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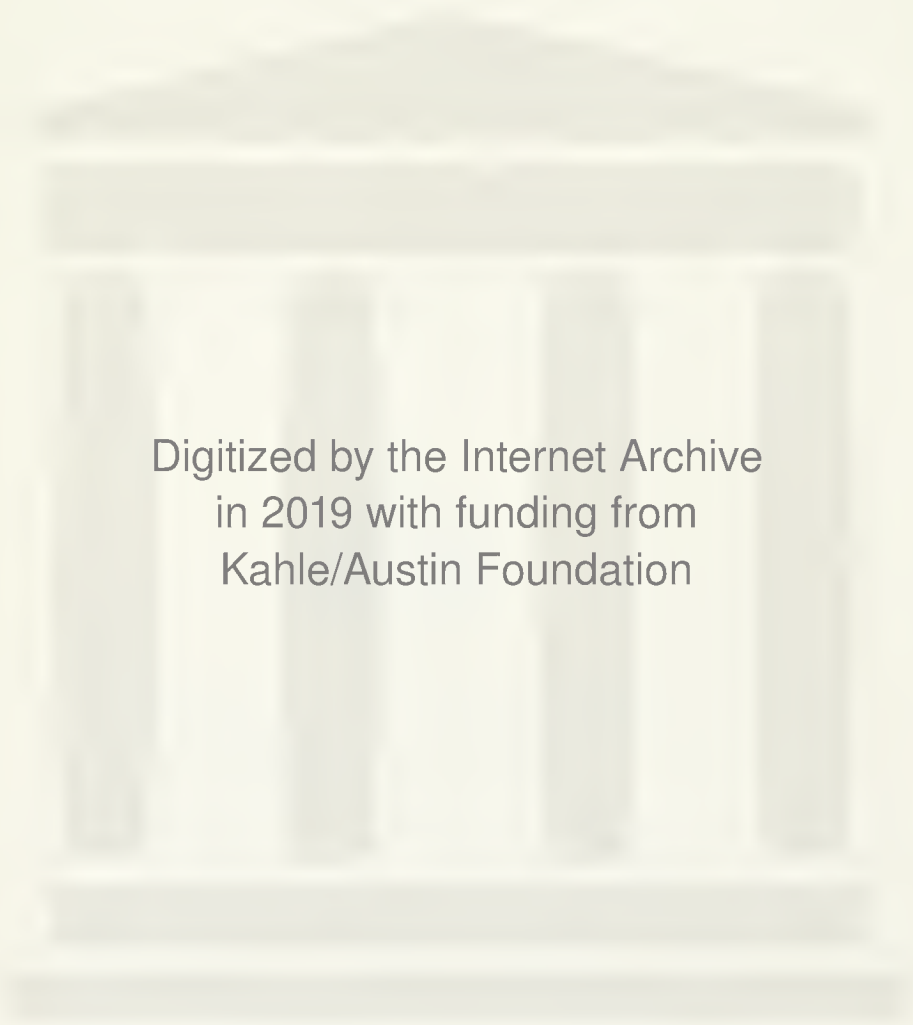

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The chemistry of cyclo-octatetraene and its derivatives

The chemistry of cyclo-octatetraene and its derivatives

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Foreword

The story of cyclo-octatetraene began in 1911–13 with Willstätter's multistep preparation from pseudo-pelletierine, surely one of the most hopeful synthetical projects ever undertaken in organic chemistry. Although for many years doubt was cast on the validity of this work it was proved in 1947 to have been correct. Yet in view of its inaccessibility, for thirty years after its discovery the likelihood of ever being able either to solve the fascinating theoretical speculation as to whether cyclo-octatetraene was an aromatic compound akin to benzene, or to investigate its properties in any detail, seemed wholly remote.

The writer recalls the almost incredible news reaching this country in 1945 that Reppe had prepared cyclo-octatetraene in kilogram quantities by the polymerisation of acetylene, and his wonder on seeing this beautiful yellow liquid in bulk. Since 1945, and indeed a few years before in Germany, the investigation of this remarkable compound has been pursued in chemical laboratories throughout the world, and has revealed an astonishing variety of chemical behaviour, little of which could have been foretold by application of chemical theory or by analogy with the behaviour of other substances, and in which, in contrast with benzenoid compounds, the cyclo-octatetraene nucleus seldom retains its original structure.

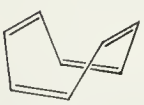
It has long been evident that a comprehensive account of the chemistry of cyclo-octatetraene was needed, not only to summarise the great volume of work that has been done with it but, on the basis of the information disclosed, to lay the foundations of a real knowledge of the chemistry of this hydrocarbon. This timely book by Dr G. I. Fray in collaboration with Dr R. G. Saxton fulfils both these objectives, and generations of chemists who will continue to investigate this versatile hydrocarbon will be grateful to be able to 'look it up in Fray and Saxton'.

W. BAKER

For
Joyce and Patricia

Preface

Z,Z,Z,Z-Cyclo-octatetraene (COT) (I) has played an outstanding role in many aspects of theoretical and synthetical chemistry. As [8]annulene, the next higher vinylogue of benzene, it is of fundamental importance for the understanding of cyclic alternating π-systems. As a medium-ring polyene, it undergoes a wide variety of reactions which are often accompanied by skeletal transformations, and it is the progenitor of a large number of interesting species including, for example, cyclobutadiene (II), semibullvalene (III), the homotropylium cation (IV), the dianion (V), 1H-azonine (VI), basketene (VII), bullvalene (VIII), [16]annulene (IX) and triamantane (X).



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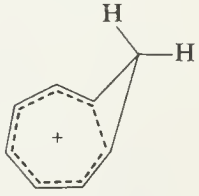

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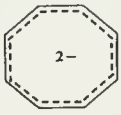

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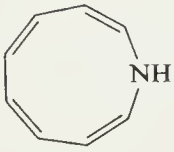

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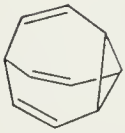

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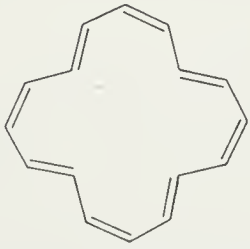

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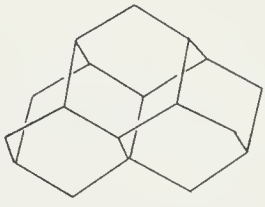

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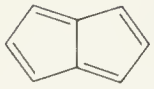

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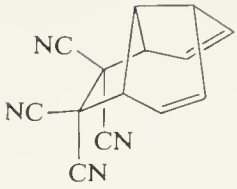

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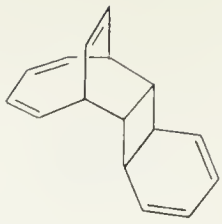


(XIII)

COT also forms an exceptional variety of complexes with transition metals. In addition to the interest, from the viewpoint of bonding theory, of these multifarious derivatives (some of which exhibit intriguing fluxional behaviour), modifications of the attached C_8H_8 ligand may occur, leading to systems such as pentalene (XI). Moreover, reactions of metal-coordinated COT can provide routes to systems which are not readily available by the conventional transformations of organic chemistry; examples include the dihydrotriquinacene-derivative (XII) and the COT dimer (XIII).

We feel that our interest in such a molecule needs no apology, and the rapid development of its chemistry during the last decade provides some justification for a new summary of existing knowledge. In chapter 1, the formation, physical properties and chemical reactions of COT are outlined, while chapter 2 deals with substituted (and annulated) derivatives of the parent compound; in order to keep the length of the book within bounds, benzo-derivatives and analogues containing hetero-atoms, e.g. azocines, have been omitted. Chapter 3 attempts to cover, as far as possible, the known chemistry of those compounds which are immediately derivable from COTs. By means of an appendix, prepared after the main typescript had been submitted, we have been able to include additional material from the later literature (up to the end of 1976).

We are indebted to previous reviewers of this field, notably the following:

L. E. Craig, *Chem. Rev.*, 1951, **49**, 103

R. A. Raphael, in *Non-Benzenoid Aromatic Compounds* (ed. D. Ginsburg), Interscience, 1959, chapter VIII

G. Schröder, *Cyclooctatetraen*, Verlag Chemie, Weinheim, 1965

H. P. Figeys, *Topics in Carbocyclic Chem.*, 1969, **1**, 269

L. A. Paquette, *Tetrahedron*, 1975, **31**, 2855.

July 1977

G.I.F.
R.G.S

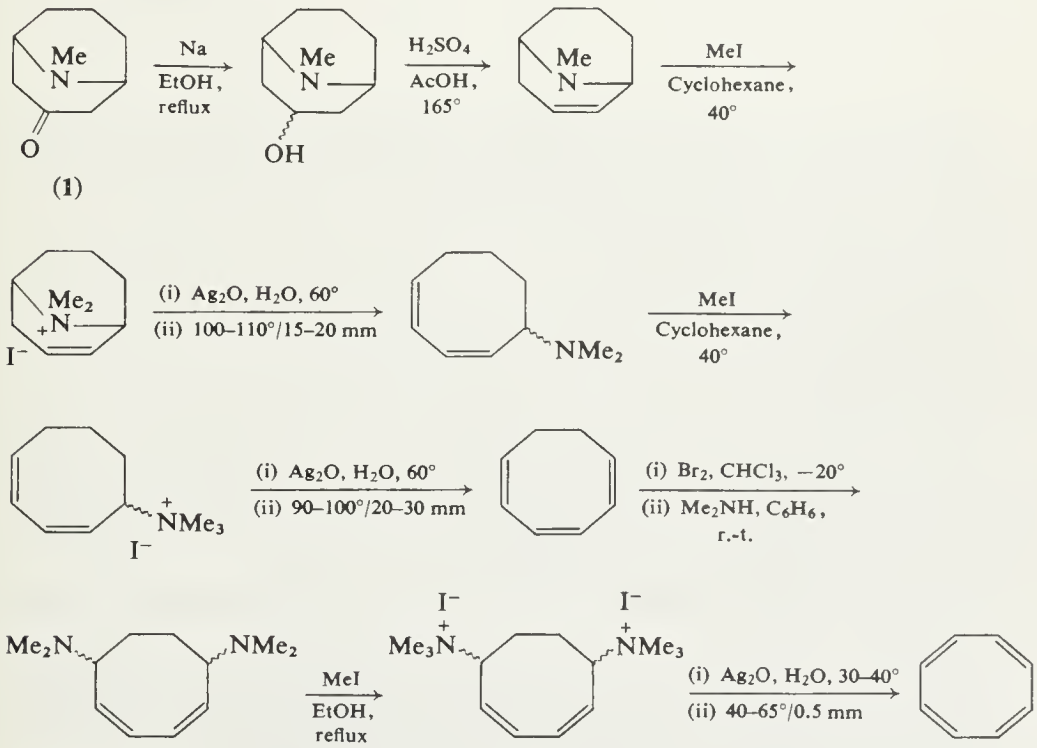
1

Cyclo-octatetraene

1. Formation

Cyclo-octatetraene was first described in 1911 by Willstätter and Waser,[1] who obtained it from pseudo-pelletierine (**1**), an alkaloid from the bark of the pomegranate tree, by a lengthy degradation proceeding *via* cyclo-octa-1,3,5-triene (see also ref.,2). The resulting sample of COT probably contained *ca.* 30% of styrene,[3] and its authenticity did not go unchallenged (for a review of the evidence, see ref. 4). However, the original reaction sequence was repeated some thirty-six years later by Cope and Overberger[3, 5] (scheme 1), and Willstätter's claim was completely vindicated.

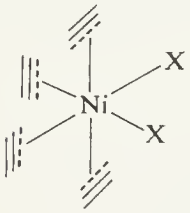
Scheme 1



This type of approach to COT may be simplified by starting from the readily available cyclo-octa-1,5-diene, but the introduction of the additional double

bonds by means of the Hofmann elimination procedure,[6,7] or by dehydrobromination,[8–10] results in poor yields of a product which is contaminated with styrene, benzocyclobutene etc.

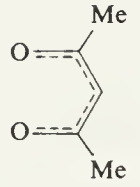
In 1940, the important discovery that COT could be produced by the cyclotetramerisation of acetylene was made in the laboratories of Badische Anilin- & Soda-Fabrik AG, by Reppe *et al.*[11] The reaction is best carried out (up to 70% conversion) in dry tetrahydrofuran or dioxan at 85–90° and a pressure of 15–25 atmospheres, in the presence of nickel(II) compounds such as the cyanide or chelate 'ato' complexes from acetylacetone, acetoacetic esters, salicylaldehyde, *N*-alkylsalicylaldimines etc.[11–15] (a much less efficient conversion results from the use of $(CH_2{=}CH.CN)_2Ni$[16]). The process has been reviewed,[17–19] and Schrauzer[15,18] has proposed a mechanism involving an intermediate octahedral nickel complex (**2**) (but see appendix). (For a discussion of bonding in this type of complex, see refs. 20, 21. An earlier hypothesis proposed the intermediacy of a cyclobutadiene complex (**3**)[22].)



(2)

(3)

X = CN; XX =



etc.

Among the by-products of the Reppe process are benzene, styrene, naphthalene, azulene, *Z*-1-phenylbuta-1,3-diene, vinylcyclo-octatetraene, and a $C_{12}H_{12}$ fraction of unknown constitution.[23–26] .

Octadeuteriocyclo-octatetraene may be prepared by similar cyclotetramerisation of dideuterioacetylene.[27]

COT has been identified as one of the products of the thermal polymerisation of acetylene,[28,29] and very low yields of COT result from u.v. irradiation of acetylene.[30,31]

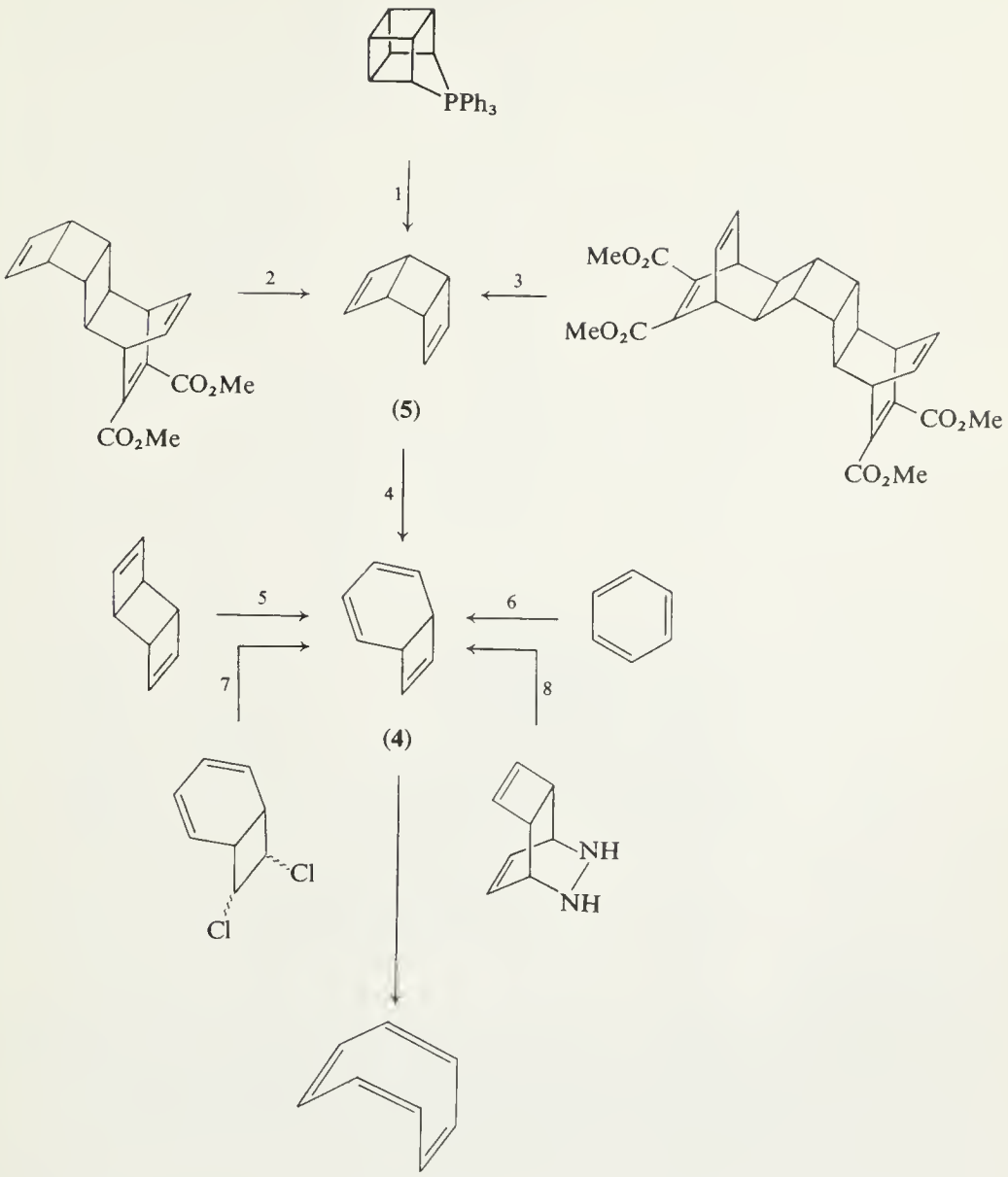
COT is also formed by various isomerisation processes occurring in other C_8H_8 compounds. Reactions which generate bicyclo[4.2.0]octa-2,4,7-triene (**4**), unless carried out at low temperatures,[32] lead to COT *via* valence isomerism (see p. 10); examples are given in scheme 2.

Other skeletal rearrangements leading to COT are outlined in schemes 3 and 4.

Additionally, COT is a minor photo-product of basketene (**6**)[55] and of the dimethyl acetylenedicarboxylate adduct (**7**),[56] and it has been detected amongst the pyrolysis products of the β-lactone (**8**)[57] and of α-cellulose.[58]

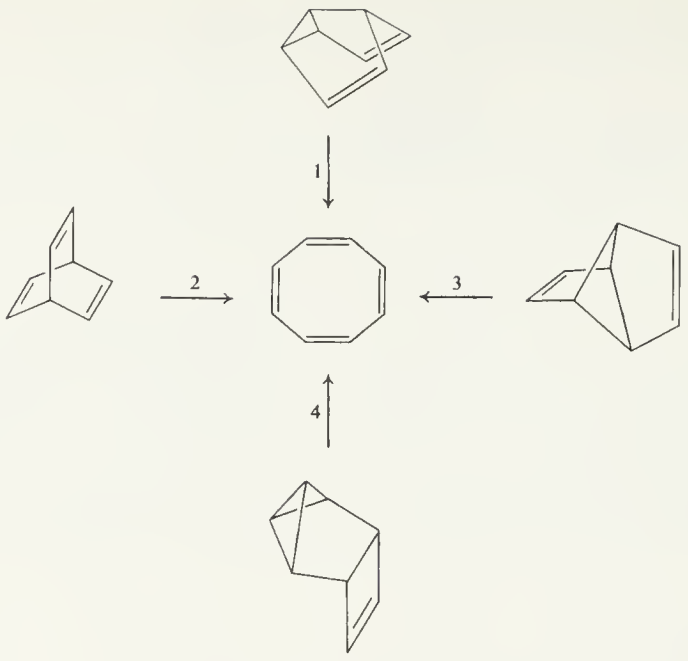
Finally, COT has been identified as one of the constituents responsible for the odour of tomatoes,[59] and may therefore be a natural product!

Scheme 2



Reaction	Reagents and conditions	Yield (%)	Ref.
1	120°	85[a]	33
2	140–160°	—	34
3	*ca.* 150°	—	34
4	(>100°), 90–121°	—	(35), 36
5	*o*-Dichlorobenzene, 140°	100	35
	or e.g. $AgBF_4$, Me_2CO, reflux	100	37
6	HC≡CH, *hv*	(Very low)	38
7	NaI, $NaHSO_3$, Me_2CO, r.-t. → 50°	35	39
8	MnO_2, n-hexane, r.-t.	75–80	40

[a] Mixture of (5) and COT (4:1).



Reaction	Reagents and conditions	Yield (%)	Ref.
1	$AgNO_3$, MeOH(aq.), 80°	100	41
	or 427°/30 mm (flow system)	56	(42), 43
2	*hν*, methylcyclohexane	20	44
3	*hν* (Pyrex), e.g. isopentane, −60°	Up to 29	45
4	400–500°	—	46
	or e.g. $AgClO_4$, Me_2CO, r.-t.	—	46

2. Purification

The purification of COT by fractional distillation and low-temperature crystallisation has been described in detail.[60]

For separation by liquid–solid column chromatography, see ref. 44.

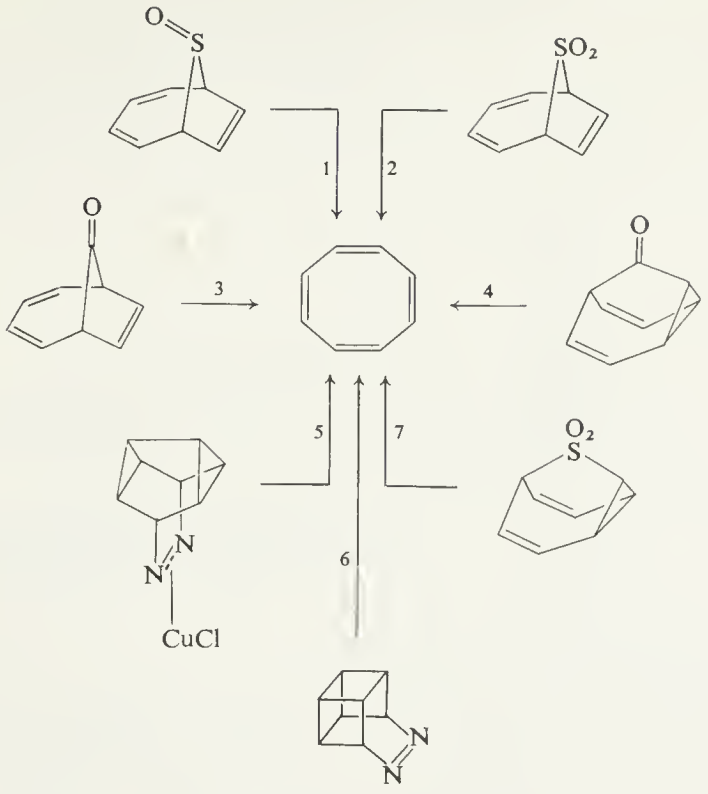
For the use of gas–liquid chromatography, see e.g. refs. 9, 40, 44, 49; for other gas-chromatographic data see refs. 61, 62.

COT may also be purified *via* its silver nitrate complex $(COT)_2(AgNO_3)_3$ (see p. 51), from which it is readily regenerated by treatment with aqueous sodium chloride.[63]

COT forms an inclusion complex with thiourea,[64] but no use of this property appears to have been made.

COT is somewhat sensitive to air and light, and is best stored in the dark below room-temperature, in the presence of a free-radical inhibitor such as hydroquinone. Even so, samples of COT which have been kept for some time inevitably contain dimeric and polymeric material (see pp. 12–13, 34).

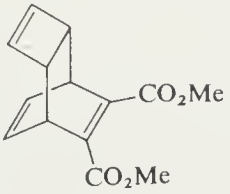
Scheme 4



Reaction	Reagents and conditions	Yield (%)	Ref.
1	*hv*	—	47
2	345° (g.l.c.)	100	48
	or *hv* (Corex), Me_2CO, Et_2O[a]	—	—
3	*hv* (Pyrex), Et_2O or THF	80–82	(50), 51, 52
4	*hv*	—	50
5	25°	100	41
6	*hv*	(Low)	53
7	240° (flow system)	100	54

[a] Conditions used for 1,4-dideuteriocyclo-octatetraene (40%).[49]

(6)



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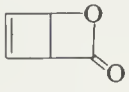


(8)

3. Physical properties

COT is a yellow liquid, with a strong distinctive odour.

Boiling-point (°C)	142–143	Pressure (mm Hg)	760	Ref. 11
	48		31	65
	42–42.5		17	11
Melting-point (°C)	−4.7			27, 66
	−4.5 to −3.5			63
Triple-point (K)	268.48			66
Density (g cm^{-3})	0.9382	Temperature (°C)	0	11
	(0.9206), 0.9209		20	(11), 60
	0.9196		25	60
	0.9117		30	60
Viscosity (cP)	1.42	Temperature (°C)	20	60
	1.30		25	60
	1.18		30	60

Heat capacity (12–330 K): see ref. 66

Vapour pressure (0–75 °C): see ref. 66

Heat of fusion (cal mol^{-1})	2694.6	66
Heat of combustion (25 °C) (kcal mol^{-1})	−1084.9	67
	−1086.5	68
Heat of hydrogenation (25 °C) (kcal mol^{-1})	−97.96	69

Refractive index (Na_D)[a]	1.5379	Temperature (°C)	20	60
	(1.5348), 1.5350		25	(63), 60, 69
	1.5323		30	60

[a] For measurements at other wavelengths, see ref. 60.

Dielectric constant (20 °C)	2.74	11
First ionisation potential (adiabatic)[a] (eV)	7.99	70
	8.0	71
	8.04	72
	8.06	73

[a] For higher ionisation potentials, see refs. 71, 72.

Electron affinity (kcal mol^{-1})	13.3	74

Half-wave reduction potentials: see e.g. refs. 65, 75–82

Magnetic susceptibility (cm^3 mol^{-1})	−0.0000539	83, 84
Magnetic rotation (μrad)	1009	85

The following have been calculated from thermochemical data:

Heat of vaporisation (25 °C) (cal mol^{-1})		10300	Ref. 66
Entropy (cal deg^{-1} mol^{-1})	(Liquid, 25 °C)	52.65	66
	(Gas, 25 °C, 1 atm)	78.10	66
Heat of formation (kcal mol^{-1})	(Liquid, 25 °C)	60.82	68
	(Gas, 25 °C)	71.0	86, 87
		71.1	88, 89
		71.12	90
		71.3	91
		71.9	69
Heat of isomerisation to styrene (kcal mol^{-1})	(Liquid, 25°C)	−36.10	68
	(Gas, 25 °C)	−36.3	69
Empirical (thermochemical) resonance energy (stabilisation energy) (kcal mol^{-1})		2.4	69
		3.0	92
		3.3	93
		3.6	69
		4.8	67

For other calculations, see table 5, p. 11.

U.v. spectrum. COT exhibits a broad weak absorption band with a maximum near 280 nm (table 1), which tails into the visible region;[94,95] there is strong 'end-absorption', with a shoulder at *ca.* 205 nm[95,96] (ε 20000[97]). The absorption curve is reproduced in refs. 60, 94, 98. (Measurements have also been made in the gas phase[94,95].)

Table 1

Solvent	$\lambda_{max.}$ (nm)	ε	Ref.
MeOH	280	350	94
EtOH	280	435	94
n-Heptane	280	235	94
$CHCl_3$	282	200	99
Cyclohexane	283	255	94
Iso-octane	283	250	98
CCl_4	288	320	94

I.r. spectrum. The C=C stretching vibration in COT gives rise to an absorption band with $\nu_{max.}$ (liquid film) 1634,[99] 1635[27] cm^{-1}. The spectrum is reproduced in refs. 27, 60; for complete lists of the principal absorption maxima, see refs. 27, 99. (Measurements have also been made in the gas phase[27,99].)

Raman spectrum. See refs. 27, 100, 101.

N.m.r. spectra. The ^1H n.m.r. spectrum of COT shows a singlet resonance at −341 Hz relative to tetramethylsilane, i.e. at τ 4.32 (60 MHz; neat liquid).[102]

For the p.m.r. of solid COT, see ref. 103.

The ^1H n.m.r. spectrum is temperature-dependent with respect to the ^{13}C satellites of the proton signal, owing to the conformational mobility of the molecule (see p. 9). At very low temperatures these satellites are essentially double doublets; for the coupling constants, see table 2.

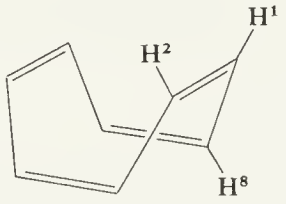


Table 2

$J(H^1–H^2)$ (Hz)	$J(H^1–H^8)$ (Hz)	Ref.
11.4	*ca.* 2.5	104
11.48	3.87	105
11.8	—	106

From the ^{13}C n.m.r. spectrum, $J(^{13}C–H) = 155$ Hz.[107]

The presence of a weak paramagnetic ring-current in COT has been inferred from measurements of solvent shifts.[108]

Mass spectrum. The major ions in the mass spectrum of COT, together with their relative abundances and appearance potentials, are listed in ref. 73.

For the doubly-charged ion mass spectrum of COT, see ref. 109.

For the collisional activation spectrum of field-ionised COT, see ref. 110.

Photo-electron spectrum. See refs. 71, 72, 111, 112.

Trapped electron impact spectrum. See ref. 113.

For electron attachment studies see refs. 114, 115.

Magnetic circular dichroism. The MCD curve of COT is reproduced in ref. 98.

4. Structure

X-ray[116] and electron diffraction[117–119] studies of COT show that the eight-membered ring exists in a non-planar 'tub' form (D_{2d} symmetry), with the bond lengths and angles listed in tables 3 and 4.

Although the non-planarity of COT in its ground state prevents *substantial* overlap of the adjacent π-orbitals, certain through-bond and through-space interactions may exist.[72,85,87]

The observed u.v. absorption (see p. 7) has been explained on the basis of interactions between the excited π-systems.[121,122]

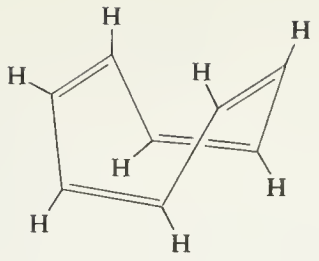


Table 3

Bond	Length (Å)	Ref.
C=C	1.330	116
	1.334	118
	1.340	119
C—C	1.456	116
	1.462	118
	1.476	119
C—H	1.090	118
	1.100	119

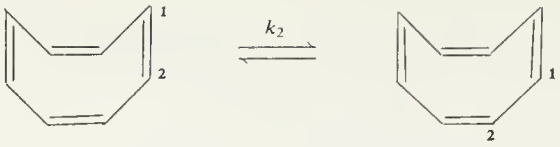
Table 4

		Ref.
Angle C(=C)(—C)—	126.1°	119
	126.5°	118
	126.8°	116
Angle C(=C)(—H)—	117.6°	119
	118°	118
Torsion angle around C—C	56°	116
	58°	120

Conformational inversion and valence tautomerism. At ordinary temperatures, the tub-shaped COT molecule undergoes rapid ring-inversions (see e.g. ref. 123).

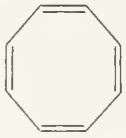
This process may be studied in substituted COTs by variable-temperature n.m.r. spectroscopy (see p. 94); for calculations of the energy barrier, see refs. 124–127.

In addition to this conformational change, two kinds of valence tautomerism occur. The first involves bond-shift in the eight-membered ring, the single and double bonds exchanging their positions.

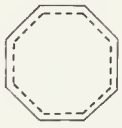


For measurements of the rate constant k_2, see refs. 104, 106, 128, 129 ($E_a = 10.9$,[129] 14.5[104] kcal mol^{-1}; $\Delta G^{\ddagger} = 13.3$,[104] 13.7[106] kcal mol^{-1}).

It is generally assumed that the ring-inversion and bond-shift processes occur *via* the planar transition states (***A***) and (***B***) respectively, (***A***) containing alternate double and single bonds (alternating bond lengths, D_{4h} symmetry), but (***B***) having D_{8h} symmetry (equal bond lengths). Theoretical studies[125,127,130–133] predict that structure (***A***) should be more stable than the



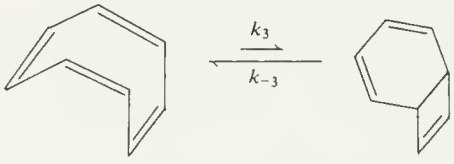
(***A***)



(***B***)

delocalised form (***B***) (which is 'anti-aromatic'). It follows that inversion should proceed more rapidly than bond-shift, and indeed this is found for substituted COTs in which it is possible to discriminate between the two processes (see p. 94).

The second type of valence tautomerism displayed by COT results in a low concentration (*ca.* 0.01 % at 100°) of bicyclo[4.2.0]octa-2,4,7-triene (**4**)[134–136] (a disrotatory 6π electrocyclisation is thermally allowed by the Woodward–Hoffmann rules).



(**4**)

For values of k_3, see refs. 128, 136 ($E_a = 27.2$ kcal mol^{-1};[128] $\Delta H^{\ddagger} = 27.4$,[135] 28.1[136] kcal mol^{-1}); for k_{-3}, see ref. 128 ($E_a = 18.7$ kcal mol^{-1} [32]).

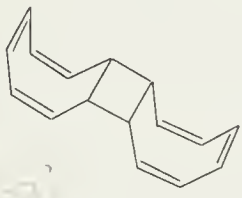
The theoretical importance of COT as [8]annulene has led to numerous calculations of various aspects of its structure and properties (table 5) (for general discussions, see e.g. refs. 137–139). Calculation of the properties of the lowest $\pi \rightarrow \pi^*$ triplet state of COT leads to the conclusion that it may be regarded as 'aromatic'.[154]

Table 5

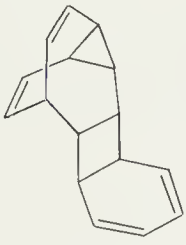
	Ref.
Molecular geometry	124, 125, 127, 140–142
Symmetry force constants	143
Mean amplitudes of vibration	143
Strain	95, 130, 144–147
Thermodynamic functions	90
Bond energies	142
Orbital energies	72
Total energy	125, 145, 148
Bond length–bond overlap correlation	149
π-Binding energy	150
Resonance	92, 95, 130, 150, 151
Index of aromaticity	152
U.v. spectrum	92, 95
π-Electron transition energies	96, 153
Heat of formation	88, 111, 124, 144, 145
Ionisation potential	111, 124

5. Thermal oligomerisation

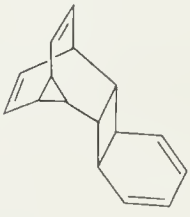
The thermal dimerisation of COT was first observed by Reppe *et al.*,[11] and Jones[155,156] later showed that four different products of formula $C_{16}H_{16}$ could be isolated. At *ca.* 100° (or at 20° under high pressure[157]) the two main dimeric products are compounds of m.p. 52–53°[156,158] and 76–77°[156,159] respectively (for the best preparative procedure, see ref. 160); at higher temperatures (130–170°) two other dimers, melting at 41.5°[11,155] and 38.5°[155] respectively, are produced. The structures of these products are now known to be (**9**), (**10***a* ⇌ **10***b*), (**11**), and (**12**) severally.



(**9**)

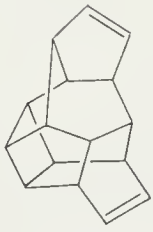


(**10***a*)



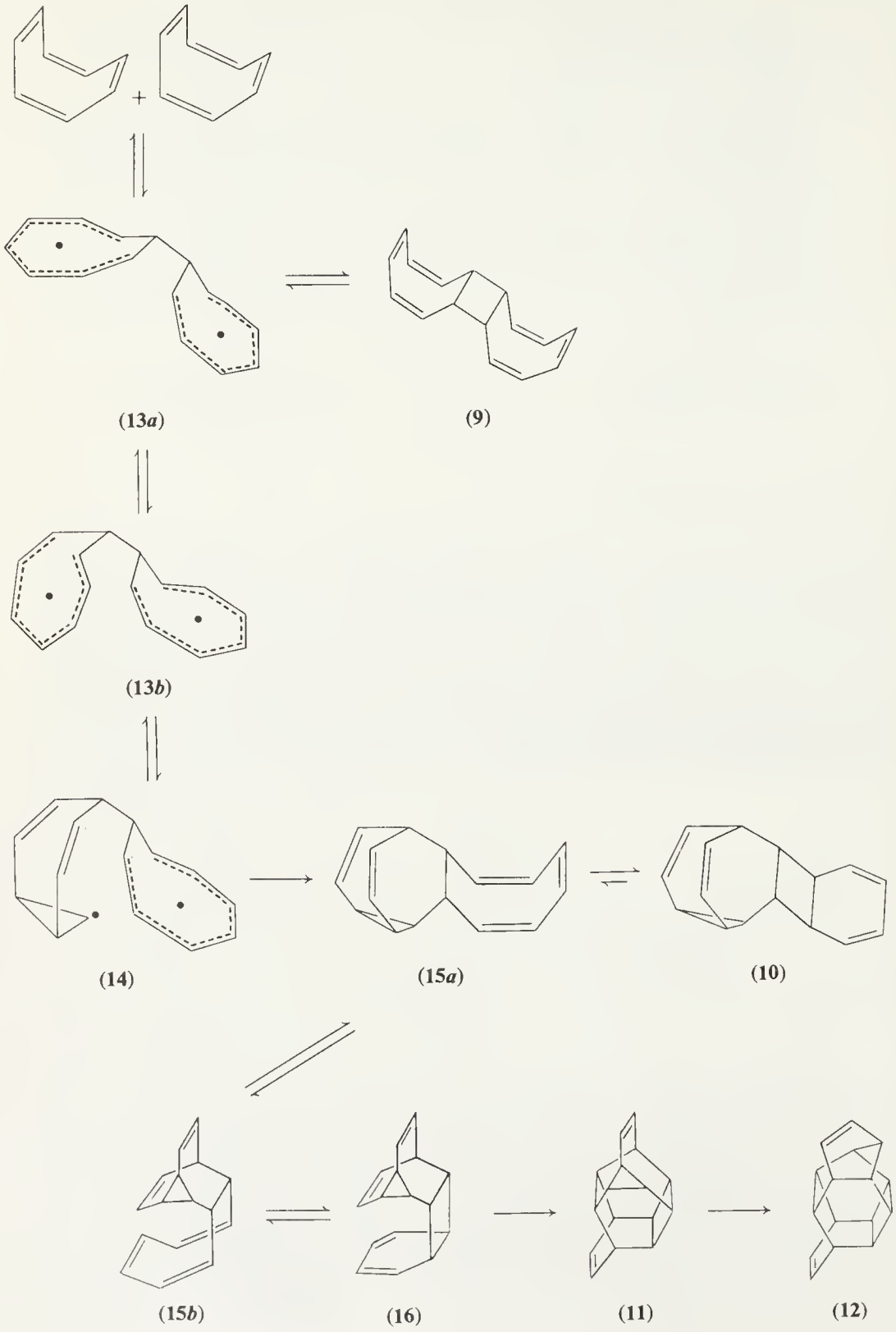
(**10***b*)

(**11**)



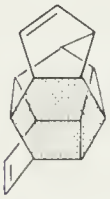
(**12**)

Scheme 5

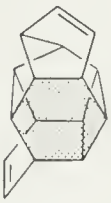


Structure (**12**) for the dimer of m.p. 38.5° was determined by an X-ray crystallographic examination of its silver nitrate complex;[161,162]* the co-dimer, m.p. 41.5°, may be assigned structure (**11**) from spectral evidence.[165] The temperature-dependent p.m.r. spectrum of the dimer of m.p. 76–77° reveals the presence of a fluxional 3,4-homotropilidene system, in which rapidly reversible valence isomerism occurs *via* the Cope rearrangement;[159,166] its structure is therefore represented as (**10*a*** $\rightleftharpoons$ **10*b***) (for the ^{13}C n.m.r. spectrum, see ref. 167). The remaining thermal dimer, m.p. 52–53°, possesses structure (**9**),[34,168] oxidative cleavage to *cis,cis,cis*-cyclobutanetetracarboxylic acid indicating the stereochemistry of the ring-fusions.[34]

Schröder and Oth[169] have proposed the following mechanism (scheme 5) for the formation of these remarkable products. Dimer (**9**), which is formed slowly even at room-temperature,[156] is presumed to result from a non-concerted [2 + 2] cycloaddition of two molecules of COT, the reaction intermediate being represented as the diradical (**13*a***). If dimer (**9**) is heated at *ca.* 100°, COT is regenerated,[159] but formation of dimer (**10**) also occurs (and may be made quantitative by using high pressure[157]). It is proposed that inversion of one of the eight-membered rings in (**13*a***), leading to the conformer (**13*b***), is followed by ring-closure of the rearranged diradical (**14**) to give the valence tautomer (**15*a***) of dimer (**10**). At higher temperatures the cage-like dimer (**12**) accumulates, and has been shown to result from dimer (**11**).[158,165] Inversion of the cyclohexa-1,3-diene system in dimer (**10**), which is possible *via* the conformationally mobile valence tautomer (**15*a*** $\rightleftharpoons$ **15*b***), would lead to a structure (**16**) capable of an intramolecular Diels–Alder reaction with the formation of dimer (**11**). Conversion of this product into dimer (**12**) may then proceed *via* a vinylcyclopropane → cyclopentene rearrangement, as suggested by Moore.[165] This mechanistic scheme suffers from the defect that it provides no explanation for the *stereospecific* formation of dimer (**9**). The conversion of dimer (**11**) into dimer (**12**), rather than into the alternative rearrangement product (**17**), also requires explanation. However, inspection of molecular models indicates that the shaded six-membered ring in structure (**12**) is in the form of a half-chair,



(**12**)

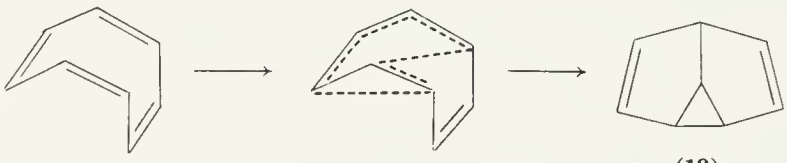


(**17**)

* Although it was not realised at the time, this assignment was not completely unambiguous, because of the possibility of silver-catalysed rearrangement (see e.g. ref. 163). N.m.r. spectral studies show, however, that there is no skeletal rearrangement when dimer (**12**) is converted into its silver nitrate complex.[164]

whereas in structure (**17**) the corresponding ring is forced to adopt a distorted boat-form;[164] this difference may account for the exclusive formation of dimer (**12**) in the vinylcyclopropane rearrangement, if the transition states leading to the alternative structures (**12**) and (**17**) are closely related to the respective products.

Alternative suggestions concerning the formation of the COT dimers have been made by Iwamura and Morio.[170] On the basis of a theoretical study it was concluded that the conversion of COT into semibullvalene (**18**) is symmetry-allowed as a thermal process ($[{}_{\pi}4_a + {}_{\pi}2_a]$).



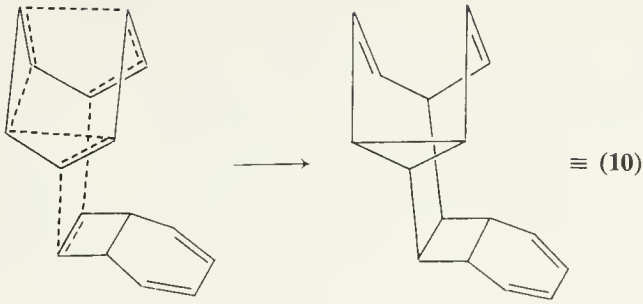
(**18**)

It was then claimed that dimers (**10**)–(**12**) could result from thermally-allowed cycloadditions of semibullvalene and bicyclo[4.2.0]octa-2,4,7-triene, *via* the transition states (*C*)–(*E*) (scheme 6) which were shown to contain Hückel arrays of molecular orbitals (see ref. 171). However, closer examination of the structure which would be obtained by reaction of the components in mode (*E*) shows that it would represent, not dimer (**12**), but an impossibly strained system (**19**). As an alternative possibility, it was proposed that dimers (**9**) and (**10**) could arise from an intermediate dimer (**20**) (*cf.* (**193**), p. 68) *via* the transition states (*F*) and (*G*) (scheme 7) respectively.[170] Again a correction is necessary; transition state (*F*) would not lead to dimer (**9**), but to the *anti*-isomer (**21**) (see p. 320). Another hypothetical intermediate (**22**), derived from (**20**), was also visualised as a possible precursor of dimers (**11**) and (**12**)[170] (scheme 8).

For the co-dimerisation of COT and monosubstituted COTs, see pp. 101–2.

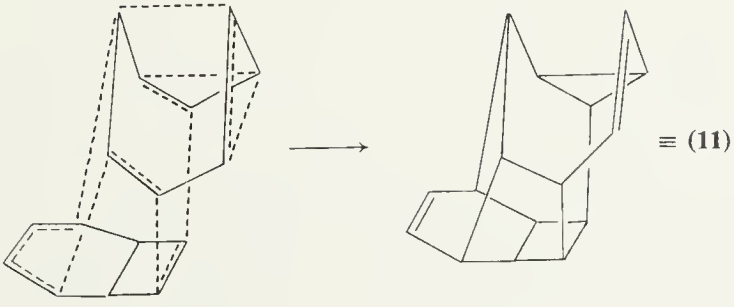
Residues from the distillation of dimerised COT contain a tetramer, $C_{32}H_{32}$,[159] which also results when dimer (**10**) is heated[172] (see p. 368). The tetramer molecule possesses two fluxional homotropilidene systems, and is formulated as the Diels–Alder adduct (**23**) derived from two molecules of dimer (**10**)[172] (only one of the four interconverting forms is shown). The illustrated stereochemistry has not been proved, but represents that which would result from [4 + 2] cycloaddition on the unhindered face of each component and in the *endo*-manner.

Scheme 6



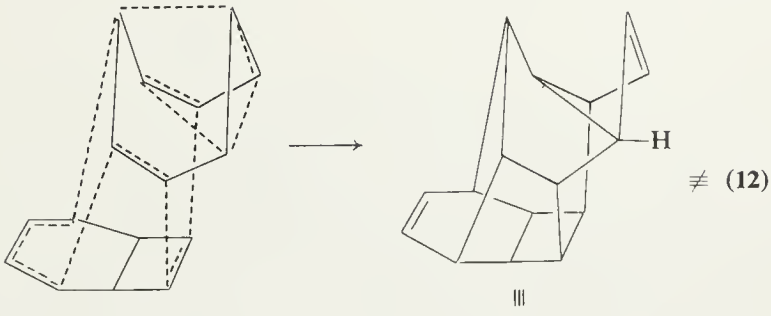
≡ **(10)**

(*C*)



≡ **(11)**

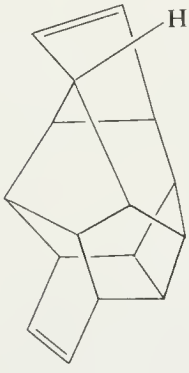
(*D*)



≠ **(12)**

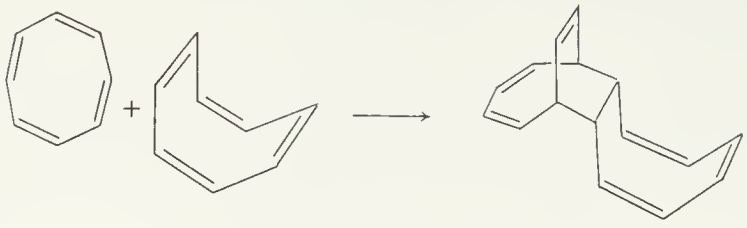
(*E*)

≡

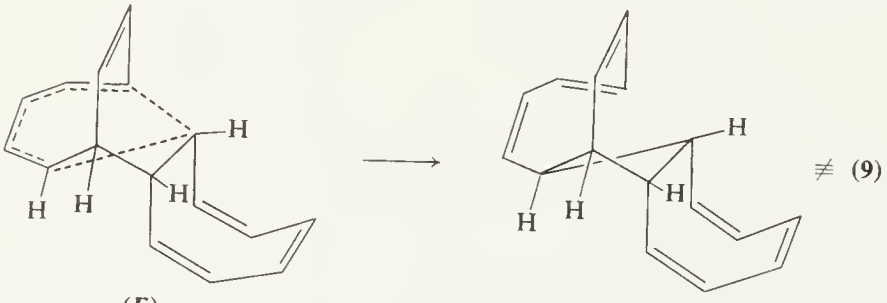


(19)

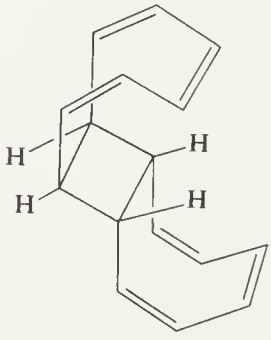
Scheme 7



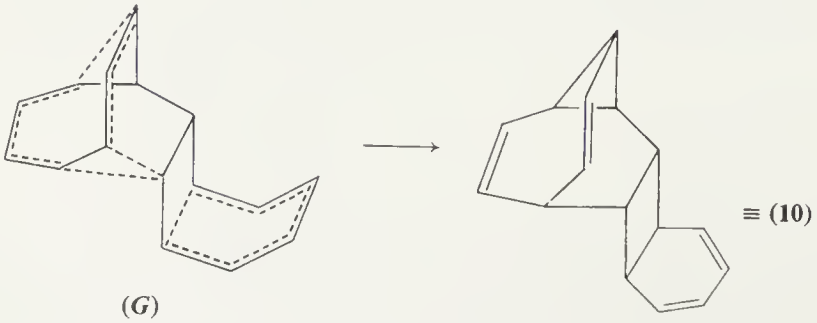
(20)



(*F*) III

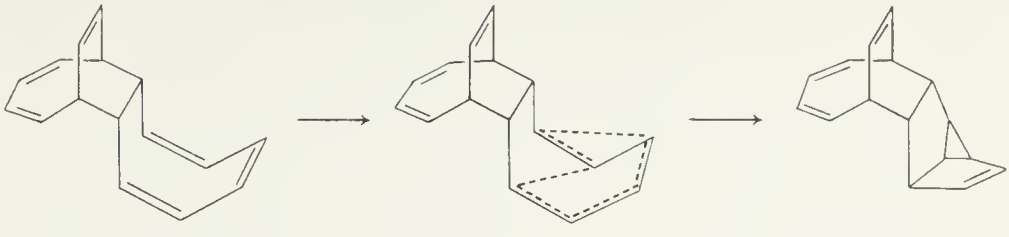


(21)

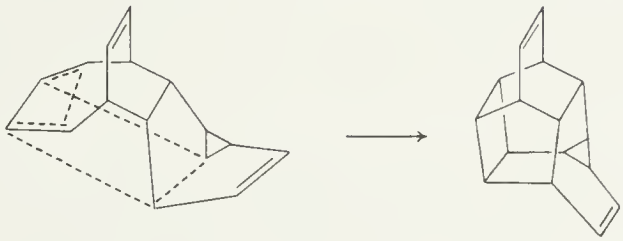


(*G*)

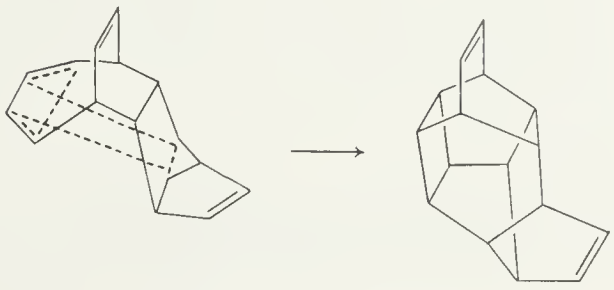
Scheme 8



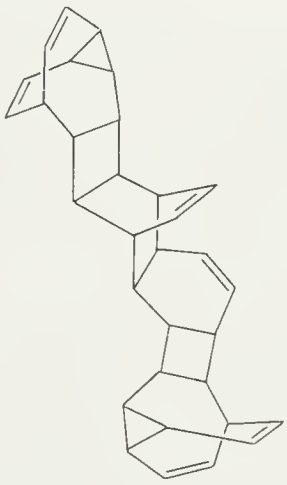
(20) (22)



≡ (11)



≡ (12)

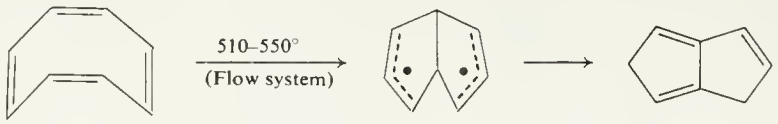


(23)

6. Thermolysis, photolysis and radiolysis

Thermolysis. At 520°/30 mm (flow system; residence time *ca.* 1–3 s), COT undergoes a degenerate structural rearrangement, detectable by the observation of deuterium scrambling in 1,4-dideuteriocyclo-octatetraene[49] (see also p. 118).

Under slightly more vigorous conditions, *ca.* 510–550° (flow system; residence time *ca.* 7.5 s), the dihydropentalene (**24**) is formed (up to *ca.* 40%), possibly *via* the diradical (**25**).[173]

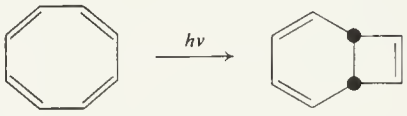


(**25**) (**24**)

At higher temperatures, in the gas or liquid phase, styrene, benzene, acetylene, etc. are produced.[174]

In the presence of a palladium catalyst, at 400° the main product (50%) is ethylbenzene.[175]

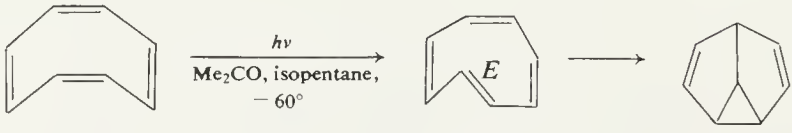
Photolysis. Direct photolysis of COT in the gas phase,[176–179] in solution,[180] or in a frozen matrix,[181] affords styrene, benzene and acetylene. Some evidence has been adduced[180,181] for the intermediate formation of bicyclo[4.2.0]octa-2,4,7-triene (**4**), which in principle could result from a photochemically-allowed disrotatory closure of the cyclobutene ring in a 4π electrocyclic process.



(**4**)

(The above evidence has been questioned,[182] but u.v. irradiation of the bicyclic triene (**4**) at −65° in the presence of acetone is known to give benzene[183].)

In isopentane containing acetone, at −60°, u.v. irradiation of COT leads to semibullvalene (**18**) (*ca.* 42% yield based on unrecovered COT); it has been postulated that initial photo-isomerisation to *Z,Z,Z,E*-cyclo-octatetraene (**26**) could be followed by a photochemical intramolecular $[{}_{\pi}2_s + {}_{\pi}2_s + {}_{\pi}2_a]$ cycloaddition.[183,184]



(**26**) (**18**)

COT effects efficient 'quenching' of triplet benzophenone,[185] and is widely used as a specific triplet-state quencher in dye-laser studies (see e.g. refs. 185–187). (For fluorescence quenching, see ref. 188.)

Radiolysis. COT is remarkably stable to γ-radiation,[189] and has a powerful retarding effect on the radiation-induced polymerisation of vinyl monomers.[190] (For one-electron oxidation and reduction, see refs. 191, 192; for radiolysis studies in the presence of COT, see e.g. refs. 193–195.)

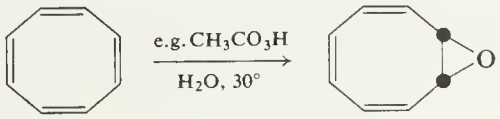
7. Oxidation, and reactions with electrophiles

Oxygen. COT polymerises in the presence of air,[11] but the nature of the initiation reaction has not been elucidated. COT apparently does not undergo dye-sensitised photo-oxygenation (singlet oxygen).[196]

Oxidation of COT with air in the presence of a mixed metal oxide catalyst at 370° gives benzoic acid (70%).[11]

Ozone. Ozonolysis of COT in chloroform gives, after work-up with acetic acid–aqueous hydrogen peroxide, a mixture containing oxalic acid, glycollic acid, ethane-1,1,2,2-tetracarboxylic acid and succinic acid.[197] When ozonolysis is carried out in methanol, however, the product is glyoxal.[198]

Peracids. COT may be converted into the mono-epoxide (**27**)[199] (52–55%) by the action of peracetic,[200] perbenzoic,[11,201] or monoperphthalic[202] acid.

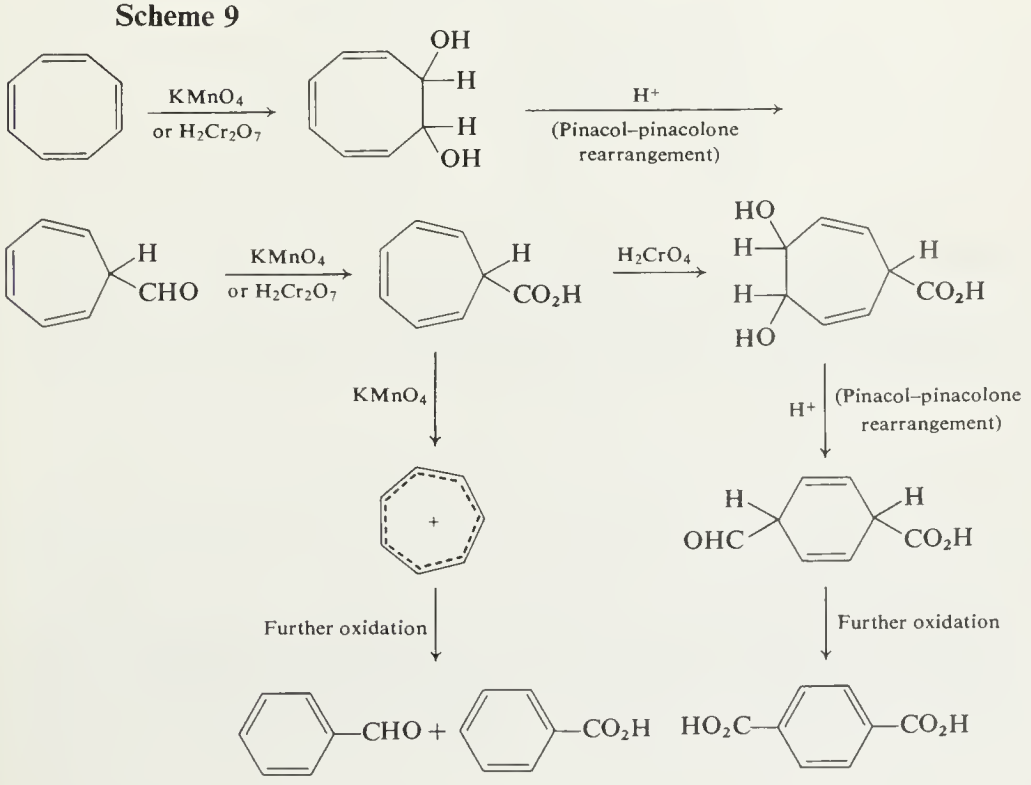


(27)

With performic acid, the products are phenylacetaldehyde (20%) and phenylacetic acid (49%).[39]

Potassium permanganate, chromic acid. Aqueous potassium permanganate oxidises COT to benzaldehyde and benzoic acid, whereas chromic acid gives in addition to these products, terephthalic acid.[11,203]

Scheme 9



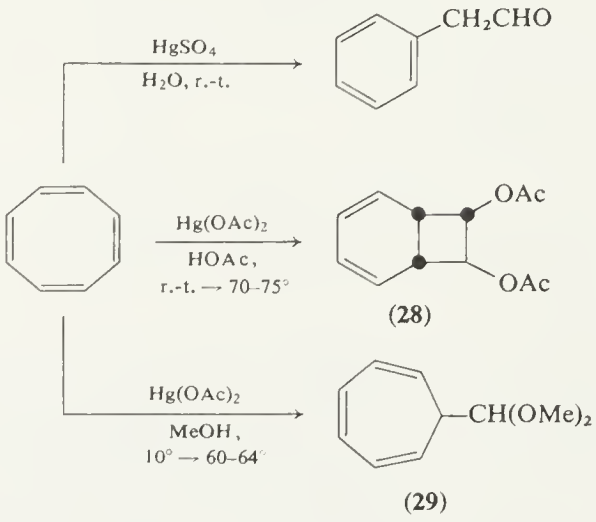
In an oxidation using permanganate in aqueous sulphuric acid containing acetone, Ganellin and Pettit[204] were able to obtain evidence for the intermediate formation of tropylium sulphate, and suggested that acid permanganate and chromic acid oxidations might proceed according to scheme 9.

Sodium hypochlorite. Alkaline hypochlorite solution oxidises COT to benzaldehyde, benzoic acid and terephthaldialdehyde.[11]

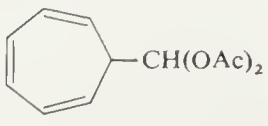
Selenium dioxide. Oxidation of COT with selenium dioxide gives (in poor yield) terephthalic acid, together with *o*-phthalaldehyde, phenylglyoxal and cyclo-octatrienone.[205]

Mercury(II) *and lead*(IV) *salts.* A suspension of mercury(II) sulphate in water oxidises COT to phenylacetaldehyde (up to 70%).[11,206]

Mercury(II) acetate in acetic acid yields the bicyclic diacetoxy-compound (**28**) (up to 84%),[206,207] but in methanol the product is the acetal (**29**) (88%).[206]



Lower yields of the products (**28**) and (**29**) are obtained with lead(IV) acetate in acetic acid (or benzene) and methanol respectively;[208] however, with lead(IV) acetate in acetic acid containing boron trifluoride, the main product is the diacetate (**30**) (up to 34%).[208,209]



(**30**)

In these reactions, the initial step is presumably an electrophilic attack on COT by $(AcO)Hg^+$ or $(AcO)_3Pb^+$; for a possible mechanism for the ring-contraction processes, see ref. 210.

Cobalt(II) *salts.* The oxidation of COT with cobalt(II) ions in a rapid-mixing flow system gives rise to a radical cation (**31**), the e.s.r. spectrum of which supports a non-planar structure.[211]

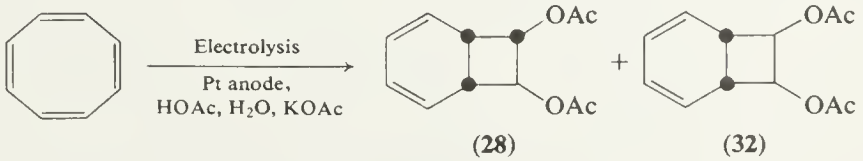
$$\text{COT} \xrightarrow[CF_3CO_2H]{Co^{2+}} \text{COT}^{+\cdot} \quad \textbf{(31)}$$

(For theoretical calculations on $COT^{+\cdot}$, see ref. 124.)

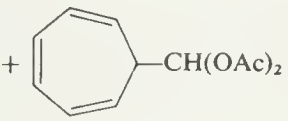
For the production of $COT^{+\cdot}$ by γ-irradiation of COT in a frozen matrix, see ref. 191.

Electrolytic oxidation. The electrochemical oxidation of COT at a mercury anode gives phenylacetaldehyde in good yield.[212]

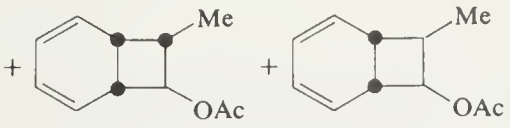
In acetic acid containing sodium or potassium acetate, with a carbon anode, a mixture of the diacetoxy-compounds (**28**), (**32**) and (**30**) is produced; the use of a platinum anode leads, additionally, to the acetoxy-methyl-derivatives (**33**) and (**34**) in low yields.[209]



(28) **(32)**

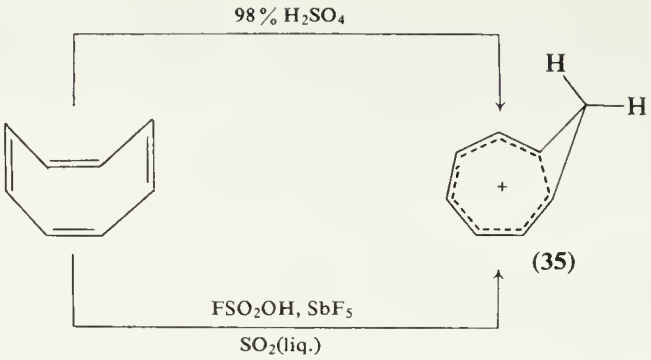


(30)



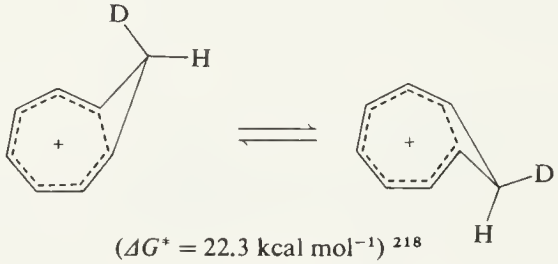
(33) **(34)**

Protonation. Dissolution of COT in concentrated sulphuric acid generates the homotropylium cation,[213,214] the p.m.r. spectrum of which provides compelling evidence for the non-classical structure (**35**);[214–217] this formulation is also supported by the u.v. spectrum[218] and by volume diamagnetic susceptibility data.[219] Comparison of this species with the protonated complexes of COT with certain transition metal carbonyls is instructive.[214] The same cation is obtained in a 'super-acid' medium.[220]



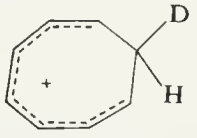
Summaries of the structural evidence for (**35**) have been given by Winstein[221,222] (for theoretical discussions, see refs. 223, 224).

At −10° in D_2SO_4, initially *ca.* 80%* of the incoming deuterium appears with *endo*-stereochemistry, but eventually becomes distributed uniformly between the *endo*- and *exo*-positions through ring-inversion[218] (a circumambulatory rearrangement may be excluded;[226] for a theoretical study, see refs. 223, 227).



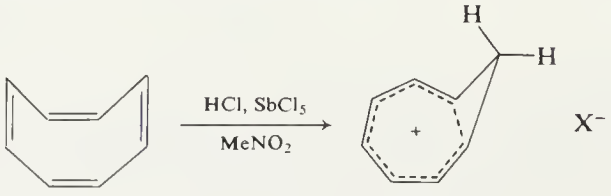
($\Delta G^{\ddagger} = 22.3$ kcal mol^{-1}) [218]

If the ring-inversion proceeds *via* the planar classical cyclo-octatrienyl cation (**36**), then the above value of $\Delta G^{\ddagger}$ represents the difference in free energy between the classical and non-classical cations.[218]



(**36**)

A crystalline homotropylium salt (**37*a***) may be formed from COT by the action of hydrogen chloride and antimony(v) chloride.[213]



(**37**)

a: X = $SbCl_6$

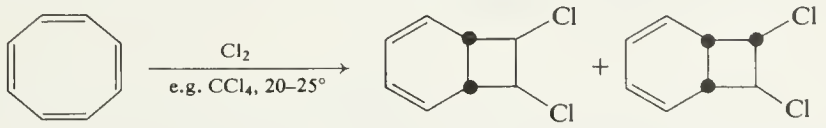
b: X = $SbBrCl_5$

Using hydrogen bromide, the analogous salt (**37*b***) is produced.[213]

* In FSO_2OD at −70°, 75%.[225]

Halogenation. Chlorine and bromine add to COT with the formation of di-, tetra- and hexahalides;[11] no octahalide has been reported.

Reaction of COT with one equivalent of chlorine gives a mixture of the stereoisomeric bicyclic dichlorides (**38**) and (**39**) (*ca.* 4:1, total yield up to 82%);[11,39,228] rearrangement of the *cis*-isomer (**38**) to the *trans*-compound (**39**) is rapid above 70°, and is catalysed by acids.[228]

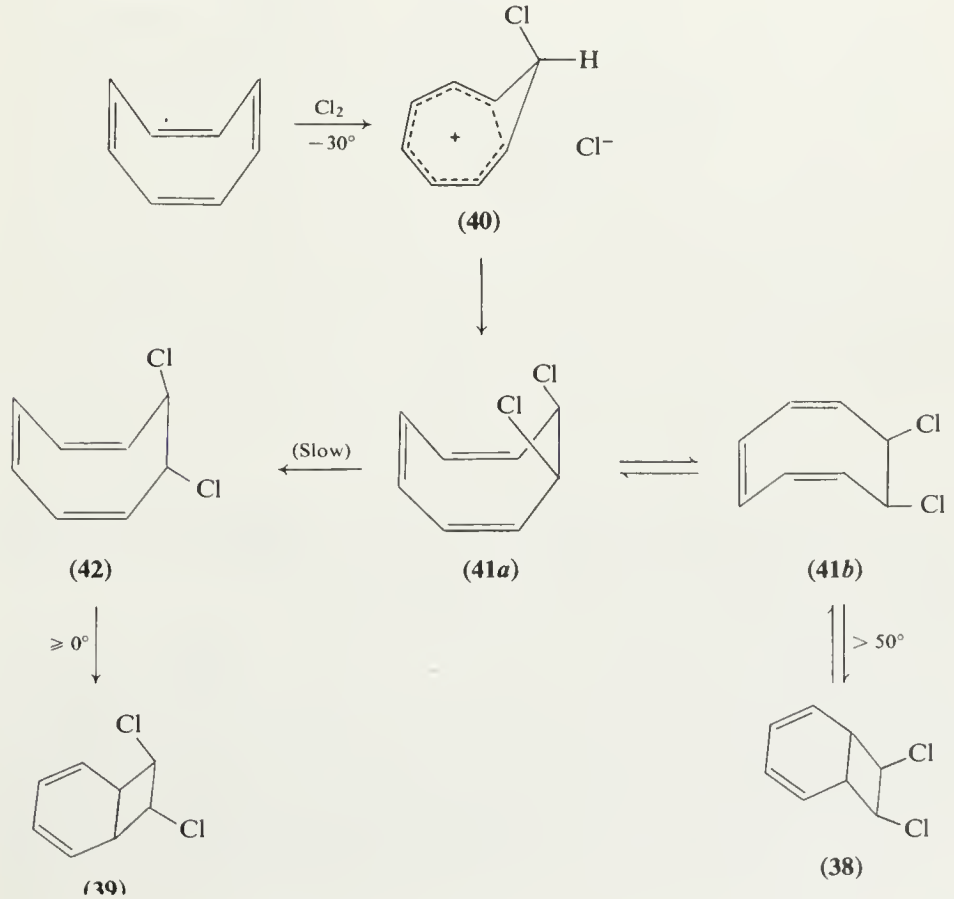


(**38**) (**39**)

(Chlorination of COT may also be accomplished with sulphuryl chloride (see p. 34).)

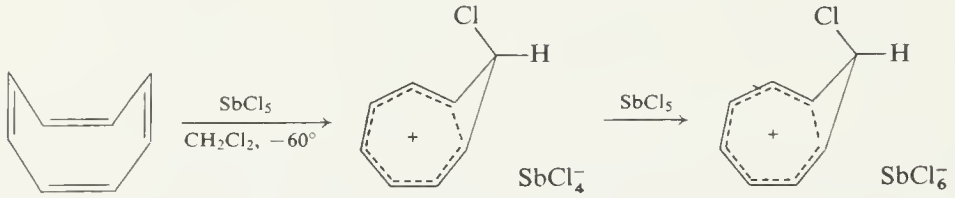
Careful examination of the chlorination reaction has been made by Huisgen *et al.*,[225,229,230] the multi-stage reaction being shown in scheme 10. The initial reaction apparently proceeds *via* the *endo*-8-chlorohomotropylium ion (**40**), which undergoes exclusive *endo*-attack by chloride ion to form the monocyclic *cis*-dichloride (**41***a* ⇌ **41***b*). Slow epimerisation of the *cis*- to the *trans*-

Scheme 10



dichloride (**42**) occurs, and at temperatures $\geq 0°$ irreversible valence isomerism leads to the bicyclic *trans*-dichloride (**39**). Above 50° the valence isomerisation (**41***b* $\rightleftharpoons$ **38**) is mobile, the equilibrium mixture containing 80% of the bicyclic *cis*-dichloride (**38**) at 70°.

In connection with these studies, it was found that COT reacts with two equivalents of antimony(v) chloride at low temperature to give the *endo*-8-chlorohomotropylium salt (**43**) (94%).[230]

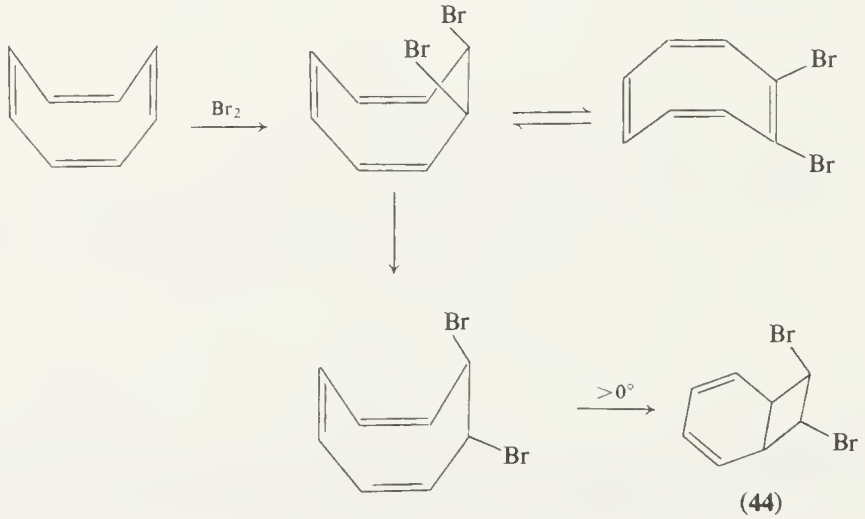


(43)

For tetra- and hexachlorides of COT, see ref. 11.

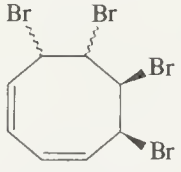
In the analogous bromination of COT, no bicyclic *cis*-dibromide is formed, the exclusive product above 0° being the *trans*-dibromide (**44**)[231] (scheme 11).

Scheme 11

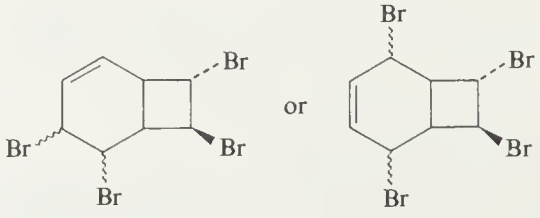


(44)

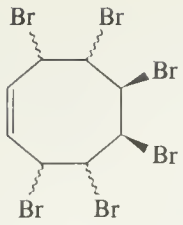
Further reaction with bromine gives tetra- and hexabromides,[11] the structures of which have been partially solved, and are illustrated below (each compound is likely to be a mixture of stereoisomers).[232]



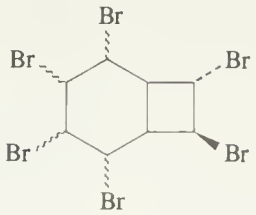
m.p. 144–145°



m.p. 87–88°

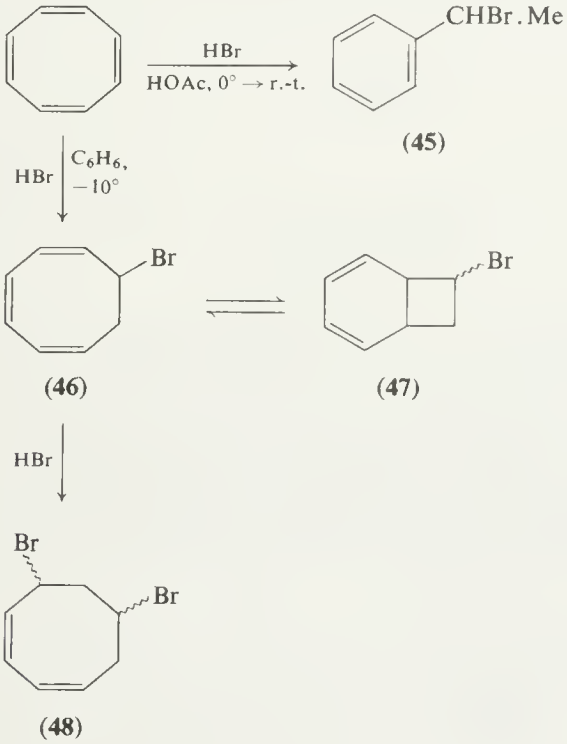


m.p. 150–151°



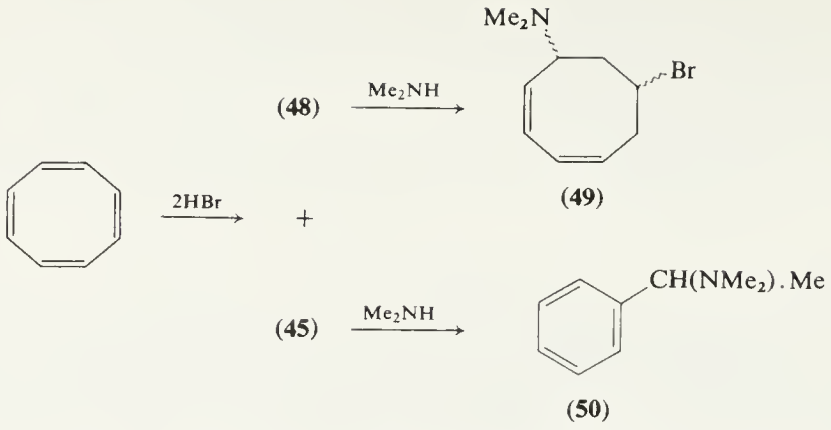
m.p. 97–98°

Hydrogen bromide. Reaction of COT with hydrogen bromide in acetic acid at 0° gives 1-bromoethylbenzene (**45**) (70%).[11] However, in benzene at −10° the product is 7-bromocyclo-octa-1,3,5-triene (**46**) (53%), isolated in admixture with its valence tautomer (**47**) (30%); addition of a further molecule of hydrogen bromide yields the dibromocyclo-octa-1,3-diene (**48**) (52%).[233] The

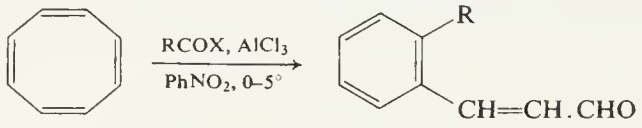


results obtained by Overberger *et al.*,[234] who employed two equivalents of hydrogen bromide (in benzene, or in the absence of solvent), and then treated the product with dimethylamine, may now be clarified (scheme 12). The principal product (68–69%) must have been derived from the dibromide (**48**), and may be assigned structure (**49**); the minor product (5–6%) was shown to have structure (**50**), arising from the benzylic bromide (**45**).

Scheme 12



Acylation. Reaction of COT with acetyl bromide or propionyl chloride in the presence of aluminium chloride results in the formation of *o*-alkylcinnamaldehydes (**51**) in very low yields (2–3%).[235]

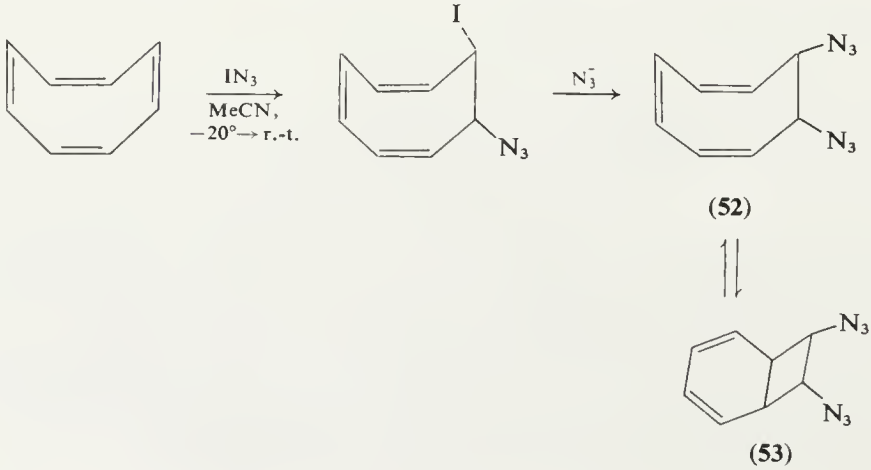


(**51**)

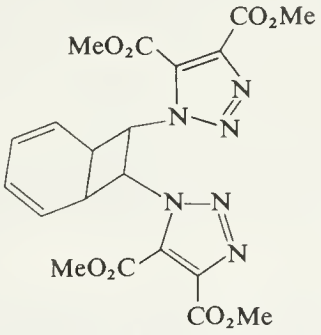
R = Me, X = Br
or R = Me.CH_2, X = Cl

Extensive polymerisation of COT is inevitable under these conditions. (For substitution of the iron tricarbonyl complex of COT, see pp. 82–3, 202.)

Iodine azide. Iodine azide, prepared *in situ* from iodine monochloride and an excess of sodium azide in acetonitrile, reacts with COT to form the *cis*-1,2-diazide (**52**) (80–90%); this is thought to arise from an initial *trans*-addition followed by S_N2 displacement of iodide ion.[236] The product (isolated as the

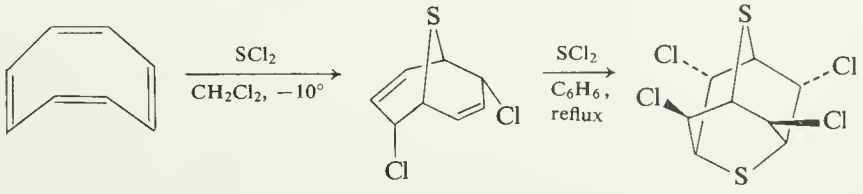


bicyclic valence isomer (**53**)) is an explosive oil, and was characterised as the adduct (**54**) resulting from 1,3-dipolar addition of the azide groups to dimethyl acetylenedicarboxylate.



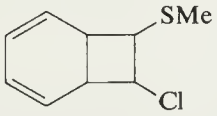
(**54**)

Sulphur dichloride. The addition of sulphur dichloride to COT at low temperature affords the sulphur-bridged product (**55**) (*ca.* 30%).[237,238] Reaction of this product with a second molecule of sulphur dichloride yields the dithia-adamantane (**56**) (20%).[237,238]

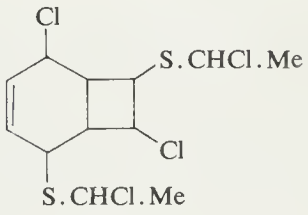


(**55**) (**56**)

Alkanesulphenyl chlorides. COT reacts with methanesulphenyl chloride in chloroform at −10° to give, in very high yield, a product formulated as (**57**).[239]



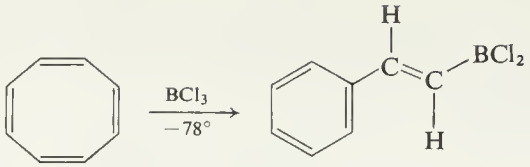
(**57**)



(**58**)

With two equivalents of 1-chloroethanesulphenyl chloride in tetrahydrofuran at room-temperature, there was obtained a crude product for which structure (**58**) was suggested.[240] In the absence of structural evidence, these formulations are doubtful (*cf.* ref. 241).

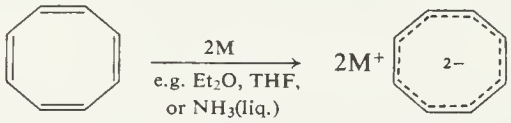
Boron trichloride. Boron trichloride reacts with COT at low temperature to yield the styryldichloroborane (**59**) (34%).[242]



(59)

8. Reduction, and reactions with nucleophiles

Reduction with metals. COT reacts with the alkali metals in e.g. ethers[11,243,244] or liquid ammonia[63,99] to form the planar 'aromatic' dianion (**60**) (see pp. 48–9).



(**60**)

M = Li, Na, K etc.

In the presence of less than two equivalents of alkali metal, an equilibrium is established with the radical anion (**61**).[243–246]

$$COT + COT^{2-} \rightleftharpoons 2COT^{\cdot-} \quad (61)$$

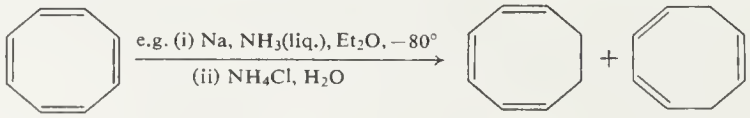
(The position of this equilibrium is controlled by ion-pairing, and is therefore dependent on the solvent (see p. 49).) The radical anion (**61**), which may also be generated by electrolytic reduction of COT (see p. 29), likewise appears to be planar, on the evidence of e.s.r.[243,246,247] and u.v.[248] spectroscopy, and of polarography[65,249] (see, however, ref. 75).

For the e.s.r. spectrum of the monodeuterio-system, see ref. 250.

For the formation of $COT^{\cdot-}$ by γ-irradiation of COT in a frozen matrix, see ref. 191.

The electron-transfer processes occurring in the reduction of COT to its dianion (**60**) have been examined in some detail (see e.g. refs. 65, 246, 251–255), and the species (**60**) and (**61**) have been the subject of numerous theoretical studies (see e.g. refs. 70, 122, 124, 125, 248, 256–258).

Protonation of the dianion (**60**), using water or alcohol, leads to mixtures of the cyclo-octatrienes (**62**) and (**63**); the systems which have been employed to generate COT^{2-} for this purpose include lithium–ether,[11,63] triphenylmethyl-sodium–ether,[259] sodium–liquid ammonia,[11,63] sodium–liquid ammonia–ether,[260] sodium–*N*-methylaniline–ether[7] and sodium–*N*-ethylaniline–ether.[261]



(**62**) (**63**)

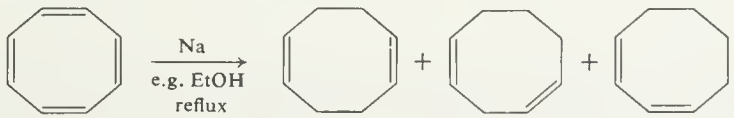
For the deuteriation of COT^{2-} with deuterium oxide, see p. 173.

For the reduction of octadeuteriocyclo-octatetraene, see ref. 262.

The relative proportions of the trienes (**62**) and (**63**) obtained after work-up are variable, since the 1,3,6-triene (**63**) may be converted into the 1,3,5-triene (**62**) in the presence of base.[63, 261] If the products are heated during work-up, further complications may arise from the thermal conversion of (**63**) into (**62**), which equilibrates with bicyclo[4.2.0]octa-2,4-diene (**64**) (see pp. 214–15).

(**63**) (**62**) (**64**)

Sodium in boiling alcohols reduces COT to a mixture of the cyclo-octadienes (**65**)–(**67**);[261, 263] the relative proportions of the products depend on the reaction temperature and the duration of heating, possibly owing to base-catalysed isomerisations.[263]



(**65**) (**66**) (**67**)

(The dienes (**65**)–(**67**) can be separated by selective extraction with aqueous silver nitrate[263].)

Zinc in aqueous–alcoholic sulphuric acid,[263] or in aqueous–alcoholic sodium hydroxide,[264] gives a mixture of the cyclo-octatrienes (**62**) and (**63**) in which the 1,3,6-triene predominates (up to 84 % yield[265]). In aqueous–alcoholic potassium hydroxide, however, the main product is apparently the 1,3,5-triene.[264]

Electrolytic reduction. The reduction of COT in aqueous ethanol, using a mercury cathode, affords a mixture of the cyclo-octatrienes (**62**) and (**63**), the 1,3,6-isomer predominating.[261] A controlled-potential electrolysis may be achieved in aqueous lithium chloride.[266] In dry *N*,*N*-dimethylformamide the almost exclusive product (after the addition of water) is the 1,3,5-triene (**62**).[65]

For the electrochemical behaviour of COT in aqueous sulphuric acid, see ref. 267.

The radical anion (**61**) may be generated electrochemically, and in e.g. dimethylformamide this species is stable to disproportionation (in the absence of alkali metal ions).[65, 268]

Mechanistic studies on the electrochemical reduction of COT are described in refs. 65, 75, 77, 79–82, 249, 269–273.

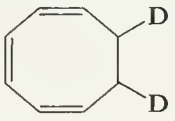
Catalytic hydrogenation. Hydrogenation of COT in the presence of platinum,[2, 3] palladium-on-carbon in glacial acetic acid,[11] Raney nickel in methanol,[274] or

with a chromium–nickel catalyst in methanol under pressure,[11] yields cyclo-octane. It is possible to limit the uptake of hydrogen to three equivalents, however, since the double bond of *Z*-cyclo-octene is unusually resistant to hydrogenation.[275,276] Thus with palladium-on-calcium carbonate in methanol,[11,277] Raney nickel in ethanol,[278] or Raney nickel alloy in aqueous sodium hydroxide,[264] *Z*-cyclo-octene can be isolated in good yields.

Hydrogenation of COT in the presence of $[(CPD)Cr(CO)_3]_2$* affords a mixture of the cyclo-octadienes (**65**)–(**67**) in the ratio 46:29:25.[279]

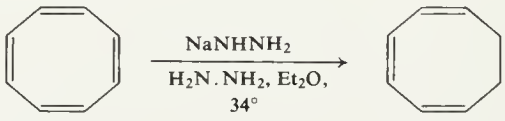
For the hydrogenation of COT in the presence of $[Co(CN)_5]^{3-}$, see ref. 280.

Catalytic deuteriation of COT in the presence of $(Ph_3P)_3RhCl$ leads to the dideuteriocyclo-octa-1,3,5-triene (**68**).[281]



(**68**)

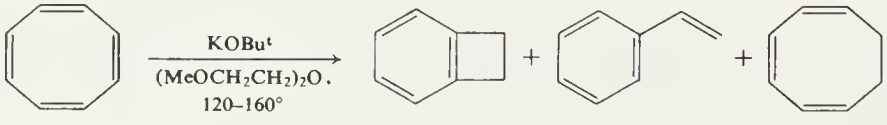
Sodium hydrazide. Reduction of COT with sodium hydrazide in the presence of hydrazine gives cyclo-octa-1,3,5-triene (**62**) (85%), apparently uncontaminated with the 1,3,6-triene (**63**).[282]



(**62**)

Alkali metal alkoxides. Although COT is stable towards alkali metal alkoxides at room-temperature, reaction begins to occur above *ca.* 110°.[283]

With potassium t-butoxide in diglyme, COT affords a mixture of products containing benzocyclobutene (**69**) (up to 44%), styrene and cyclo-octa-1,3,5-triene.[8,9]

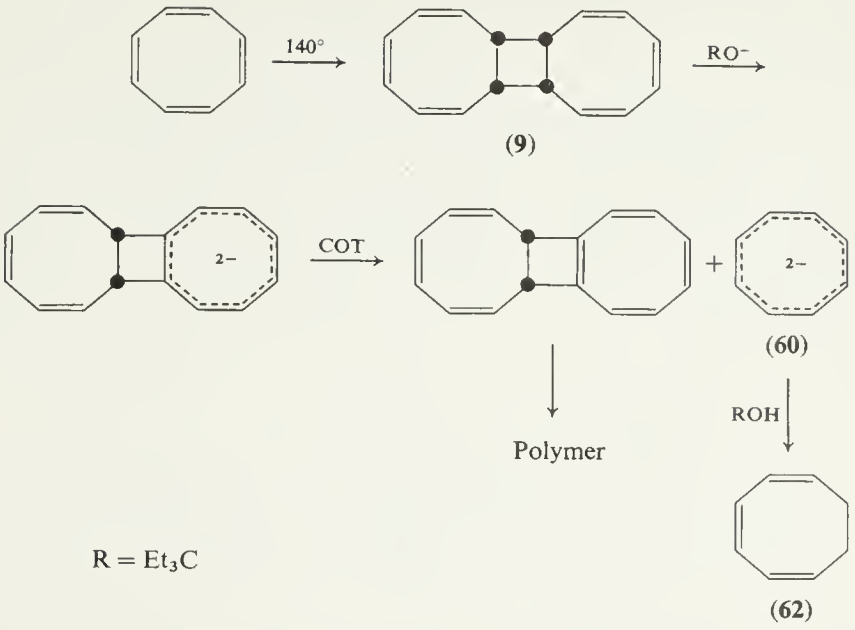


(**69**)

Reaction of COT with potassium triethylmethoxide in triethylmethanol at 140° gives cyclo-octa-1,3,5-triene (up to 30%), together with polymeric material.[283,284] Schröder[283] has proposed that deprotonation of the COT dimer now known to possess structure (**9**) is followed by electron-transfer to COT, protonation of the dianion (**60**) then leading to the cyclo-octatriene (**62**) (scheme 13).

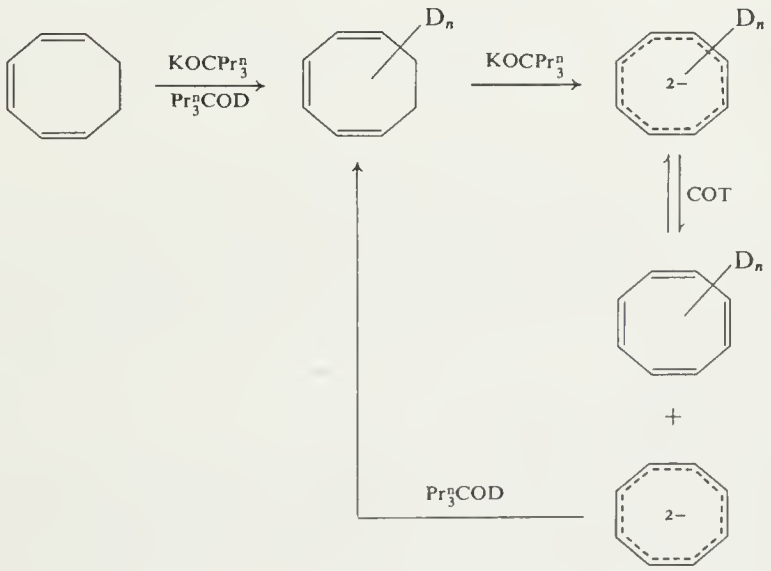
* CPD = cyclopentadienyl.

Scheme 13



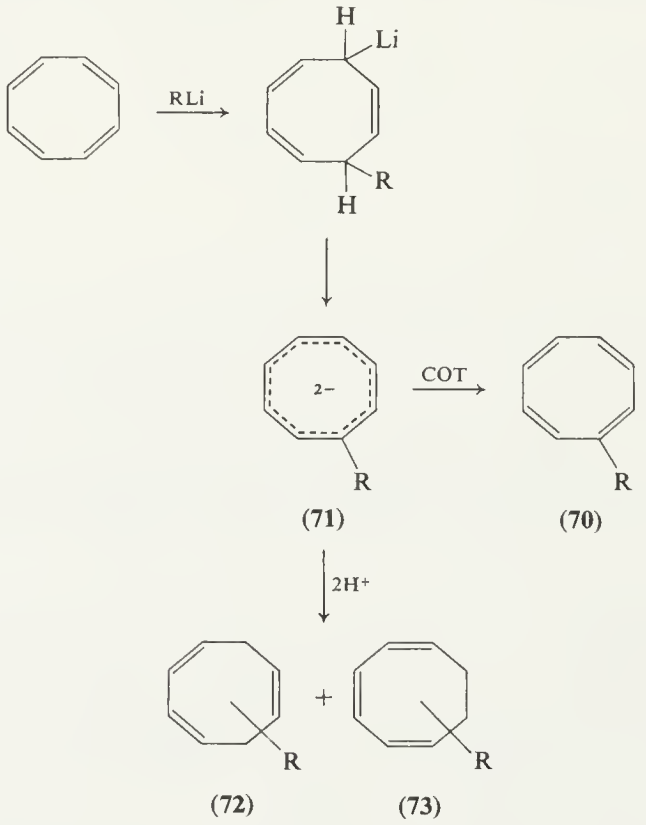
If a mixture of COT and potassium tripropylmethoxide in Pr^n_3COD, together with cyclo-octa-1,3,5-triene, is kept at 65° for a prolonged period, the recovered COT is found to be deuteriated; base-catalysed deuterium-exchange in cyclo-octa-1,3,5-triene, followed by proton-abstraction, is thought to result in deuteriated COT^{2-}, which by electron-transfer yields deuteriated COT[284] (scheme 14). (This deuteriation of COT is also catalysed by dimer (9)[284].)

Scheme 14



Organo-compounds of lithium, sodium and magnesium. Alkyl- or aryl-lithiums, or phenylsodium, react with COT in ether to afford, after aqueous work-up, low yields (up to *ca.* 30%) of alkyl- or arylcyclo-octatetraenes (**70**) (see p. 80), together with cyclo-octatrienes and their substituted derivatives.[285,286] With n-butyl- or s-butyl-lithium in pentane, only butylcyclo-octatrienes are obtained (18% and 24% respectively).[286] These reactions may proceed *via* the substituted dianion (**71**), which by electron-transfer to COT could generate substituted COTs (**70**), and by protonation could form substituted cyclo-octatrienes (**72**) and (**73**) (scheme 15).

Scheme 15



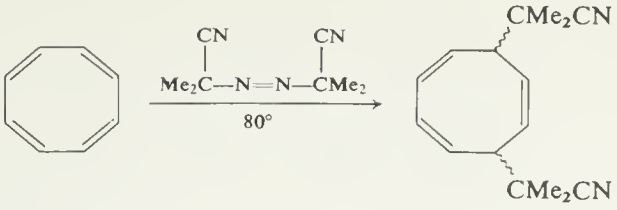
R = Et, Bu^n, Bu^s, Ph, *p*-$Me_2N.C_6H_4$

The reaction with phenylmagnesium bromide in ether gives a 45% yield of biphenyl (together with cyclo-octatrienes); in a control experiment only 6.6% of biphenyl was formed by a coupling reaction during the preparation of the Grignard reagent.[285]

9. Reactions with free radicals

The reactivity of COT towards methyl[287] and ethyl[288] radicals has been measured.

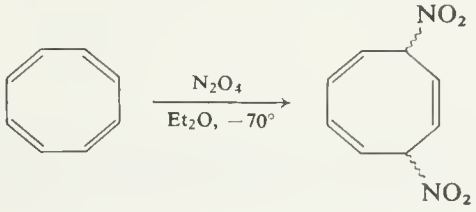
With α-cyanoisopropyl radicals, generated from azobis(isobutyronitrile) at



(74)

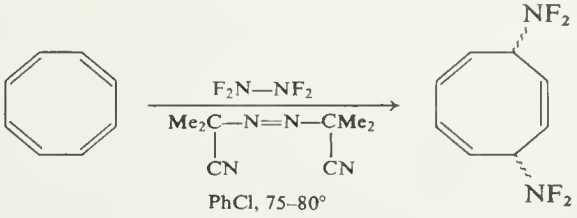
80°, COT forms the 5,8-disubstituted cyclo-octa-1,3,6-triene (**74**) (5.5%).[289]

Reaction with dinitrogen tetroxide at low temperature produces the dinitro-compound (**75**) (33%).[290]



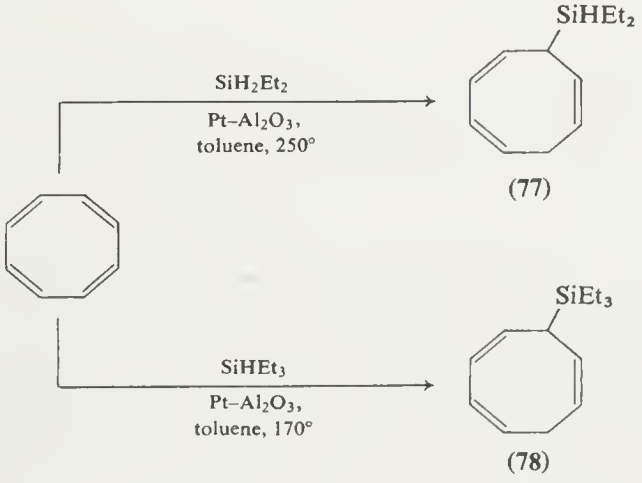
(75)

The analogous product (**76**) (65–70%) is obtained by the action of difluoroamino radicals, generated from tetrafluorohydrazine.[291]



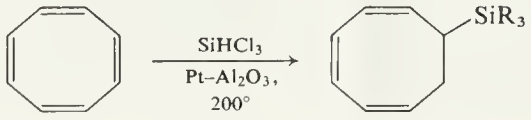
(76)

The stereochemistry of the products (**74**)–(**76**) is not certain, but the substituent groups are likely to adopt a *trans*-relationship (see refs. 289–291).



The reaction of diethyl- or triethylsilane with COT in the presence of a platinum catalyst results in similar 1,4-addition to give the products (**77**) (26%) and (**78**) (21%) respectively (together with other, ill-defined compounds).[292]

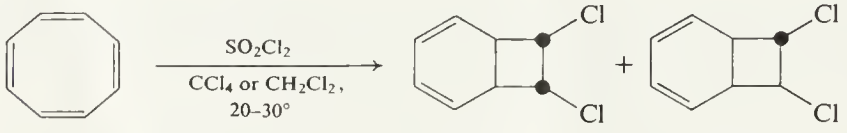
Trichlorosilane, however, affords the 1,2-addition product (**79*a***) (33%) characterised as the triethyl-derivative (**79*b***) obtained by reaction with ethylmagnesium bromide.[292]



(**79**)

a: R = Cl
b: R = Et

The chlorination of COT with sulphuryl chloride, which is assumed to proceed *via* a free-radical mechanism, gives a mixture of the bicyclic dichlorides (**38**) and (**39**) (*ca.* 4:1, total yield 68.5%).[11,228]



(**38**) (**39**)

Further reaction with sulphuryl chloride yields tetrachloro-derivatives.[11]

10. Polymerisation

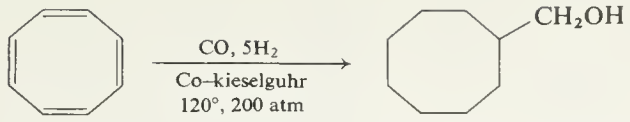
Unwanted polymers are frequently encountered in reactions of COT, which forms polymeric material on heating,[11] u.v. irradiation,[179] or mere storage[1,2,11] (even under nitrogen[60]). A wide variety of reagents, including air,[11] aluminium chloride,[235] tetranitromethane[293] and sodium,[294] can induce polymer formation.

COT inhibits the bulk polymerisation of vinyl monomers (initiated by dibenzoyl peroxide); a long induction period is followed by the formation of polymer in which COT is incorporated.[288]

11. Carbonylation

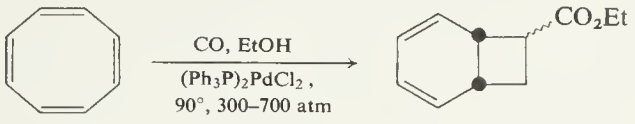
Reppe *et al.*[11] reported that COT reacts with carbon monoxide in the presence of $Ni(CO)_4$ and water (at 270° and 200 atm) to give a mixture of carboxylic acids, but the products were not characterised.

Hydroformylation of COT, using carbon monoxide and five equivalents of hydrogen in the presence of a cobalt catalyst, affords cyclo-octylmethanol (**80**).[11]



(80)

Carbon monoxide in the presence of ethanol and $(Ph_3P)_2PdCl_2$ gives the bicyclic ester (**81**) (33%).[295]



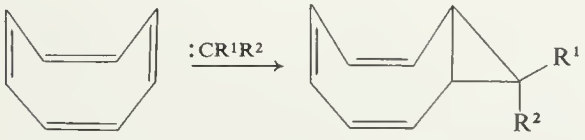
(81)

12. Cycloadditions

The following cycloaddition reactions of COT are classified according to the scheme devised by Huisgen.[296]

2 + 1 → 3

Carbenes, nitrenes etc. The reaction of carbenes $:CR^1R^2$ with COT affords



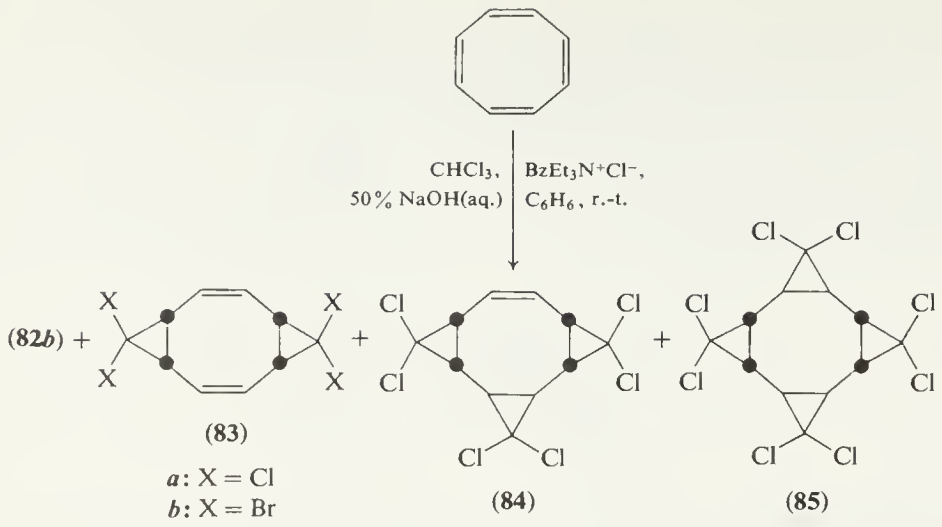
(82)

a: $R^1 = R^2 = H$
b: $R^1 = R^2 = Cl$
c: $R^1 = R^2 = Br$
d: $R^1 = R^2 = CN$
e: $R^1 = H, R^2 = Cl$
f: $R^1 = Cl, R^2 = H$
g: $R^1 = H, R^2 = Me$
h: $R^1 = CO_2Et, R^2 = H$
i: $R^1 = H, R^2 = CO_2Et$
j: $R^1 = CO_2Me, R^2 = H$
k: $R^1 = H, R^2 = CO_2Me$

bicyclo[6.1.0]nona-2,4,6-trienes (**82**) (2:1, 3:1 and 4:1 adducts may result from further addition of the carbene (see below)).

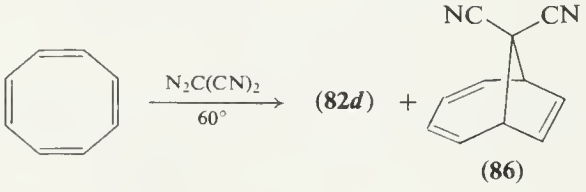
The parent hydrocarbon (**82*a***) is best produced by using di-iodomethane in the presence of a zinc-copper couple;[297,298] an alternative procedure employs diazomethane in the presence of copper(I) chloride (yield 25–30%).[299]

Dichloro- or dibromocarbene, generated from chloroform or bromoform and potassium t-butoxide, gives the adduct (**82*b***) or (**82*c***) respectively, allegedly in good yield.[297] The use of chloroform and aqueous sodium hydroxide in the presence of a phase-transfer catalyst leads to a mixture of the 1:1 (**82*b***) (22–24%),[300,301] 2:1 (**83*a***) (16–25%),[300,301] 3:1 (**84**) (10%)[301] and 4:1 (**85**) (3%)[301] adducts (see also ref. 302). The 2:1 dibromocarbene-adduct (**83*b***) has



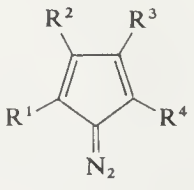
been prepared by a similar procedure.[303]

Thermally-generated dicyanocarbene (from dicyanodiazomethane) in COT forms the adduct (**82*d***) (70%),[304] together with a smaller yield of the isomer (**86**);[305] these 1,2- and 1,4-additions apparently result from singlet and triplet dicyanocarbene respectively.[305]

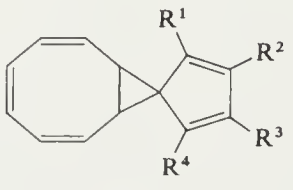


COT reacts with dichloromethane in the presence of methyl-lithium to give a *ca.* 3:1 mixture of the *syn-* and *anti*-compounds (**82*e***) and (**82*f***) (30–56%).[306, 307] It was reported, however, that these products were formed only when the methyl-lithium solution had been prepared from methyl bromide; if the reagent was derived from methyl iodide, the reaction product (obtained in low yield) was the *syn*-9-methyl-derivative (**82*g***).[307]

The copper-catalysed decomposition of ethyl diazoacetate in COT gives mainly the *anti*-9-ethoxycarbonyl-derivative (**82*h***) (40%);[308–311] the ratio of *anti-* to *syn*-product, (**82*h***):(**82*i***), is 19:1.[312] The corresponding methyl esters, (**82*j***) and (**82*k***), may be prepared similarly.[313, 314]



(87)

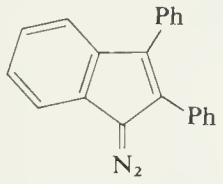


(88)

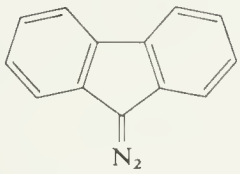
Table 6

	R^1	R^2	R^3	R^4	Yield (%) of (**88**)	Ref.
a	H	H	H	H	40–50	315
b	H	Ph	Ph	Ph	23	316

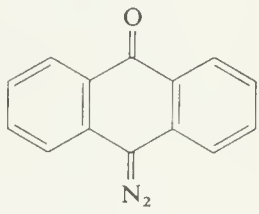
Photolysis of the diazocyclopentadienes (**87**) in COT leads to the spiro-compounds (**88**) in moderate yields[315,316] (table 6). Similar products are formed from the diazo-compounds (**89**)–(**91**)[316] (table 7).



(**89**)



(**90**)

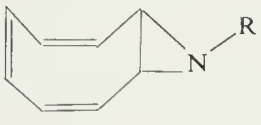


(**91**)

Table 7

Carbene precursor	Yield (%) of adduct	Ref.
(**89**)	32	316
(**90**)	42	316
(**91**)	27	316

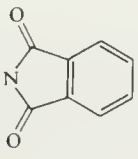
Cyanonitrene, generated thermally from cyanogen azide at *ca.* 80°, reacts with COT to form a mixture of the labile 1,2-addition product (**92*a***) and the more stable 1,4-adduct (**93**).[317,318] (In a side reaction, cyanogen azide itself reacts with COT to give compound (**94**) (see p. 42).) The product composition varies with the solvent, and with concentration, and it is believed that the 1,2-adduct results from the singlet nitrene while the 1,4-adduct is produced by a two-step process from triplet nitrene[317] (*cf.* the addition of $:C(CN)_2$, p. 36).

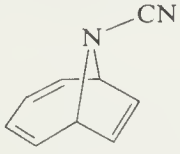


(**92**)

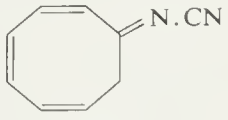
a: R = CN
b: R = CO_2Et

c: R =





(**93**)

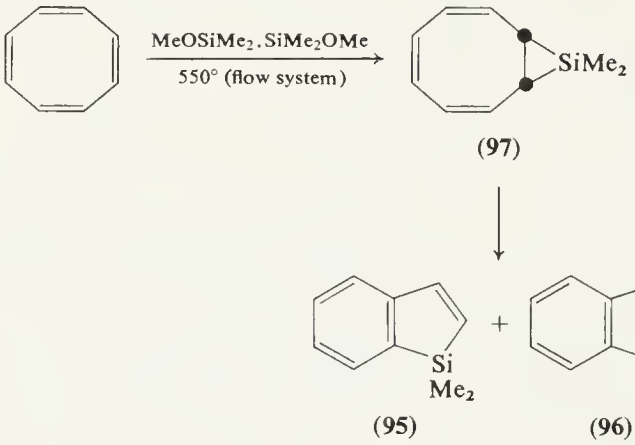


(**94**)

Ethoxycarbonylnitrene (from *N*-(*p*-nitrobenzenesulphonyloxy)urethan and triethylamine) and COT furnish the 1,2-adduct (**92***b*) (35–40%).[319]

Lead(IV) acetate oxidation of *N*-aminophthalimide in an excess of COT produces the analogous product (**92***c*) (42%).[320]

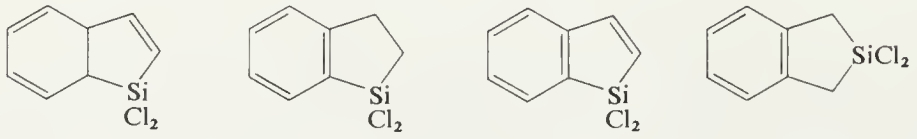
COT reacts with the disilane $MeOSiMe_2.SiMe_2OMe$ at 550° to give the products (**95**) (30%) and (**96**) (15%); the reaction probably occurs *via* the $:SiMe_2$-adduct (**97**)[321] (*cf.* the thermal rearrangement of bicyclo[6.1.0]nonatrienes (**82**), p. 264).



(**97**)

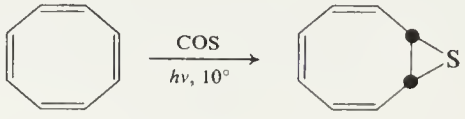
(**95**) (**96**)

With hexachlorodisilane, at the same temperature, a mixture of the products (**98**) (8%), (**99**) (13%), (**100**) (17%) and (**101**) (7%) is obtained.[322]



(**98**) (**99**) (**100**) (**101**)

Sulphur. Sulphur atoms, generated by photolysis of carbonyl sulphide, allegedly add to COT to form the thi-iran (**102**)[323] (but see appendix).

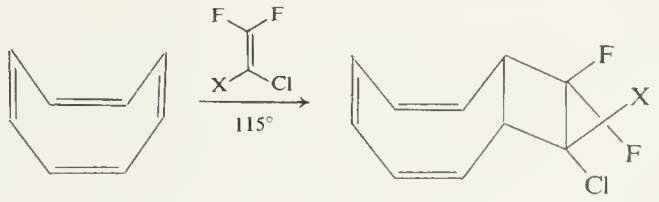


(**102**)

2 + 2 → 4

Dimerisation. The thermal [2 + 2] dimerisation of COT has already been described (see p. 11). 'Mixed' dimers are formed in very low yields by the reaction of COT with monosubstituted COTs (see pp. 101–2).

Polyhaloethylenes. 1,1-Dichloro-2,2-difluoroethylene[324] and 1-chloro-1,2,2-trifluoroethylene[325] add to COT at *ca.* 115° to give low yields of the bicyclo-[6.2.0]deca-2,4,6-trienes (**103**) (table 8).

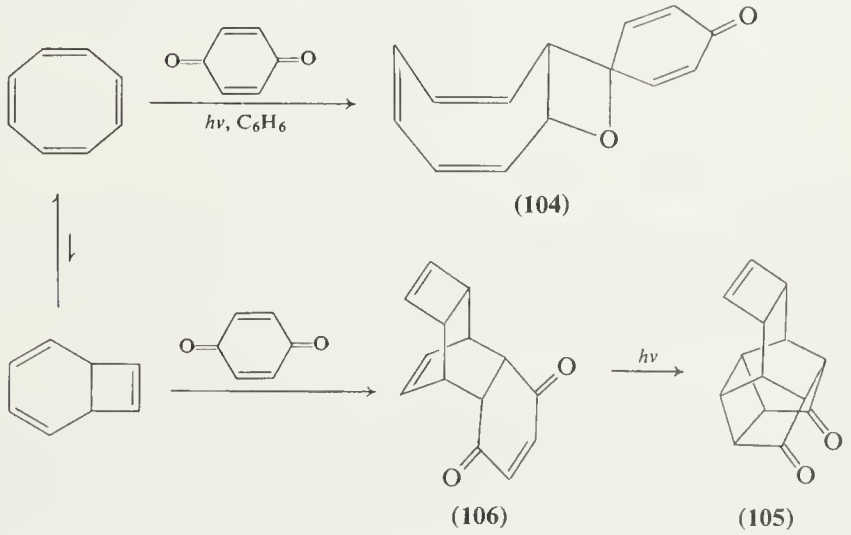


(**103**)

Table 8

	X	Yield (%)	Ref.
a	F	8	325
b	Cl	7	324

p-Benzoquinone. The photo-addition of *p*-benzoquinone to COT gives a product formulated as the oxetan (**104**) (up to 30%),[326,327] although this structure has been disputed (see p. 46). A by-product (*ca.* 3% yield) of the photo-reaction is the cage-compound (**105**), presumably arising from the thermal Diels–Alder adduct (**106**) (see pp. 42–3).

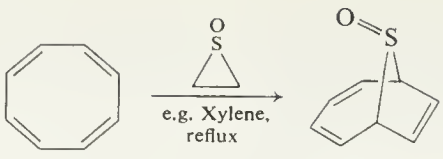


(**104**)

(**106**) (**105**)

4 + 1 → 5

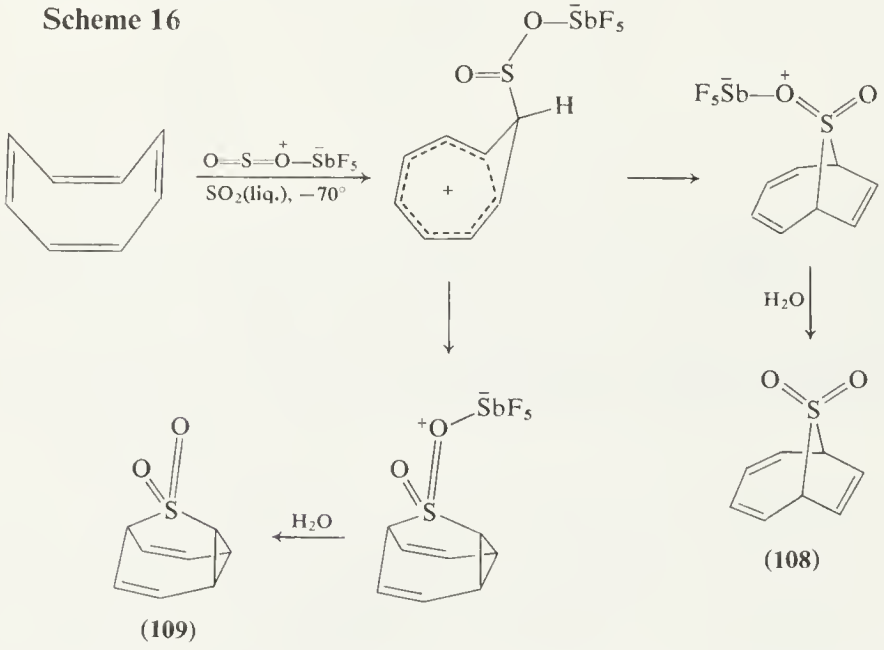
Sulphur monoxide. Sulphur monoxide, generated by the thermolysis of ethylene sulphoxide, reacts with COT to form the 1,4-adduct (**107**) (single stereoisomer; 15–30%).[47,328]



(107)

Sulphur dioxide. COT does not undergo reaction with sulphur dioxide under normal conditions, but in the presence of antimony(v) fluoride in liquid sulphur dioxide at −70°, the adduct (**108**) is formed (95%) (after aqueous work-up).[48] Careful control of the hydrolysis conditions enables up to 12% of 9-thiabarbaralane 9,9-dioxide (**109**) to be isolated.[54] The suggested mechanistic routes to these products are shown in scheme 16.

Scheme 16



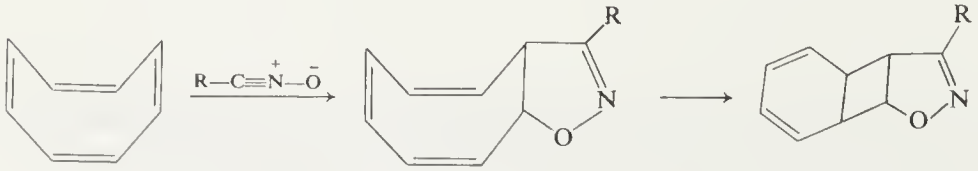
(108)

(109)

Triplet carbenes and nitrenes. The formation of the 1,4-adducts (**86**) and (**93**), from dicyanocarbene and cyanonitrene respectively, has already been described (see pp. 36, 37).

2 + 3 → 5

1,3-*Dipolar reagents.* Nitrile oxides reacts with COT at 0–20° to give, initially, 1:1 adducts of structure (**110**), which by valence isomerisation yield the tricyclic products (**111**)[329–333] (table 9). Adduct (**111***c*) reacts further with

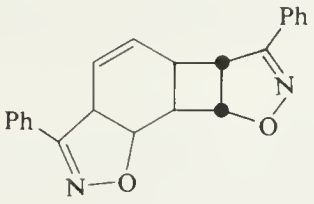


(110) **(111)**

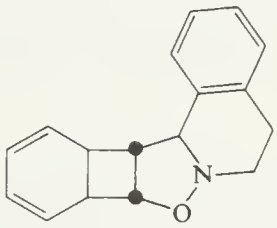
Table 9

	R	Yield (%) of (**111**)	Ref.
a	H	8	329, 333
b	Me	38	331
c	Ph	83, (50)	330, (331), 332
d	*p*-Br.C_6H_4	70	331
e	*m*-NO_2.C_6H_4	75	331

benzonitrile oxide; structure (**112**) has been suggested for the major product.[331]



(**112**)

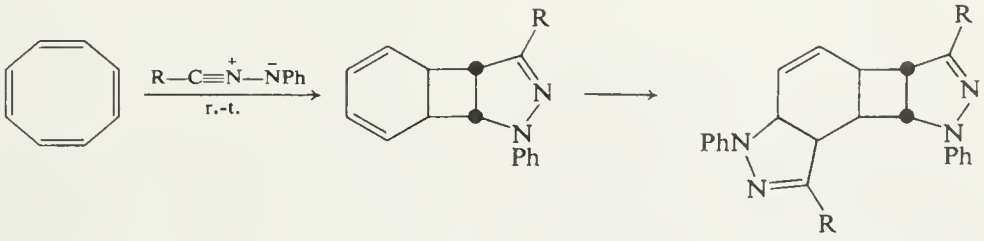


(**113**)

(For other reactions of the system (**111**), see refs. 331, 332, 334.)

Reaction of COT with the nitrone 3,4-dihydroisoquinoline *N*-oxide, at 65°, gives the adduct (**113**) (50%).[335]

Nitrile imines react in a similar fashion, affording 1:1 adducts (**114**); however, 2:1 adducts (**115**) result unless a large excess of COT is present[336] (table 10).



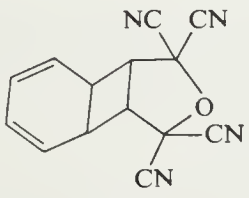
(**114**) (**115**)

Table 10

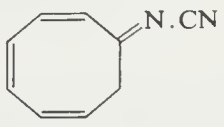
	Yield (%)	
R	(**114**)	(**115**)
Ph	62	65
p-Cl.C_6H_4	68	50[a]

[a] Two isomeric 2:1 adducts isolated.

COT reacts with tetracyanoethylene oxide at 80° to form the adduct (**116**) (28%).[337]



(**116**)

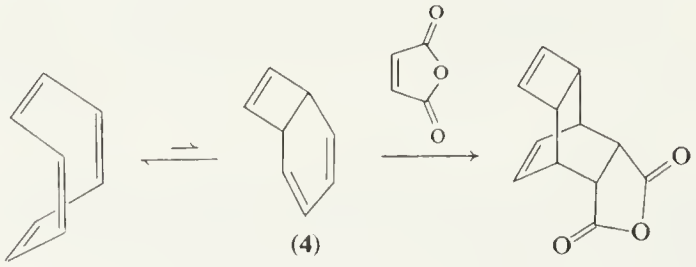


(**94**)

Cyanogen azide reacts with COT at room-temperature, with slow evolution of nitrogen, to give compound (**94**) (73%);[317] the initial reaction is almost certainly a 1,3-dipolar addition (*cf.* ref. 338).

4 + 2 → 6

Dienophiles. Although the 'tub' conformation of COT does not provide the near-planar diene system necessary for a concerted [4 + 2] (Diels–Alder) cycloaddition, such a system is available in the valence tautomer bicyclo[4.2.0]-octa-2,4,7-triene (**4**);* reaction of COT with e.g. maleic anhydride thus leads



(**4**) (**117**)

Table 11

Dienophile	Solvent	Temp. (°C)	Yield (%)	Ref.
Acrylic acid	—	180–200	29	11
'Acrylic ester'	—	—	—	345
Acrylonitrile	Chlorobenzene	180	13	39
Fumaroyl chloride	—	130–140	73	340
Maleic anhydride	*o*-Dichlorobenzene	160–170	82	11
N-Phenylmaleimide	*o*-Dichlorobenzene	Reflux	87	346
Tetracyanoethylene[a]	Benzene	Reflux	92, (63)	134, (347)
Dicyanomaleimide	Dioxan	100	—	134, 135
p-Benzoquinone[b]	*o*-Dichlorobenzene	140	—	11
2,3-Dichloro-5,6-dicyano-*p*-benzoquinone	Benzene	Reflux	—	350
1,4-Naphthoquinone	Xylene	Reflux	16[c]	11
Benzoylacetylene	—	140–150	30[d]	351
Dimethyl acetylene-dicarboxylate	—	150–155	51	352
	—	100	82	353
Diethyl acetylene-dicarboxylate	—	160–170	—	11
Dicyanoacetylene	THF	56	17	354

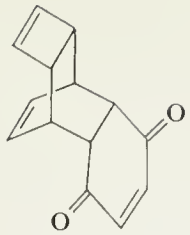
[a] For the reaction of 1,4-dideuteriocyclo-octatetraene with tetracyanoethylene, see ref. 49.

[b] At 140–150° in benzene under 30 atm of nitrogen a 2:1 adduct is formed;[11] since the *endo*-stereochemistry of the 1:1 adduct (**106**) has been proved by photo-caging[348] (see p. 330), the stereochemistry of the 2:1 adduct may be represented as (**118**), by analogy with related compounds (*cf.* ref. 349).

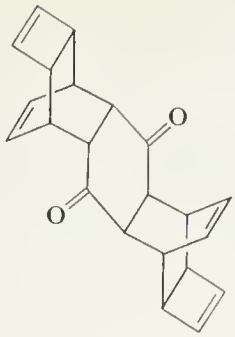
[c] The isolated product was the dehydro-derivative (**119**).

[d] The isolated product was benzophenone (see pp. 343–4).

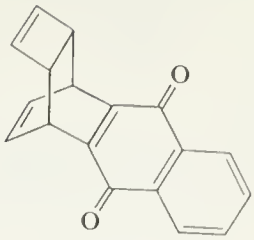
* For reactions of dienophiles with isolated bicyclo[4.2.0]octa-2,4,7-triene, see refs. 32, 40.



(106)



(118)



(119)

to the adduct (**117**).[11,135] The stereochemistry of this product, the evidence[135,339–343] for which has culminated in an X-ray structure determination,[344] is that which would be expected to result from *endo*-addition of the dienophile to the less hindered face of the diene system.

Similar adducts, possessing the basic tricyclo[4.2.2.$0^{2,5}$]decane skeleton of compound (**117**), are produced from the dienophiles listed in table 11.

U.v. irradiation of maleic anhydride in an excess of COT at 8° gives a 12% yield of the Diels–Alder adduct (**117**).[355,356] In a similar dark (thermal) reaction the yield of the product is 3%, and the difference has been ascribed to the production of bicyclo[4.2.0]octa-2,4,7-triene (**4**) by photo-isomerisation of COT.[356]

The reaction of benzyne (generated from benzenediazonium-2-carboxylate at *ca.* 40°) with COT is complex. The products (combined yield 25%) include the 1:1 adducts (**120**), (**121**) and (**122**), phenanthrene and 9,10-dihydro-9-phenylphenanthrene (**123**) (major product).[357] The proposed routes to these products are outlined in scheme 17. The reaction appears to be very sensitive to metal catalysis, and in the presence of e.g. silver fluoroborate the adduct

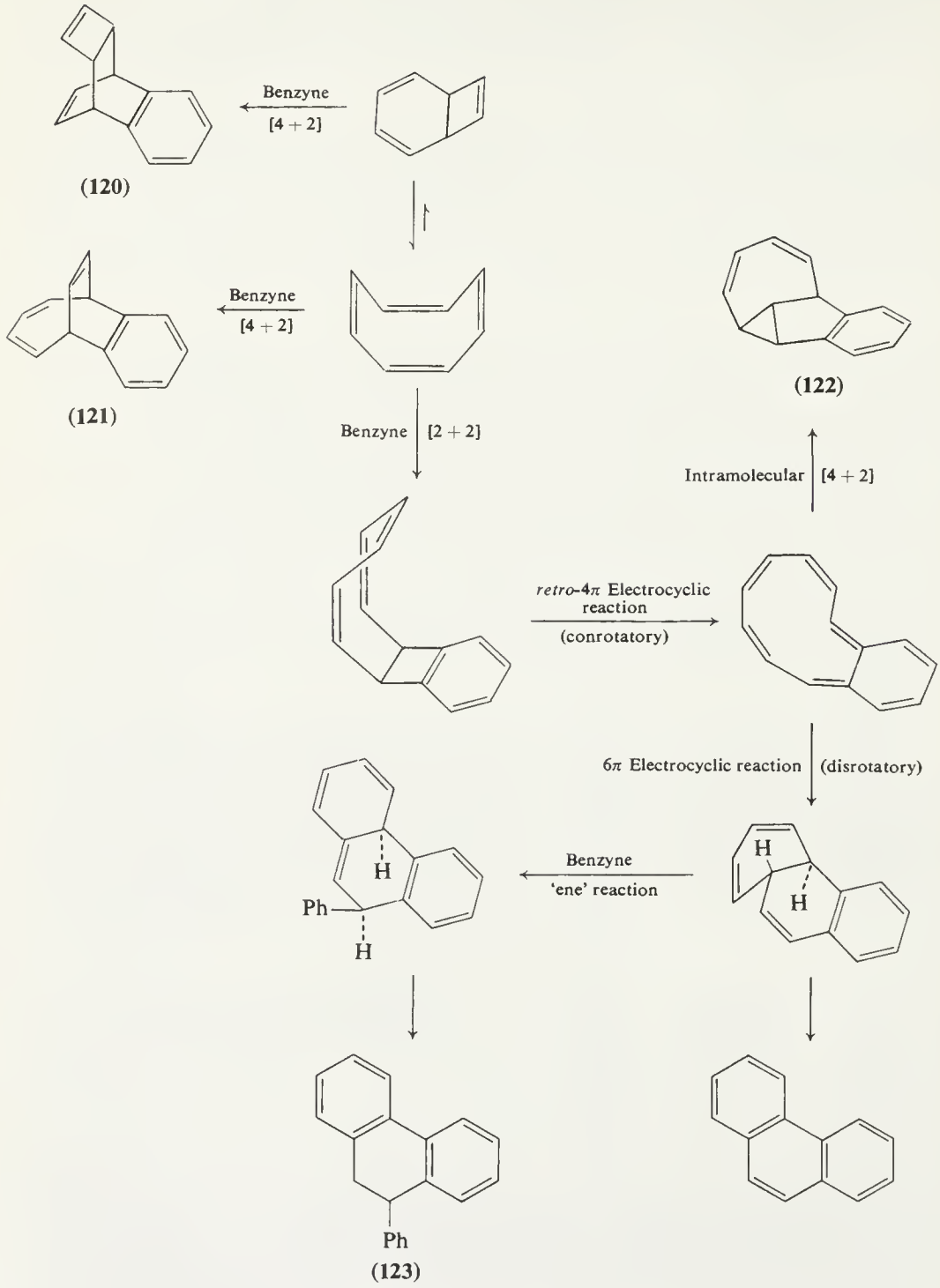
Table 12 (see scheme 17)

Catalyst	Ratio (**123**):(**122**)	Relative yield (%) (**120**)	(**121**)	(**122**)	Phenanthrene	Biphenylene
—	26:1	28	31	12	14	14
$AgBF_4$	1:11	6	8	80	1	1

(**122**) predominates[358] (table 12). It has been suggested[359,360] that a benzyne–silver complex is involved in the silver-catalysed reaction, and the steps leading to the adduct (**122**) have been visualised as shown in scheme 18.[360]

When COT is heated with poor dienophiles, such as vinylene carbonate or citraconic anhydride, its rate of dimerisation exceeds that of the addition to the valence tautomer (**4**), and the isolated products are derived from COT dimers (see pp. 365, 369).

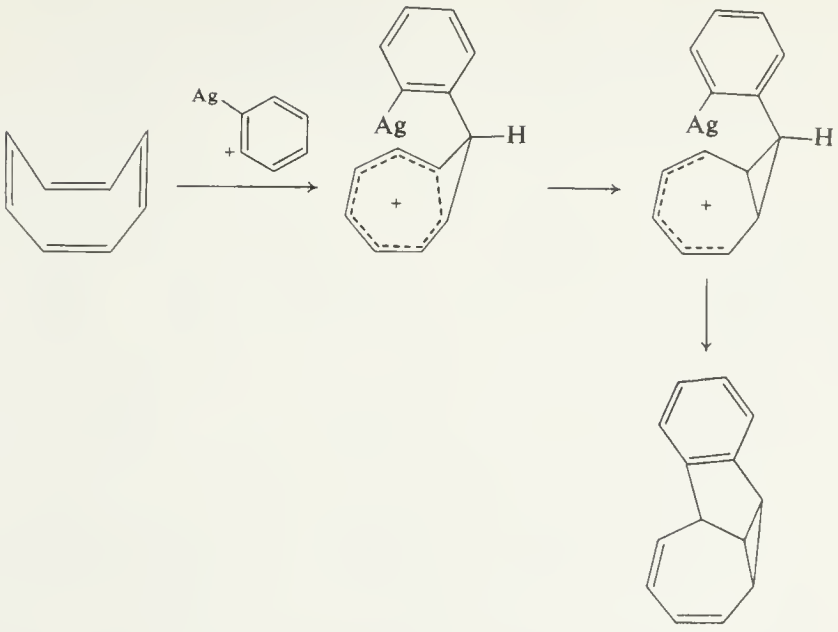
Scheme 17



COT reacts slowly at 100° with bis(trifluoromethyl)ketene to give the adduct (**124**).[361]

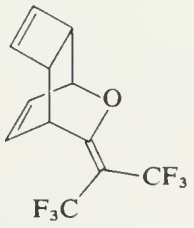
With 4-phenyl-1,2,4-triazoline-3,5-dione at 100°, a 1:1 mixture of the iso-

Scheme 18



(122)

meric adducts (**125*a***)[362] and (**126*a***)[363] is produced (total yield up to 63%[364]). At room-temperature in benzene or acetone, however, the adduct (**126*a***) is formed almost exclusively[363] (37%[364]). Huisgen *et al.*[364] have postulated



(124)

(scheme 19) that the formation of the 1,4-addition product (**126*a***) proceeds *via* the zwitterion (**127*a***); at room-temperature the production of adduct (**125*a***), which requires the intermediacy of bicyclo[4.2.0]octa-2,4,7-triene (**4**), is suppressed.

Exclusive 1,4-addition to COT occurs with chlorosulphonyl isocyanate, which affords the adduct (**128**) (up to 73%).[365–367] Initial electrophilic attack on COT is again proposed.[366]

A similar reaction takes place with the *N*-sulphonylurethan (**129**), generated from the oxathiadiazine (**130**) at 80°; the product (formed in low yield) is the 1,4-adduct (**131**).[368]

Scheme 19

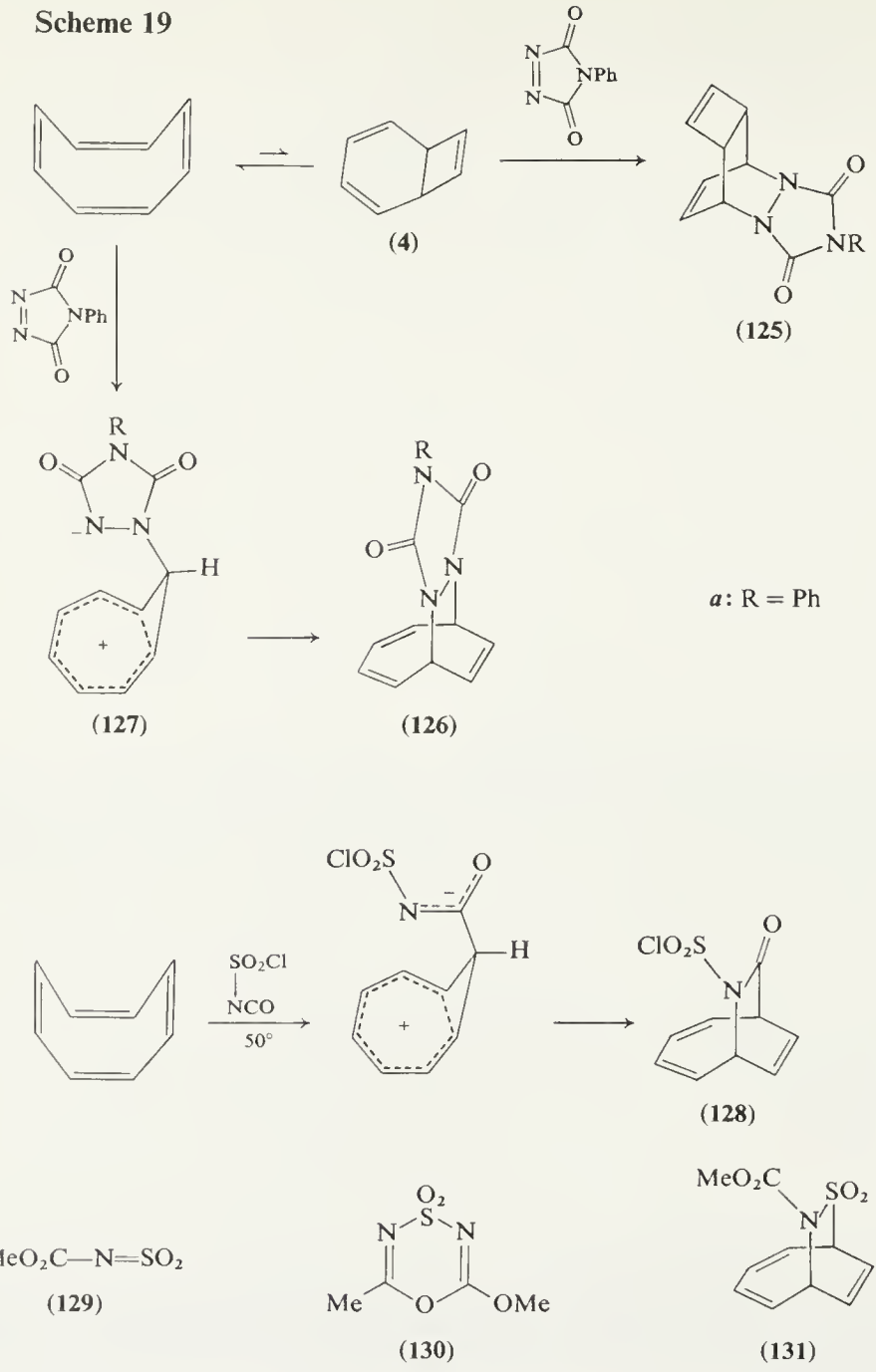
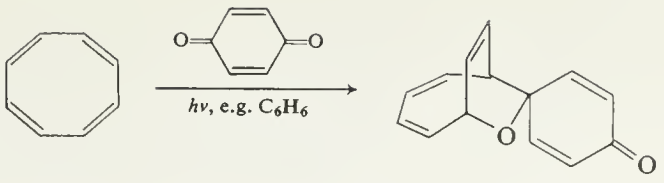
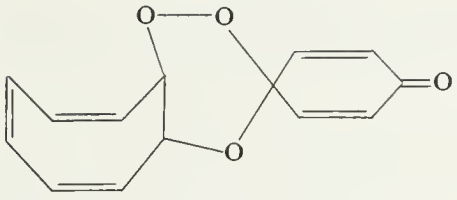


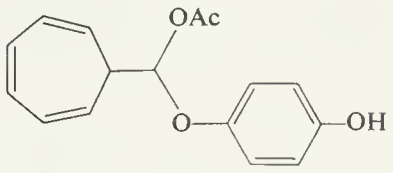
Photo-addition. The photo-addition of *p*-benzoquinone to COT, using an argon ion-laser, yields the adduct (**132**) (77%), and the authors[369,370] dispute structure (**104**) for the product obtained by conventional irradiation (see p. 39); it is not certain, however, that the two photo-adducts are identical. In the presence of air, the adduct (**132**) (31%) is accompanied by the peroxide (**133**) (49%); in glacial acetic acid the products are (**134**) (58%) and (**135**) (26%).[369,370]



(132)



(133)



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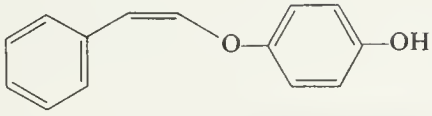
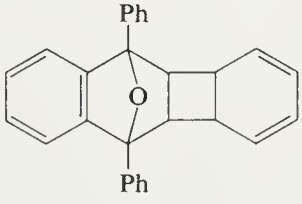


(135)

2 + 4 → 6

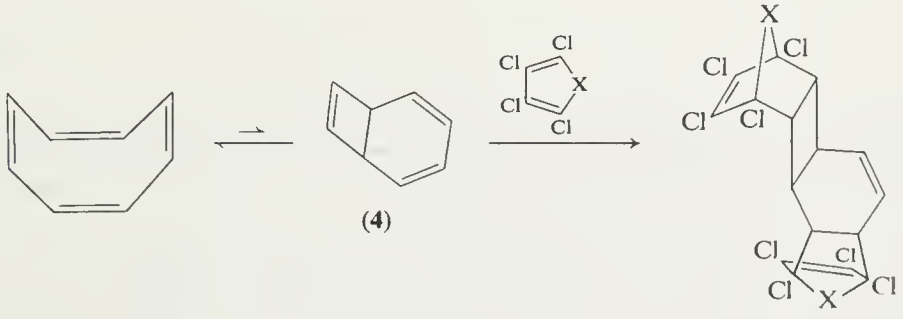
Electron-deficient dienes. COT functions as a dienophile towards electron-deficient diene systems, probably *via* its valence tautomer (**4**).

With 1,3-diphenylbenzo[*c*]furan, two isomeric products (presumably *endo*- and *exo*-adducts) of structure (**136**) are formed.[371]



(136)

Tetrachlorocyclopentadienone ketals at 100–150° give 2:1 adducts of structure (**137**) (table 13); no 1:1 adducts could be isolated.[372]



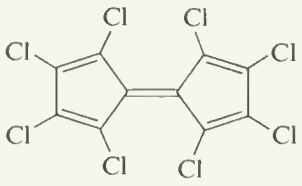
(4)

(137)

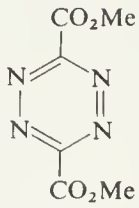
Table 13

	X	Conditions	Yield (%)
a	$C(OMe)_2$	Xylene, reflux	27
b		*ca.* 100°	65

Reactions of COT with octachlorofulvalene (**138**),[373] and with the tetrazine (**139**),[374] have been reported, but the structures of the products are not known.



(**138**)



(**139**)

13. Reactions with metals and their derivatives

COT can bond to metals in an unparalleled variety of ways. It may act, not only as an electron-donor, but also as an acceptor, and its high affinity for electrons is reflected in its reactions with electropositive metals to form ionic compounds containing the dianion COT^{2-}. In some transition metal complexes, the eight-membered ring flattens completely to become an *octahapto*-system which approximates to the planar dianion. In other cases, however, COT retains its 'tub' conformation and acts as a mono-olefin, or a chelating 1,5-diene (1,2,5,6-*tetrahapto*)- system. Yet again, the COT ligand may adopt intermediate conformations in which the ring is partly flattened, and behave as a 1,3-diene (1,2,3,4-*tetrahapto*-) or a 1,3,5-triene (1,2,3,4,5,6-*hexahapto*-) system. In addition, examples of σ-bonding and π-allyl bonding are known in COT–metal compounds. In its multinuclear complexes containing metal–metal bonds, more complicated bonding systems may occur, and the C_8H_8 ligand is sometimes transformed from the monocyclic tetraene into a different species.

Group IA

The alkali metals. COT reacts with lithium,[11,63,244] sodium,[11,63] potassium[99,244,375] and rubidium[376] in ethers, liquid ammonia or hexamethylphosphoramide to form salts of type (**140**).

$$\text{COT} \xrightarrow[\text{e.g. } Et_2O,\ THF,\ \text{or } NH_3(\text{liq.})]{2M} 2M^+\ COT^{2-} \quad (\mathbf{140})$$

M = Li, Na, K, Rb

(For preparative procedures, see e.g. refs. 377, 378 (dilithium salt in ether); 379 (dipotassium salt in 1,2-dimethoxyethane); 380, 381 (dipotassium salt in tetrahydrofuran); 382 (dipotassium salt in liquid ammonia).)

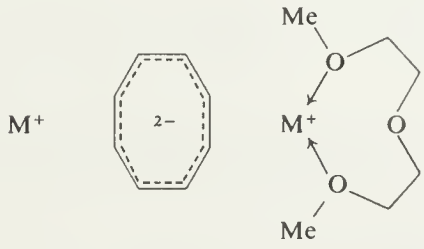
Solutions of these alkali metal derivatives are also produced by electron-transfer to COT from the species (**141**)[259] and (**142**).[383]

$Na^+ (Ph_3C)^-$ (**141**)

$2K^+ (Ph_2C—CPh_2)^{2-}$ (**142**)

The alkali metal cyclo-octatetraenides may be obtained as crystalline solvates (see e.g. refs. 244, 375, 384–386); in solution (in various ethers) they appear to exist as contact ion-pairs.[376] (For the solubilities of the sodium and potassium salts in tetrahydrofuran and hexamethylphosphoramide, see ref. 387.)

The spectra of the cyclo-octatetraenides are consistent with the presence of a planar monocyclic dianion (D_{8h} symmetry),[99,244,245,375] and X-ray crystallographic studies confirm the planarity of COT^{2-} in the solvated derivatives (**143**).[385,386]



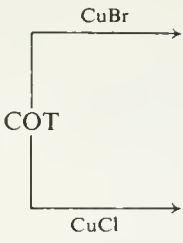
(**143**) *a*: M = K; *b*: M = Rb

The COT dianion obeys the Hückel $(4n + 2)$ rule; moreover, it sustains a diamagnetic ring-current.[244] The addition of two electrons to the non-planar COT molecule is thus attended by ring-flattening, the electrons entering the non-bonding π-orbital of a planar 'aromatic' Hückel-system, the resonance energy of which must be more than sufficient to compensate for the compressional strain involved in flattening the ring. (For theoretical studies on COT^{2-}, see e.g. refs. 122, 124, 125, 248, 257.)

Group IB

Copper, silver, gold. The formation of crystalline addition compounds of COT by the action of aqueous silver nitrate, or ammoniacal copper(I) chloride, was first mentioned by Reppe *et al.*[11]

COT reacts readily with finely-ground copper(I) chloride and bromide (best in the presence of e.g. benzonitrile), or with solutions of these halides in acrylonitrile. Under these conditions copper(I) bromide affords the 1:1 complex (**144***a*), while copper(I) chloride forms the 1:2 compound (**145***a*).[388]



(COT)CuX (**144**) *a*: X = Br; *b*: X = Cl

(COT)$(CuX)_2$ (**145**) *a*: X = Cl; *b*: X = CF_3CO_2

A 1:2 complex (**145*b***) results (65%) from the reaction of COT with copper(I) trifluoroacetate.[389]

$$\text{COT} \xrightarrow[C_6H_6,\ \text{r.-t.}]{Cu(OCOCF_3)} \textbf{(145}b\textbf{)}$$

Reduction of copper(II) halides with sulphur dioxide in the presence of COT gives complexes of the type (**144**)[390] (table 14). However, slight alterations

$$\text{COT} \xrightarrow[EtOH,\ 0°]{CuX_2,\ SO_2} \textbf{(144)}$$

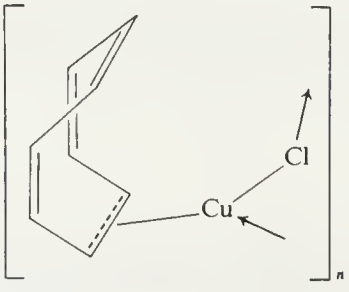
Table 14

	X	Yield (%)
a	Br	76
b	Cl	55

in the reaction conditions may lead to the formation of type (**145**) products;[390] complex (**145*a***) (79%) results when triphenyl phosphite is employed as the reducing agent.[391]

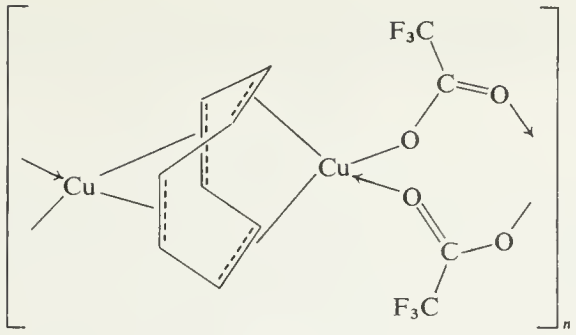
$$\text{COT} \xrightarrow[MeOH,\ \text{r.-t.}]{CuCl_2.2H_2O,\ (PhO)_3P} \textbf{(145}a\textbf{)}$$

The structure of (COT)CuCl (**144*b***) contains chains of –Cu–Cl– units, with only one double bond of COT interacting closely with each copper atom: the carbon atoms of the co-ordinated double bond, the associated copper atom and the attached chlorine atoms are approximately co-planar.[392]



(**144*b***)

In contrast, the i.r. spectrum of (COT)$(CuCl)_2$ (**145*a***) indicates that all four of the COT double bonds are equivalent;[391] the suggested structure for (COT)$[Cu(OCOCF_3)]_2$ (**145*b***) incorporates bridging or chelating trifluoroacetate groups.[389]



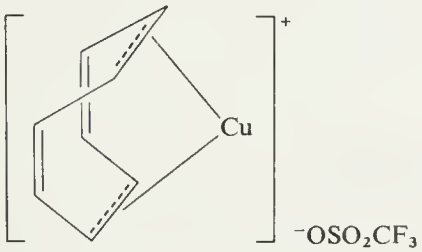
(**145***b*)

Reaction of COT with the benzene complex of copper(I) trifluoromethanesulphonate affords the cationic species (**146**) (86%).[393,394] The structural

$$\text{COT} \xrightarrow[\text{EtCOMe}]{\text{(Benzene) } [Cu(OSO_2CF_3)]_2} [(\text{COT})\text{Cu}]^+ \ {}^-OSO_2CF_3$$

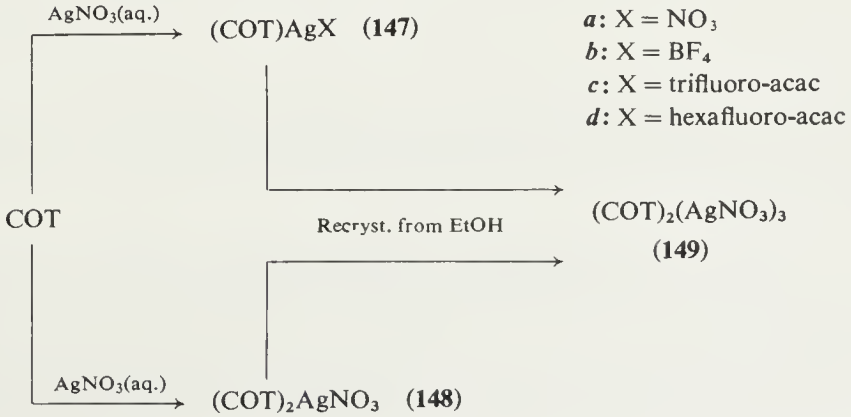
(**146**)

evidence indicates that in (**146**) the COT forms a 1,2,5,6-*tetrahapto*-system, but that rapid intermolecular ligand-exchange occurs in solution at normal temperatures.[393–395]



(**146**)

COT reacts readily with silver nitrate to give 1:1 (**147***a*) or 2:1 (**148**) complexes; both of these products disproportionate when heated, forming a 2:3

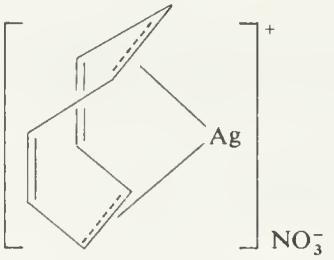


complex (**149**).[63] With silver tetrafluoroborate, only the 1:1 complex (**147*b***) is produced, the reaction being insensitive to the COT:salt ratio.[396]

$$\text{COT} \xrightarrow[\text{e.g. Toluene, } 0^\circ]{AgBF_4} \textbf{(147}b\textbf{)}$$

If COT is treated with aqueous silver nitrate followed by the sodio-derivative of trifluoro- or hexafluoroacetylacetone, the complex (**147*c***) (52%) or (**147*d***) (34%) is precipitated.[397]

X-ray studies show that (COT)$AgNO_3$ (**147*a***) contains a tub-shaped COT ring, bound to silver *via* two non-adjacent double bonds.[398,399] In the crystal,



(**147*a***)

these units form infinite chains by longer-range interactions. (For spectra of (**147*a***), see ref. 99; for ^{13}C n.m.r. shifts of COT in the presence of silver nitrate, see ref. 400.) The p.m.r. spectra of the complexes (**147*c***) and (**147*d***) show a singlet resonance for the COT protons, presumably due to rapid exchange of COT in solution.[397]

Treatment of COT with gold(I) or gold(III) chloride affords the complexes (**150**) (84%) or (**151**) (75%).[401]

$$\text{COT} \xrightarrow[CH_2Cl_2,\ -45^\circ]{AuCl} \text{(COT)AuCl} \quad \textbf{(150)}$$

$$\text{COT} \xrightarrow[SO_2(\text{liq.}),\ -78^\circ \rightarrow -40^\circ]{AuCl_3} \text{(COT)}Au_2Cl_4 \quad \textbf{(151)}$$

Group IIA

Magnesium. COT reacts with magnesium in tetrahydrofuran, in the presence of a catalytic amount of magnesium bromide; the solvated cyclo-octatetraenide (**152**) separates.[402]

$$\text{COT} \xrightarrow[\text{THF, } 20^\circ]{Mg,\ MgBr_2} \text{(COT)Mg.2}\tfrac{1}{2}\text{THF} \quad \textbf{(152)}$$

Group IIIA

The lanthanides. COT reacts with dipyridinium hexachlorocerate(IV), with

the elimination of hydrogen chloride, to give the compound (**153**) (40%)[403] (*cf.* titanium, zirconium and hafnium (below) and molybdenum (p. 59)).

$$\text{COT} \xrightarrow[C_6H_6,\ \text{reflux}]{(PyH^+)_2[CeCl_6]^{2-}} (C_8H_7)_2CeCl_2 \quad (\mathbf{153})$$

The addition of COT to a solution of europium or ytterbium in liquid ammonia yields the cyclo-octatetraenide (**154**).[404]

$$\text{COT} \xrightarrow[NH_3(\text{liq.})]{2M} (\text{COT})M \quad (\mathbf{154})$$

a: M = Eu
b: M = Yb

The presence of M^{2+} ions in these products is indicated by the e.p.r. spectrum of (**154*a***) and the diamagnetism of (**154*b***).[404]

The actinides. At *ca.* 150°, COT reacts with finely-divided thorium, uranium or plutonium (prepared from the hydrides) to afford the bis(cyclo-octatetraene) compound (**155**) (up to 57%); the reaction is catalysed by mercury vapour.[405]

$$\text{COT} \xrightarrow[Hg,\ 150^\circ]{M} (\text{COT})_2M \quad (\mathbf{155})$$

M = Th, U, Pu

(For the structure of complexes of this type, see p. 186.)

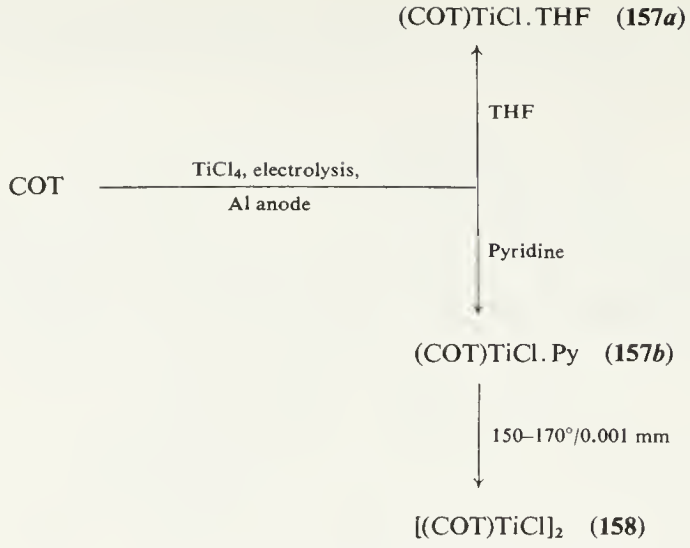
Group IVA

Titanium, zirconium, hafnium. The tetrachlorides of titanium, zirconium and hafnium react thermally with COT to form supposedly σ-bonded bis(cyclo-octatetraenyl) species (**156**) (92–95%), hydrogen chloride being eliminated[406] (*cf.* cerium (above) and molybdenum (p. 59)).

$$\text{COT} \xrightarrow[C_6H_6,\ \text{reflux}]{MCl_4} (C_8H_7)_2MCl_2 \quad (\mathbf{156})$$

M = Ti, Zr, Hf

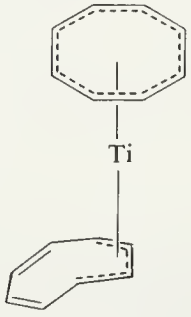
The electrochemical reduction of titanium(IV) chloride in tetrahydrofuran containing COT, using an aluminium anode, leads to the solvated complex (**157*a***) (68%); with pyridine as the solvent the same compound may be isolated as the pyridinate (**157*b***) (77%), which when heated under reduced pressure loses its co-ordinated solvent to form the dimeric species (**158**).[407]



Preliminary electrochemical reduction of titanium(IV) chloride, followed by further electrolysis in the presence of COT, produces bis(cyclo-octatetraene)-titanium (**159**) (45%).[407]

$$\text{COT} \xrightarrow[\text{Al anode, THF}]{\text{TiCl}_3\text{, electrolysis}} (\text{COT})_2\text{Ti} \quad (\mathbf{159})$$

In this product (**159**) the titanium atom is attached symmetrically to one (planar) eight-membered ring, but is bonded to the other (non-planar) ring *via* four carbon atoms only.[408] (For the i.r. spectrum, see ref. 409.)



(**159**)

In solution, a fluxional process has been detected (by variable-temperature n.m.r. studies), in which the planar and non-planar rings exchange their respective conformations; if the planar ring is a COT dianion, the conformational change involves an intramolecular redox reaction, in which two electrons are transferred from one ligand to the other.[410]

$$(\text{COT})^{2-}\text{Ti}(\text{COT}) \rightleftharpoons (\text{COT})\text{Ti}(\text{COT})^{2-}$$

The analogous zirconium complex (**160**) is formed (15%) by electrolytic reduction of zirconium(IV) chloride in the presence of COT when a magnesium anode is used, but with an aluminium anode the dichloride (**161**) is obtained

$(COT)_2Zr$ **(160)**

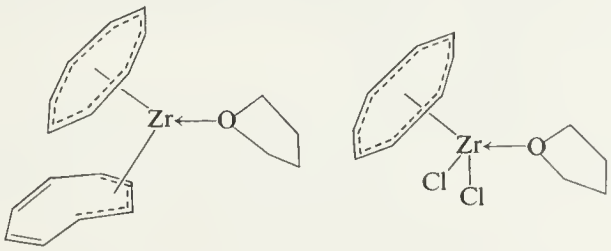
Mg anode

COT — $ZrCl_4$, electrolysis, THF

Al anode

$(COT)ZrCl_2.THF$ **(161)**

(83%).[402,411] The structure of the tetrahydrofuranate of the zirconium complex (**160**) has been established as (**160*a***), again featuring one planar and one non-planar COT ring;[412] the structure of the dichloride (**161**) is as shown.[413]

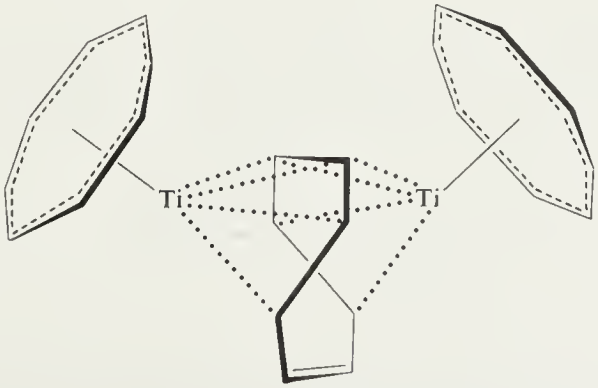


(160*a*) **(161)**

The use of titanium(IV) butoxide in the electrosynthesis leads to another type of complex (**162**) (27%).[407]

$$COT \xrightarrow[\text{Al anode, THF}]{\text{Ti(OBu)}_4\text{, electrolysis}} (COT)_3Ti_2 \quad \textbf{(162)}$$

In this product (**162**), each titanium atom is bonded symmetrically to a planar eight-membered ring and to four carbon atoms of a central non-planar ring, in a double sandwich structure.[414,415] The same product (**162**) also results



(162)

(80%) when COT reacts with titanium(IV) butoxide in the presence of triethylaluminium; however, the use of a large excess of COT in this reaction produces $(COT)_2Ti$ (**159**) (80%), since $(COT)_3Ti_2$ reacts with COT.[416]

$$COT \xrightarrow[80°]{Ti(OBu)_4,\ Et_3Al} \underset{\textbf{(162)}}{(COT)_3Ti_2} \xrightarrow[80°]{COT} \underset{\textbf{(159)}}{(COT)_2Ti}$$

The zirconium complex (**160**) may be obtained (65%) by a similar process.[417]

$$COT \xrightarrow[Toluene,\ -45°\rightarrow\ 90°]{Zr(OBu)_4,\ Et_3Al} (COT)_2Zr \quad \textbf{(160)}$$

It should be noted, however, that the triethylaluminium used must be free from diethylaluminium hydride, which with zirconium(IV) butoxide and COT produces the complex hydride (**163**).[417]

$$COT \xrightarrow{Zr(OBu)_4,\ Et_2AlH} (COT)ZrH_2 \quad \textbf{(163)}$$

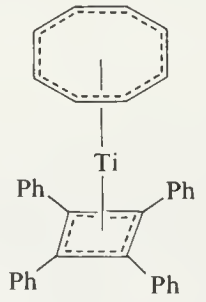
Treatment of COT with tetra-allylzirconium also leads to (**160**) (98%).[417]

$$COT \xrightarrow[45\text{–}55°]{(CH_2{=}CHCH_2)_4Zr} (COT)_2Zr \quad \textbf{(160)}$$

Reaction of titanium(III) chloride with isopropylmagnesium bromide in the presence of COT and diphenylacetylene gives the complex (**164**) (11%).[418]

$$COT \xrightarrow[\substack{PhC{\equiv}CPh,\ Et_2O,\\ -78°\rightarrow r.\text{-}t.}]{TiCl_3,\ Pr^iMgBr} (COT)Ti(C_4Ph_4) \quad \textbf{(164)}$$

The structural evidence suggests that the product (**164**) is a sandwich compound containing a tetraphenylcyclobutadiene ligand.[418]

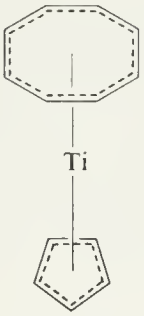


(164)

Electrolysis of $(CPD)TiCl_3$, or (better) $(CPD)_2TiCl_2$, in the presence of COT gives the 'mixed' complex (**165**) (25%).[407]

$$\text{COT} \xrightarrow[\text{Al anode, THF}]{\text{e.g. } (\text{CPD})_2\text{TiCl}_2,\ \text{electrolysis}} (\text{COT})\text{Ti}(\text{CPD}) \quad \textbf{(165)}$$

This is known to be a sandwich compound containing planar ligands.[419]



(165)

(For the e.p.r. spectrum, see ref. 420; for the photo-electron spectrum, see ref. 421.)

Group VA

Vanadium, niobium, tantalum. For ion-molecule reactions of $(\text{CPD})\text{V}(\text{CO})_4$ with COT, see ref. 422.

COT reacts with $[\text{Li}(\text{THF})_4]^+[\text{Ph}_6\text{Ta}]^-$ to give the ionic complex (**166**) (23%), readily convertible to (**167**) (80%).[423]

$$\text{COT} \xrightarrow[\text{THF, reflux}]{[\text{Li}(\text{THF})_4]^+[\text{Ph}_6\text{Ta}]^-} [\text{Li}(\text{THF})_4]^+[(\text{COT})_3\text{Ta}]^- \quad \textbf{(166)}$$

$$[\text{Li}(\text{THF})_4]^+[(\text{COT})_3\text{Ta}]^- \xrightarrow[\text{EtOH, r.-t.}]{[\text{Ph}_4\text{As}]^+\text{Cl}^-} [\text{Ph}_4\text{As}]^+[(\text{COT})_3\text{Ta}]^- \ \textbf{(167)}$$

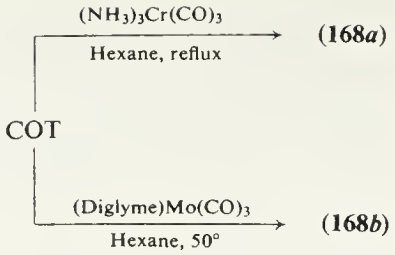
Group VIA

Chromium, molybdenum, tungsten. COT displaces acetonitrile from $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ to give the carbonyl complex (**168*a***) (9%);[424] the analogous molybdenum and tungsten compounds (**168*b***)[424] and (**168*c***)[425,426] may be obtained in a similar manner (37% and 28% respectively). In related processes,

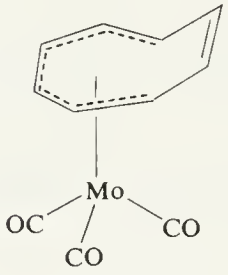
$$\text{COT} \xrightarrow[\text{Hexane, reflux}]{(\text{MeCN})_3\text{M}(\text{CO})_3} (\text{COT})\text{M}(\text{CO})_3 \quad \textbf{(168)}$$

a: M = Cr
b: M = Mo
c: M = W

COT reacts with $(\text{NH}_3)_3\text{Cr}(\text{CO})_3$ to give (**168*a***) (20%),[427] and with (diglyme)$\text{Mo}(\text{CO})_3$ to yield (**168*b***) (60–70%).[214] A low yield (5%) of the chro-

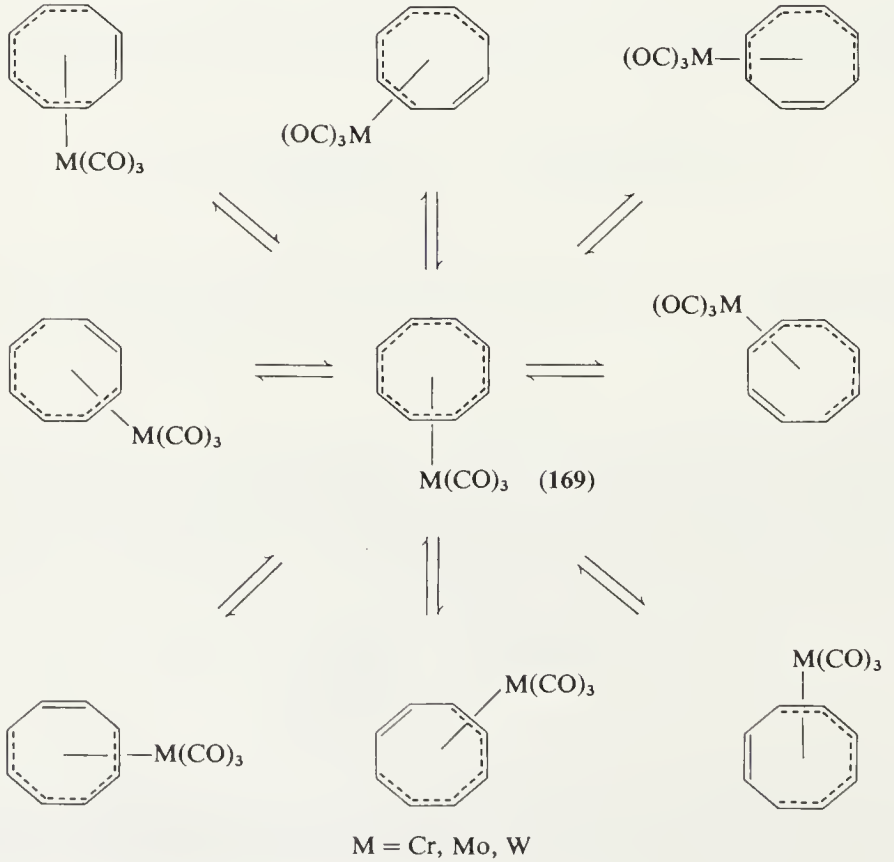


mium complex (**168***a*) also results from the reaction of COT with $Cr(CO)_6$ in acetonitrile.[424]



(**168***b*)

Scheme 20



M = Cr, Mo, W

In (COT)Mo(CO)$_3$ (**168***b*) the COT ring is partly flattened, the molybdenum atom being associated with six approximately coplanar carbon atoms (although not equidistant from each).[428]

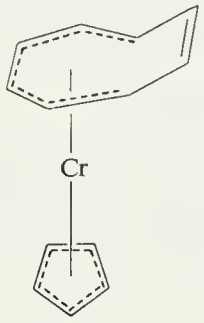
The complexes (**168**) are fluxional in solution, the metal atom apparently moving around the ring (these shifts must necessarily involve ring-deformations).[214,424,427,429,430] The results of variable-temperature ^{13}C n.m.r. studies on the complexes (**168**) suggest that the mechanism of the fluxional process may involve random shifts in a symmetrical intermediate (**169**)[431,432] (scheme 20).

For the mass spectrum of (COT)Cr(CO)$_3$ (**168***a*), see ref. 433.

Treatment of (CPD)$CrCl_2$.THF with isopropylmagnesium bromide in the presence of COT, followed by u.v. irradiation, affords the complex (**170**) (68%).[434]

$$\text{COT} \xrightarrow[\text{(ii) } h\nu]{\text{(i) (CPD)}CrCl_2\text{.THF, } Pr^iMgBr,\ Et_2O,\ -50^\circ \rightarrow \text{r.-t.}} \text{(COT)Cr(CPD)} \quad \textbf{(170)}$$

The probable instantaneous structure of this fluxional molecule is as shown.



(170)

Treatment of COT with $Mo(CO)_6$ gives a product (**171**) (*ca.* 3%), believed to incorporate a COT dimer.[435,436]

$$\text{COT} \xrightarrow[\text{Petroleum (b.p. 100–120°), reflux}]{Mo(CO)_6} (C_{16}H_{16})Mo(CO)_4 \quad \textbf{(171)}$$

Reaction between COT and molybdenum(VI) chloride oxide leads to the product (**172**)[437] (*cf.* cerium (p. 53) and titanium, zirconium and hafnium (p. 53)).

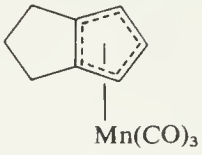
$$\text{COT} \xrightarrow[C_6H_6,\ \text{reflux}]{MoOCl_4} (C_8H_7)_2MoOCl_2 \quad \textbf{(172)}$$

Group VIIA

Manganese. Reaction of COT with $Mn_2(CO)_{10}$ affords (in low yield) the complex (**173**), containing a C_8H_9 ligand.[438]

$$\text{COT} \xrightarrow[150^\circ]{Mn_2(CO)_{10}} (C_8H_9)Mn(CO)_3 \quad \textbf{(173)}$$

The structure of the product incorporates a bicyclo[3.3.0]octadienyl system[438] (*cf.* ruthenium (pp. 66, 69)).

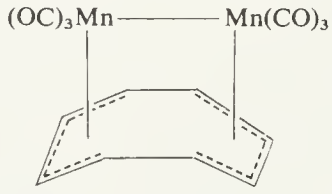


(173)

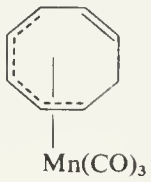
With $[HMn(CO)_4]_3$, COT gives the complexes **(174)** (1.6%) and **(175)** (6.4%).[439]

$$\text{COT} \xrightarrow[\text{Hexane, reflux}]{[HMn(CO)_4]_3} (COT)Mn_2(CO)_6 \quad \textbf{(174)}$$
$$+ \quad (C_8H_9)Mn(CO)_3 \quad \textbf{(175)}$$

The first of these products **(174)** is apparently fluxional, and has the structure shown below[440]; the C_8H_9 ligand in **(175)** contains a free olefinic bond.[439]



(174)

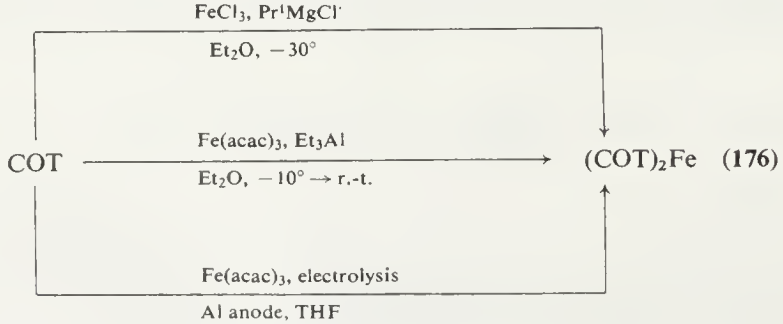


(175)

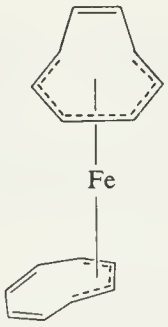
For ion-molecule reactions of $(CPD)Mn(CO)_3$ with COT, see ref. 422.

Group VIII

Iron, ruthenium, osmium. Treatment of COT with iron(III) chloride in the presence of isopropylmagnesium chloride gives the product **(176)** (20%).[441]

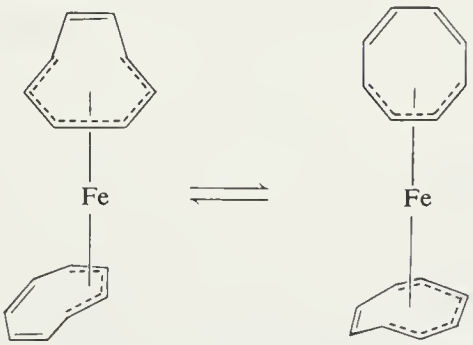


A higher yield (*ca.* 75%) of this product results from a reaction employing $Fe(acac)_3$ and triethylaluminium.[442,443] Electrolysis of $Fe(acac)_3$ in the presence of COT, using an aluminium anode, also gives (**176**).[411] In the crystal, $(COT)_2Fe$ (**176**) possesses a structure in which one of the COT rings uses a 1,3,5-triene system for coordination, while the other ring is attached *via* a 1,3-diene system (this is, of course, in accordance with EAN considerations).[444] The conformations adopted by the two ligands resemble those found in $(COT)Mo(CO)_3$ (**168*b***) and $(COT)Fe(CO)_3$ (**177**) (see p. 62) respectively. In



(176)

solution, $(COT)_2Fe$ (**176**) exhibits fluxional behaviour, of two kinds.[445] In the first process, the two ligands exchange roles, the changes of coordination being accompanied by changes of conformation. At –84° the 'triene' ligand is



'frozen', but the protons of the 'diene' ring continue to appear equivalent in the p.m.r. spectrum;[445] rapid 1,2-shifts of the iron atom are probably involved. (For 'broad-line' n.m.r. studies on the solid, see refs. 446, 447; for the ^{57}Fe Mössbauer spectrum, see ref. 448.)

COT reacts with $Fe(CO)_5$ under the influence of heat[449–451] or u.v. radiation[452,453] to afford $(COT)Fe(CO)_3$ (**177**) (up to 72%) and a binuclear compound '*trans*'-$(COT)Fe_2(CO)_6$ (**178**) (up to 31%).

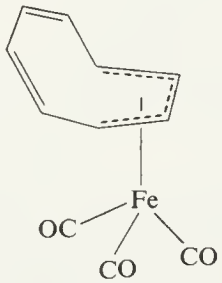
$$\text{COT} \xrightarrow[\text{Ethylcyclohexane, reflux or hexane, } h\nu]{\text{Fe(CO)}_5} \begin{matrix}(\text{COT})\text{Fe(CO)}_3 \quad \textbf{(177)} \\ + \text{ '}\textit{trans}\text{'-}(\text{COT})\text{Fe}_2(\text{CO})_6 \quad \textbf{(178)}\end{matrix}$$

A second binuclear complex has been found amongst the products of the thermal reaction;[450] it was originally formulated as $(COT)Fe_2(CO)_7$, but is now known to be $(COT)Fe_2(CO)_5$[454,455] (see p. 199).

A very efficient conversion (up to 80%) of COT into $(COT)Fe(CO)_3$ (**177**) results from the reaction with $Fe(CO)_5$ in the presence of trimethylamine *N*-oxide.[456]

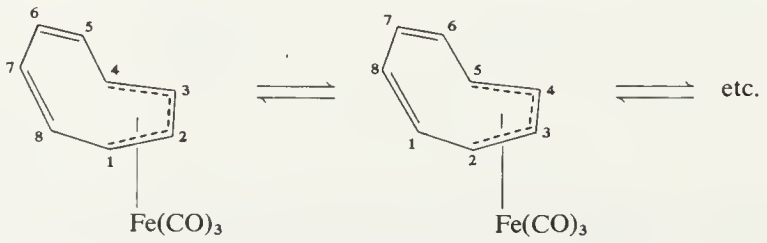
$$\text{COT} \xrightarrow[\text{Me}_3\text{NO, e.g. } C_6H_6,\ 0°\text{, then reflux}]{\text{Fe(CO)}_5} (\text{COT})\text{Fe(CO)}_3 \quad \textbf{(177)}$$

The structure of the tricarbonyl complex (**177**), obtained by X-ray studies, features 1,3-diene-to-metal bonding.[457,458] The molecule is fluxional in



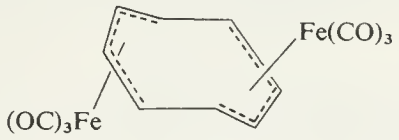
(177)

solution, the iron atom undergoing a sequence of extremely rapid 1,2-shifts.[459]



This fluxional process is sufficiently fast, even at −150°, to preclude n.m.r. observation of the protons in their instantaneous environments; 'wide-line' n.m.r. studies indicate that the molecule possesses considerable motional freedom even in the crystal.[455,460] The limiting ^{13}C n.m.r. spectrum, however, is observable below −120°,[461] and the nature of the rearrangement process has been elucidated by examination of the analogous ruthenium complex (see p. 65). (For other spectral data, see refs. 99 (u.v., i.r. and p.m.r.); 462, 463 (i.r. and Raman); 433, 464 (mass spectrum); 465 (chemical ionisation mass spectrum); 466, 467 (^{57}Fe Mössbauer).)

In '*trans*'-$(COT)Fe_2(CO)_6$ (**178**), the COT ligand exists in a 'chair' form with the $Fe(CO)_3$ groups attached on opposite sides of the ring;[457,458,468] the molecule is non-fluxional. (For the u.v., i.r. and p.m.r. spectra, see ref. 99; for the mass spectrum, see ref. 464; for ^{57}Fe Mössbauer spectral data, see ref. 466.)

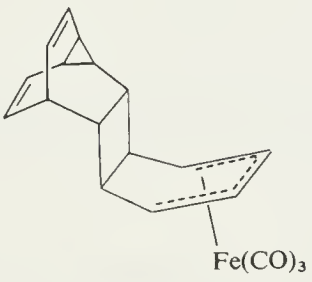


(178)

Prolonged irradiation of $Fe(CO)_5$ in the presence of an excess of COT leads to two complexes in which the ligands are COT dimers.[469,470] Complex (**179**), m.p. 118°, is the chief product (58%) when the radiation is mainly in the visible region; when shorter wavelengths are used, complex (**180**), m.p. 172°, predominates (27%).[470]

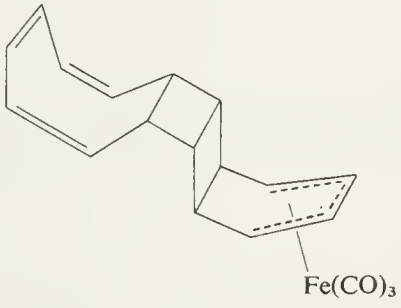
$$\text{COT} \xrightarrow[C_6H_6,\ h\nu,\ \text{reflux}]{Fe(CO)_5} \begin{array}{l} (C_{16}H_{16})Fe(CO)_3 \quad (\mathbf{179}) \quad \text{m.p. } 118° \\ + (C_{16}H_{16})Fe(CO)_3 \quad (\mathbf{180}) \quad \text{m.p. } 172° \end{array}$$

Structure (**179**) may be assigned to the product of m.p. 118°,[470] while the higher-melting isomer has been shown to possess structure (**180**).[470,471]



(179)

(Stereochemistry assumed)



(180)

These products may also be obtained from COT and $(COT)Fe(CO)_3$ (see p. 64), and from the appropriate COT dimers (see pp. 367–8, 371).

The reaction of COT with $Fe_2(CO)_9$ gives not only $(COT)Fe(CO)_3$ (**177**) and '*trans*'-$(COT)Fe_2(CO)_6$ (**178**) but also '*cis*'-$(COT)Fe_2(CO)_6$ (**181**) (and allegedly a third isomer of formula $(COT)Fe_2(CO)_6$).[454]

$$\text{COT} \xrightarrow{Fe_2(CO)_9} \begin{array}{l} (COT)Fe(CO)_3 \quad (\mathbf{177}) \\ + \text{ '}\textit{trans}\text{'-}(COT)Fe_2(CO)_6 \quad (\mathbf{178}) \\ + \text{ '}\textit{cis}\text{'-}(COT)Fe_2(CO)_6 \quad (\mathbf{181}) \end{array}$$

The complex (**181**) appears to be isostructural with the ruthenium analogue[472,473] (see p. 65).

The thermal reaction of COT with $Fe_3(CO)_{12}$ affords the tricarbonyl complex (**177**) (up to 88%).[474,475]

$$\text{COT} \xrightarrow[\text{Petroleum (b.p. 120–130°), reflux}]{Fe_3(CO)_{12}} (\text{COT})Fe(CO)_3 \quad (\mathbf{177})$$

The same product (**177**) is also formed from COT and the cycloheptatriene complex $(CHT)Fe(CO)_3$.[450]

$$\text{COT} \xrightarrow[\text{Ethylcyclohexane, reflux}]{(CHT)Fe(CO)_3} (\text{COT})Fe(CO)_3 \quad (\mathbf{177})$$

U.v. irradiation of COT in the presence of $(COT)Fe(CO)_3$ leads to the complexes of dimeric COT (**179**) and (**180**)[469,470,476] (see p. 63).

$$\text{COT} \xrightarrow[C_6H_6,\ h\nu]{(COT)Fe(CO)_3} (\mathbf{179}) + (\mathbf{180})$$

COT displaces cyclohepta-1,4-diene from the complex (cyclohepta-1,4-diene)Fe(CO)(cyclohexa-1,3-diene) to give the product (**182**).[477]

(COT)Fe(CO)(cyclohexa-1,3-diene) (**182**)

For the reaction of COT with ^{103}Ru atoms, see ref. 478.

With ruthenium(III) halides, COT gives polymeric complexes (**183**).[435]

$$\text{COT} \xrightarrow[\text{EtOH}]{RuX_3} [(\text{COT})RuX_2]_n \quad (\mathbf{183}) \qquad X = Cl, Br, I$$

COT reacts thermally or photochemically with $Ru_3(CO)_{12}$. When u.v. light is used to promote the reaction, the main product is the tricarbonyl complex (**184**) (60%), which is accompanied by the binuclear pentacarbonyl complex (**185**).[479]

$$\text{COT} \xrightarrow[\text{Cyclohexane, } h\nu]{Ru_3(CO)_{12}} (\text{COT})Ru(CO)_3 \quad (\mathbf{184}) + (\text{COT})Ru_2(CO)_5 \quad (\mathbf{185})$$

In refluxing heptane, the products include the tricarbonyl (**184**) (12%), the pentacarbonyl (**185**) (34%), the '*cis*'-hexacarbonyl (**186**) (32%), and possibly the '*trans*'-hexacarbonyl (**187**);[480] additionally, the pentalene complex (**188**),[481] a complex (**189**) containing two (different) C_8H_9 ligands,[482] and two complexes (**190**) and (**191**) of a COT dimer,[483,484] have been isolated. Compounds (**185**) (60%) and (**186**) (30%) are obtained in refluxing xylene,[479] but reaction in

$$\text{COT} \xrightarrow[\text{Heptane, reflux}]{Ru_3(CO)_{12}} \begin{array}{ll} (COT)Ru(CO)_3 & \textbf{(184)} \\ + (COT)Ru_2(CO)_5 & \textbf{(185)} \\ + \text{'}cis\text{'-}(COT)Ru_2(CO)_6 & \textbf{(186)} \\ + \text{'}trans\text{'-}(COT)Ru_2(CO)_6 & \textbf{(187)} \\ + (\text{Pentalene})Ru_3(CO)_8 & \textbf{(188)} \\ + (C_8H_9)_2Ru_3(CO)_6 & \textbf{(189)} \\ + (C_{16}H_{16})Ru(CO)_3 & \textbf{(190)} \\ + (C_{16}H_{16})Ru_2(CO)_5 & \textbf{(191)} \end{array}$$

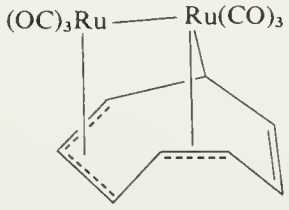
refluxing octane affords yet another complex (**192**) as the principal product (87%).[480]

$$\text{COT} \xrightarrow[\text{Octane, reflux}]{Ru_3(CO)_{12}} (COT)_2Ru_3(CO)_4 \quad \textbf{(192)}$$

The tricarbonyl compound (**184**) is isostructural with $(COT)Fe(CO)_3$ (**177**),[485] and undergoes a similar fluxional process[472, 479, 486] (see p. 62). In this case the limiting p.m.r. spectrum is observable (at −147°), and the rearrangement mechanism has been established by computer-simulation of the spectrum.[487] (For the mass spectrum of $(COT)Ru(CO)_3$ (**184**), see ref. 464.)

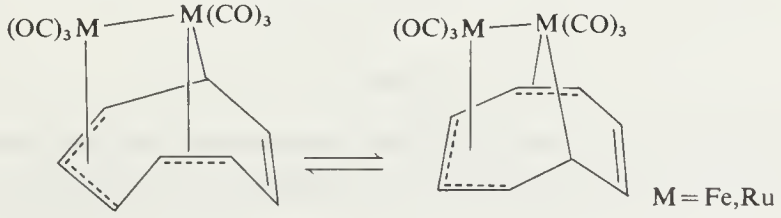
Similarly, $(COT)Ru_2(CO)_5$ (**185**) appears to be isostructural with the fluxional $(COT)Fe_2(CO)_5$ (see p. 199),[472, 480] and '*trans*'-$(COT)Ru_2(CO)_6$ (**187**) with the non-fluxional '*trans*'-$(COT)Fe_2(CO)_6$ (**178**) (see p. 63).[472] (For the mass spectrum of $(COT)Ru_2(CO)_5$ (**185**), see ref. 464.)

The structure of crystalline '*cis*'-$(COT)Ru_2(CO)_6$ (**186**) features, in addition to a metal–metal bond, a π-allyl system, an olefin–metal bond, and a carbon–metal σ-bond (at least as rough approximations).[473]



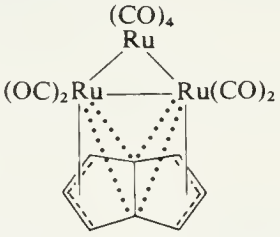
(**186**)

The observed p.m.r. spectrum of this compound[472] and that of the apparently isostructural '*cis*'-$(COT)Fe_2(CO)_6$ (**181**)[454] indicate that these molecules must either rearrange in solution to a more symmetrical structure, or that they are fluxional by virtue of a process such as the following.[473, 488]



(For the mass spectrum of '*cis*'-$(COT)Ru_2(CO)_6$, see ref. 464.)

The pentalene complex (**188**), the formation of which involves dehydrogenative transannular ring-closure of COT, possesses an instantaneous structure which may be represented as shown.[481] The molecule is fluxional,

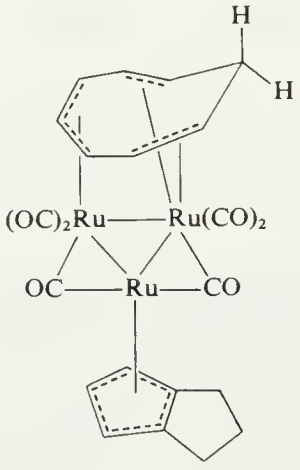


(188)

and the following oscillatory process is suggested to account for the observed p.m.r. spectrum.[481]

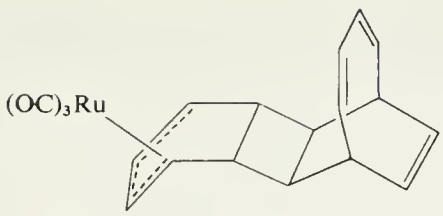
(CO groups omitted)

An X-ray structure determination has shown that the complex $(C_8H_9)_2Ru_3(CO)_6$ (**189**) incorporates two different C_8H_9 ligands[489] (*cf.* the structures of $(C_8H_8.SiMe_3)Ru_2(SiMe_3)(CO)_5$ and $(C_8H_9)Ru(GeMe_3)(CO)_2$, p. 69).

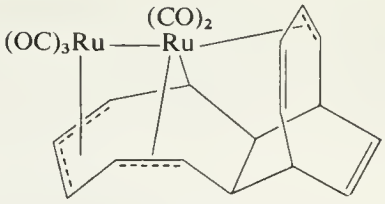


(189)

The complex $(C_{16}H_{16})Ru(CO)_3$ (**190**) contains the illustrated dimeric-COT ligand,[483] a valence isomer of which is contained in the diruthenium complex

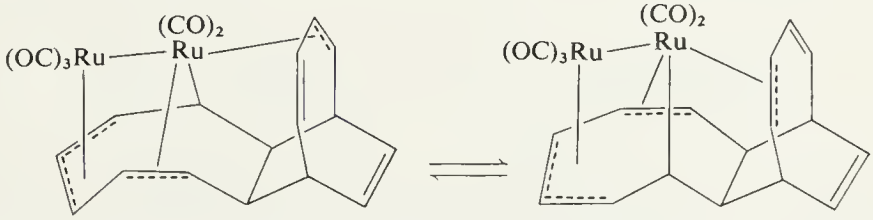


(190)

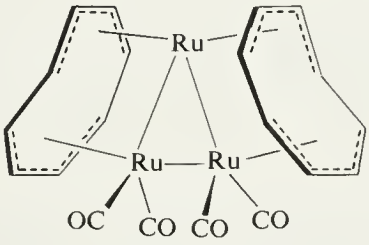


(191)

(**191**).[484] The fluxional process occurring in $(C_{16}H_{16})Ru_2(CO)_5$ (**191**) appears to involve a rearrangement of the bonding in the unbridged C_8 ring, similar to that postulated for '*cis*'-$(COT)Ru_2(CO)_6$ (**186**) (see p. 65), with a concomitant 1,3-shift within the other metal-bonded ring.[484]



The fluxional $(COT)_2Ru_3(CO)_4$ (**192**) is somewhat inadequately represented by the structure below;[490] the 'wide-line' p.m.r. spectrum of the solid is temperature-dependent.[491] Each COT ring is attached to two ruthenium



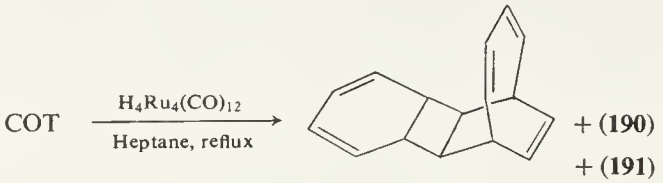
(192)

atoms, but the precise nature of the ring-to-metal bonding is not clear; it seems to be intermediate between the arrangements illustrated below.[490]

(One C_8 ring and CO groups omitted)

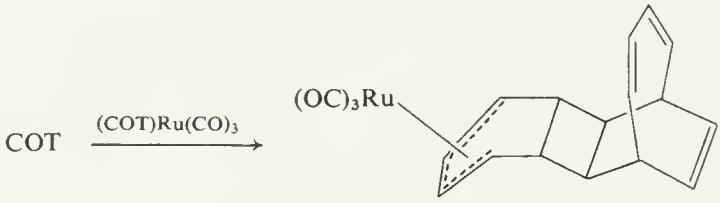
Treatment of COT with the hydridocarbonylruthenium cluster $H_4Ru_4(CO)_{12}$ affords, in addition to complexes of COT and of cyclo-octatriene, the free

COT dimer (**193**) together with the ruthenium carbonyl complexes (**190**) and (**191**).[483] The suggestion that (**193**) and (**190**) may be formed *via* $(COT)Ru(CO)_3$



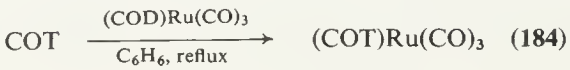
(**193**)

(**184**) is supported by the formation of the complex (**190**) from COT and $(COT)Ru(CO)_3$.[483]

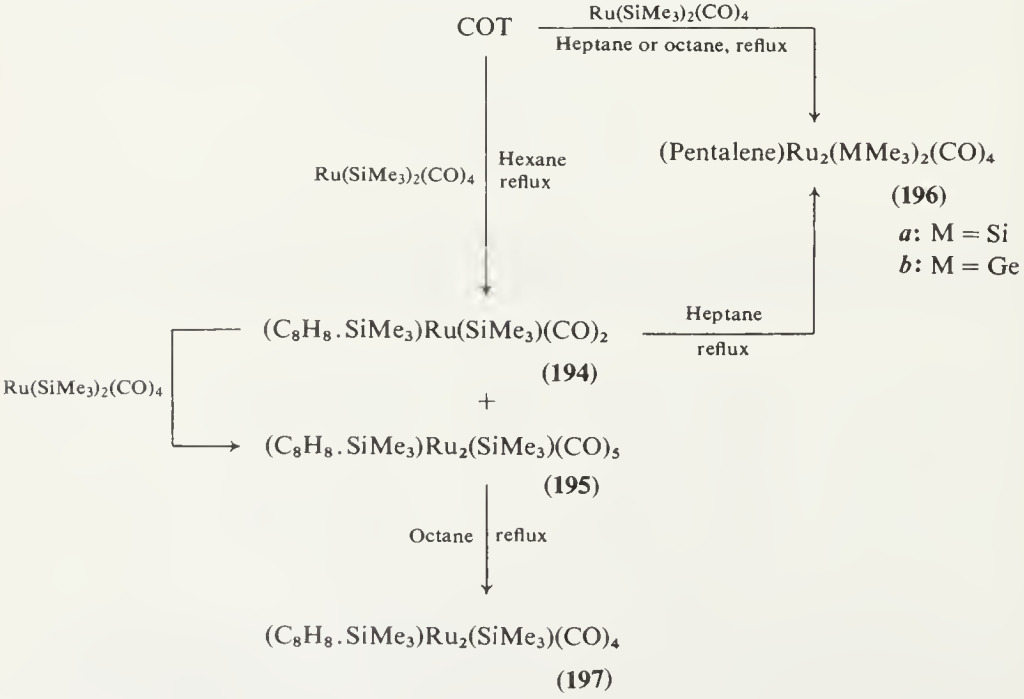


(**190**)

Displacement of cyclo-octa-1,5-diene from $(COD)Ru(CO)_3$* with COT provides a high-yield preparation of the tricarbonyl complex (**184**).[492]



With $Ru(SiMe_3)_2(CO)_4$ in refluxing hexane, COT affords the complex (**194**);[482] a minor product is (**195**), which is best obtained from (**194**).[493] At



* COD = cyclo-octa-1,5-diene.

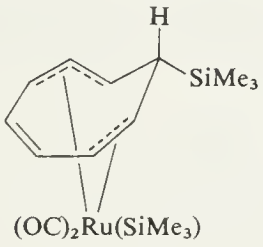
higher temperatures (**194**) gives the pentalene complex (**196*a***),[482] while (**195**) loses carbon monoxide to yield (**197**).[493]

Similar reactions occur with $Ru(GeMe_3)_2(CO)_4$, but in this case the pentalene complex (**196*b***) is accompanied by several by-products,[494] two of which have been identified as (**198*a***) and (**199**) respectively.[482]

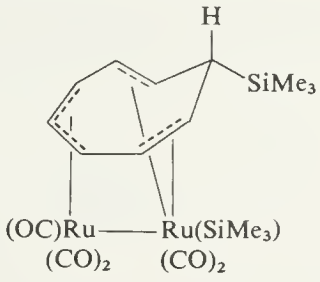
$(COT)Ru_2(MMe_3)_2(CO)_4$ (**198**) *a*: M = Ge; *b*: M = Si

$(C_8H_9)Ru(GeMe_3)(CO)_2$ (**199**)

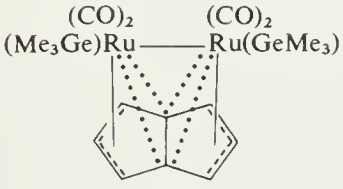
The structures of the products (**194**),[482] (**195**).[493] (**196*b***),[494] (**197**),[493] (**198*a***)[482] and (**199**)[482] are illustrated below. Compound (**194**) is fluxional, the n.m.r.



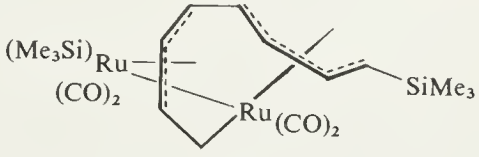
(**194**)



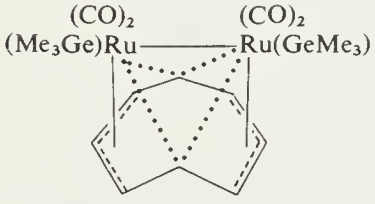
(**195**)



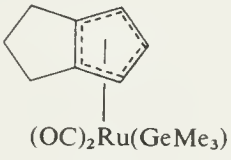
(**196*b***)



(**197**)

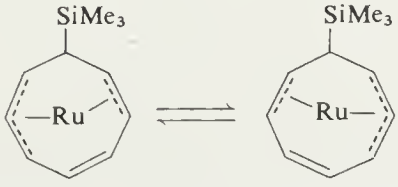


(**198*a***)



(**199**)

spectra being consistent with the operation of an oscillatory process as shown.[482]

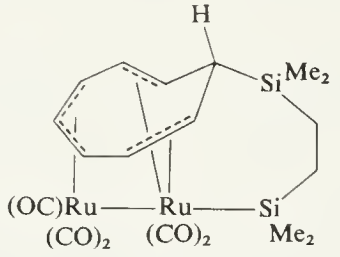


(SiMe$_3$ and CO groups on metal omitted)

The structures (**195**), (**196**), (**198**) and (**199**) may be compared with those of complexes (**189**) (see p. 66), (**188**) (see p. 66), $(COT)Fe_2(CO)_5$ (see p. 199) and (**173**) (see p. 60) severally. In complex (**197**), the C_8 ring has opened to form a chain, carrying an $SiMe_3$ group on one end and a σ-bonded Ru atom on the other; the octatetraene chain takes up a conformation such that each of the metal atoms is η^4-bonded.[493]

The reaction of COT with $[Ru(SiMe_3)(CO)_4]_2$ yields the complexes (**188**)[481] and (**198***b*).[482]

Among the products from COT and $Me_2Si.[CH_2]_2.SiMe_2.Ru(CO)_4$ is the complex (**200**).[493] In the formation of compound (**200**), one $SiMe_2$ group



(**200**)

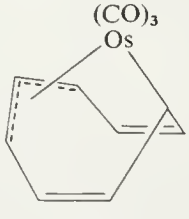
migrates to carbon while the other remains bonded to ruthenium; the metal-to-ring bonding is similar to that in complex (**195**) (see p. 69).

COT reacts with $Os_3(CO)_{12}$ under the influence of u.v. light to give a product $(COT)Os(CO)_3$ (**201**), which is *not* an analogue of the iron and ruthenium tricarbonyl complexes (**177**) and (**184**); in refluxing cyclohexane, however, it isomerises to give a compound (**202**) which is isostructural with these complexes.[495,496]

$$\text{COT} \xrightarrow[h\nu,\ C_6H_6]{Os_3(CO)_{12}} \beta\text{-(COT)Os(CO)}_3 \quad (\mathbf{201})$$

$$\beta\text{-(COT)Os(CO)}_3 \xrightarrow[\text{reflux}]{\text{Cyclohexane}} \alpha\text{-(COT)Os(CO)}_3 \quad (\mathbf{202})$$

The following structure has been suggested for the thermally labile β-isomer (**201**).[495,496]



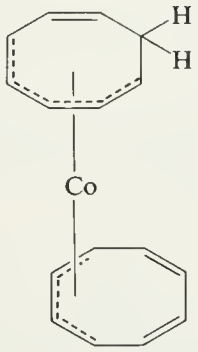
(**201**)

The p.m.r. spectrum of the stable isomer (**202**) is fully resolved at a higher temperature than for the analogous iron and ruthenium complexes (**177**) and (**184**)[496, 497] (see pp. 62, 65). Thus for the series (COT)M(CO)$_3$ (M = Fe, Ru, Os) the ease of the fluxional process, occurring *via* 1,2-shifts of the metal atom, decreases with increasing atomic number of the metal.

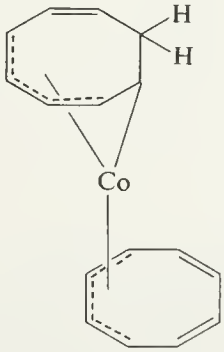
Cobalt, rhodium, iridium. Reduction of cobalt(II) chloride with sodium borohydride in the presence of COT gives a small yield (4%) of the complex (**203**).[498]

$$\text{COT} \xrightarrow[\text{EtOH, } -30° \rightarrow \text{r.-t.}]{CoCl_2,\ NaBH_4} \text{(Cyclo-octatrienyl)Co(COT)} \quad \textbf{(203)}$$

On the basis of the ^{1}H n.m.r. spectrum, the crude structures (**203*a***) and (**203*b***) both appear to be possibilities, although (**203*a***) is favoured; the molecule is seemingly fluxional[498] (for a revised structure, see appendix).

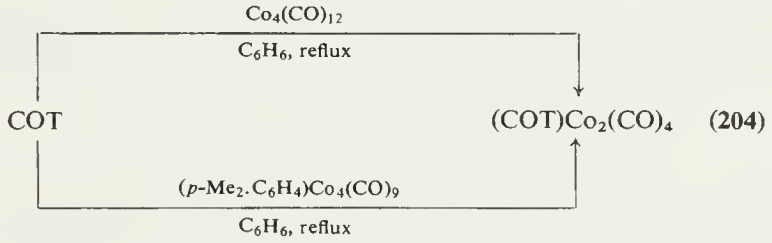


(**203*a***)



(**203*b***)

With $Co_4(CO)_{12}$ a binuclear, apparently fluxional complex (**204**) is produced (2%); a better yield (26%) results from the use of (p-Me_2.C_6H_4)$Co_4(CO)_9$.[499]



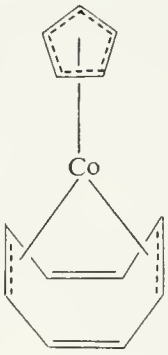
COT displaces carbon monoxide from (CPD)$Co(CO)_2$ to afford the product (**205**) (up to 30%).[474, 500, 501]

$$\text{COT} \xrightarrow[ca.\ 140°]{\text{(CPD)Co(CO)}_2} \text{(CPD)Co(COT)} \quad \textbf{(205)}$$

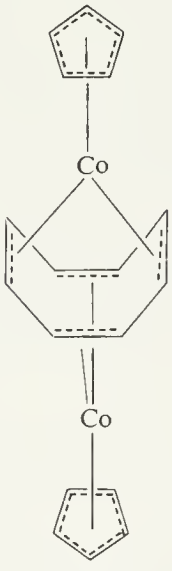
The 'mixed' complex (**205**) is obtained in better yield by using u.v. irradiation,[99, 502] and under these conditions the binuclear complex (**206**) is also formed.[502]

$$\text{COT} \xrightarrow[h\nu]{\text{(CPD)Co(CO)}_2} \underset{\textbf{(205)}}{} + \underset{\textbf{(206)}}{\text{(CPD)}_2\text{Co}_2\text{(COT)}}$$

Complexes (**205**) and (**206**) are formulated as shown below; structure (**206**) has been confirmed by X-ray studies.[503] (For u.v., i.r. and p.m.r. spectra of



(205)

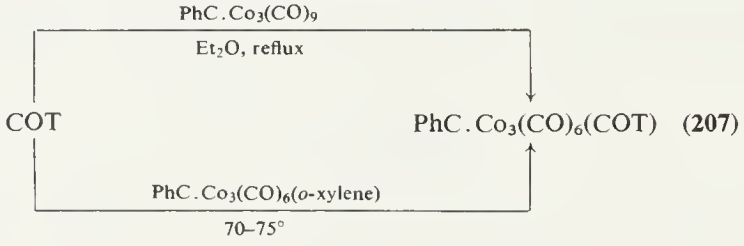


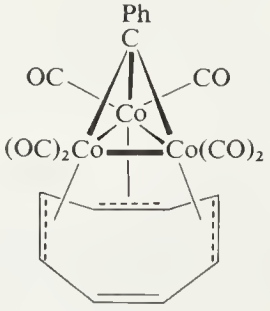
(206)

(**205**) and (**206**), see ref. 99.)

For ion-molecule reactions of COT with $(CPD)Co(CO)_2$, see ref. 422.

With $PhC.Co_3(CO)_9$, COT displaces carbon monoxide to give the fluxional complex (**207**) (9%); the same product is formed (16%) from $PhC.Co_3(CO)_6$-





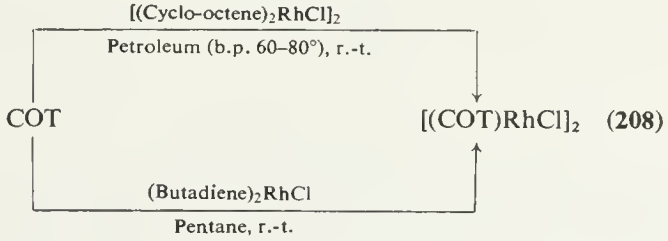
(207)

(*o*-xylene) by displacement of the xylene.[504] In the product (**207**), all three metal atoms in the metal cluster are bonded to the COT ligand.[504,505]

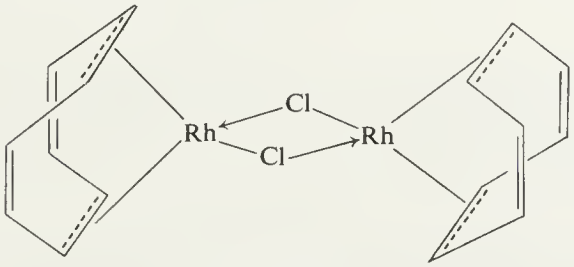
COT reacts with hydrated rhodium(III) chloride to form the dimeric rhodium(I) complex (**208**).[339,506]

$$\text{COT} \xrightarrow[\text{EtOH}]{RhCl_3.3H_2O} [(\text{COT})RhCl]_2 \quad (\mathbf{208})$$

The same product is obtained in high yields (85–100%) by displacement reactions using $[(\text{cyclo-octene})_2RhCl]_2$[507] or $(\text{butadiene})_2RhCl$.[508]

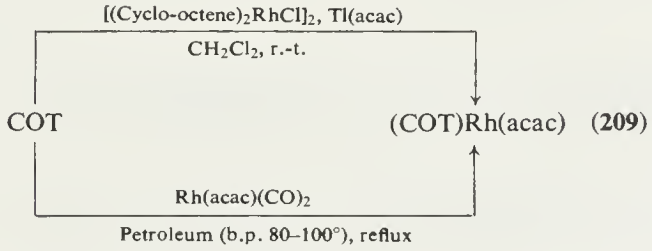


On the basis of the spectral evidence, the structure of the dimeric complex (**208**) is believed to be as shown.[507]



(**208**)

Treatment of $[(\text{cyclo-octene})_2RhCl]_2$ with thallium(I) acetylacetonate, followed by reaction with COT, affords the complex (**209**) (83%);[509] the same product results (87%) from the treatment of COT with $Rh(acac)(CO_2)$.[510]



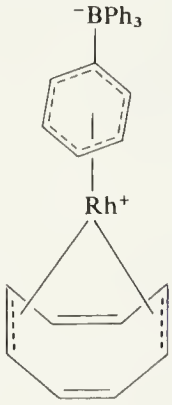
With $Rh_4(CO)_{12}$, COT forms the complex (**210**) (77%).[499]

$$\text{COT} \xrightarrow[C_6H_6,\ \text{reflux}]{Rh_4(CO)_{12}} (\text{COT})_2Rh_4(CO)_8 \quad (\mathbf{210})$$

Reaction of hydrated rhodium(III) chloride with sodium tetraphenylborate in the presence of COT gives the neutral complex (**211**) (70–80%).[511]

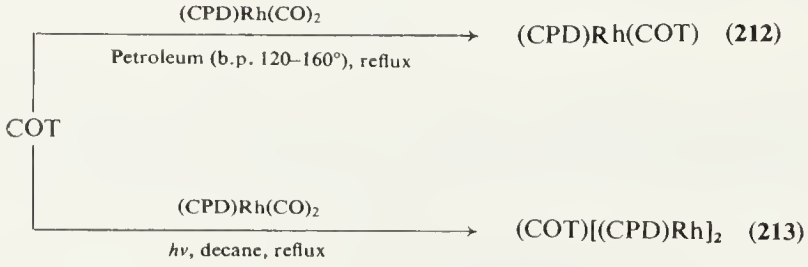
$$\text{COT} \xrightarrow[\text{MeOH(aq.), r.-t. or 50°}]{\text{RhCl}_3.3\text{H}_2\text{O, NaBPh}_4} (\text{COT})\text{Rh.BPh}_4 \quad (\mathbf{211})$$

In this product (**211**), the tetraphenylborate anion is co-ordinated to Rh^+ *via* one of the phenyl rings, and the suggested structure is as follows.[511]



(**211**)

As with analogous cobalt compound, COT displaces carbon monoxide from $(CPD)Rh(CO)_2$. The thermal reaction affords the product (**212**) (11%),[474] while a photochemical procedure results in the binuclear compound (**213**) (62%).[512]

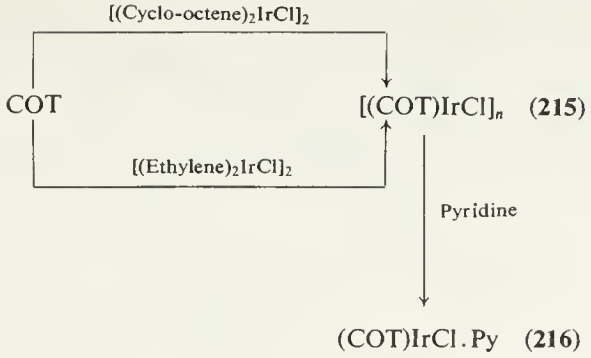


The displacement of cyclo-octa-1,5-diene from the perchlorate $[(COD)Rh.Bipy]^+ ClO_4^-$ yields the corresponding COT complex (**214**).[513]

$$\text{COT} \xrightarrow[\text{MeOH, } CH_2Cl_2\text{, r.-t.}]{[(\text{COD})\text{Rh.Bipy}]^+ ClO_4^-} [(\text{COT})\text{Rh.Bipy}]^+ \; ClO_4^- \quad (\mathbf{214})$$

Bipy = 2,2′-bipyridyl

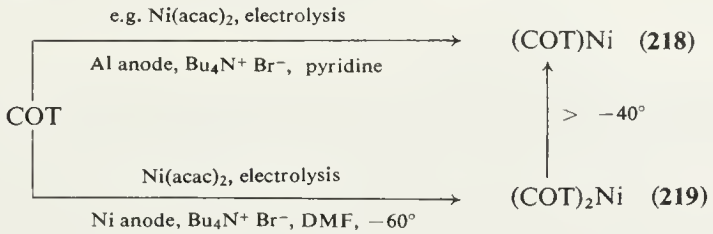
COT reacts with $[(\text{cyclo-octene})_2IrCl]_2$ or $[(\text{ethylene})_2IrCl]_2$ to afford the COT complex (**215**) (63%), which is probably polymeric; in pyridine, however, the monomeric pyridinate (**216**) is formed.[514]



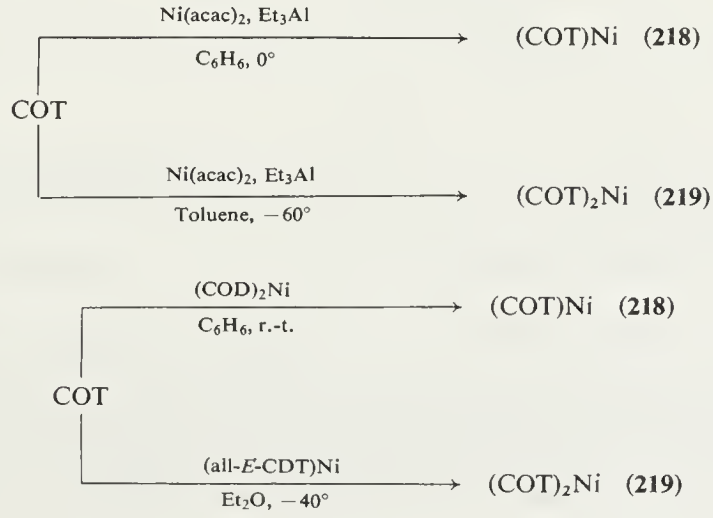
The acid H_3IrCl_6 apparently reacts with COT to give the hydrido-iridium(III) complex (**217**) (see ref. 515).

$$\text{COT} \xrightarrow[\text{EtOH}]{H_3IrCl_6} [(\text{COT})IrHCl_2]_n \quad (\mathbf{217})$$

Nickel, palladium, platinum. Electrolysis of $Ni(acac)_2$ in the presence of COT, using a nickel or an aluminium anode, produces cyclo-octatetraenenickel (**218**) in high yields.[411,516,517] By working at –60°, the reaction can be made to give the bis(cyclo-octatetraene) complex (**219**), which decomposes above *ca.* –40° to yield the mono(cyclo-octatetraene) compound (**218**).

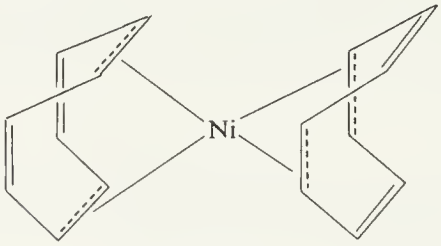


The reaction of $Ni(acac)_2$ with triethylaluminium in the presence of COT affords an alternative route to these products (**218**) (95%) and (**219**) (78.5%).[518]



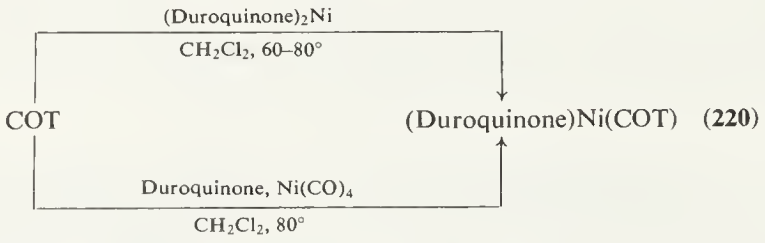
The same products (**218**) and (**219**) are also formed in high yields by displacement reactions, using the cyclo-octa-1,5-diene or all-*E*-cyclododeca-1,5,9-triene complex of nickel(0).[518]

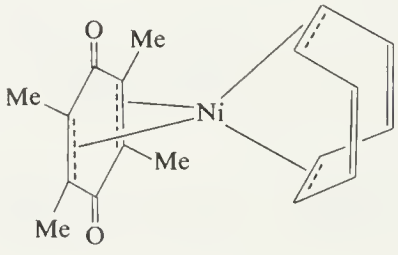
In the solid state, (COT)Ni (**218**) appears to be polymeric[518, 519] (see appendix); $(COT)_2Ni$ (**219**) is monomeric.[518]



(**219**)

The action of COT on the duroquinone complex of nickel(0) yields the 'mixed' product (**220**) (40%),[520] and this is also formed (65%) by reaction of COT with duroquinone and $Ni(CO)_4$.[520] The proposed structure of (duroquinone)Ni(COT) (**220**) is shown below; for a theoretical discussion, see ref. 521.





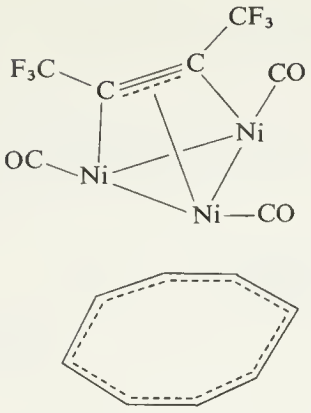
(**220**)

In the presence of COT, the mass spectrum of (CPD)Ni(NO) shows that $[(CPD)Ni(COT)]^+$ ions are formed.[522]

COT reacts with $(F_3C.C{\equiv}C.CF_3)_3Ni_4(CO)_4$ to give the complex (**221**).[523]

$$COT \xrightarrow{(F_3C.C{\equiv}C.CF_3)_3Ni_4(CO)_4} (COT)(F_3C.C{\equiv}C.CF_3)Ni_3(CO)_3 \quad (221)$$

The structure of this product, which is fluxional, incorporates a nickel cluster sandwiched between a planar COT ligand and the hexafluoro but-2-yne ligand, but the nature of the metal-to-ring bonding is not clear.[523]



(**221**)

COT displaces benzonitrile from palladium complexes of the type $(PhCN)_2PdX_2$ to give the products (**222**)[99, 524, 525] (table 15). (For heats of

$$\text{COT} \xrightarrow[C_6H_6,\ \text{r.-t.}]{(PhCN)_2PdX_2} (\text{COT})PdX_2 \quad (\mathbf{222})$$

Table 15

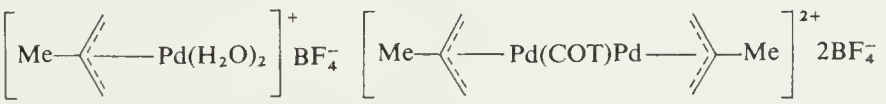
X	Yield (%)	Ref.
Cl	86	524
Br	*ca.* 10	525

reaction, see ref. 526.) A square planar geometry for $(COT)PdCl_2$ (red) has been established; a (yellow) dimeric form also exists.[527]

In the presence of methanol, COT reacts with disodium tetrachloropalladate(II) to afford the dimeric complex (**223**), which apparently contains a 7-methoxycyclo-octa-1,3,5-triene ligand.[524]

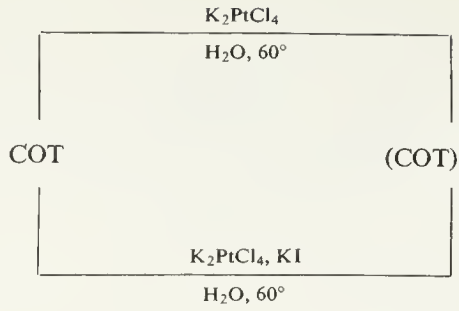
$$\text{COT} \xrightarrow[\text{MeOH, r.-t.}]{Na_2PdCl_4.4H_2O} [(C_8H_9.OMe)PdCl]_2 \quad (\mathbf{223})$$

Reaction of COT with the cationic π-allyl complex (**224**) gives the product (**225**).[528]



(**224**) (**225**)

The platinum(II) complex (**226*a***) results from the reaction of COT with dipotassium tetrachloroplatinate(II); in the presence of potassium iodide, the corresponding di-iodide (**226*b***) is produced (93%).[529] (For spectra of complexes of the type (**226**), see refs. 99, 530; for ^{81}Br n.q.r. measurements on $(COT)PtBr_2$, see ref. 531.)



(226)

a: X = Cl
b: X = I

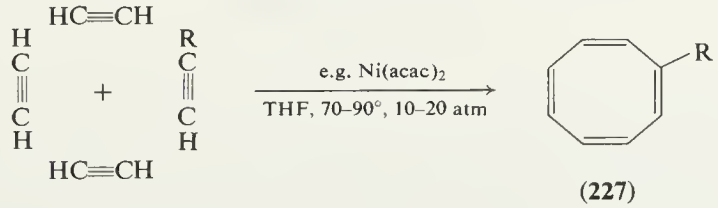
2

Substituted cyclo-octatetraenes

1. Monosubstituted derivatives

Formation

(*a*) '*Mixed*' *cyclotetramerisation of acetylenes.* The cyclotetramerisation of acetylene in the presence of nickel catalysts (see p. 2) may be adapted to produce substituted COTs, monosubstituted derivatives (**227**) being formed by the co-reaction of three molecules of acetylene and one molecule of a substituted acetylene; not unexpectedly, the yields are low (table 16).



(**227**)

Table 16

R	Yield (%)	Ref.
Me	16	(532), 533
$CH{=}CH_2$	20	13
Pr^n	25	533
Bu^n	16	(532), 533
Ph	17	(532), 533
CH_2OH	17	534
$[CH_2]_2OH$	24	534
$[CH_2]_3OH$	8	535
CH(OH)Me	11	535
$C(OH)Me_2$	13	535
CO.Me	1.5	535
$[CH_2]_2NMe_2$	8	534
$[CH_2]_3CN$	11	535

Vinylcyclo-octatetraene is a by-product of the Reppe synthesis of COT.[24,25]

(*b*) *Photochemical cycloadditions of monosubstituted acetylenes to benzene.* The u.v. irradiation of suitable monosubstituted acetylenes in benzene leads to monosubstituted COTs (table 17), presumably *via* intermediate bicyclo[4.2.0]-octatrienes.

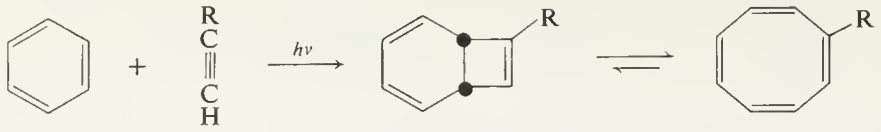
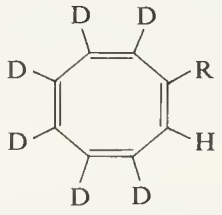


Table 17

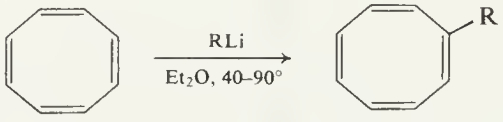
R	Yield (%)	Ref.
Bu^n	—	38
Bu^t	—	38
Ph	0.6	536
CO_2Me	8	536

Although the yields are very low, this reaction provides a useful one-step synthesis, from hexadeuteriobenzene, of the deuteriated products (**228**; R = Ph,[49] CO_2Me,[49] CO_2Et,[123] CN[49]).



(228)

(*c*) *Syntheses using organo-lithiums and analogous reagents.* Alkylation or arylation of COT may be effected with organo-lithiums, monosubstituted COTs being produced together with cyclo-octatrienes and their substituted derivatives (see p. 32); the yields are low (table 18). Phenylcyclo-octatetraene may also be prepared (22%) from COT using phenylsodium in refluxing benzene.[285]



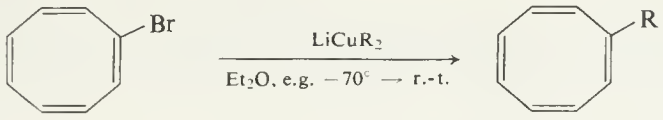
(227)

Table 18

R	Yield (%)	Ref.
Et	29	286
Bu^n	14.5	286
[a] Ph	25	285, (538)
p-Me.C_6H_4	29	539
p-Bu^t.C_6H_4	22	539
p-Ph.C_6H_4	16	539
2,4,6-Me_3.C_6H_2	6 (crude)	539
p-Me_2N.C_6H_4	27, [21]	285, (538), [539]

[a] For the deuteriated derivative (**227**; R = C_6D_5), see ref. 537.

Superior yields of alkyl and aryl derivatives of COT result from the coupling reaction between bromocyclo-octatetraene and lithium 'organocuprates' (table 19); this is undoubtedly the method of choice for the preparation of monoalkyl- and monoarylcyclo-octatetraenes.



(227)

Table 19

R	Yield (%)	Ref.
Me	93[a]	540
Cyclopropyl	95, (90)	541, (542)
$CH{=}CH_2$	88	541
Ph	58	540
p-$MeO.C_6H_4$	80	541

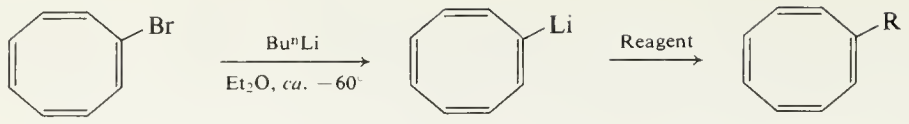
[a] A lower yield (73%) results from the use of methyl-lithium.[540]

Metal–halogen exchange between n-butyl-lithium and bromocyclo-octatetraene affords cyclo-octatetraenyl-lithium, and this product may be used *in situ* for the preparation of a wide variety of COT derivatives (table 20). Similar

Table 20 (refers to the equation at the top of p. 82)

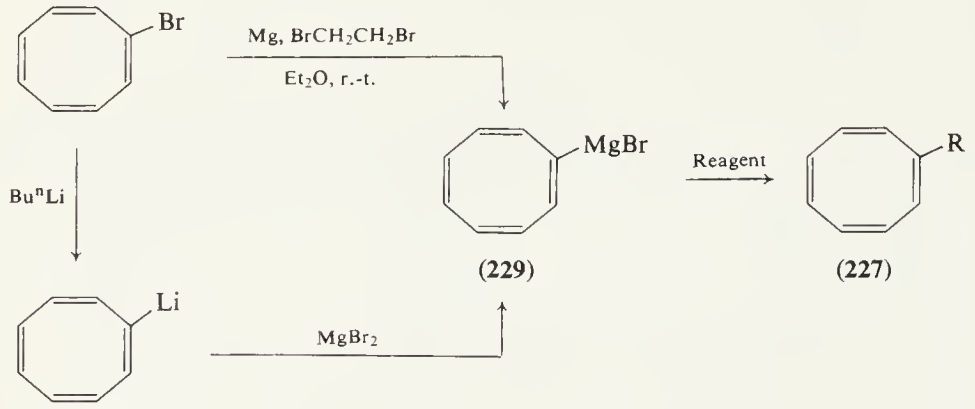
Reagent	R	Yield (%)	Ref.
D_2O	D	—	250
MeI	Me	(24), 81	(540), 543
$CoCl_2$ (catalyst)	Cyclo-octatetraenyl	24	544
Ethylene oxide	$[CH_2]_2OH$	[60], 70	(545), [546], 547
PhCHO	CH(OH)Ph	47	548
$CH_2{=}CH.CHO$	$CH(OH).CH{=}CH_2$	43	548
$CH_2{=}CH.CO_2Et$ (CuCl)	$[CH_2]_2.CO_2Et$	5	547
HCO_2Me	CHO	79	541
$Fe(CO)_5$	CHO[a]	45	541
$Me.CH{=}CH.CN$	$CO.CH{=}CHMe$	75	548
PhCN	CO.Ph	(57), 63	(544), 548
CO_2	CO_2H	58.5	549
$(CN)_2$	CN	25	541
$FClO_3$	F	*ca.* 10	550
Me_3SiCl	$SiMe_3$	80	551
$(Allyl)Me_2SiCl$	$SiMe_2(allyl)$	50	551
$(CPD)FeCl(CO)_2$	$Fe(CO)_2(CPD)$	10	551
Me_3GeBr	$GeMe_3$	55	551
Me_3SnCl	$SnMe_3$	55	551
I_2	I	50	540

[a] The product is the iron tricarbonyl complex of (227; R = CHO).



(227)

conversions have been effected using the Grignard reagent (**229**) generated from bromocyclo-octatetraene (table 21).

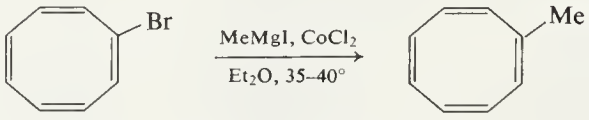


(229) (227)

Table 21

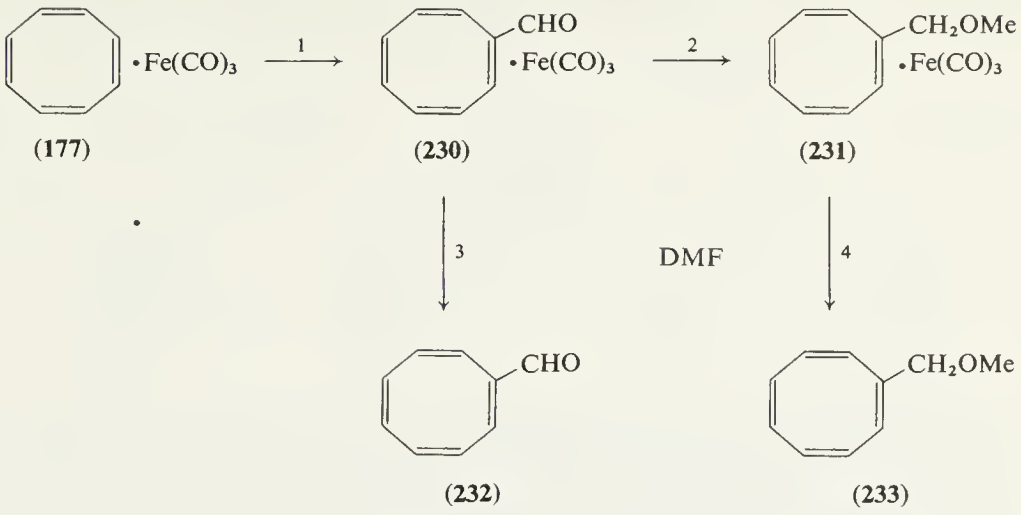
Reagent	R	Yield (%)	Ref.
CH_2=CH.CH_2Br (LiCl, CuCl)	CH_2.CH=CH_2	44	547
Oxetan	$[CH_2]_3OH$	51	547
Ethylene oxide	$[CH_2]_2OH$	21	547
CH_2=CH.CO_2Et (CuCl)	$[CH_2]_2CO_2Et$	20	547
CO_2	CO_2H	59	160
$(CN)_2$	CN	Up to 40	541

A coupling reaction between bromocyclo-octatetraene and methylmagnesium iodide (in the presence of cobalt(II) chloride) yields methylcyclo-octatetraene (36%).[160]



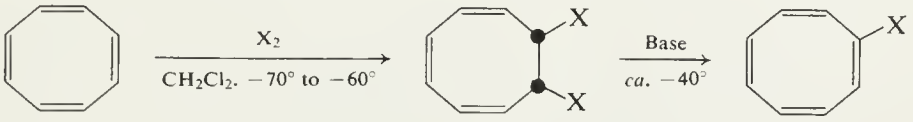
(*d*) *Syntheses using the tricarbonyliron complex of COT.* It is possible to effect electrophilic substitution of the COT ring using the tricarbonyliron complex (**177**). Thus Vilsmeier-Haack formylation yields the aldehyde complex (**230**) (60%), the functional group of which may be modified, if required, to give e.g. the methoxymethyl-compound (**231**); decomposition of these complexes with cerium(IV) ions occurs in high yield to afford the monosubstituted COTs (**232**) and (**233**)[552] (scheme 21).

Scheme 21



Reaction	Reagents and conditions	Yield (%)
1	$POCl_3$, $HCONMe_2$, 4°	60
2	(i) $NaBH_4$, EtOH, 0° (ii) 64% HPF_6(aq.), 20° (iii) MeOH, r.-t.	74
3	$Ce(NO_3)_4.2NH_4NO_3$, EtOH	80
4	$Ce(NO_3)_4.2NH_4NO_3$, EtOH	90

(*e*) *Syntheses involving dehydrohalogenation.* The base-induced elimination of hydrogen halide from the appropriate 7,8-dihalocyclo-octa-1,3,5-triene (**234**) (see pp. 23–4) may be used to prepare the chloro- and bromo-derivatives of COT (table 22). Chloro- and bromocyclo-octatetraene are also formed



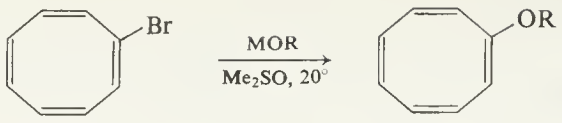
(**234**)

Table 22

X	Base	Yield (%)	Ref.
Cl	KOBu^t	74–83	540
Br	KOBu^t	85	540
Br	NaOMe	16	540

(26–50%) by the action of phenyl-lithium[553] or potassium t-butoxide[554] on the bicyclic dihalides (**38**/**39**) and (**44**) (pp. 23, 24).

Further treatment of bromocyclo-octatetraene with sodium or potassium alkoxides, or phenoxide, produces alkoxy- or aryloxy-derivatives of COT (**235**) (table 23). The intermediacy of 1,2-didehydrocyclo-octatetraene (**236**) in the reaction of bromocyclo-octatetraene with potassium t-butoxide has

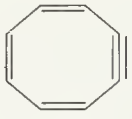


(235)

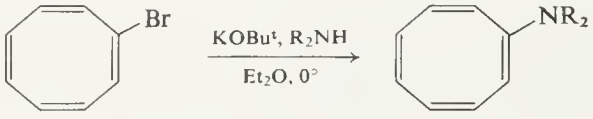
Table 23

M	R	Yield (%)	Ref.
Na	Me	75, (69)	540, (554)
K	Et	70–80	554
K	Bu^t	70–80	554, (555)
K	Ph	73	540

been demonstrated by trapping experiments with phenyl azide, tetracyclone, etc. (see p. 164), and generation of the 'yne' (**236**) in the presence of secondary amines leads to the dialkylamino-derivatives of COT (**237**)[541] (table 24).



(236)

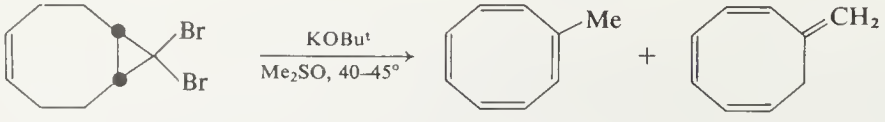


(237)

Table 24

R	Yield (%)
Me	79
Et	—

(*f*) *Syntheses involving skeletal transformations.* Methylcyclo-octatetraene is generated (33%), together with other hydrocarbons from which it is not completely separable, by treatment of the dibromocarbene-adduct (**238**) with potassium t-butoxide.[556]



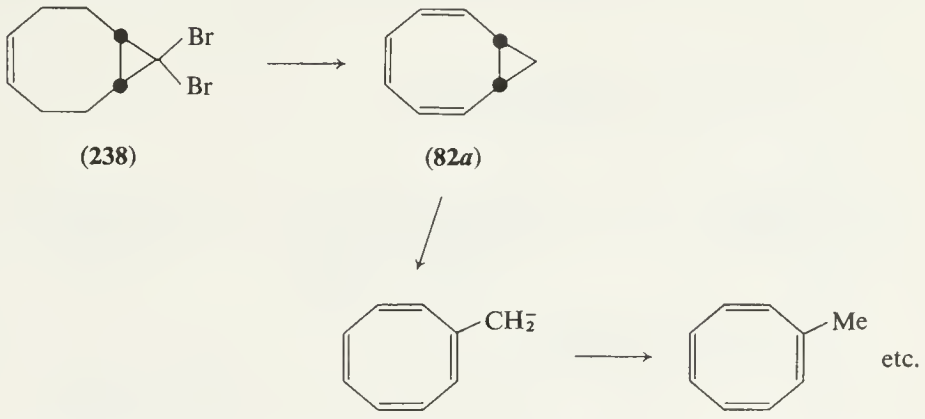
(238)

+ bicyclic hydrocarbons

The proposed intermediate in this formation of methylcyclo-octatetraene is bicyclo[6.1.0]nona-2,4,6-triene (**82*a***), which on similar treatment with base

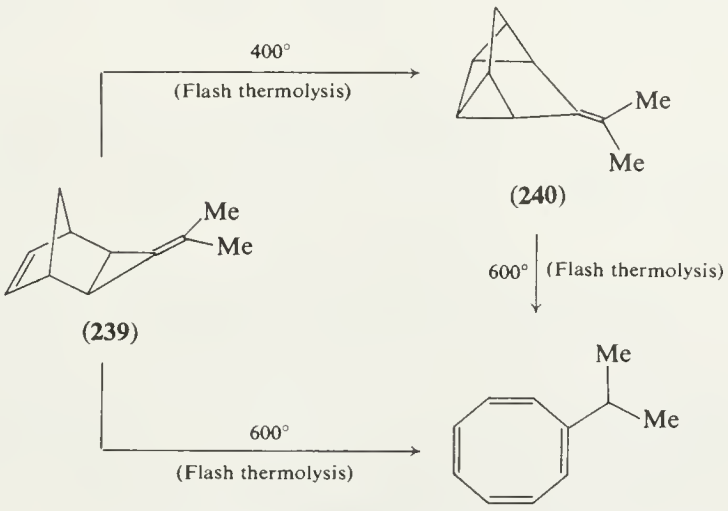
gives the same mixture of products (47 % yield of methylcyclo-octatetraene)[556] (scheme 22).

Scheme 22

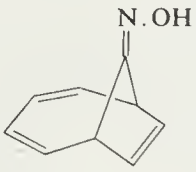


(238) (82*a*)

Flash thermolysis of the tricyclic diene (**239**), or of its initial thermolysis product (**240**), gives isopropylcyclo-octatetraene (29 % or 40 % respectively).[557]



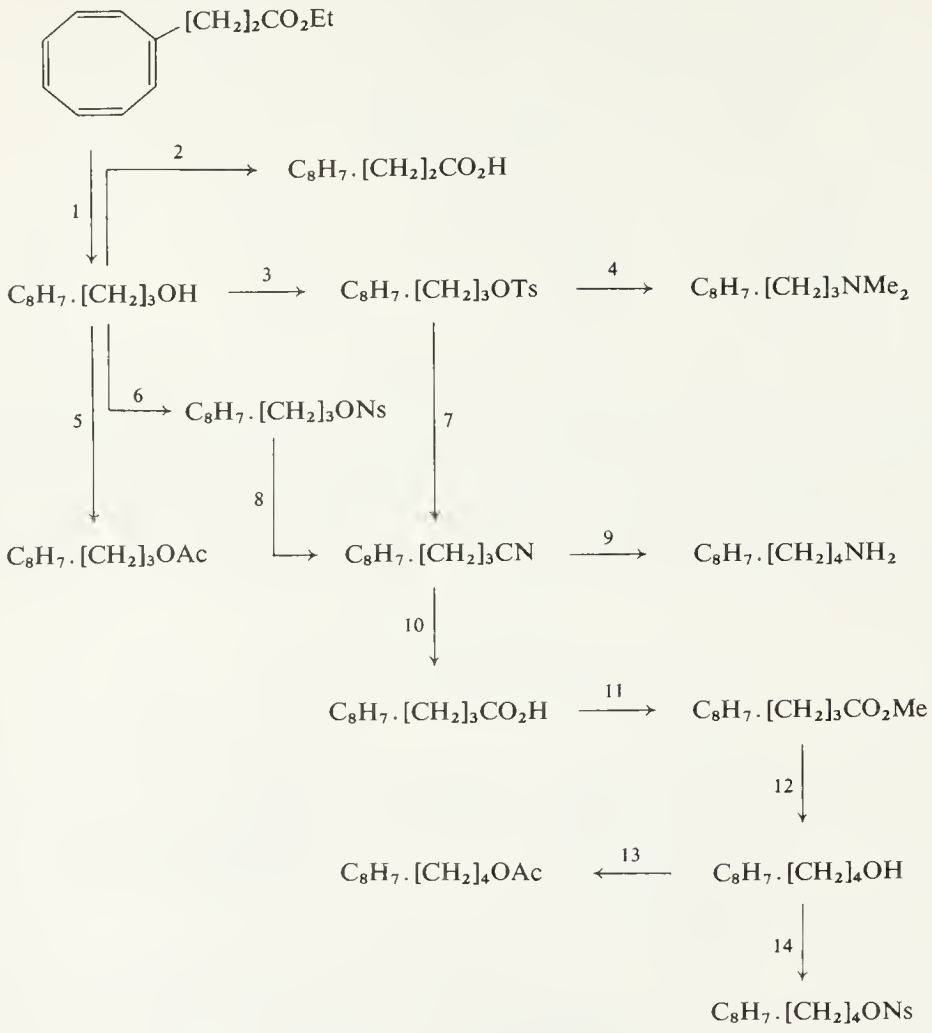
Cyanocyclo-octatetraene is formed (57 %) by treatment of the oxime (**241**) with toluene-*p*-sulphonyl chloride[52] (see p. 297).



(241)

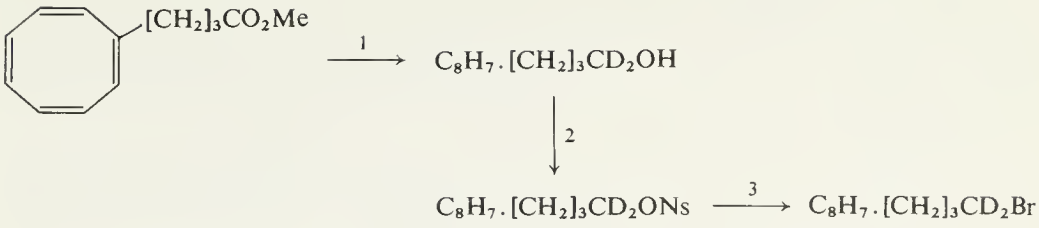
(*g*) *Functional group transformations.* The transformations outlined in schemes 23–36 lead to a further variety of monosubstituted COTs.

Scheme 23



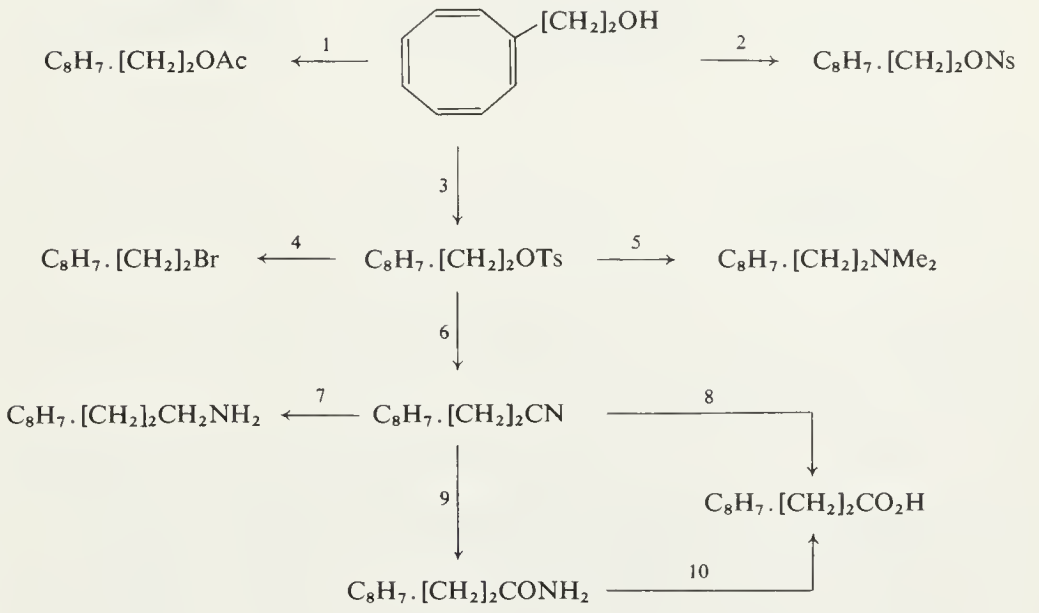
Reaction	Reagents and conditions	Yield (%)	Ref.
1	$LiAlH_4$, Et_2O, r.-t.	90	547
2	CrO_3, H_2SO_4(aq.), Me_2CO, 25°	37	535
3	*p*-Me.C_6H_4.SO_2Cl, pyridine, 0°	96	535
4	Me_2NH, C_6H_6, r.-t.	54	535
5	Ac_2O, pyridine, 0° → r.-t.	—	547
6	*p*-NO_2.C_6H_4.SO_2Cl, pyridine, 0°	—	547
7	KCN, EtOH(aq.), reflux	74	535
8	NaCN, DMF, r.-t.	100	547
9	$LiAlH_4$, Et_2O, reflux	39	535
10	NaOH(aq.), reflux	69, (67)	535, (547)
11	CH_2N_2, Et_2O	100	547
12	$LiAlH_4$, Et_2O, r.-t.	91	547
13	Ac_2O, pyridine, 0° → r.-t.	—	547
14	*p*-NO_2.C_6H_4.SO_2Cl, pyridine, 0°	—	547

Scheme 24



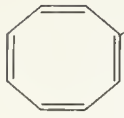
Reaction	Reagents and conditions	Yield (%)	Ref.
1	$LiAlD_4$, Et_2O	91	558
2	*p*-$NO_2.C_6H_4.SO_2Cl$	—	558
3	$PyH^+ Br^-$, DMF	93	558

Scheme 25



Reaction	Reagents and conditions	Yield (%)	Ref.
1	Ac_2O, *ca.* 100°	91	534
	or Ac_2O, pyridine, r.-t.	95 (crude)	546, (547)
2	*p*-$NO_2.C_6H_4.SO_2Cl$, pyridine, 0°	82	547
3	*p*-$Me.C_6H_4.SO_2Cl$, pyridine	92	534
4	$CaBr_2$, $MeO[CH_2]_2OH$, 50°	72	534
5	Me_2NH, C_6H_6, r.-t.	53	534
6	KCN, EtOH(aq.), reflux	78	534
7	$LiAlH_4$, Et_2O, reflux	56	534
8	NaOH(aq.), reflux	90	534
9	H_2O_2, Na_2CO_3, Me_2CO(aq.), r.-t.	36	559
10	$NaNO_2$, HCl, dioxan(aq.), r.-t.	35	559

Scheme 26



$[CH_2]_2OH$ —1→ $C_8H_7.CH_2.CO_2H$ —2→ $C_8H_7.CH_2.CD_2OH$

$C_8H_7.CH_2.CO_2H$ —3→ $C_8H_7.CH_2.CO_2Me$ —4→ $C_8H_7.CD_2.CO_2Me$

$C_8H_7.CD_2.CO_2Me$ —5→ $C_8H_7.CD_2.CH_2OH$

Reaction	Reagents and conditions	Yield (%)	Ref.
1	CrO_3, H_2SO_4(aq.), Me_2CO	61	546
2	$LiAlD_4$, Et_2O, reflux	61	546
3	CH_2N_2, Et_2O, $-5° \rightarrow$ r.-t.	81 (crude)	546
4	Na, MeOD, 50°	—	546
5	$LiAlH_4$, Et_2O, reflux	—	546

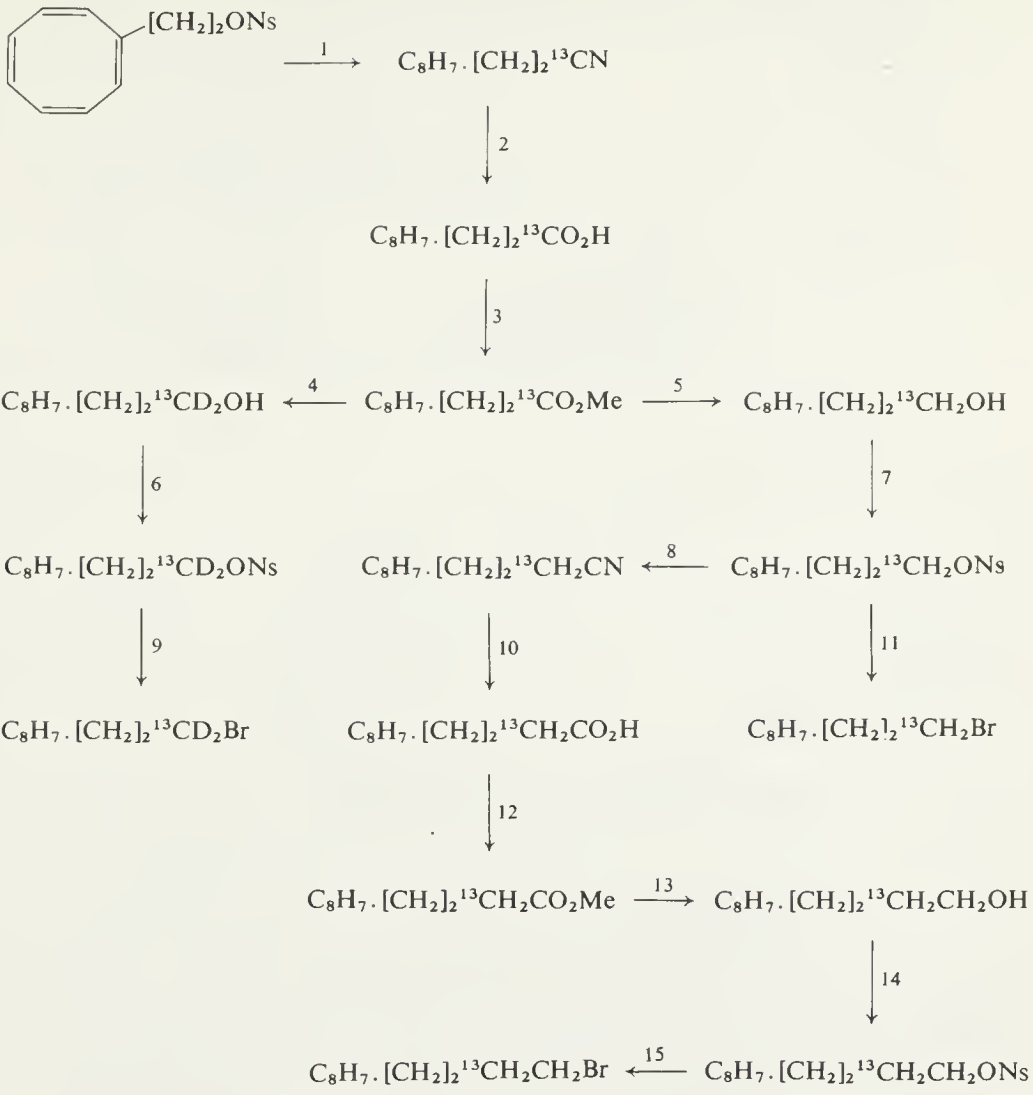
Scheme 27

$[CH_2]_2CO_2Me$ —1→ $C_8H_7.[CH_2]_2CD_2OH$

$C_8H_7.[CH_2]_2CD_2OH$ —2→ $C_8H_7.[CH_2]_2CD_2ONs$ —3→ $C_8H_7.[CH_2]_2CD_2Br$

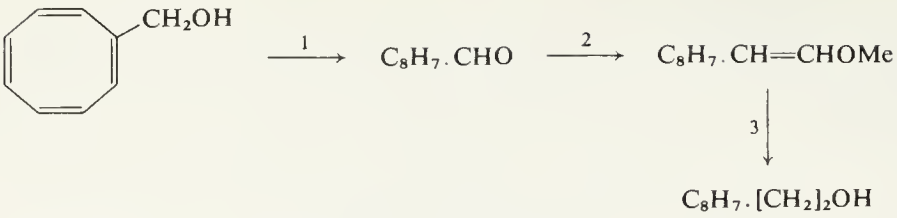
Reaction	Reagents and conditions	Yield (%)	Ref.
1	$LiAlD_4$	90	558
2	p-$NO_2.C_6H_4.SO_2Cl$	87	558
3	$PyH^+ Br^-$, DMF	70	558

Scheme 28



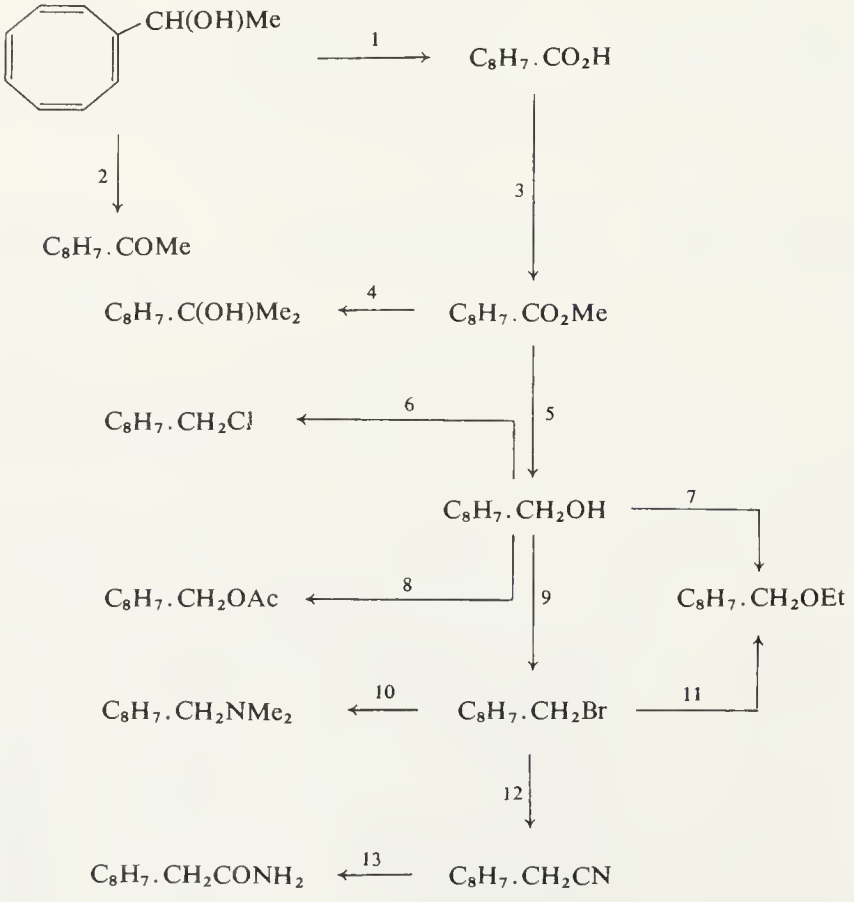
Reaction	Reagents and conditions	Yield (%)	Ref.
1	$Na^{13}CN$, DMF	87	558
2	NaOH(aq.)	87	558
3	CH_2N_2	95	558
4	$LiAlD_4$	95	558
5	$LiAlH_4$	95	558
6	*p*-$NO_2.C_6H_4.SO_2Cl$	—	558
7	*p*-$NO_2.C_6H_4.SO_2Cl$	80	558
8	NaCN, DMF	—	558
9	$PyH^+ Br^-$, DMF	97	558
10	NaOH(aq.)	—	558
11	$PyH^+ Br^-$, DMF	91	558
12	CH_2N_2	—	558
13	$LiAlH_4$	—	558
14	*p*-$NO_2.C_6H_4.SO_2Cl$	—	558
15	$PyH^+ Br^-$, DMF	—	558

Scheme 29



Reaction	Reagents and conditions	Yield (%)	Ref.
1	MnO_2–C, $CHCl_3$, r.-t.	85	546
2	Ph_3P=CHOMe, EtOH, r.-t.	94 (crude)	546
3	(i) $Hg(OAc)_2$, THF(aq.), r.-t.; (ii) $NaBH_4$, NaOH(aq.), r.-t.	91 (crude)	546

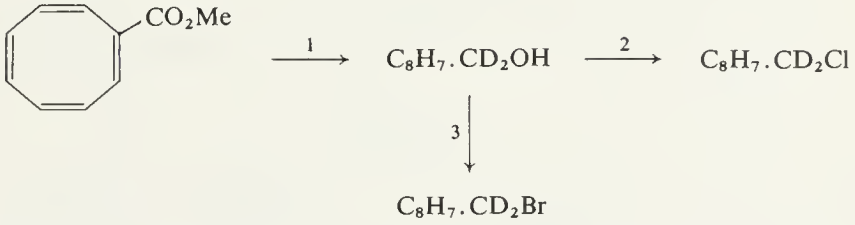
Scheme 30



Reaction	Reagents and conditions	Yield (%)	Ref.
1	NaOBr(aq.), 10° → r.-t.	37	535
2	CrO_3, H_2SO_4(aq.), Me_2CO, 0°	53	535
3	CH_2N_2, Et_2O, r.-t.	89	549
4	MeMgI, Et_2O	16	535
5	$LiAlH_4$, Et_2O, r.-t.	99	210, (560)

6	$SOCl_2$, pyridine, $CHCl_3$, r.-t.	33	210, (560)
	or *N*-chlorosuccinimide, Me_2S, CH_2Cl_2, $-30° \rightarrow 0°$	77	210
7	$KOBu^t$, EtBr, THF, r.-t.	75	210
8	—	—	561
9	PBr_3, pyridine, hexane, $0° \rightarrow$ r.-t.	65	559
10	Me_2NH, C_6H_6, r.-t.	43	559
11	NaOEt, EtOH, r.-t.	95	210
12	KI, KCN, THF(aq.), reflux	44	559
13	H_2O_2, Na_2CO_3, Me_2CO(aq.), r.-t.	74	559

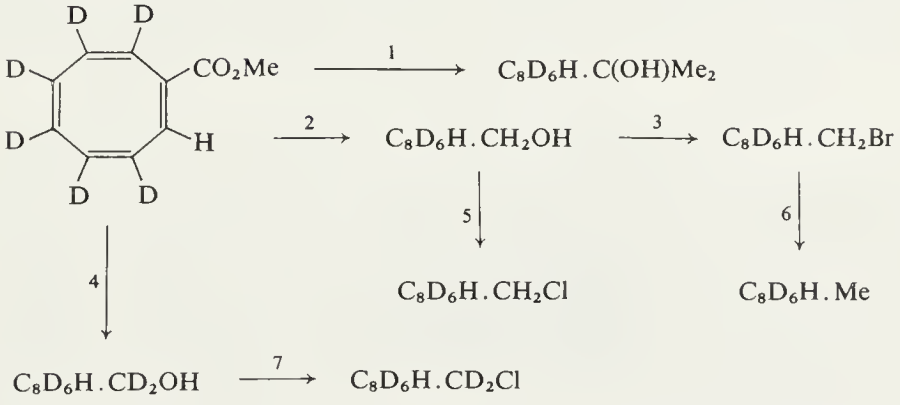
Scheme 31



Reaction	Reagents and conditions	Yield (%)	Ref.
1	$LiAlD_4$, Et_2O, r.-t.	76	210, (558), (560)
2	$SOCl_2$, pyridine, $CHCl_3$, r.-t.	35	210, 560
3	PBr_3	94[a]	558

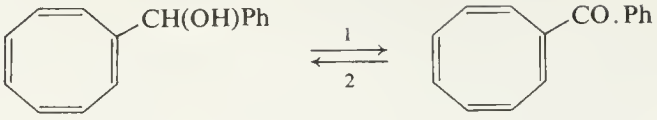
[a] Overall yield from the methyl ester.

Scheme 32



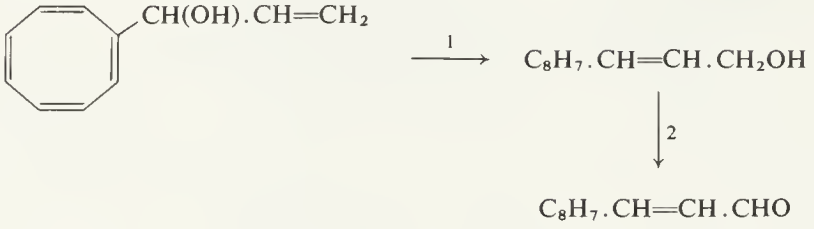
Reaction	Reagents and conditions	Yield (%)	Ref.
1	MeMgI	—	123
2	$LiAlH_4$, Et_2O, $0° \rightarrow 25°$	64	49
3	Ph_3PBr_2, DMF, 25°	84	49
4	$LiAlD_4$, Et_2O, r.-t.	95	210
5	*N*-Chlorosuccinimide, Me_2S, CH_2Cl_2, $-30° \rightarrow 0°$	60	210
6	$LiAlH_4$, Et_2O, reflux	67	49
7	*N*-Chlorosuccinimide, Me_2S, CH_2Cl_2, $-30° \rightarrow 0°$	65	210

Scheme 33



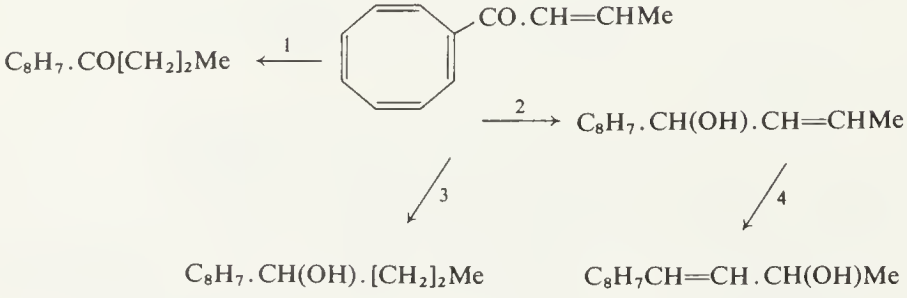
Reaction	Reagents and conditions	Yield (%)	Ref.
1	CrO_3-pyridine, C_6H_6, r.-t.	66	548
2	$LiAlH_4$, Et_2O, reflux	89	544

Scheme 34



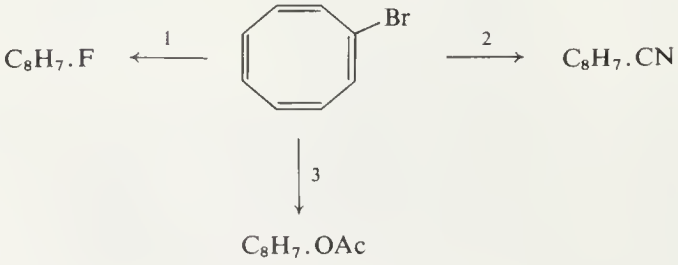
Reaction	Reagents and conditions	Yield (%)	Ref.
1	HCl, Me_2CO(aq.), r.-t.	56	548
2	CrO_3-pyridine, C_6H_6, r.-t.	40	548

Scheme 35



Reaction	Reagents and conditions	Yield (%)	Ref.
1	$LiAlH_4$, Et_2O, 0°	67	548
2	$Al(OPr^i)_3$, toluene, reflux	8	548
3	KBH_4, MeOH(aq.), reflux	85	548
4	HCl, Me_2CO(aq.), r.-t.	87	548

Scheme 36



Reaction	Reagents and conditions	Yield (%)	Ref.
1	AgF, pyridine, r.-t.	67	562
2	$K_4Ni_2(CN)_6$, KCN, MeOH, r.-t.	8	541
3	AgOAc, HOAc, 80°	39	540

Structure

The bond lengths and angles in the eight-membered ring of cyclo-octatetraene-carboxylic acid (obtained by X-ray crystallography[563]) are tabulated (table 25).

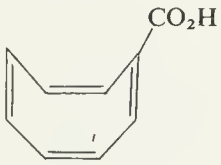
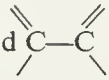


Table 25

Bond	Length (Å)	
C=C	1.322	
C—C	1.470	
Angle 		126°
Torsion angle around 		57°

A monosubstituted COT possessing a *rigid* non-planar eight-membered ring should be capable of existing in two enantiomeric forms, (**227***a*) and (**227***b*), and early attempts were made to effect the separation of such forms (see e.g. refs. 285, 549). When rapid ring-inversion and/or bond-shift processes are

Scheme 37

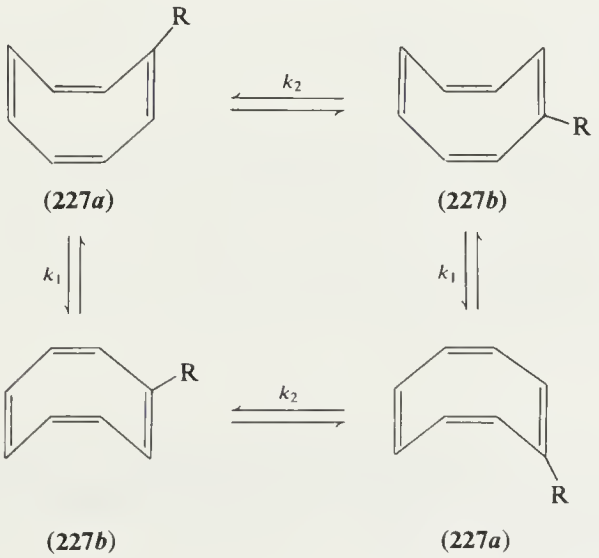
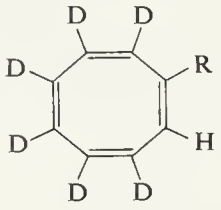


Table 26. Ring-inversion

R	Temp. (°C)	k_1 (s^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})	Ref.
$CHMe_2$	−25	—	14.8	564
$C(OH)Me_2$[a]	−2	7.8	14.7	123
OEt	0	604	12.5	104
$OCHMe_2$	0	361	12.7	104

[a] Substituent group in the hexadeuteriocyclo-octatetraene (**228**).



(**228**)

Table 27. Bond-shift

R	Temp. (°C)	k_2 (s^{-1})	$\Delta G^{\ddagger}$ (kcal mol^{-1})	Ref.
$C(OH)Me_2$[a]	−2	*ca.* 0.1	*ca.* 17.1	123
$C(OH)Me_2$[a]	41	5.4	17.4	123
CO_2CH_2Me[a]	40	126	15.3	123
OMe	0	(0.45), 0.61	16.2	(554), 104
OEt	0	0.88	16.0	104
$OCHMe_2$	0	1.86	15.6	104
$OCMe_3$	0	(6), 7.29	14.9	(554), 104
F	−33	*ca.* 44	*ca.* 12	550

[a] Substituent group in the hexadeuteriocyclo-octatetraene (**228**).

operating (see scheme 37), such attempts have no chance of success.

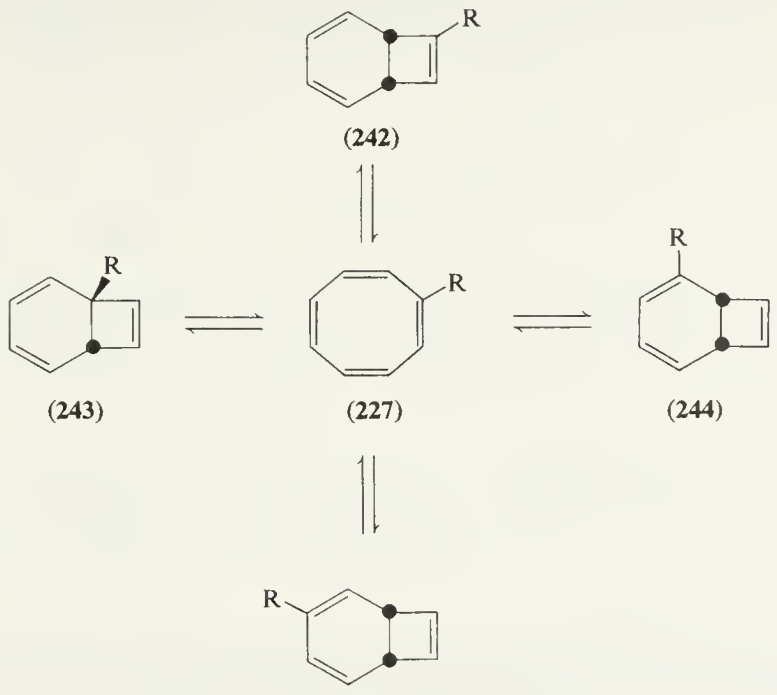
Ring-inversion and bond-shift processes may be studied in suitable substituted COTs by means of variable-temperature n.m.r. spectroscopy, and the available results are collected in tables 26 and 27.

Four different bicyclic valence tautomers, (**242**)–(**245**), are possible for a monosubstituted COT (scheme 38); however, Diels–Alder adducts are mostly derived from the 7-substituted compound (**242**), since this reacts more rapidly than the others (see pp. 101–2). (Values of the Eyring parameters for (**227**; R = Ph) → (**242**; R = Ph) are given in ref. 135.)

Reactions

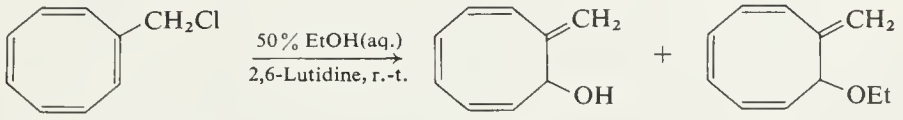
(*a*) *Functional group transformations.* Most of these naturally lead to other substituted COTs (see pp. 86–92); however, the following reactions result in derivatives which are not COTs.

Scheme 38



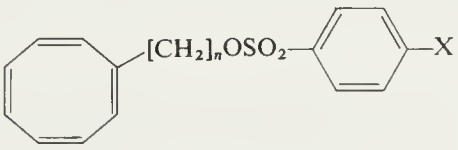
(242) (243) (227) (244) (245)

Hydrolysis of the chloromethyl-derivative (**246**) in buffered aqueous ethanol leads to a mixture of the methylenecyclo-octatrienes (**247**) (*ca.* 66%) and (**248**) (*ca.* 22%); these products are extremely acid-sensitive, rearranging to *o*-tolylacetaldehyde.[210]



(246) (247) (248)

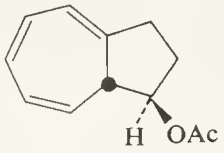
The operation of π-bond participation in solvolytic reactions of suitable monosubstituted COTs is revealed by studies using the sulphonate esters (**249**).



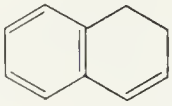
(**249**)

a: $n = 2$, X = Br
b: $n = 2$, X = NO_2
c: $n = 3$, X = NO_2
d: $n = 4$, X = NO_2

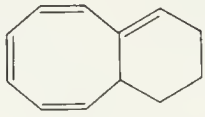
The acetolysis (NaOAc–HOAc) of (**249***a*) or (**249***b*) gives rise to varying amounts of the tetrahydroazulene (**250**), the dihydronaphthalene (**251**), and other products, [545–547] and that of (**249***d*) to the bicyclic tetraene (**252**) etc.[547] (very little rearrangement is observed with (**249***c*)[547]).



(**250**)

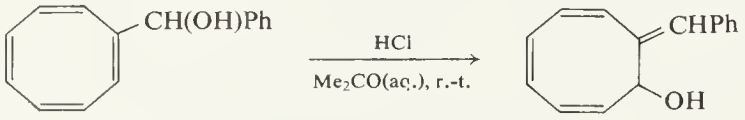


(**251**)



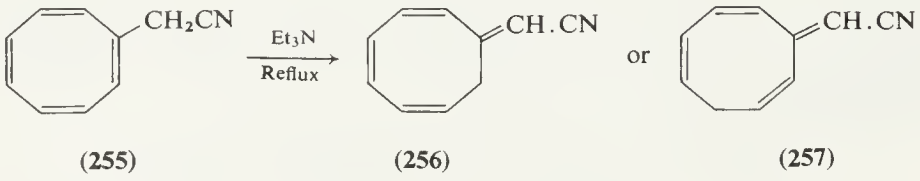
(**252**)

Acid-catalysed rearrangement of the alcohol (**253**) gives the product (**254**) (83%).[548]

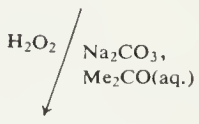


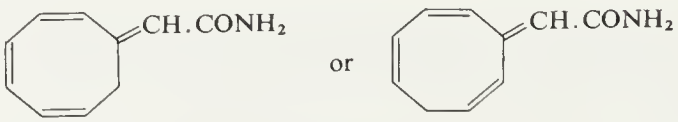
(**253**) (**254**)

Treatment of the nitrile (**255**) with triethylamine yields a product formulated as either (**256**) or (**257**) (87%), which may be converted into the amide (**258**) or (**259**) (32%).[559]



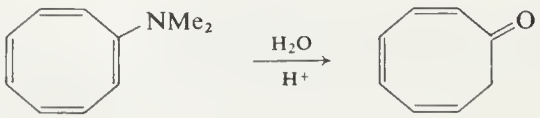
(**255**) (**256**) (**257**)



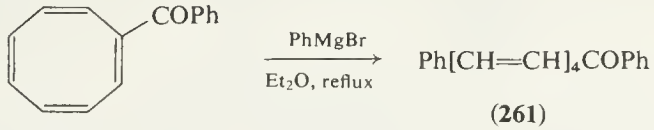


(**258**) (**259**)

N,*N*-Dimethylaminocyclo-octatetraene is hydrolysed extremely readily in the presence of acids, forming cyclo-octa-2,4,6-trienone.[541]

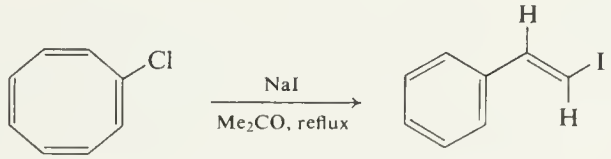


With phenylmagnesium bromide, the benzoyl-derivative (**260**) undergoes 1,4-addition and subsequent ring-opening, with the formation of the acyclic ketone (**261**) (20%).[544]



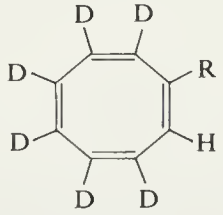
(**260**) (**261**)

Treatment of chlorocyclo-octatetraene with sodium iodide gives *E*-β-iodostyrene (**262**) (72%)[553] (*cf.* the thermal rearrangement of halocyclo-octatetraenes, below).



(**262**)

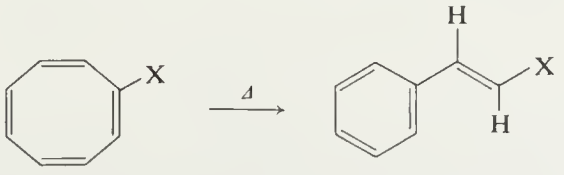
(*b*) *Thermolysis.* The operation of a degenerate rearrangement in certain monosubstituted COTs when subjected to a temperature of *ca.* 550° (flow system) is revealed by protium scrambling in the hexadeuterio-derivatives (**228**)[49] (see p. 80). (For carbon and hydrogen scrambling in the mass spectrometry of monosubstituted COTs, see ref. 558.)



(**228**)

R = Me, Ph, CO_2Me

The acetoxy-, fluoro-, chloro- and bromo-derivatives of COT undergo thermal rearrangement to give *E*-β-substituted styrenes (**263**) (table 28); the isomerisation is accelerated by acids.[566] The mechanism of the rearrangement



(**263**)

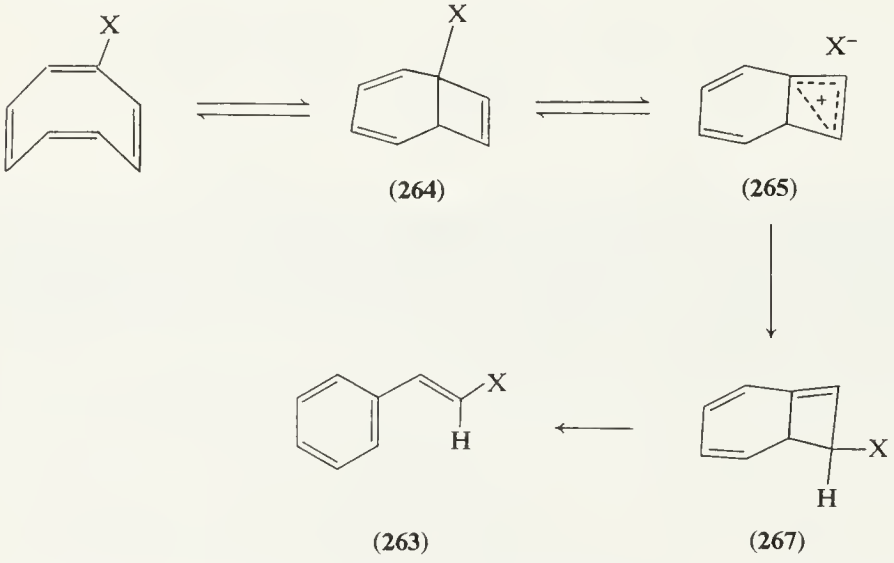
Table 28

X	Temp. (°C)	Yield (%)	Ref.
OAc	120[a]	100	565
F	100	12	562
Cl	200–210	91	553, (565)
Br	90–103	84	553, (566)

[a] In the presence of acetic acid.

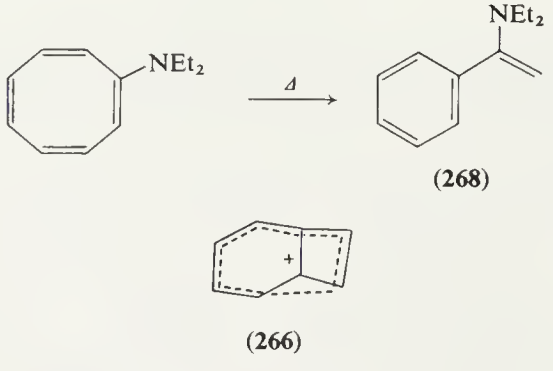
has been elucidated,[566, 567] and is illustrated in scheme 39. Ionisation of the valence tautomer (**264**) generates a cation which may be formulated as a homocyclopropenium ion (**265**).* Ion-recombination can give the strained

Scheme 39



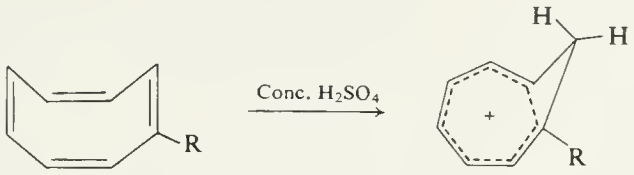
cyclobutene derivative (**267**), in which conrotatory ring-opening leads to the *E*-styrene (**263**) (very little of the *Z*-isomer is produced).

In contrast, *N*,*N*-diethylaminocyclo-octatetraene rearranges to give the α-substituted styrene (**268**).[541]



* Or, alternatively, as the homotropylium ion (**266**).[562]

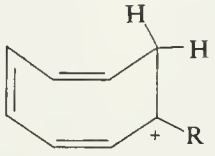
(*c*) *Reactions with electrophiles.* Protonation of methyl- or phenylcyclo-octatetraene occurs preferentially on the 'inside' of the 'tub' structure (*cf.* COT, p. 22), and affords only one isomer (**269**) of the six possible homotropylium ions.[215]



(**269**)

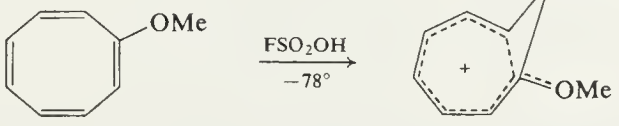
R = Me, Ph

It is proposed that the cation (**270**), the most stable of the possible classical structures, is an intermediate in this conversion (or alternatively, that the transition state resembles (**270**)).[215] Similarly, protonation of methoxycyclo-

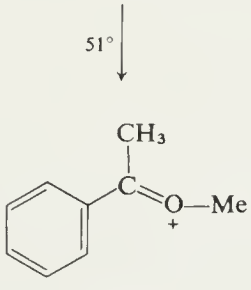


(**270**)

octatetraene gives the homotropylium ion (**271**), but this rearranges at 51° to (**272**), which on hydrolysis yields acetophenone.[568] In FSO_2OD, *ca.* 75%



(**271**)

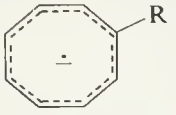


(**272**)

of the resulting homotropylium ions contain deuterium in the *endo*-position.[568]

For the addition of bromine to monosubstituted COTs, see ref. 569 (for the low-temperature bromination of bromocyclo-octatetraene, see refs. 43, 565).

(*d*) *Reduction.* The anion radicals (**273**) derived from monosubstituted COTs have been studied by means of e.s.r. spectroscopy (table 29). For theoretical studies, see also refs. 258, 575.



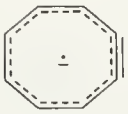
(**273**)

Table 29

R	Ref.
D	250
Me	247, 570
Et	247, 537, 570, 571
Pr^n	247, 570
Bu^n	247, 570
[a]Ph	80, 572–574
p-Me.C_6H_4	539
p-Bu^t.C_6H_4	539
p-Ph.C_6H_4	539
2,4,6-Me_3.C_6H_2	539
p-Me_2N.C_6H_4	539
Cyclo-octatetraenyl	574
OBu^t	537, 571

[a] For the deuteriated species (**273**; R = C_6D_5), see ref. 537.

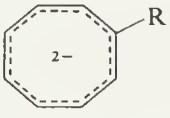
Bromocyclo-octatetraene reacts with potassium in tetrahydrofuran-hexamethylphosphoramide to generate the anion radical (**274**).[576]



(**274**)

For the polarographic reduction of methoxycyclo-octatetraene, see refs. 75, 577.

The reported monosubstituted COT^{2-} species (**275**) are listed in table 30.



(**275**)

Table 30

R	Ref.
Me	578
Ph	80
OMe	578
$OCHMe_2$	579

Examples of the catalytic hydrogenation of monosubstituted COTs to give cyclo-octane derivatives (**276**) are listed in table 31; in some instances the intermediate cyclo-octene (**277**) may be isolated (see p. 30).

(**227**) (**277**) (**276**)

Table 31

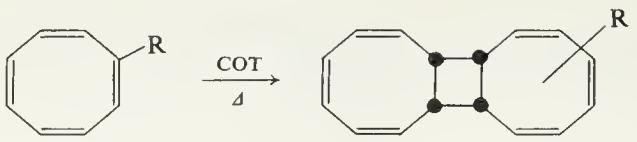
R	Catalyst and solvent	Yield (%)	Ref.
Me	PtO_2,[a] HOAc	53	533
Et	PtO_2,[a] HOAc	69	286
Pr^n	PtO_2,[a] HOAc	64	533
Bu^n	PtO_2,[a] HOAc	60	(286), 533
$CH{=}CH_2$	PtO_2,[a] HOAc	86, (64)[b]	24, (25)
Cyclo-octatetraenyl	PtO_2,[a] HOAc	67	544
Ph	10% Pd–C, MeOH	80	285
p-$Me_2N.C_6H_4$	10% Pd–C, MeOH	61	285
$[CH_2]_2OH$	PtO_2,[a] EtOH	84	534
CH_2OH	PtO_2,[a] EtOH	94	534
CH(OH)Ph	10% Pd–C, EtOH	67[c]	548, (549)
COPh	10% Pd–C, EtOH	38	549
COPh	1% Pd–$CaCO_3$, EtOH	66[d]	549
CO_2H	10% Pd–C, EtOH	97.5[e]	549
Cl	PtO_2,[a] HOAc, NaOAc	72[f]	553
Br	PtO_2,[a] HOAc, NaOAc	—[f]	553

[a] Pre-reduced. [b] Product (**276**; R = Et). [c] Product (**276**; R = CH_2Ph).
[d] Product (**277**; R = COPh). [e] Product (**277**; R = CO_2H). [f] Product (**276**; R = H).

(*e*) *Cycloadditions.* The [2 + 2] cycloaddition of certain monosubstituted COTs to COT itself produces very low yields of the 'mixed' dimers (**278**) (table 32), convertible into monosubstituted [16]annulenes (see p. 359).[160, 580]

The dimerisation of (**227**; R = CO_2Me, OMe) occurs at 100–150°, but the products have not been characterised.[160]

In principle, monosubstituted COTs could undergo [4 + 2] cycloadditions *via* any of the four possible bicyclic valence tautomers (**242**)–(**245**) (see p. 95). In most cases, however, the adducts are predominantly those of the 7-substituted bicyclo[4.2.0]octa-2,4,7-triene (**242**), steric factors presumably resulting



(227) (278)

Table 32

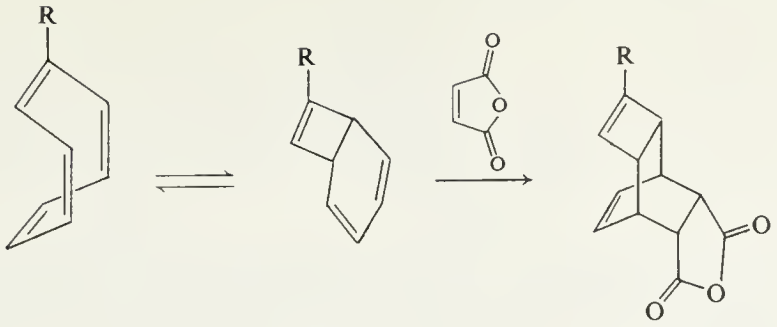
R	Temp. (°C)
Ph	100
CO_2Me	100
F	70
Cl	100

in a slower rate of addition for the 1-, 2- and 3-substituted compounds. Thus with e.g. maleic anhydride, monosubstituted COTs afford adducts of structure (**279**). The known reactions of this general type are listed in table 33. (For secondary deuterium isotope effects in Diels–Alder reactions of the hexa-

Table 33 (refers to the equation at the top of p. 103)

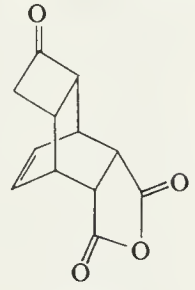
R	Dienophile	Conditions	Yield (%)	Ref.
Me	Maleic anhydride	Benzene, reflux	55	543
		Toluene, reflux	30	533
Me	Tetracyanoethylene	EtOAc, reflux	61	49
Et	Maleic anhydride	165–170°	60	533
Et	Tetracyanoethylene	—	—	567
Cyclopropyl	Maleic anhydride	Toluene, reflux	—	542
Ph	Fumaroyl chloride	EtOAc or THF, 70°	—	135
Ph	Maleic anhydride	Benzene, reflux	92, (91), [69]	135, (285), [542]
Ph	Tetracyanoethylene	EtOAc or THF, 70°	—	135
		EtOAc, reflux	58	49
Ph	Dicyanomaleimide	EtOAc or THF, 70°	—	135
Ph	*p*-Benzoquinone	Benzene, reflux	(76), 81	(285), [536], 581
CO.CH=CHMe	Maleic anhydride	*o*-Cl_2.C_6H_4, reflux	41	548
CO.Ph	Maleic anhydride	*o*-Cl_2.C_6H_4, reflux	70	548
CO_2Me	Maleic anhydride	Xylene, reflux	64 (crude)	542
CO_2Me	Tetracyanoethylene	Dioxan, reflux	62	49, (567)
OMe	Maleic anhydride	Benzene, 70°	99	582
		r.-t.	12[a]	542
OAc	Maleic anhydride	Benzene, reflux	59	543
OAc	Tetracyanoethylene	—	—	567
F	Tetracyanoethylene	EtOAc, reflux	48	562
Cl	Tetracyanoethylene	—	—	567
Br	Tetracyanoethylene	—	—	567

[a] The isolated product was the keto-anhydride (**280**).

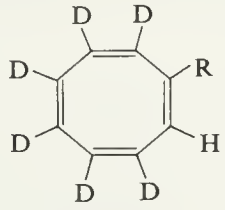


(242) (279)

deuterio-compounds (**228**; R = Me, Ph, CO_2Me, CN), see ref. 583.) Vinylcyclo-octatetraene forms a 1 : 2 adduct with maleic anhydride at 140–160°

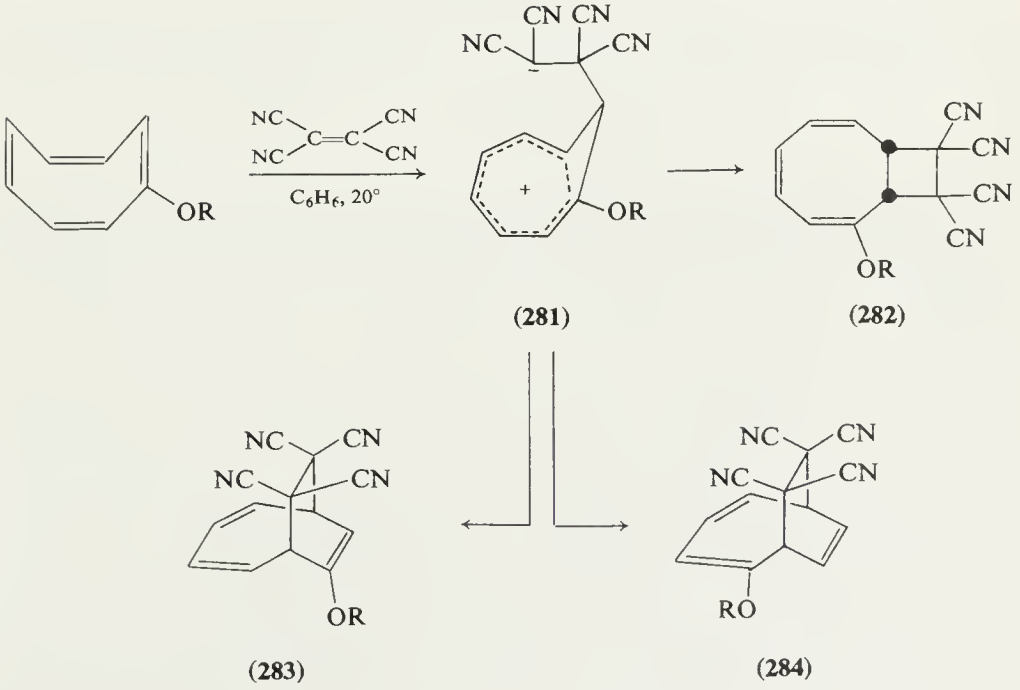


(280)



(228)

(yield 23%),[26] but the structure of the product is unknown. Phenylcyclo-octatetraene is reported to react with dimethyl acetylenedicarboxylate at 130°.[581]



(281) (282)

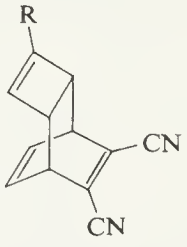
(283) (284)

Table 34

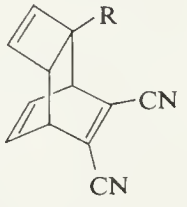
	Yield (%)		
R	(**282**)	(**283**)	(**284**)
Me	—	18	78
Ph	74	—	17

In contrast with the above reactions which proceed *via* a bicyclic valence tautomer, methoxy- and phenoxycyclo-octatetraene react directly with tetracyanoethylene (at room-temperature) *via* the homotropylium zwitterion (**281**) (which presumably gains additional stabilisation from the OR group), affording 1,2- and/or 1,4-addition products (**282**)–(**284**)[582] (table 34). (For photolysis of (**284**; R = Me), see ref. 582.)

With dicyanoacetylene, two different types of [4 + 2] adduct, (**285**) and (**286**) have been obtained[562] (table 35).



(**285**)

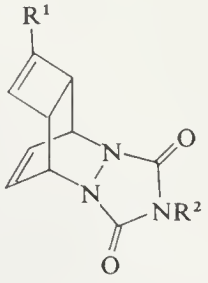


(**286**)

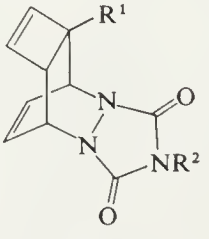
Table 35

		Yield (%)	
R	Conditions	(**285**)	(**286**)
F	Et_2O, r.-t.	—	0.9
Cl	90°	9	—

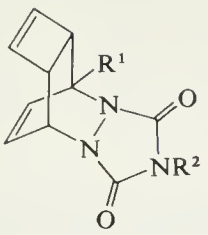
With 1,2,4-triazoline-3,5-diones, the isomers (**287**)–(**290**) may be produced, in some cases accompanied by products of 1,4-addition (**291**) (*cf.* pp. 44–6) (table 36).



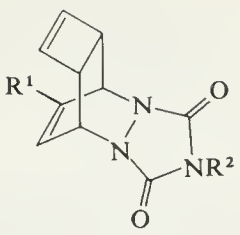
(**287**)



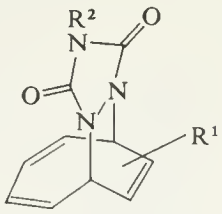
(**288**)



(289)



(290)



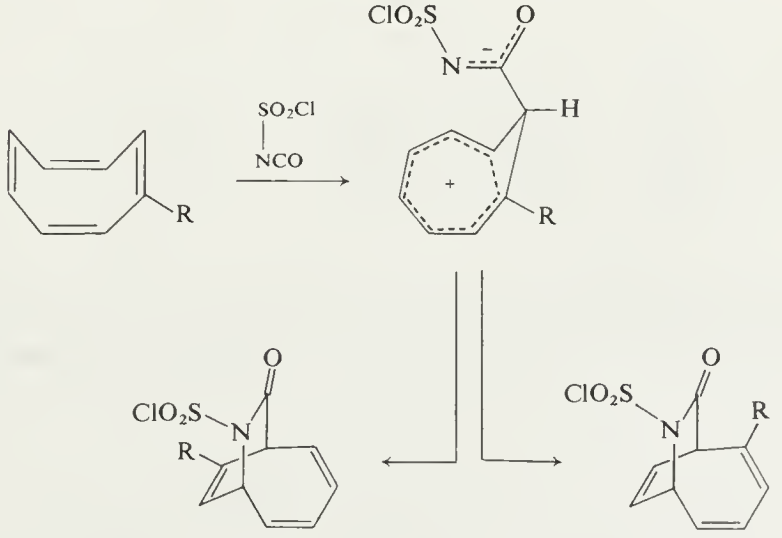
(291)

Table 36

			Yield (%)					
R^1	R^2	Conditions	(287)	(288)	(289)	(290)	(291)	Ref.
Me	Ph	EtOAc, reflux	11	—	—	—	11[a]	569
Ph	Me	EtOAc, reflux	84	—	1	—	—	569
CH_2OMe	Ph	EtOAc, reflux	42	14	7.5	—	17[a]	569
CH_2OAc	Ph	EtOAc, reflux	32	—	—	—	10[b]	569
CN	Ph	EtOAc, reflux	26	25	31	2–4	—	569
CO_2Me	Ph	EtOAc, reflux	8	—	27	2	10[c]	569
F	Me	EtOAc, 65°	—	62	—	—	—	562
F	Ph	EtOAc, reflux	—	95	—	—	—	562
Cl	Ph	EtOAc, 60°	27	30	—	—	—	567
Br	Ph	EtOAc, reflux	12	25	—	—	10[c]	567
I	Ph	EtOAc, 80°	13	—	—	—	8.5	364
I	Ph	EtOAc, 20°	—	—	—	—	12	364

[a] Two isomers. [b] Three isomers. [c] Only one isomer detected.

1,4-Addition occurs with chlorosulphonyl isocyanate (*cf.* COT, pp. 45–6), with the formation of the isomeric products (**292**) and (**293**)[367] (table 37).

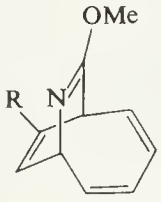


(292) (293)

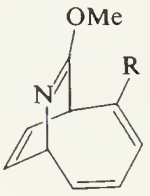
Table 37

R	Conditions	Product ratio[a] (**292**) : (**293**)	
Me	CH_2Cl_2, 0° → 20°	65	35
Ph	CH_2Cl_2, reflux	80	20
p-MeO.C_6H_4	CH_2Cl_2, 0° → r.-t.	45	55
OMe	CH_2Cl_2, −78°	17	83

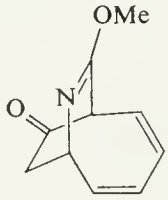
[a] The initial products were converted into the corresponding lactams, which were characterized as the imino-ethers (**294**) and (**295**); when R = OMe, two additional products were the ketones (**296**) and (**297**).



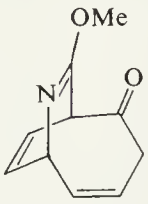
(**294**)



(**295**)

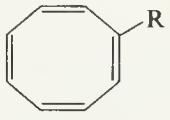


(**296**)



(**297**)

(*f*) *Formation of metal derivatives.* Silver nitrate complexes of monosubstituted COTs (**227**) are readily formed in boiling ethanol (see p. 51) (table 38).

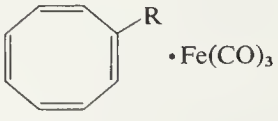


(**227**)

Table 38

R	Complex	Ref.
Me	$2(Me.C_8H_7).3AgNO_3$	533
Et	$Et.C_8H_7.2AgNO_3$	533
Pr^n	$Pr^n.C_8H_7.2AgNO_3$	533
Ph	$Ph.C_8H_7.AgNO_3$	285
COPh	$PhCO.C_8H_7.AgNO_3$	544

The iron tricarbonyl complexes (**298**) result from the action of iron carbonyls on monosubstituted COTs (table 39). N.m.r. studies indicate that for



(**298**)

Table 39

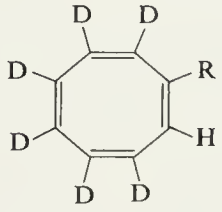
R	Reagents and conditions	Yield (%)	Ref.
Me	$Fe_2(CO)_9$, hexane, reflux	49	584, (585)
CH_2D[a]	$Fe_2(CO)_9$, hexane, reflux	—	586
Et	—	—	585
CPh_3	—	—	585, 587
Ph	$Fe_2(CO)_9$, hexane, reflux	50	588
	$Fe_3(CO)_{12}$, benzene, reflux[b]	60	(585), 590
CO_2Me	$Fe_2(CO)_9$, hexane, reflux	80	(585), 588, (591)
OMe	$Fe_2(CO)_9$, Et_2O, reflux	32[c]	588
Br	—	—	587
$SiMe_3$	$Fe_2(CO)_9$, heptane	40[d]	551
$SiMe_2$(allyl)	$Fe_2(CO)_9$, heptane	60	551
$GeMe_3$	$Fe_2(CO)_9$, heptane	60	551
$SnMe_3$	$Fe_2(CO)_9$, heptane	10[d]	551
$Fe(CO)_2$(CPD)	$Fe_2(CO)_9$, heptane	7	551

[a] Substituent group in (**228**).

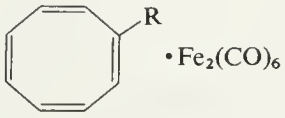
[b] Photoactivation of the reaction with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ in benzene may also be used; with $Fe(CO)_5$ (no solvent) a binuclear complex (**299**) is an additional product.[589]

[c] The cyclo-octatrienone complexes (**300**) (10%) and (**301**) (5%) are also formed.

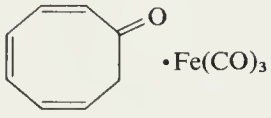
[d] A binuclear complex (**299**) (*ca.* 2%) is also formed.[551]



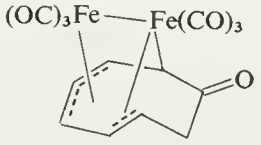
(**228**)



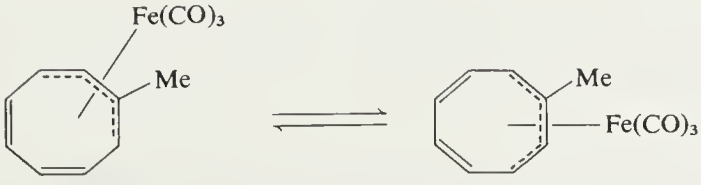
(**299**)



(**300**)



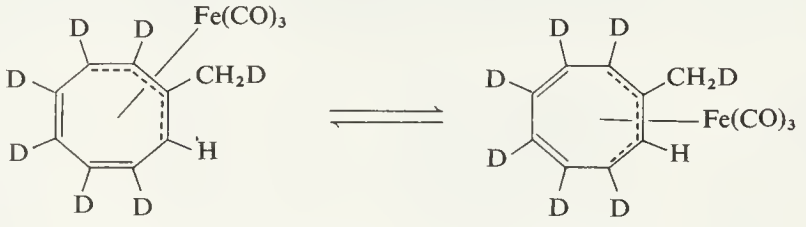
(**301**)



(**302***a*) (**302***b*)

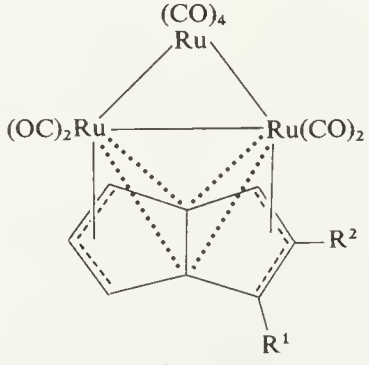
the complex (**298**; R = Me), in the most favourable arrangement of the co-ordinated diene system the methyl group is attached to one of its internal carbon atoms, and that the valence tautomerism (**302*a***) ⇌ (**302*b***) is rapid at room temperature.[592, 593] Examination of the deuteriated derivative (**303*a*** ⇌ **303*b***) has provided confirmation.[586] In contrast, electron-withdrawing groups tend to repel the $Fe(CO)_3$ group.[593]

(For mass spectra of iron tricarbonyl complexes (**298**), see ref. 594.)



(**303*a***) ($\Delta G^{\ddagger} = 7.5$ kcal mol) (**303*b***)

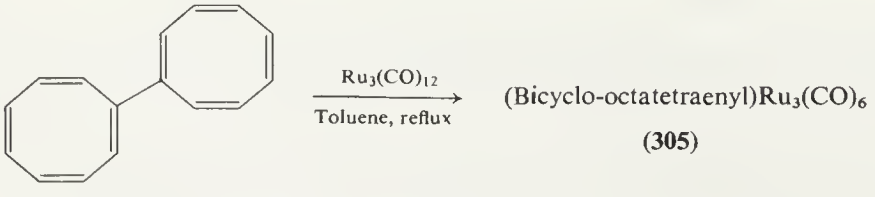
Amongst the identified products resulting from the reactions of methyl- or phenylcyclo-octatetraene with $Ru_3(CO)_{12}$ or $[Ru(SiMe_3)(CO)_4]_2$ are the pentalene complexes (**304**), of which the 2-substituted compounds (**304*a***) are fluxional but the 1-substituted isomers (**304*b***) are not. [595]



(**304**)

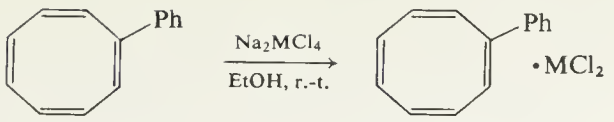
a: $R^1 = H$; R^2 = Me, Ph
b: R^1 = Me, Ph; $R^2 = H$

The reaction of bicyclo-octatetraenyl with $Ru_3(CO)_{12}$ gives the complex (**305**) (see appendix).



(**305**)

Palladium(II) and platinum(II) complexes of type (**306**) are formed by treatment of phenylcyclo-octatetraene with sodium tetrachloropalladate or



(306)

Table 40

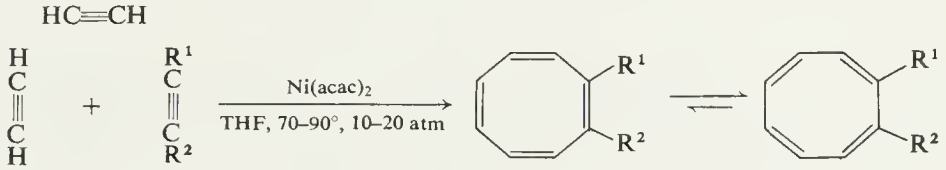
M	Yield (%)
Pd	41
Pt	24

tetrachloroplatinate[596] (table 40). (Similar complexes have been obtained from the salts Na_2MBr_4, but they have not been characterised.)

2. Disubstituted derivatives

Formation

(*a*) '*Mixed*' *cyclotetramerisation of acetylenes.* Co-reaction of acetylene and disubstituted acetylenes may be effected in the presence of nickel catalysts to afford 1,2-disubstituted COTs (**307**) in low yield (table 41).



(307)*

Table 41

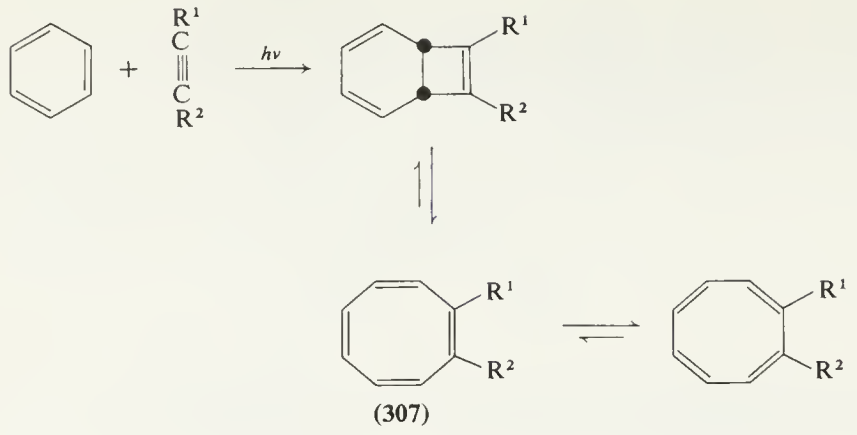
R^1	R^2	Yield (%)	Ref.
Me	Me	19	533
Ph	Ph	14	532
CH_2OAc	CH_2OAc	22[a]	597
CO_2Me	CO_2Me	10[a]	597

[a] The initial product was hydrolysed before purification.

A similar reaction involving two molecules of acetylene and two of phenylacetylene gives 1,4- and 1,5-diphenylcyclo-octatetraene (together with other isomers).[598]

(*b*) *Photochemical cycloadditions of disubstituted acetylenes to benzene.* The u.v. irradiation of certain disubstituted acetylenes in benzene produces 1,2-disubstituted COTs (table 42); in one case, evidence for the intermediacy of a bicyclo[4.2.0]octatriene has been provided.[38]

* The existence of bond-shift isomerism in 1,2-, 1,3- and 1,4-disubstituted COTs complicates their structural representation (see pp. 115–17) and their nomenclature.

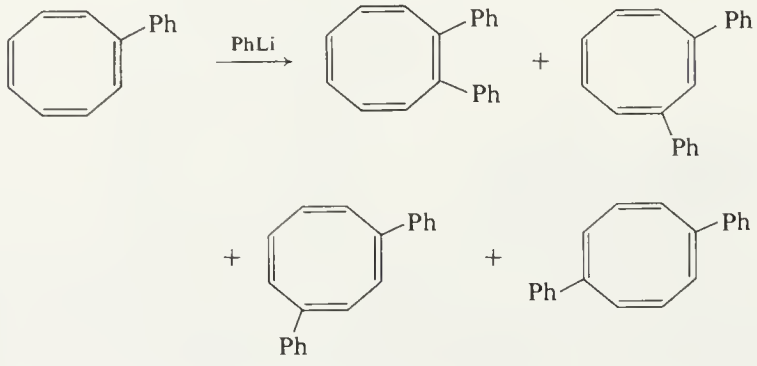


(307)

Table 42

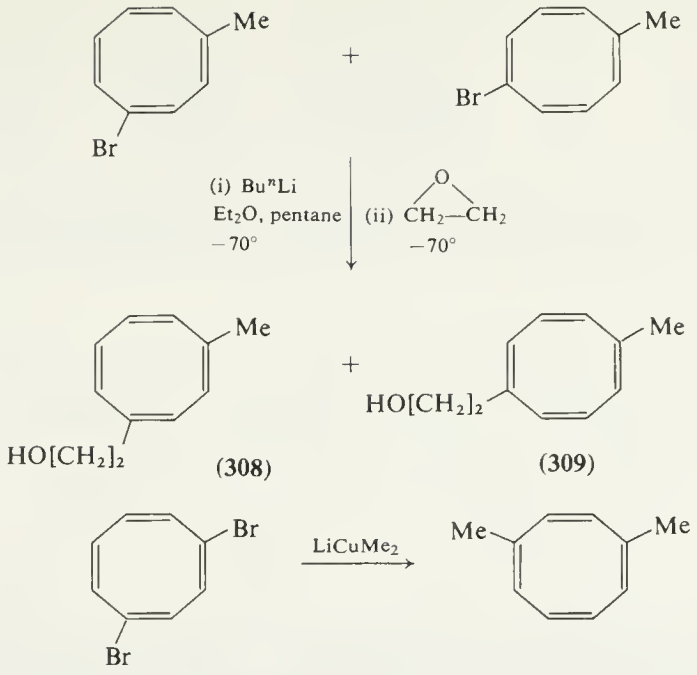
R^1	R^2	Yield (%)	Ref.
Me	CO_2Me	(45), 50	(546), 599
Ph	CO_2Me	—	38
CF_3	CF_3	(Very low)	600
CO_2Me	CO_2Me	32, (15)	536, (601, 602)

(*c*) *Syntheses using organo-lithium reagents.* The reaction of phenyl-lithium with phenylcyclo-octatetraene yields all the four possible positional isomers of the disubstituted derivative; the resulting mixture of 1,2-, 1,3-, 1,4- and 1,5-diphenylcyclo-octatetraene is separable by countercurrent distribution.[598]

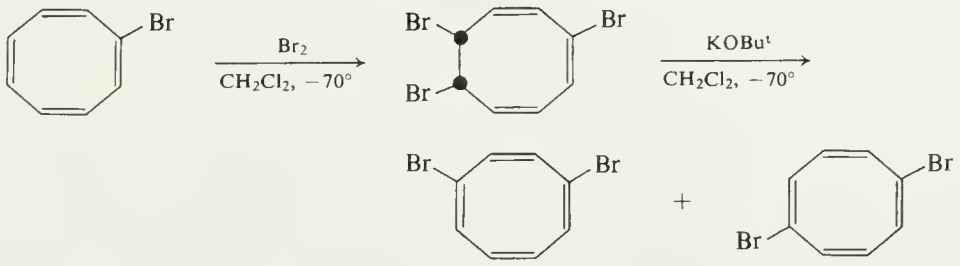


Using a mixture of 1-bromo-4-methyl- and 1-bromo-5-methylcyclo-octatetraene (from methylcyclo-octatetraene, see p. 99), halogen–metal exchange followed by reaction with ethylene oxide leads to the 1,4- and 1,5-disubstituted products (**308**) and (**309**) (overall yield from methylcyclo-octatetraene 19%; isomer ratio 3:1).[43,545,546]

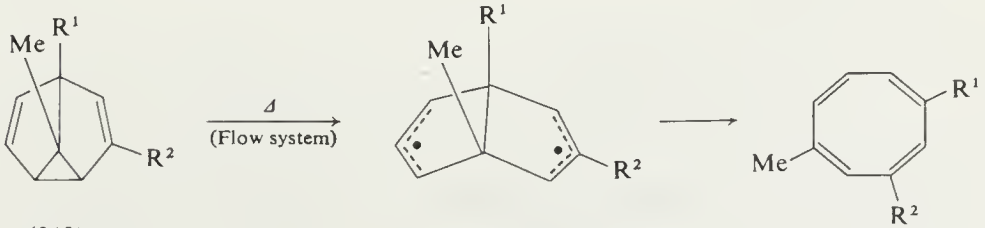
1,4-Dimethylcyclo-octatetraene is produced (95%) from the 1,4-dibromo-compound and lithium 'dimethylcuprate'[565] (but see ref. 43).



(*d*) *Syntheses involving dehydrohalogenation.* 1,4-Dibromocyclo-octatetraene may be prepared from the monobromo-compound by low-temperature bromination and subsequent dehydrobromination;[565] the product is, however, contaminated with the 1,5-dibromo-compound.[43]



(*e*) *Syntheses involving skeletal transformations.* Disubstituted COTs result from the gas-phase thermolysis of disubstituted semibullvalenes, probably *via* a diradical intermediate; thus 1,3- and 1,5-dimethylcyclo-octatetraene are obtained from the appropriate dimethylsemibullvalenes (**310**) (table 43). (For thermolytic interconversions of disubstituted COTs, see p. 118.)

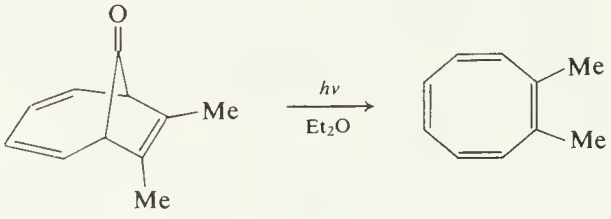


(**310**)

Table 43

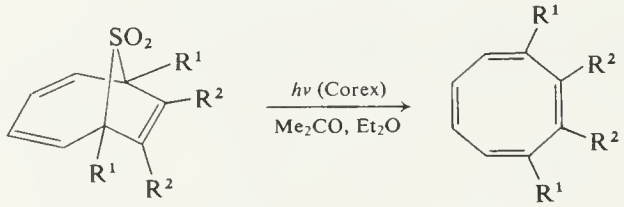
	R^1	R^2	Conditions	Yield (%)	Ref.
a	H	Me	445°/35 mm	78, (69)	43, (603)
b	Me	H	390°/30 mm	(71), 76	(42), 43

The photolytic extrusion of carbon monoxide from the disubstituted 9-oxobicyclo[4.2.1]nona-2,4,7-triene (**311**) gives 1,2-dimethylcyclo-octatetraene (85%).[604]



(**311**)

Similarly, the photolysis of disubstituted 9-thiabicyclo[4.2.1]nona-2,4,7-triene 9,9-dioxides (**312**) leads to 1,2- or 1,4-dimethylcyclo-octatetraene (table 44).



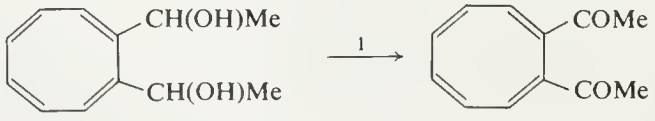
(**312**)

Table 44

	R^1	R^2	Yield (%)	Ref.
a	H	Me	11	604, (605)
b	D	Me	26	49, (606)
c	Me	H	41	43, (606)

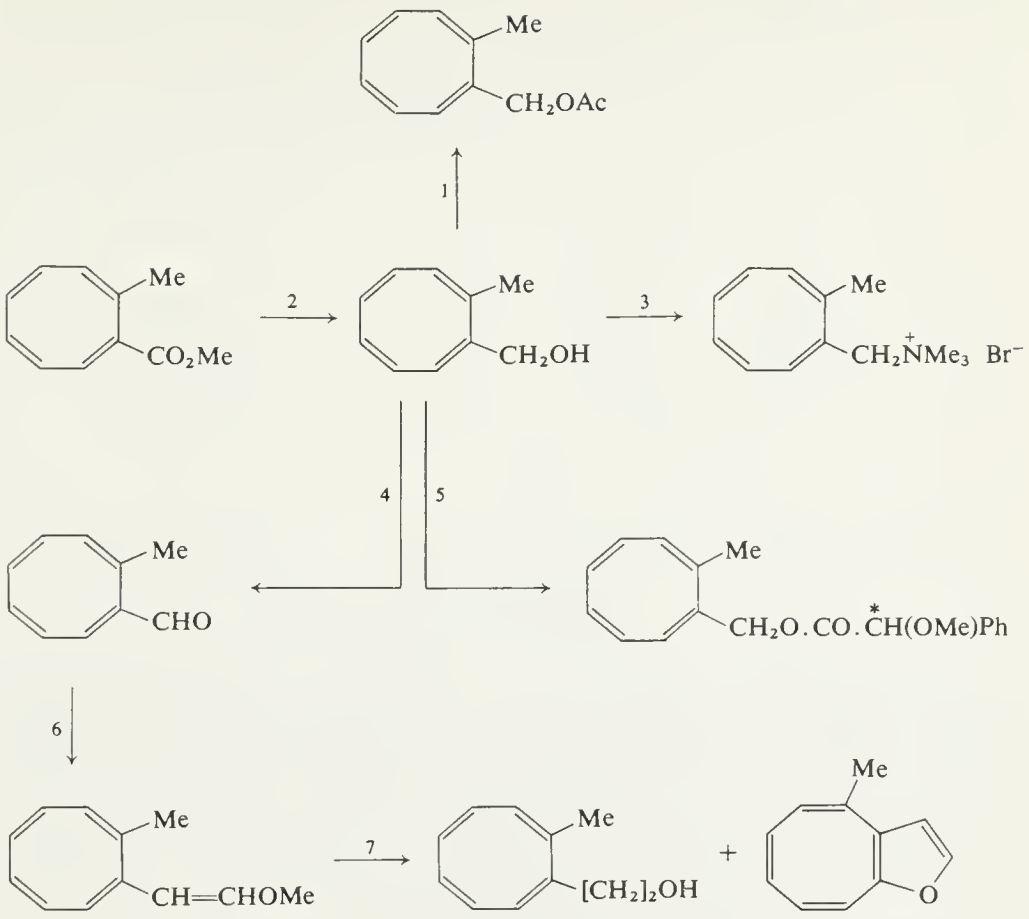
(*f*) *Functional group transformations.* The transformations outlined in schemes 40–43 result in other disubstituted COTs.

Scheme 40



Reaction	Reagents and conditions	Yield (%)	Ref.
1	CrO_3, H_2SO_4	—	607

Scheme 41



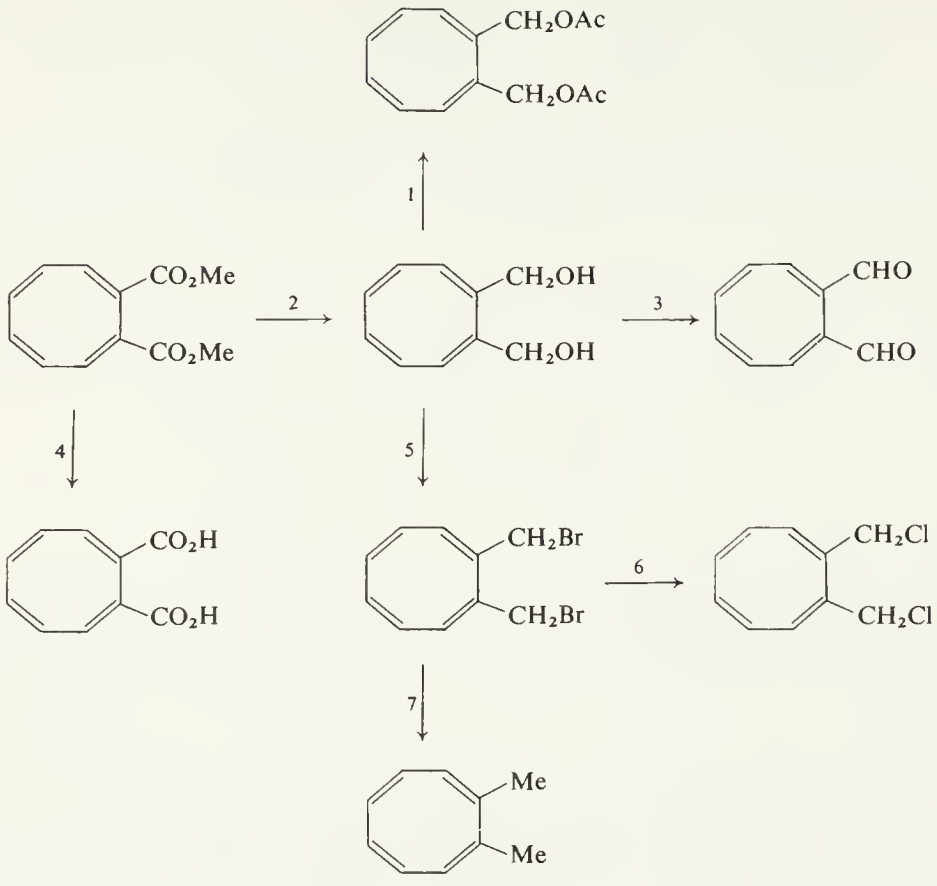
Reaction	Reagents and conditions	Yield (%)	Ref.
1	Ac_2O, *ca.* 100°	87	542
2	$LiAlH_4$, Et_2O, r.-t. or reflux	96–100, (72)	542, 546, (599)
3	(i) PBr_3, pyridine, hexane; (ii) Me_3N, MeOH	40 (overall)	599
4	MnO_2–C, $CHCl_3$, r.-t.	93 (crude)	546
5	(–)-O-Methylmandelyl chloride	—	608
6	$Ph_3P{=}CHOMe$, Et_2O, reflux	82 (crude)	546
7	(i) $Hg(OAc)_2$, THF(aq.), r.-t.; (ii) $NaBH_4$, NaOH(aq.), r.-t.	28 + 56	546

Structure

A structural peculiarity of 1,2-, 1,3- and 1,4-disubstituted COTs is that bond-shift leads to a non-enantiomeric structure (bond-shift isomer).

For a 1,2-disubstituted COT, bond-shift and ring-inversion processes result in the equilibration of two pairs of enantiomers, (**313***a*) and (**313***b*), and (**314***a*) and (**314***b*) (scheme 44). The 'skew' structure (**314**) is generally favoured,

Scheme 42

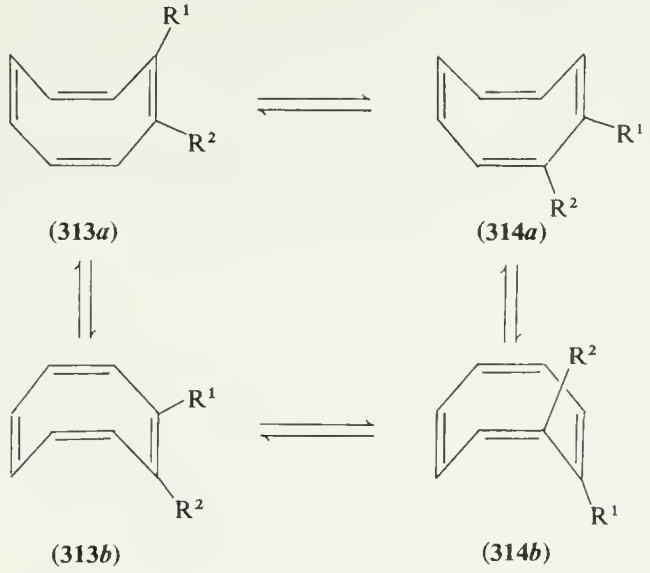


Reaction	Reagents and conditions	Yield (%)	Ref.
1	Ac_2O, *ca.* 100°	75	542
2	$LiAlH_4$, $AlCl_3$, r.-t.	82 (crude)	43, (609)
3	MnO_2, $CHCl_3$, r.-t.	15	610
	or NiO_2	Up to 40	611
4	KOH, EtOH	—	602
5	PBr_3, pyridine, Et_2O, 0–20°	53	612
	or Ph_3PBr_2, DMF, r.-t.	78	43
6	LiCl, DMF, r.-t.	90	612
7	$LiAlH_4$, Et_2O, reflux	87	43

Scheme 43

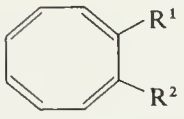
Reaction	Reagents and conditions	Yield (%)	Ref.
1	Ac_2O, pyridine, r.-t.	87 (crude)	546

Scheme 44



(When $R^1 = R^2$, (**313***a*) ≡ (**313***b*))

presumably to minimise repulsion between the substituent groups. The n.m.r. spectra of compounds (**307**; $R^1 = Me$, $R^2 = CH_2O.CO.CH(OMe)Ph$),[608] (**307**; $R^1 = Me$, $R^2 = CO_2Me$),[608] (**307**; $R^1 = Ph$, $R^2 = CO_2Me$),[613] (**307**; $R^1 = R^2 = CHO$),[610] (**307**; $R^1 = R^2 = CO_2H$)[613] and (**307**; $R^1 = R^2 = CO_2Me$)[602,613] reveal that in each case the 'skew' form predominates in



(**307**)

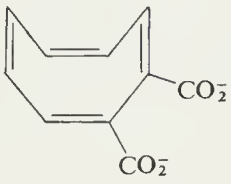
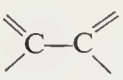


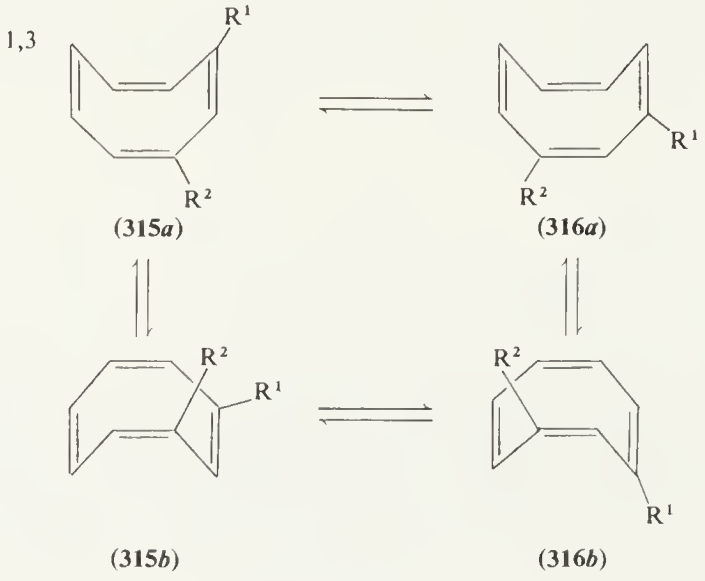
Table 45

Bond	Length (Å)
C═C	1.335
C—C	1.464
Angle 	126°
Torsion angle around 	57°

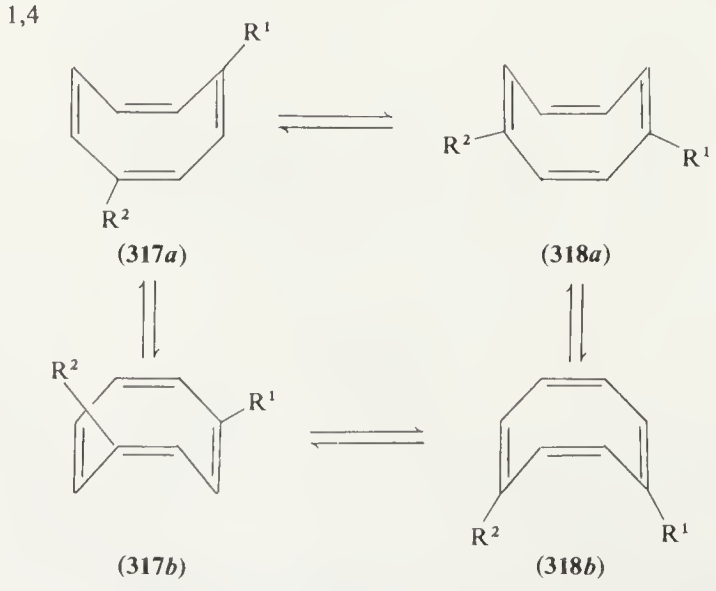
solution. The dicarboxylic acid (**307**; $R^1 = R^2 = CO_2H$) forms a cyclic anhydride only with great difficulty,[613] and its calcium salt is known to crystallise in the 'skew' configuration[614] (bond lengths and angles for the eight-membered ring are given in table 45[614]).

The rate of ring-inversion in 1,2-disubstituted COTs is relatively slow,[599,608] in accordance with the suggested planar transition state for inversion (see p. 10), and the rate of bond-shift is even slower.[608] The proportion of the less

Scheme 45



Scheme 46



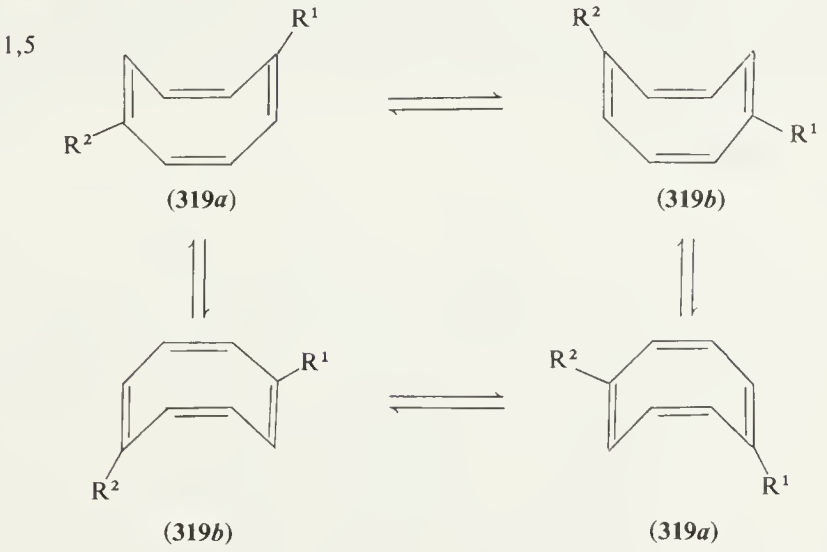
(When $R^1 = R^2$, (**318***a*) ≡ (**318***b*))

stable form (**313**) can be increased by low-temperature u.v. irradiation; e.g. for the compound (**307**; $R^1 = Me$, $R^2 = CO_2Me$) the ratio of the bond-shift isomers (**313**) : (**314**) in deuteriochloroform at 27° is *ca.* 1 : 17, but after u.v. irradiation at −50° to −30°, the ratio is *ca.* 1 : 1 (measured at −42°).[608]

Bond-shift and ring-inversion in 1,3- and 1,4-disubstituted COTs is illustrated (schemes 45 and 46).

The analogous processes in 1,5-disubstituted COTs, however, involve only the enantiomeric forms (**319***a*) and (**319***b*) (scheme 47).

Scheme 47



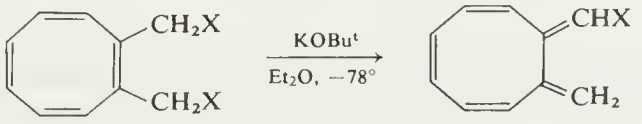
(**319***a*) (**319***b*)

(**319***b*) (**319***a*)

Reactions

(*a*) *Functional group transformations.* While most of these transformations give rise to other disubstituted COTs (see pp. 112–14) or annulated COTs (see pp. 123–4), the following reactions lead to a different system.

Treatment of 1,2-di(halomethyl)-compounds (**320**) with potassium t-butoxide yields the 1,4-dehydrohalogenated products (**321**)[612] (table 46).

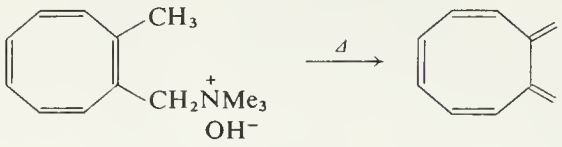


(**320**) (**321**)

Table 46

	X	Yield (%)
a	Cl	97
b	Br	83

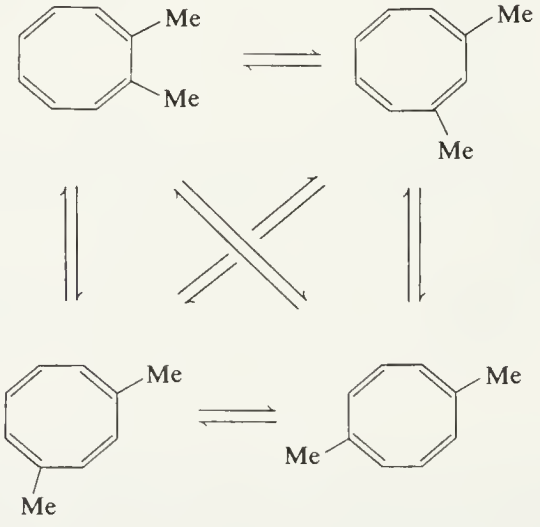
Thermolysis of the quaternary ammonium hydroxide (**322**) gives the dimethylenecyclo-octatriene (**321***c*) (35%).[599]



(**322**) (**321***c*)

(*b*) *Thermolysis.* At temperatures *ca.* 500° the dimethylcyclo-octatetraenes interconvert (scheme 48); 1,4-dimethylcyclo-octatetraene is the *initial* product from the 1,2- or the 1,5-dimethyl-derivative, and is kinetically dominant in the rearrangement of the 1,3-dimethyl-compound.[49, 603, 606] The main mechanism

Scheme 48



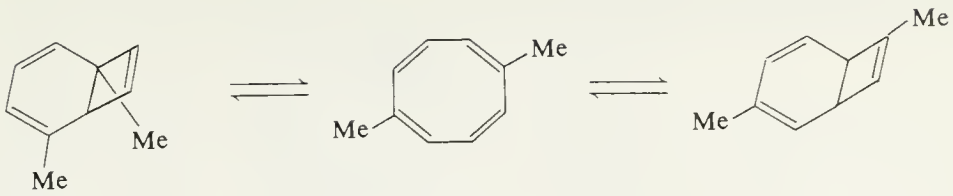
for these rearrangements is illustrated (scheme 49) for 1,5-dimethylcyclo-octatetraene; intramolecular Diels–Alder reactions in the two possible valence tautomers (**323**) and (**324**) being followed by *retro*-processes in the alternative mode.[49, 603]

1,2-Dimethylcyclo-octatetraene is known to undergo an additional *degenerate* rearrangement, revealed by scrambling of the deuterium label in the dideuterio-derivative (**325**).[49] At *ca.* 600°, fragmentation to aromatic products predominates.[49]

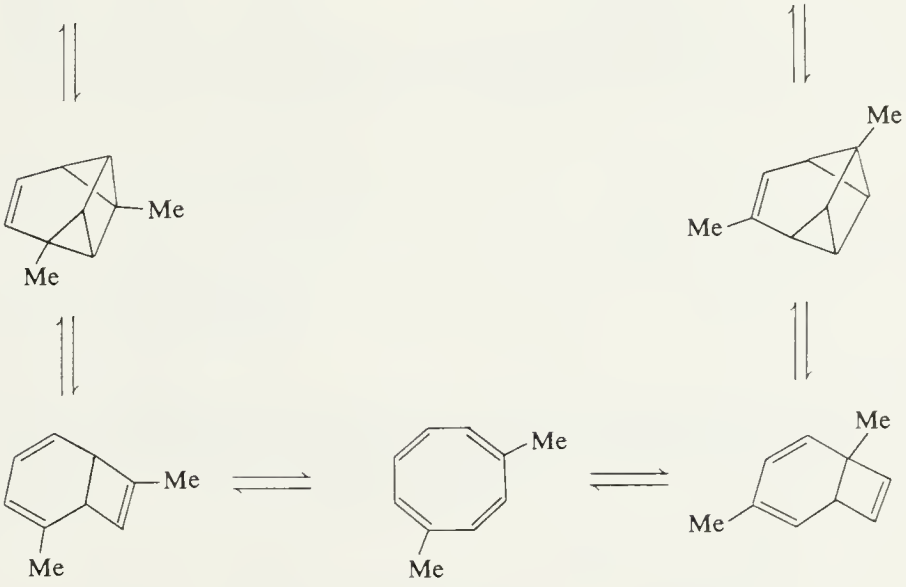
Thermal isomerisation of 1,4-dibromocyclo-octatetraene gives the dibromostyrene (**326**) (up to 92%)[565] (see pp. 97–8).

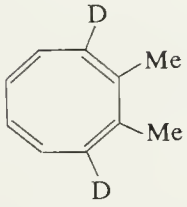
(*c*) *Bromination.* 1,4-Dinitrocyclo-octatetraene is reported to afford the dibromo-derivative (**327**).[615]

Scheme 49

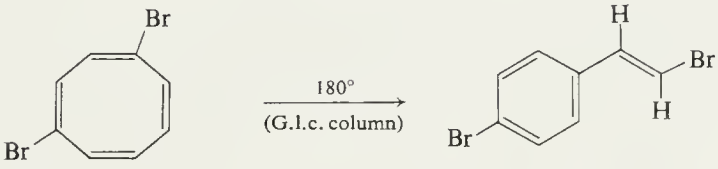


(323) (324)

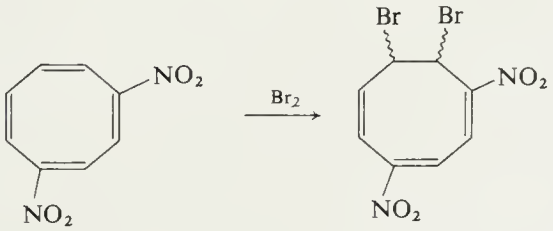




(325)

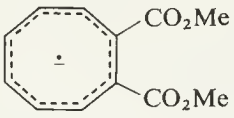


(326)



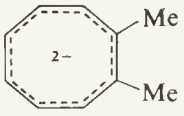
(327)

(*d*) *Reduction.* For alkali metal and electrolytic reduction of 1,2-di(methoxycarbonyl)cyclo-octatetraene to the anion radical (**328**), see ref. 616.

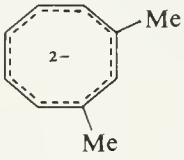


(**328**)

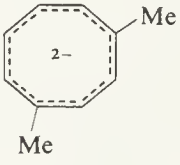
The dianions (**329**)–(**332**) are produced from the parent dimethylcyclo-octatetraenes by the action of potassium in liquid ammonia[43] (the polarographic reduction of these hydrocarbons is also described in ref. 43).



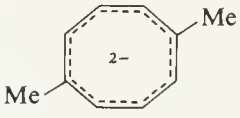
(**329**)



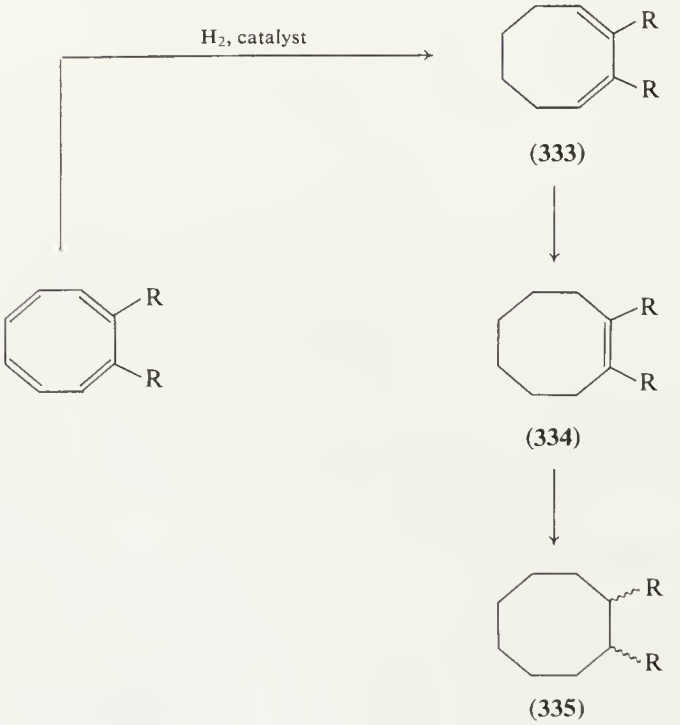
(**330**)



(**331**)



(**332**)



(**333**)

(**334**)

(**335**)

Table 47

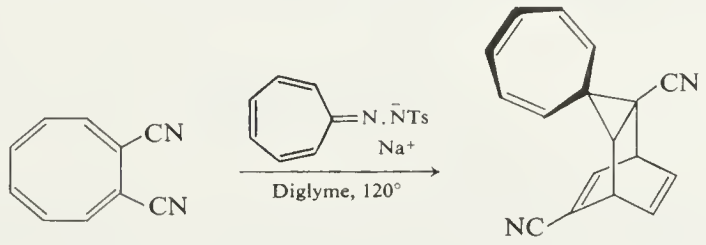
Product	R	Catalyst	Solvent	Yield (%)	Ref.
(333)	Ph	1% Pd–$CaCO_3$, then 10% Pd–C	EtOAc	17	617
(333)	CF_3	Pd–C	—	—	600
(333)	CO_2H	10% Pd–C	MeOH(aq.)	32 (crude)	536
(334)	Me	1% Pd–$CaCO_3$	MeOH	66	533
(334)	Ph	10% Pd–C	EtOAc	52	617
(334)	CO_2H	Pd–C	MeOH(aq.)	—	536
(335)	CH_2OH	PtO_2[a]	HOAc	58[b]	597

[a] Pre-reduced. [b] The product has R = Me.

The catalytic hydrogenation of 1,2-disubstituted COTs sometimes allows the isolation of 2,3-disubstituted cyclo-octa-1,3-dienes (**333**) or cyclo-octenes (**334**) (table 47).

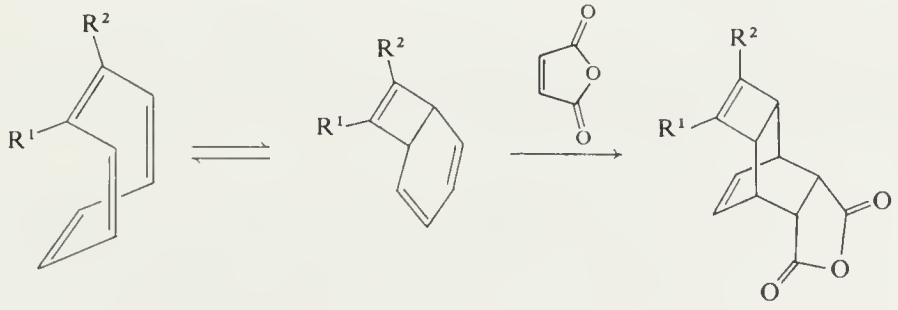
The hydrogenation of 1,3-, 1,4- or 1,5-diphenylcyclo-octatetraene over 10% Pd–C in ethanol gives the corresponding cyclo-octane (mixture of *cis*- and *trans*-isomers).[598]

(*e*) *Cycloadditions.* 1,2-Dicyanocyclo-octatetraene reacts with cycloheptatrienylidene (generated from the sodium salt of the tosylhydrazone of tropone) to afford a low yield (3%) of the product (**336**).[618]



(**336**)

1,2-Disubstituted COTs undergo Diels–Alder addition with maleic anhydride to give adducts of structure (**337**); tetracyanoethylene reacts similarly (table 48). (For the tetracyanoethylene adduct of the 3,8-dideuterio-derivative of 1,2-dimethylcyclo-octatetraene (**325**), see ref. 606.)

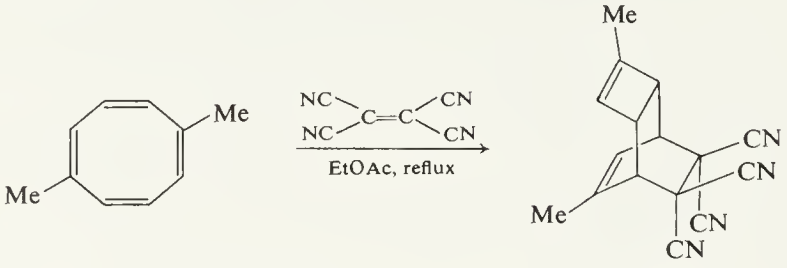


(**337**)

Table 48

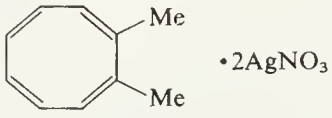
R^1	R_2	Dienophile	Conditions	Yield (%)	Ref.
Me	Me	Maleic anhydride	165°	68	533
			C_6H_6, reflux	43	542
Me	Me	Tetracyanoethylene	EtOAc, reflux	52	49
Me	CH_2OAc	Maleic anhydride	C_6H_6, reflux	69	542
CH_2OAc	CH_2OAc	Maleic anhydride	C_6H_6, reflux	90	542

1,5-Dimethylcyclo-octatetraene gives a tetracyanoethylene adduct of structure (**338**) (55%).[43]



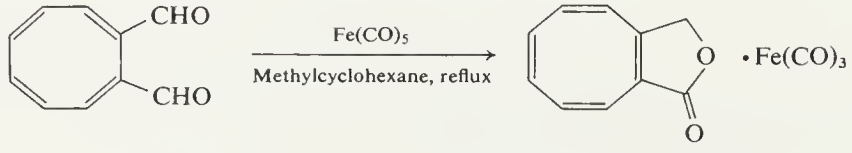
(**338**)

(*f*) *Formation of metal derivatives.* 1,2-Dimethylcyclo-octatetraene forms a silver nitrate complex (**339**) in boiling ethanol.[533]



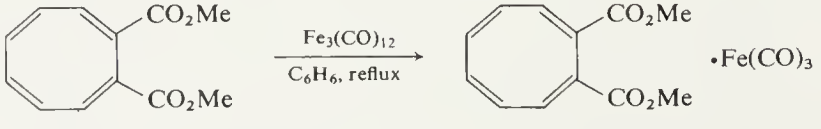
(**339**)

The 1,2-dialdehyde (**340**) reacts with $Fe(CO)_5$ to give the lactone complex (**341**) (8%).[619]



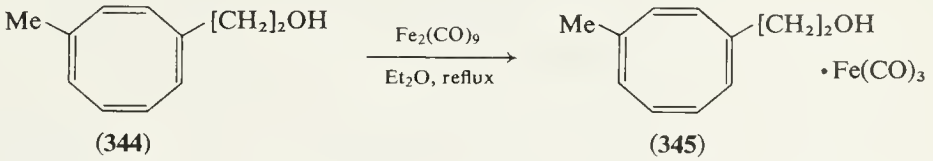
(**340**) (**341**)

Treatment of the 1,2-dicarboxylic ester (**342**) with $Fe_3(CO)_{12}$ gives a low yield (12%) of the complex (**343**).[619]



(**342**) (**343**)

The 1,4-disubstituted COT (**344**) reacts with $Fe_2(CO)_9$ to afford a complex (**345**) (crude yield 28.5%), which has been subjected (as the *p*-nitrobenzoate) to X-ray analysis.[545, 546]



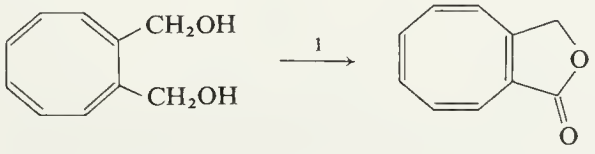
(**344**) (**345**)

3. Annulated and bridged derivatives

Formation

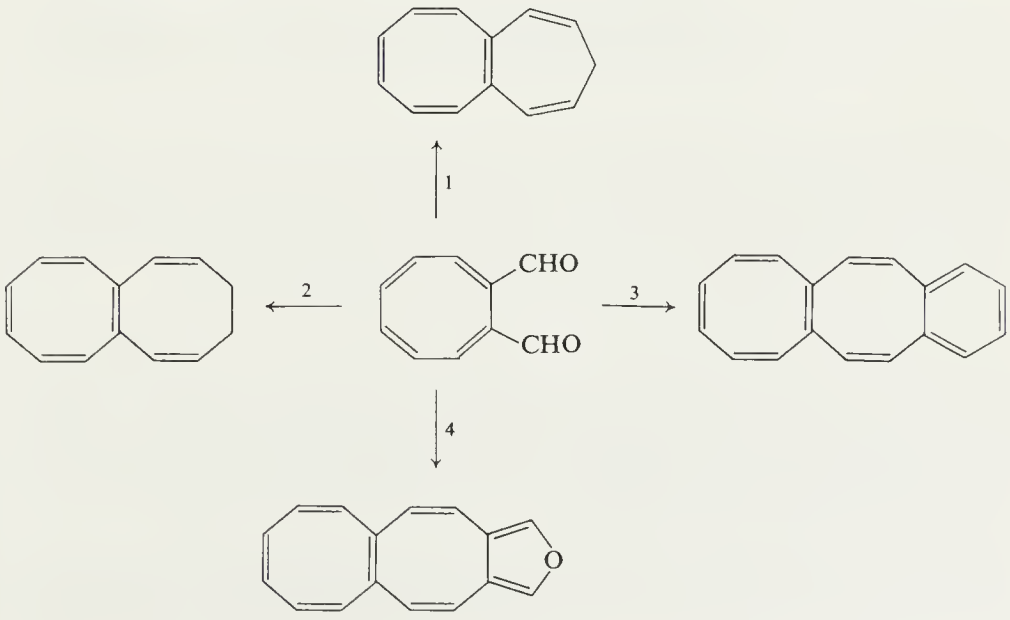
(*a*) *Cyclisation reactions of 1,2-disubstituted COTs.* A variety of annulated COT derivatives may be prepared from suitable 1,2-disubstituted COTs (schemes 50–52) (see also p. 113).

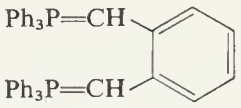
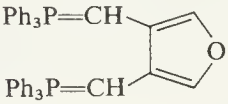
Scheme 50



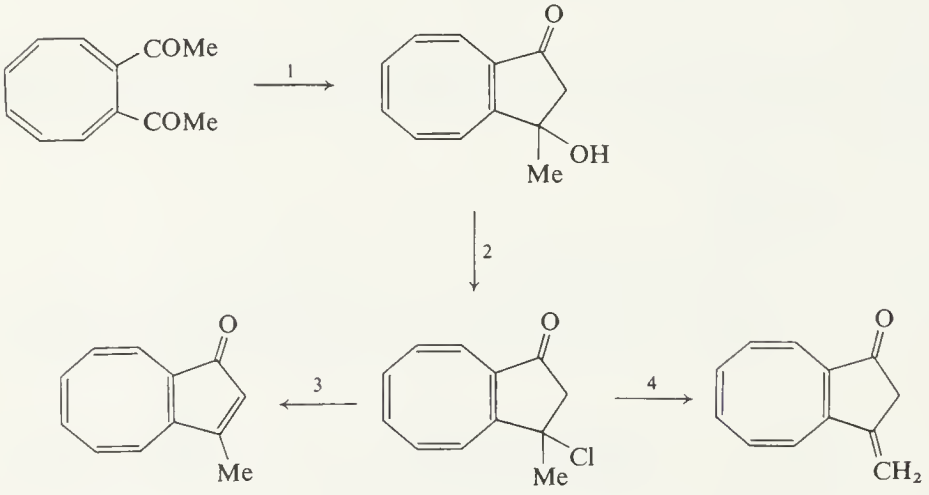
Reaction	Reagent and conditions	Yield (%)	Ref.
1	MnO_2, $CHCl_3$, r.-t.	39	610

Scheme 51



Reaction	Reagents and conditions	Yield (%)	Ref.
1	$Ph_3P{=}CH.CH_2.CH{=}PPh_3$	15	611
2	$Ph_3P{=}CH[CH_2]_2CH{=}PPh_3$	5–10	611
3		1–2	611
4	 , DMF, 90°	15	610, (620)

Scheme 52



Reaction	Reagents and conditions	Yield (%)	Ref.
1	NaOMe	—	607
2	$SOCl_2$, pyridine, Et_2O	—	607
3	Chromatography on neutral Al_2O_3	—	607
4	Chromatography on SiO_2	—	607

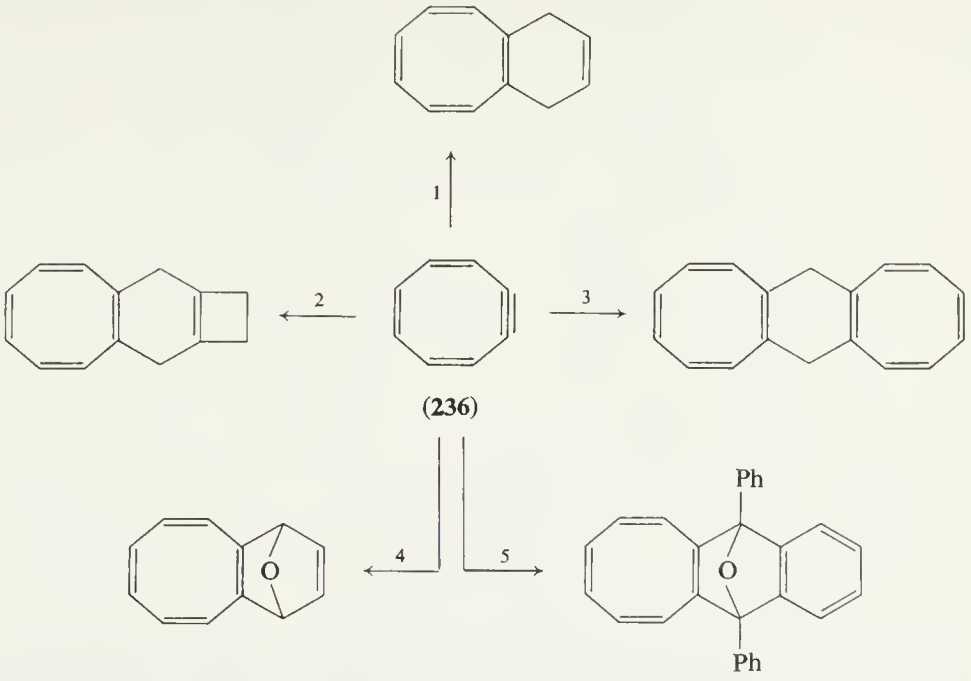
(*b*) *Cycloadditions to 1,2-didehydrocyclo-octatetraenes.* The 'yne' species (**236**), which is generated by the action of potassium t-butoxide on bromocyclo-octatetraene (see pp. 83–4), may be employed *in situ* as a dienophile for the preparation of certain annulated derivatives of COT (scheme 53).

(*c*) *Photochemical cycloadditions of acetylenes to benzenes.* U.v. irradiation of cyclo-octyne in benzene affords the annulated COT (**346**) (56%).[625] A similar reaction with toluene gives a methyl-derivative (**347**) (25–30%).[625]

An intramolecular photoaddition may be effected in the compound (**348**), leading to the product (**349**) (5%).[626]

(*d*) *Syntheses from 7,8-dimethylenecyclo-octa-1,3,5-trienes.* U.v. irradiation of

Scheme 53

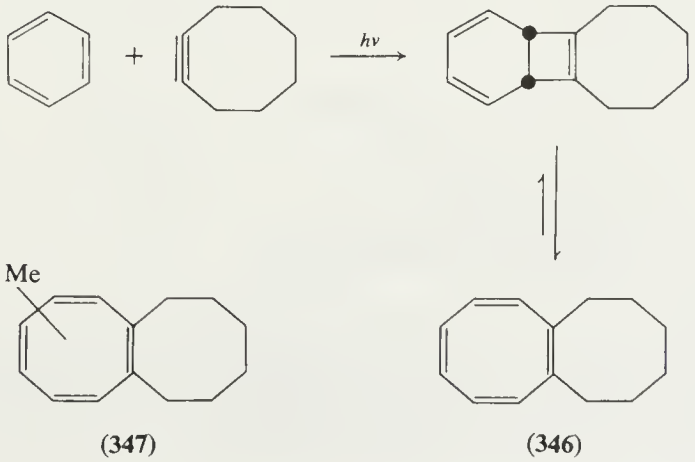


Reaction	Diene	Yield (%)	Ref.
1	Buta-1,3-diene	83[a]	621
2	1,2-Dimethylenecyclobutane	13[a]	621
3	7,8-Dimethylenecyclo-octa-1,3,5-triene	22	612, (622)
4	Furan	48	623
5	1,3-Diphenylbenzo[*c*]furan	87	624

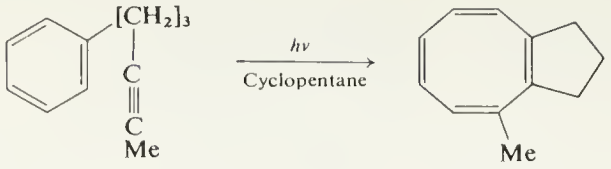
[a] Based on the bromocyclo-octatetraene consumed.

either of the dimethylenecyclo-octatrienes (**321***b*) or (**321***c*) affords the cyclised product (**350**)[627, 628] (table 49). (For the irradiation of (**321***a*), see p. 237.)

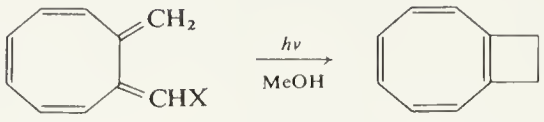
The addition of dienophiles to the dimethylene compound (**321***c*) also



(**347**) (**346**)



(348) (349)

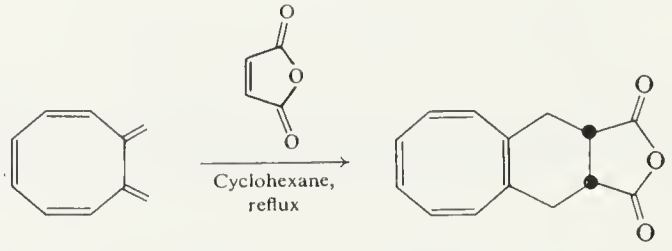


(321) (350)

Table 49

	X	Yield (%)
b	Br	*ca.* 7
c	H	*ca.* 10

leads to annulated COTs; thus maleic anhydride gives the adduct (**351**), and similar reactions occur (under the same conditions) with other dienophiles[612] (table 50). The addition of 1,2-didehydrocyclo-octatetraene (**236**) to the dimethylene compound (**321*c***) has already been mentioned (see p. 125).

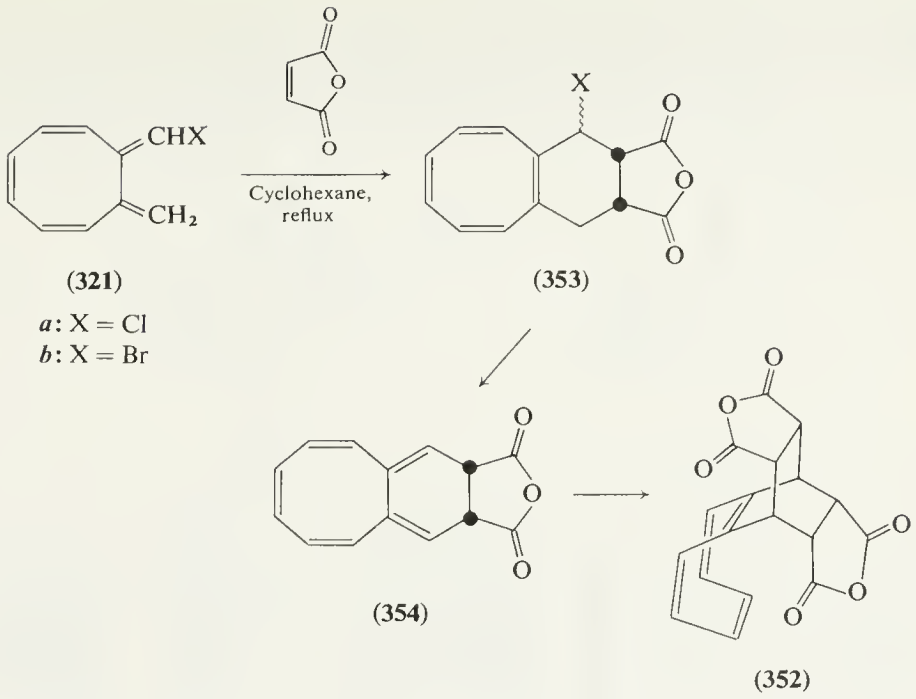


(321*c*) (351)

Table 50

Dienophile	Yield (%)
Maleic anhydride	37
p-Benzoquinone	34
Dimethyl acetylenedicarboxylate	52

Addition of maleic anhydride to the monohalodimethylene compounds (**321*a***) and (**321*b***) results in the product (**352**) (45–47%); presumably loss of hydrogen halide from the initial adduct (**353**) to give (**354**) is followed by the addition of a second molecule of the dienophile.[612]



(321)

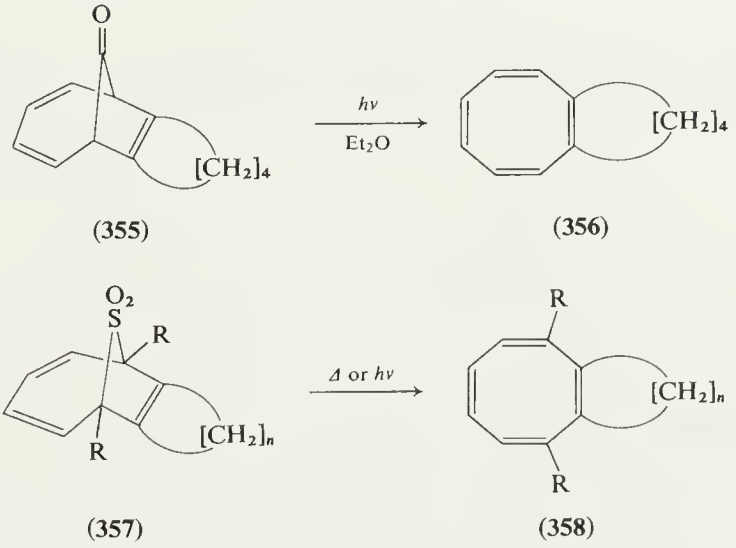
a: X = Cl
b: X = Br

(353)

(354)

(352)

(*e*) *Syntheses involving skeletal transformations*. Photolysis of the carbonyl-bridged compound (**355**) gives the product (**356**) (30%).[604]



(355)

(356)

(357)

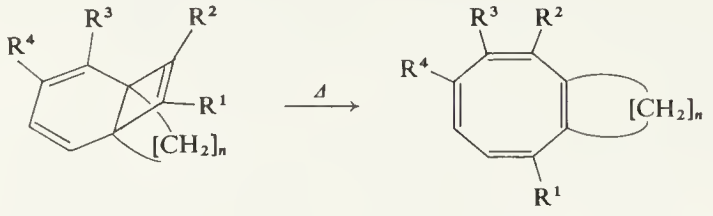
(358)

Table 51

n	R	Conditions	Yield (%)	Ref.
2	H	400°/10 mm	—	605
3	H	*hν* (Corex), Me_2CO	—	605
4	H	400°/10 mm	92	604
		hν (Corex), Me_2CO	75	604
4	D	*hν* (Vycor), Me_2CO, Et_2O	25	629
5	H	*hν* (Corex), Me_2CO	37	604

Thermolytic or photolytic extrusion of sulphur dioxide from the system (**357**) similarly leads to annulated COTs (**358**) (table 51).

Gas-phase thermolysis of the propellatriene system (**359**) also yields annulated COTs (**360**) (table 52). The rearrangement mechanism is indicated in scheme 54.[629, 630]

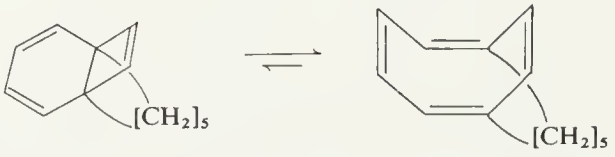


(**359**) (**360**)

Table 52

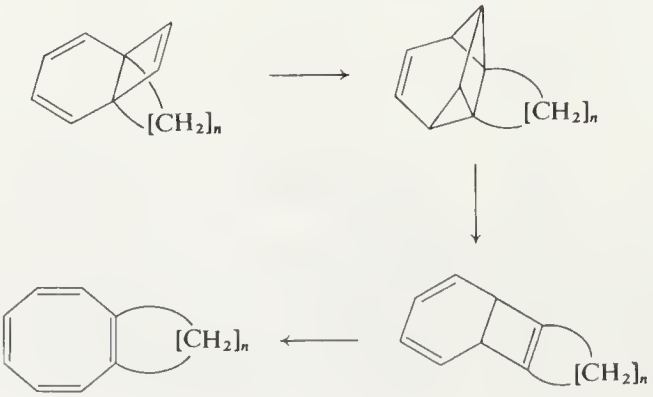
n	R^1	R^2	R^3	R^4	Conditions	Yield (%)	Ref.
3	H	H	H	H	615°/5 mm	—[a]	629, (630)
4	H	H	H	H	430°/2.5 mm	60	629, (630)
4	D	D	H	H	380°/2.5 mm	30	629, (630)
4	Me	D	H	H	480°	—	631
4	H	H	Me	H	—	—[b]	631
4	H	H	H	Me	—	—	631
4	Me	Me	H	H	500°/2.5 mm	76	629, (630)
5[c]	H	H	H	H	485°/2.5 mm	47	629, (630)

[a] The main product (by a factor of 2) is indane.
[b] The product is contaminated with an exomethylene isomer.
[c] The system (**361**) exists almost exclusively as the 1,4-bridged COT (**362**).[632]

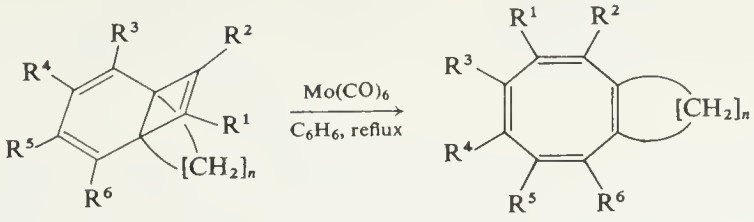


(**361**) (**362**)

Scheme 54



Skeletal rearrangement of the propellatriene system (**363**) to the bicyclic system (**364**) is catalysed by $Mo(CO)_6$ (table 53). The simplest mechanistic

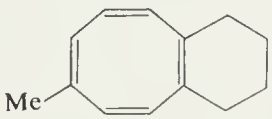


(**363**) (**364**)

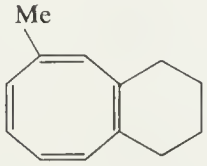
Table 53

n	R^1	R^2	R^3	R^4	R^5	R^6	Yield (%)	Ref.
4	H	H	H	H	H	H	41	633
4	D	D	H	H	H	H	—	633
4	H	H	D	H	H	D	—	631
4	H	Me	H	H	H	H	50	631
4	D	Me	H	H	H	H	—	631
4	H	H	Me	H	H	H	87[a]	631
4	H	H	H	Me	H	H	—[b]	631
4	Me	Me	H	H	H	H	*ca.* 36[c]	634
4	H	H	H	Me	Me	H	—	634
5	H	H	H	H	H	H	15[d]	633
5	D	D	H	H	H	H	—	633

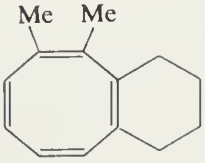
[a] Initial reaction in refluxing benzene, followed by further heating at 125°.
[b] Mixture of (**365**) and (**366**) obtained.
[c] Mixture of the double bond isomers (**367**) (*ca.* 36%) and (**368**) (*ca.* 40%) obtained, together with (**369**) (*ca.* 24%).
[d] Reaction in refluxing toluene.



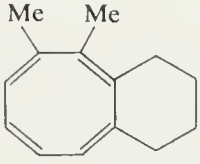
(**365**)



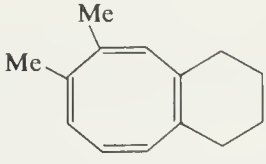
(**366**)



(**367**)



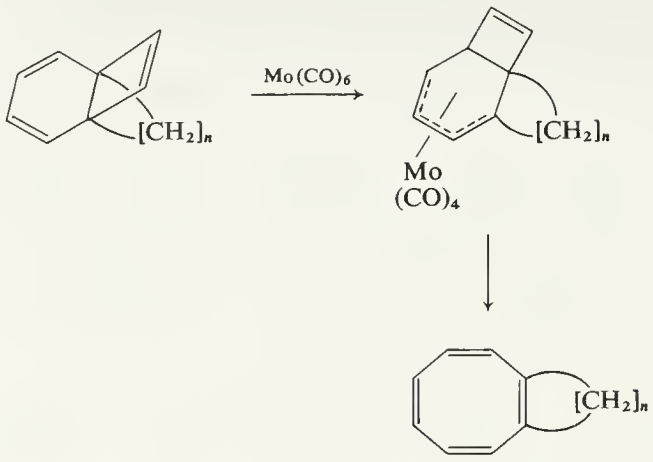
(**368**)



(**369**)

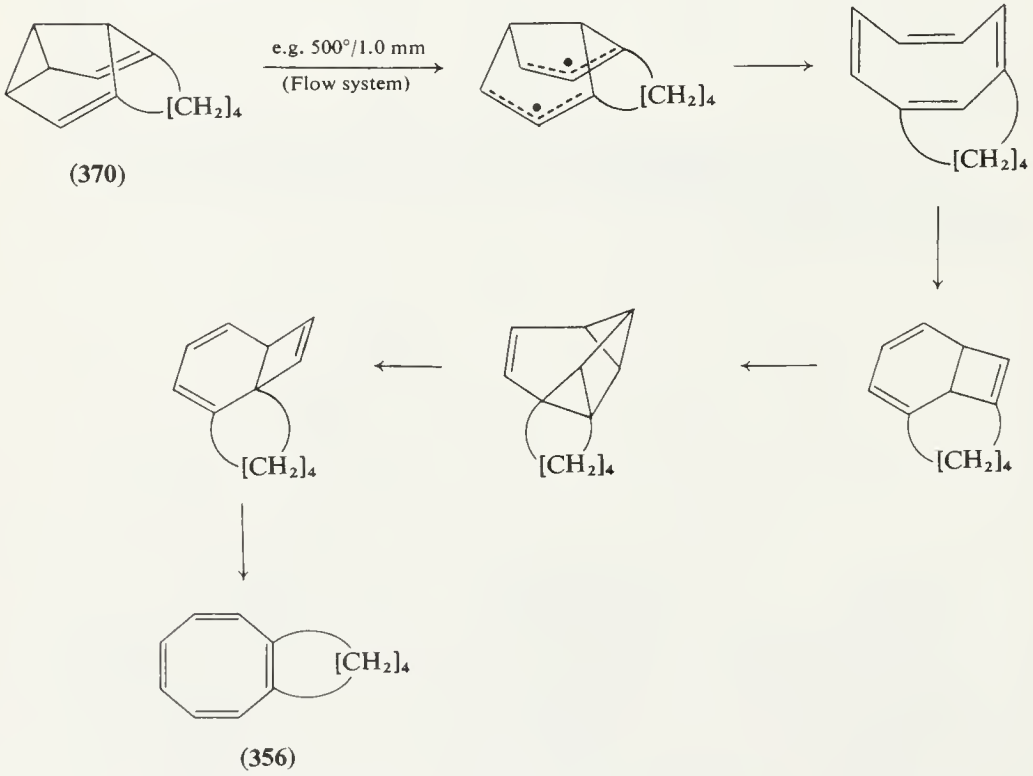
interpretation of these results involves a [1,5] sigmatropic shift of a trigonal cyclobutene carbon atom[631,634] (scheme 55).

Scheme 55



The bridged semibullvalene (**370**) rearranges at 460–500° to give the annulated COT (**356**) (69%); results obtained with deuterium-labelled starting material suggest the illustrated reaction path[42,635] (scheme 56).

Scheme 56

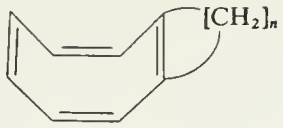


(**370**)

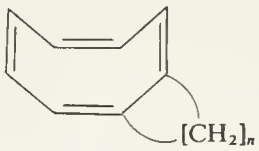
(**356**)

Structure

1,2-Annulated COTs presumably resist the bond shift process (**371***a*) → (**371***b*) when $n < 4$; when $n \geqslant 4$ very little torsional strain is imposed on structure (**371***b*) by the ring-fusion (as judged from molecular models).

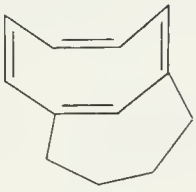


(371*a*)

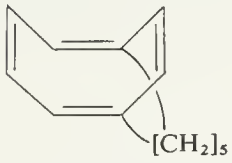


(371*b*)

The strained 1,3-bridged COT (**372**) has been invoked as an intermediate in the thermal rearrangement of the bridged semibullvalene (**370**) (see p. 130); the 1,4-bridged COT (**362**) is more stable than its valence tautomer (**361**) (see p. 128).



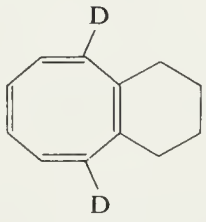
(372)



(362)

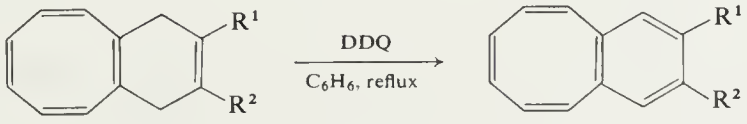
Reactions

(*a*) *Thermolysis.* Thermolysis of the annulated COT (**356**) does not result in the formation of structural isomers (*cf.* disubstituted COTs, pp. 118, 119), but at *ca.* 600° (flow system) a degenerate rearrangement occurs (see p. 17); using the 3,8-dideuterio-derivative (**373**), the stepwise shift of deuterium first to the 4,7-positions and then to the 5,6-positions may be detected.[49]



(373)

(*b*) *Dehydrogenation.* Treatment of compounds (**374**) with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone gives the corresponding benzo-derivatives (**375**) (table 54).



(374) (375)

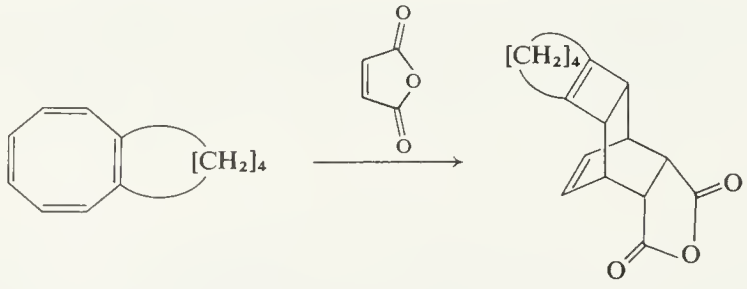
Table 54

R^1	R^2	Yield (%)	Ref.
H	H	68[a]	621
CO_2Me	CO_2Me	81	612
$-[CH_2]_2-$		99	621
$-[CH\overset{Z}{=}CH]_3-$		47[b]	612

[a] The final stage in an efficient synthesis of benzocyclo-octatetraene from COT.
[b] Using Pd–C in refluxing decalin, the yield is 36%.

(*c*) *Reduction.* For the radical anion of (**350**), see appendix.

(*d*) *Cycloadditions.* Reaction of the annulated COT (**356**) with maleic anhydride gives the adduct (**376**); analogous products are formed from other dienophiles (table 55). For tetracyanoethylene adducts of deuterio-derivatives of (**356**) etc.,



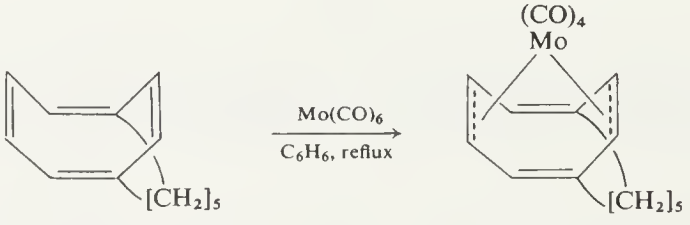
(**356**) (**376**)

Table 55

Dienophile	Conditions	Yield (%)	Ref.
Maleic anhydride	Toluene, 110°	35	542
Tetracyanoethylene	EtOAc, reflux	65	629, (630)
N-Phenyltriazolinedione	EtOAc, r.-t. reflux	83	629

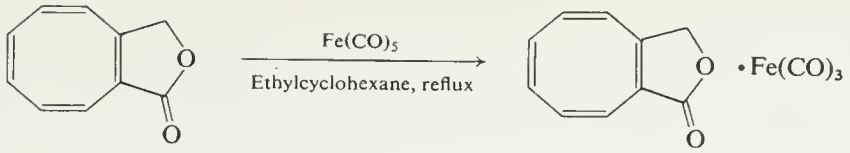
see refs. 49, 606, 629, 630, 631, 633, 635. For *N*-phenyltriazolinedione adducts of methyl-substituted derivatives (**365**)–(**369**), see refs. 629, 631, 634.

(*e*) *Formation of metal derivatives.* The 1,4-bridged COT (**362**) reacts with $Mo(CO)_6$ to give the complex (**377**) (87.5%).[633]



(**362**) (**377**)

The lactone (**378**) forms the complex (**379**) (11%) on treatment with $Fe(CO)_5$.[619]

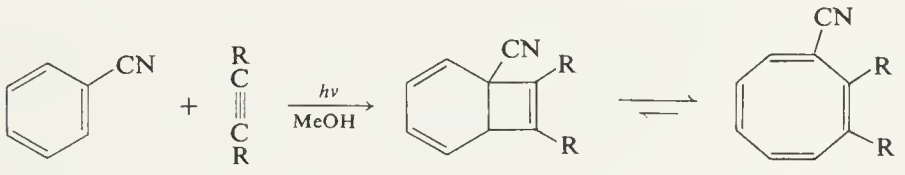


(378) (379)

4. Trisubstituted derivatives

Formation

(*a*) *Photochemical cycloadditions of disubstituted acetylenes to monosubstituted benzenes.* The photoaddition of disubstituted acetylenes to benzonitrile affords the 1,2,3-trisubstituted COTs (**380**) in very low yield[636] (table 56).

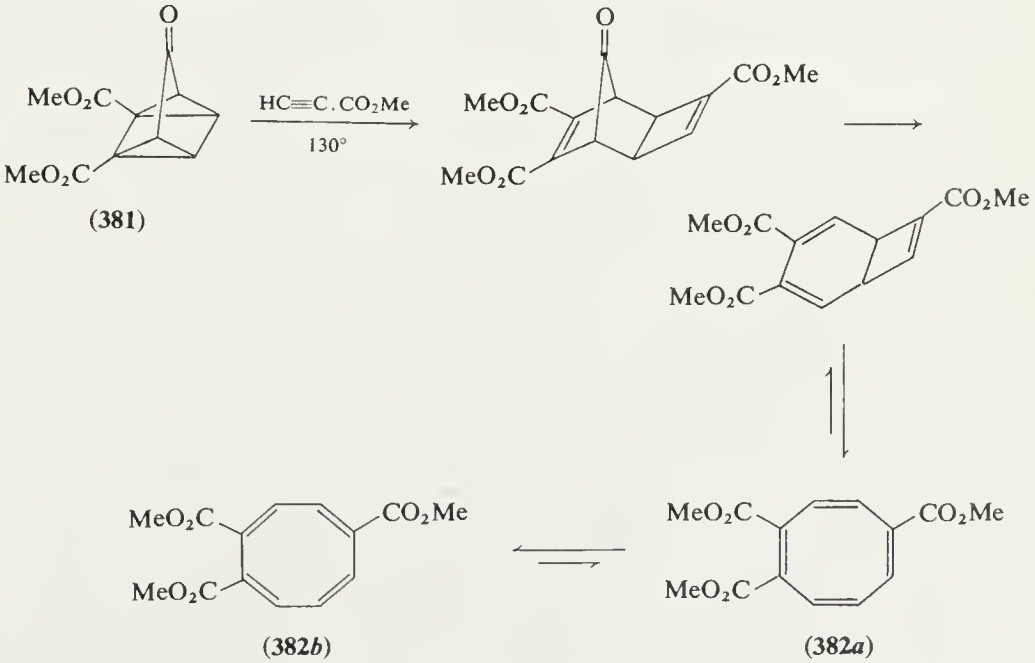


(380)

Table 56

	R	Yield (%)
a	Et	8
b	Bu^n	—

Scheme 57



(381) (382*b*) (382*a*)

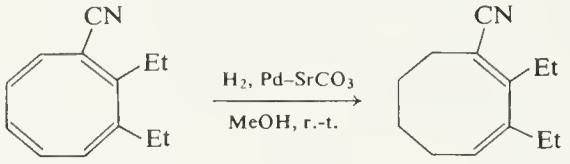
(*b*) *Synthesis involving skeletal transformation.* The reaction of methyl propiolate with the disubstituted quadricyclanone (**381**) leads to the 1,2,5-trisubstituted COT (**382**);[637] presumably [$_{\pi}2 + _{\sigma}2 + _{\sigma}2$] cycloaddition is followed by extrusion of carbon monoxide (scheme 57).

Structure

The n.m r. spectrum of compound (**382**) indicates that it exists almost exclusively in the form (**382***b*).[637]

Reactions

Hydrogenation of the trisubstituted COT (**380***a*) over Pd–$SrCO_3$ affords, as the major product, the 1,3-diene (**383**) (*ca.* 67%).[636]

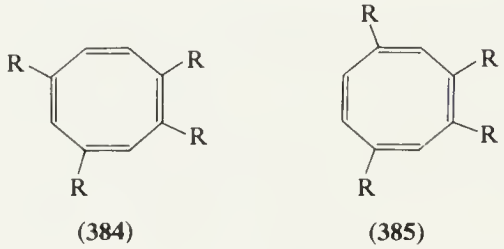


(**380***a*) (**383**)

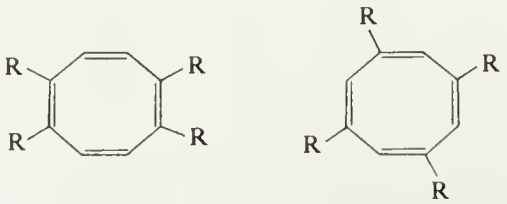
5. Tetrasubstituted derivatives

Formation

(*a*) *Cyclotetramerisation of monosubstituted acetylenes.* The cyclotetramerisation of monosubstituted acetylenes may be effected by a variety of catalysts (table 57); the observed substitution patterns in the resulting COTs are limited to 1,2,4,6 (**384**), 1,2,4,7 (**385**), 1,2,5,6 (**386**) and 1,3,5,7 (**387**). For the production



(**384**) (**385**)



(**386**) (**387**)

Table 57

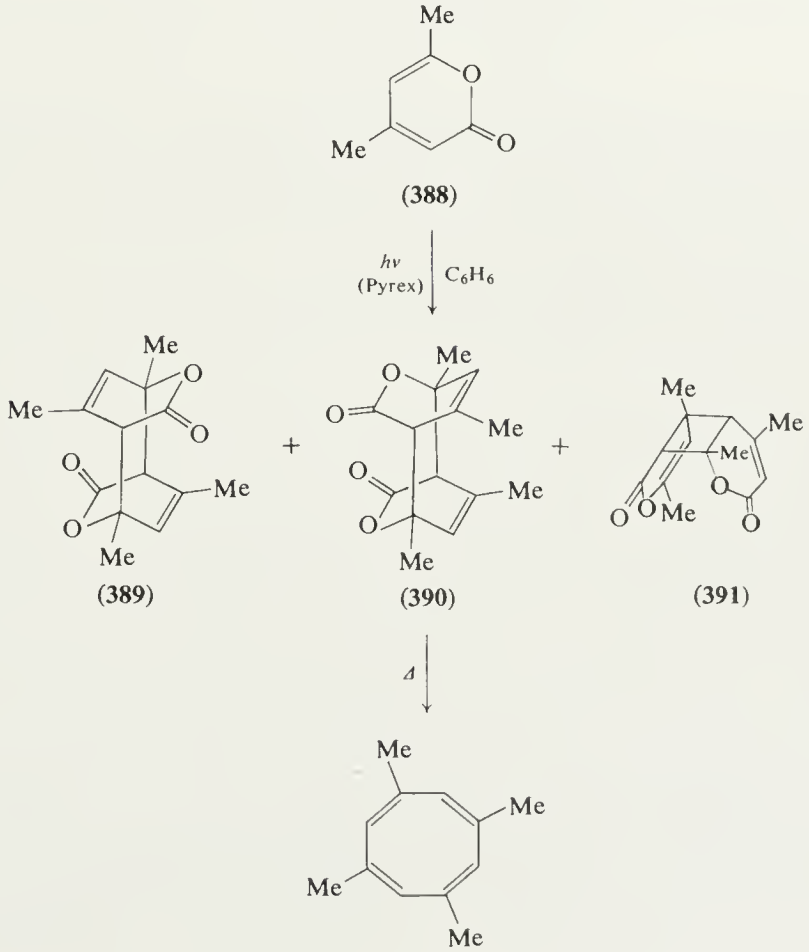
R	Catalyst and conditions	Product	Yield (%)[a]	Ref.
CH_2OH	$Ni(acac)_2$, C_6H_6, reflux	(**387**)	Up to 71	638
$C(OH)Me_2$	e.g. $Ni(acac)_2$,[b] 90–120°	(**384**) + (**385**)	40	639
CO_2Me	$Ni(PCl_3)_4$, cyclohexane, 22–55°	(**384**)	83	640
CO_2Me	$PdCl_2$, NaOAc, HOAc, 80°	(**386**)	(Very low)	641
CO_2Et	$Ni(PCl_3)_4$, cyclohexane, 25–46°	Mainly (**384**)	30	640
OEt	$NaNH_2$, NH_3(liq.), −70°	(**387**)	10–24	642
OPr^n	$NaNH_2$, NH_3(liq.), −70°	(**387**)	9.5	642

[a] Based on reacted monomer.

[b] The reaction is also catalysed by $Ni(CO)_4$, $Ni(COD)_2$, $Ni(CN)_2$, $Ni(OEt)_2$ and $NiCl_2$–$NaBH_4$.[639] For other studies using various nickel chelate 'ato' complexes, see refs. 643–645.

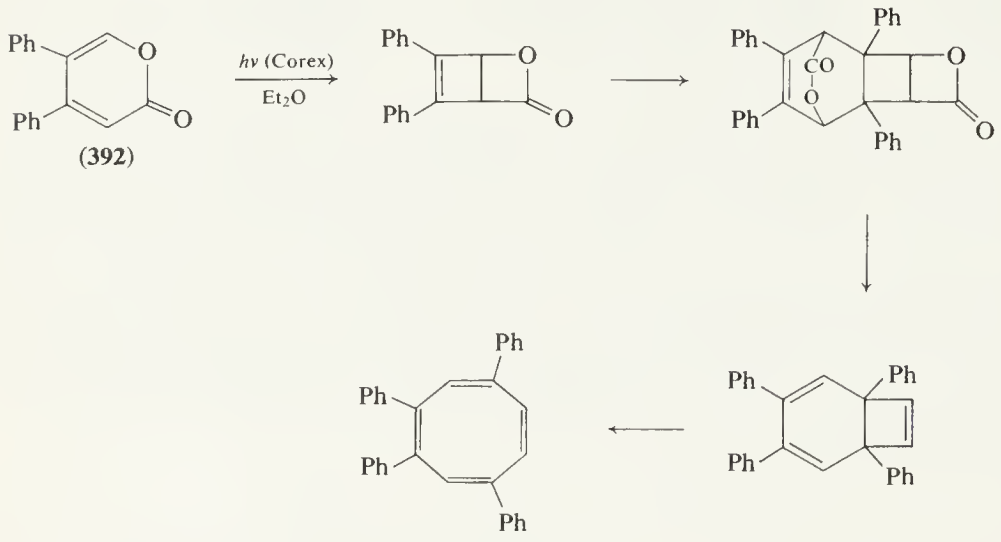
of (**387**; R = Ph) (6%) by the self-condensation of $PhC(OEt)_2Me$, see ref. 646.

(*b*) *Syntheses involving skeletal transformations.* Photo-dimerisation of 4,6-dimethyl-2-pyrone (**388**) leads to a mixture of the dimers (**389**), (**390**) and (**391**), which is readily converted to 1,3,5,7-tetramethylcyclo-octatetraene (26%, based on unrecovered starting material) by brief heating above the melting-point.[647,648]



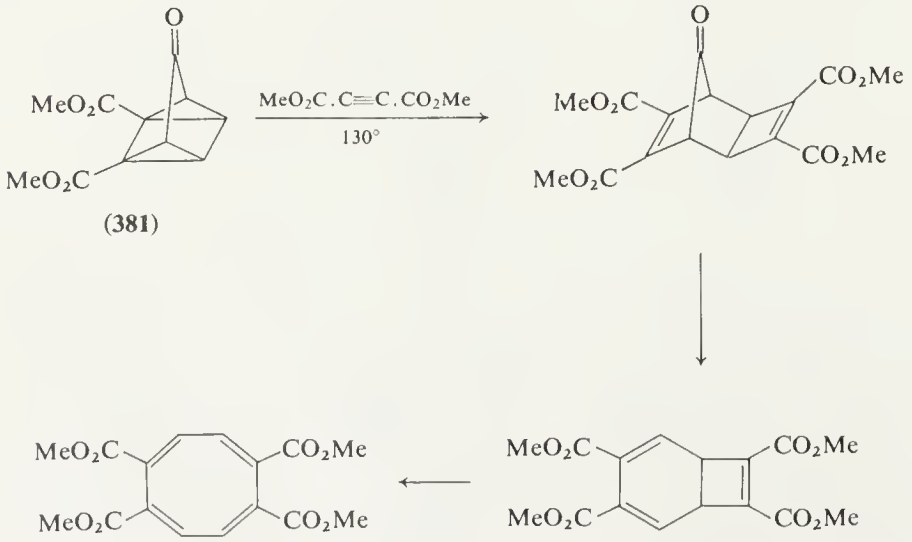
U.v. irradiation of 4,5-diphenyl-2-pyrone (**392**) gives 1,2,4,7-tetraphenyl-cyclo-octatetraene (up to 24%) (the product is itself photolabile (see p. 145)); the reaction sequence of scheme 58 is postulated.[649]

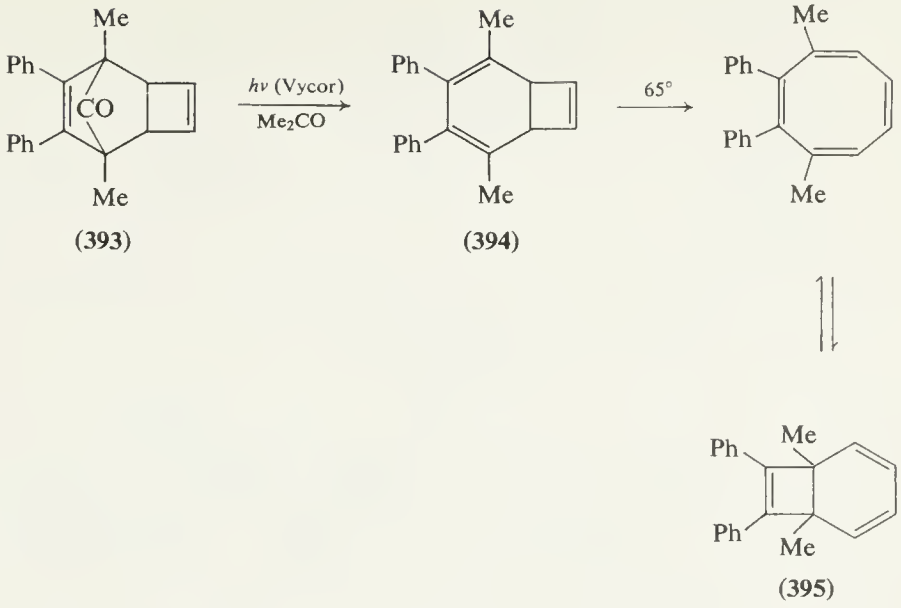
Scheme 58



The disubstituted quadricyclanone (**381**) reacts with dimethyl acetylene-dicarboxylate to afford 1,2,5,6-tetramethoxycarbonylcyclo-octatetraene[637] (*cf.* p. 133), presumably *via* a $[_{\pi}2 + _{\sigma}2 + _{\sigma}2]$ cycloaddition and subsequent loss of carbon monoxide (scheme 59).

Scheme 59





(393) (394) (395)

Photodecarbonylation of the norbornenone (**393**) gives the bicyclo[4.2.0]-octa-2,4,7-triene (**394**),[650] which is slowly transformed at 65° (half-life *ca.* 90 min.) to an equilibrium mixture of 1,6-dimethyl-7,8-diphenylcyclo-octa-tetraene and the valence tautomer (**395**)[651] (see p. 143).

The generation of disubstituted cyclobutadienes leads to tetrasubstituted dimers possessing the tricyclo[4.2.0.$0^{2,5}$]octa-3,7-diene skeleton; thermolysis of this system then affords tetrasubstituted COTs (see p. 3). Thus 1,2,4,5-, 1,2,4,7- and 1,2,5,6-tetramethylcyclo-octatetraene may be prepared by dechlorination of a mixture of the dichlorodimethylcyclobutenes (**396**), (**397**) and (**398**), followed by thermolysis of the resulting dimethylcyclobutadiene dimers (**399**), (**400**) and (**401**).[652] Thermolytic ring-opening of (**399**)–(**401**) is almost quantitative.

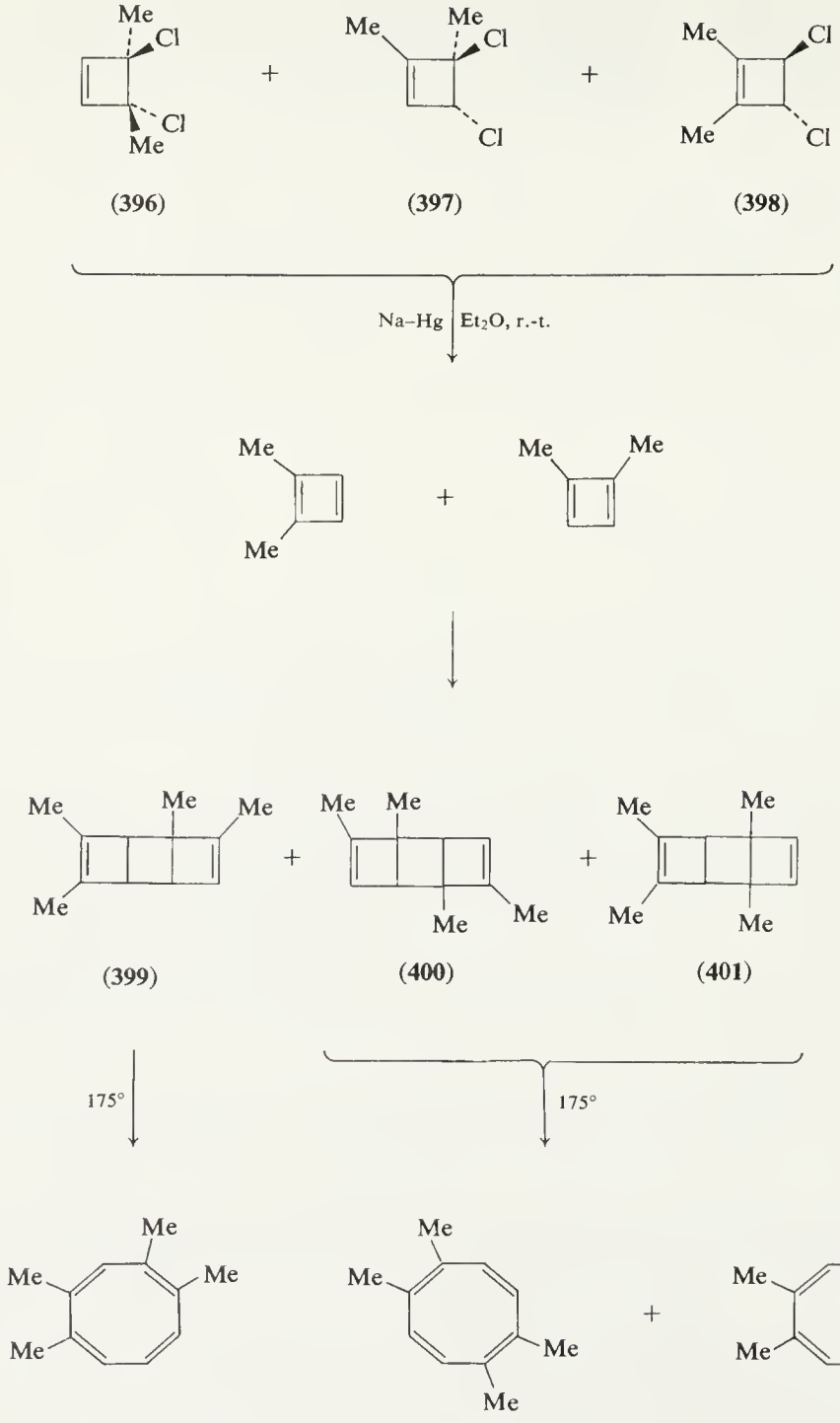
The same three tetramethylcyclo-octatetraenes result (total yield 8.8 %) from photolysis of the dimethylcyclobutenedicarboxylic anhydride (**402**)[653] (see p. 159).

1,2,4,7- and 1,3,5,7-tetraphenylcyclo-octatetraene may be obtained (24 % and 34 % respectively) from the quaternary ammonium salt (**403**) by treatment with potassium t-butoxide, without isolation of the intermediate diphenyl-cyclobutadiene dimers (**404**) and (**405**).[654]

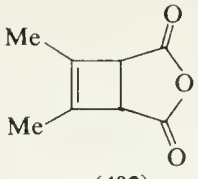
1,3,5,7-Tetramethylcyclo-octatetraene is produced (58 %) by u.v. irradiation of the tetramethylsemibullvalene (**406**).[183]

Bromination–dehydrobromination of the bicyclic diene (**408**) yields 1,2,3,8-tetramethylcyclo-octatetraene (98 %), which resists bond-shift isomerisation to the 1,2,3,4-tetramethyl-derivative[655] (see p. 142).

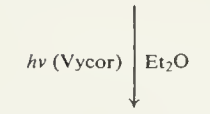
1,2,3,4-Tetramethylcyclo-octatetraene is available from the sulphone (**409**) (70–80 %).[655]

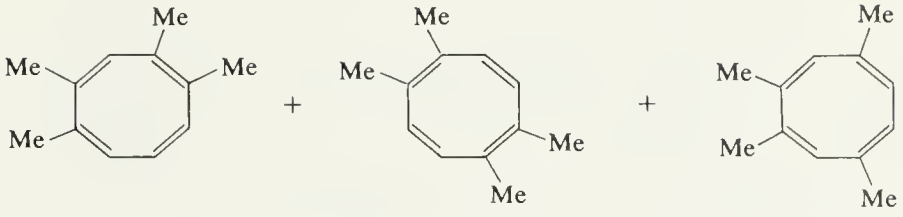


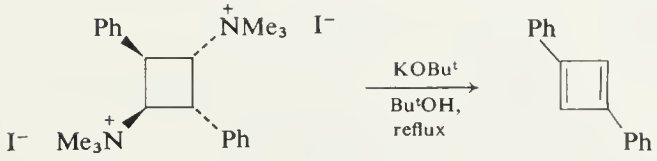
Product	Yield (%)
(399)	24
(400) + **(401)**	7.5



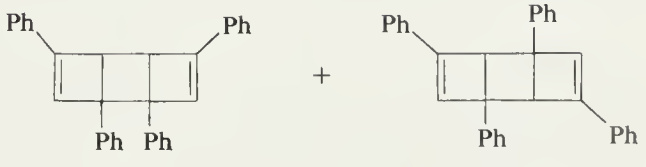
(402)



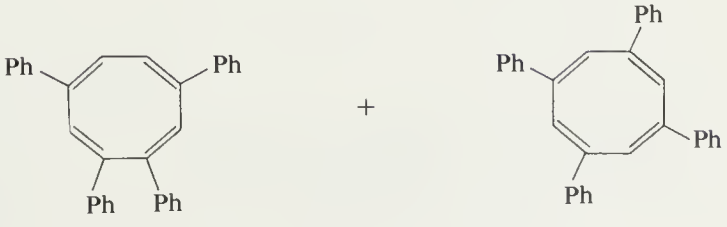


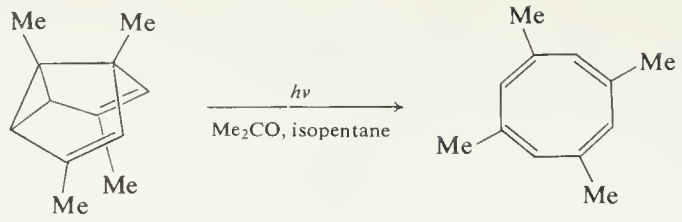


(403)

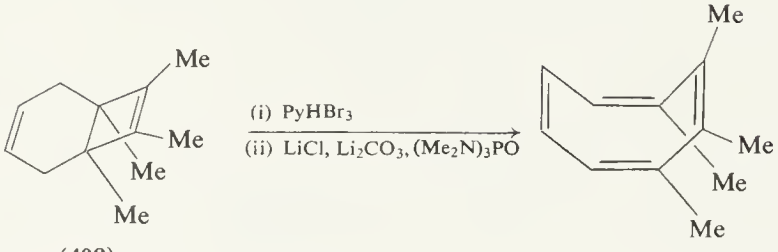


(404) **(405)**

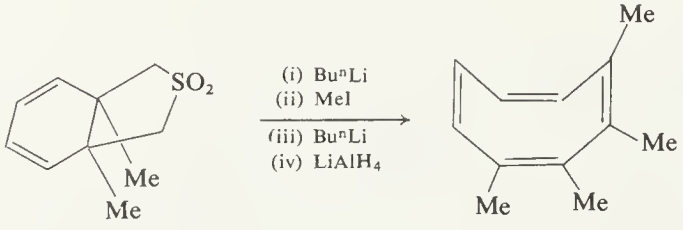




(406)



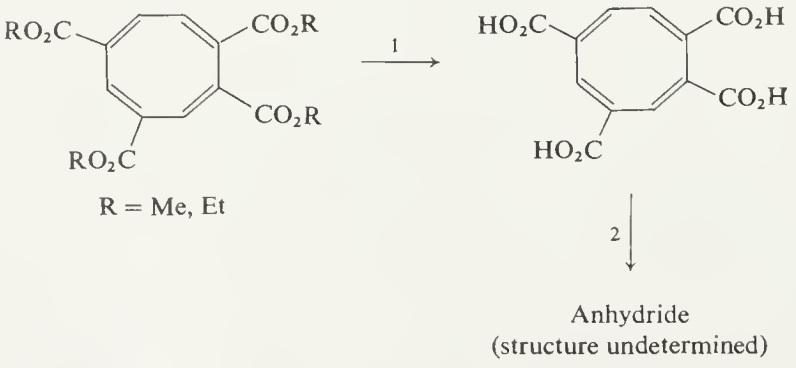
(408)



(409)

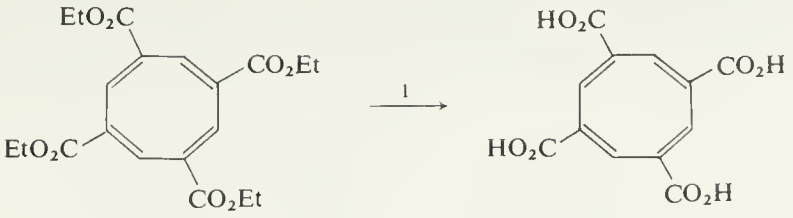
(*c*) *Functional group transformations.* The transformations in schemes 60–62 lead to other tetrasubstituted COTs. Acid treatment (as in scheme 62) of

Scheme 60



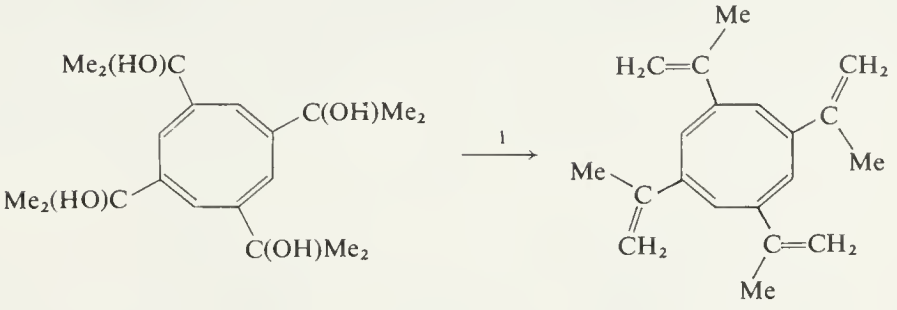
Reaction	Reagents and conditions	Yield (%)	Ref.
1	KOH, EtOH, reflux	100	640
2	100°, dioxan	—	640

Scheme 61



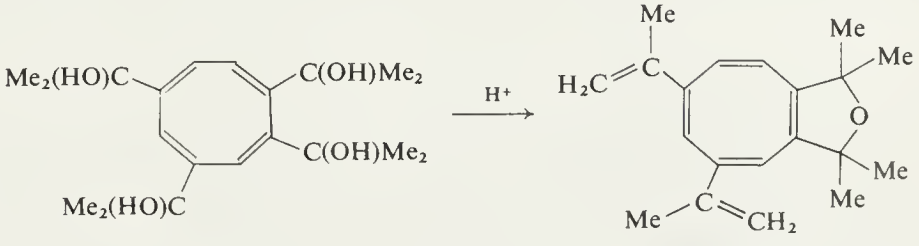
Reaction	Reagents and conditions	Yield (%)	Ref.
1	KOH, EtOH, reflux	100	640

Scheme 62

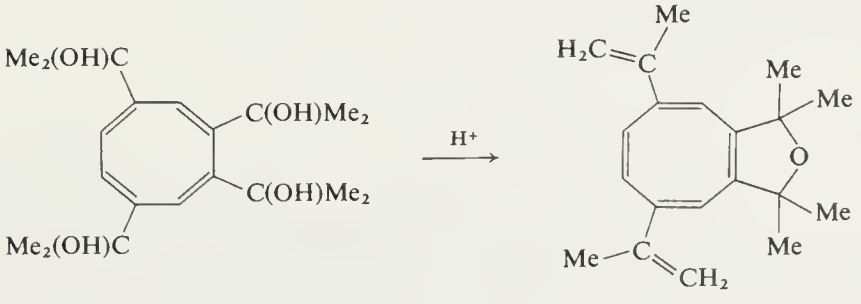


Reaction	Reagents and conditions	Yield (%)	Ref.
1	*p*-Me.C_6H_4.SO_2OH, toluene, reflux	88	639

(**410**) and (**411**) results in the cyclised products (**412**) (97%) and (**413**) (93%) respectively.[639]



(**410**) (**412**)

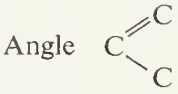


(**411**) (**413**)

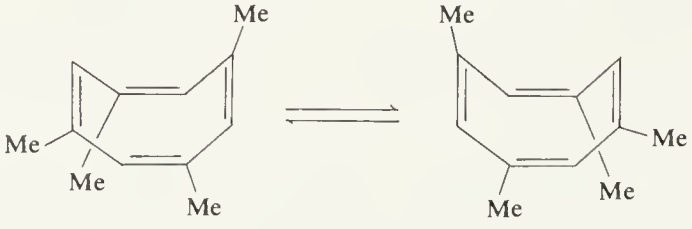
Structure

1,3,5,7-Tetramethylcyclo-octatetraene has been subjected to X-ray analysis;[656] the bond lengths and angles in the eight-membered ring are listed in table 58.

Table 58

Bond	Length (Å)
C=C	1.330
C—C	1.481
Angle 	125°

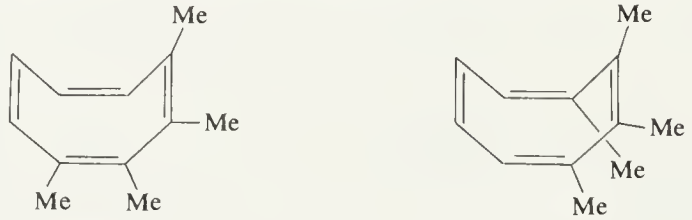
For the p.m.r. spectrum of the 1,3,5,7-tetramethyl-compound, see refs. 657–659; for the calculated barrier to ring-inversion, see refs. 126, 127. The bond-shift process (**414***a*) ⇌ (**414***b*) becomes mobile only above 120°.[657]



(**414***a*) (**414***b*)

(ΔG^{+} = *ca.* 22.5 kcal mol^{-1})

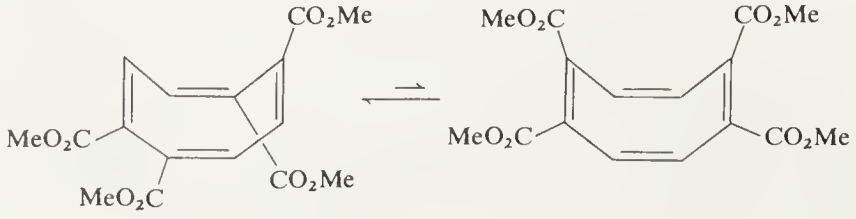
The bond-shift isomers (**415***a*) and (**415***b*) are actually isolable, the attainment of planarity by the C_8-ring being inhibited by severe substituent interactions.[655] (Interconversion can be achieved thermally or photochemically,



(**415***a*) (**415***b*)

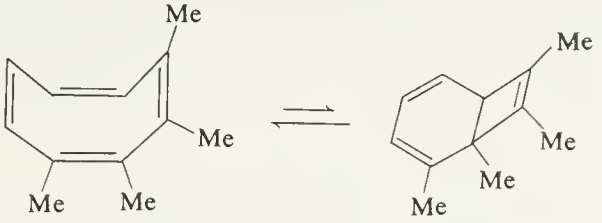
giving mixtures in which (**415***b*) predominates[655].)

P.m.r. spectral evidence indicates that the 1,2,5,6-tetramethyl ester (**416**) exists (at 30°) almost exclusively in the form (**416***a*).[637]



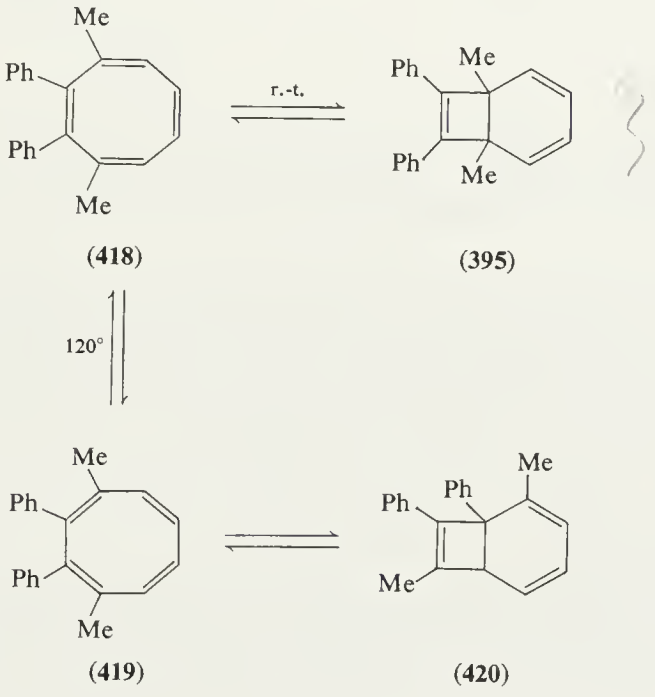
(**416***a*) (**416***b*)

The 1,2,3,4-tetramethyl-derivative (**415***a*) contains 25% of the bicyclic valence tautomer (**417**) at room-temperature;[655] ((**415***b*) is apparently homogeneous.)



(**415***a*) (**417**)

The tetrasubstituted compound (**418**) exists in equilibrium with the bicyclic isomer (**395**) (which is crystallisable), the position of the equilibrium changing very little between 0° and 100°; at 120°, however, the bond-shift isomer (**419**) emerges, together with a second bicyclic valence tautomer (**420**)[651].



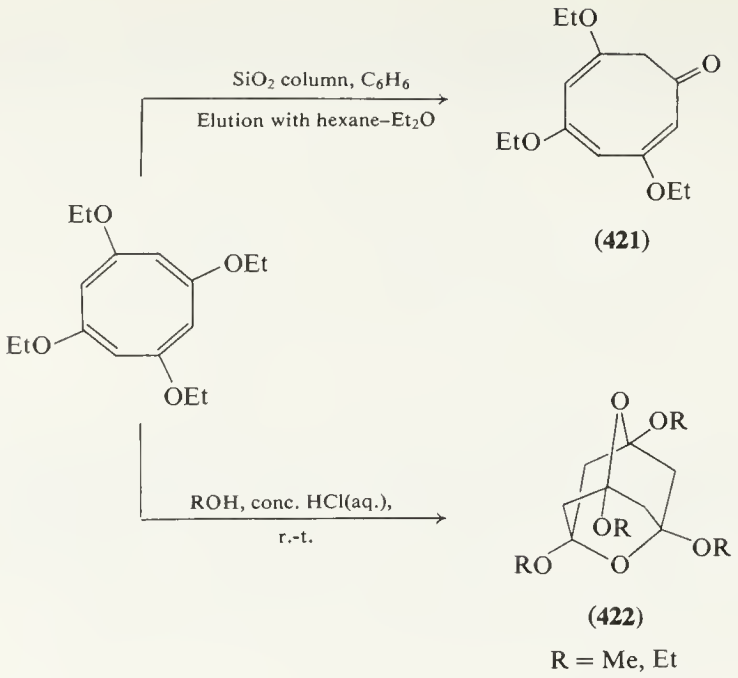
(**418**) (**395**)

(**419**) (**420**)

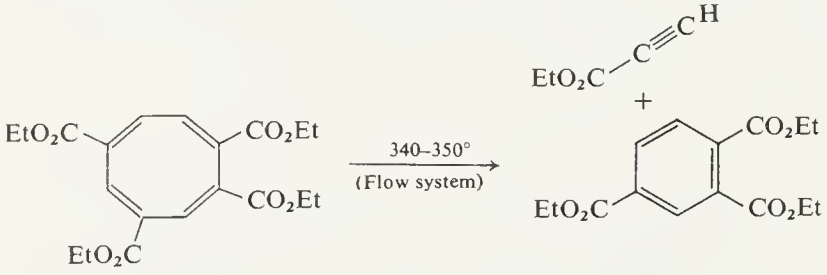
Reactions

(*a*) *Functional group transformations.* Transformations leading to other COTs have already been mentioned (see pp. 140–1).

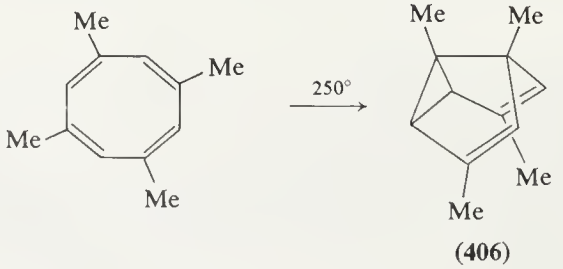
1,3,5,7-Tetraethoxycyclo-octatetraene is hydrolysed quantitatively to the cyclo-octatrienone (**421**) on a silica column, while treatment with alcohols in the presence of hydrochloric acid gives the tetra-alkoxydioxa-adamantanes (**422**) (up to 60%).[642]



(*b*) *Thermolysis.* 1,2,4,6-Tetraethoxycarbonylcyclo-octatetraene undergoes fragmentation at 340–350° to form (as the main products) the ethyl esters of propiolic and trimellitic acids.[640]

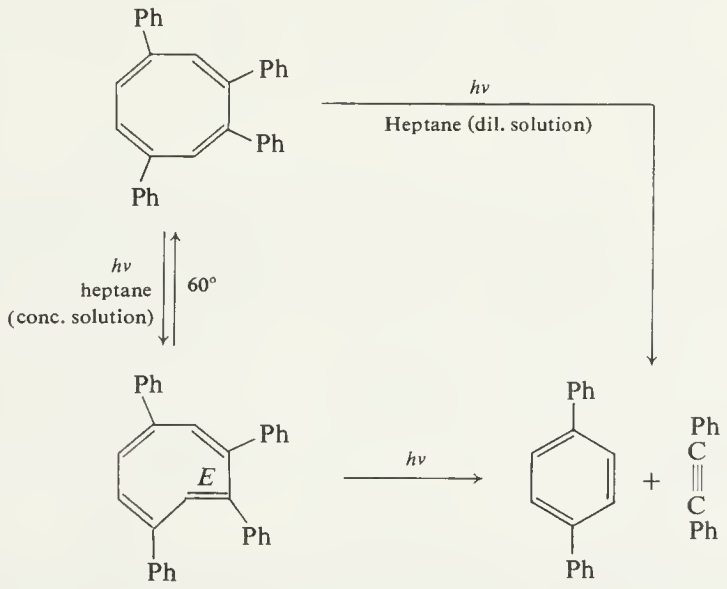


1,3,5,7-Tetramethylcyclo-octatetraene is partly converted (*ca.* 10%) at 250° into the semibullvalene (**406**)[183] (*cf.* semibullvalene, p. 169).



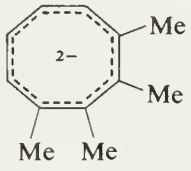
(**406**)

(*c*) *Photolysis.* U.v. irradiation of 1,3,6,8-tetraphenylcyclo-octatetraene in dilute solution effects fragmentation to *p*-terphenyl (25%) and diphenylacetylene (20%).[660,661] In concentrated solution however, a photo-isomer formulated as the *Z,Z,Z,E*-cyclo-octatetraene (**423**) accumulates; this is surprisingly stable, reverting to the starting material at 60° with a half-life of *ca.* 1 h[182,660] (but see appendix).

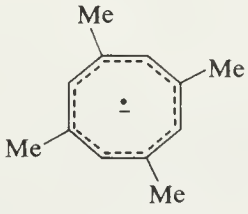


(**423**)

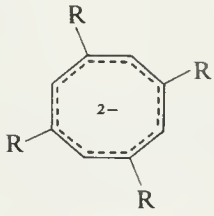
(*d*) *Reduction.* Polarographic studies of the reduction of the stable bond-shift isomers 1,2,3,4- and 1,2,3,8-tetramethylcyclo-octatetraene indicate the difficulty experienced by these systems in attaining a planar conformation, but they both afford the dianion (**424**) with potassium in ND_3.[655]



(**424**)



(**425**)



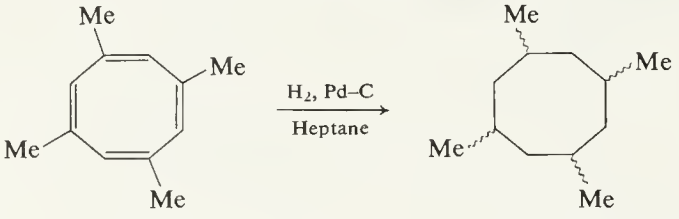
(**426**)

a: R = Me
b: R = Ph

The anion radical (**425**) of 1,3,5,7-tetramethylcyclo-octatetraene may be generated by the action of sodium or potassium in hexamethylphosphoramide,[537,571,662] or electrolytically.[662] For the p.m.r. spectrum of the dianion (**426*a***), see refs. 658, 659.

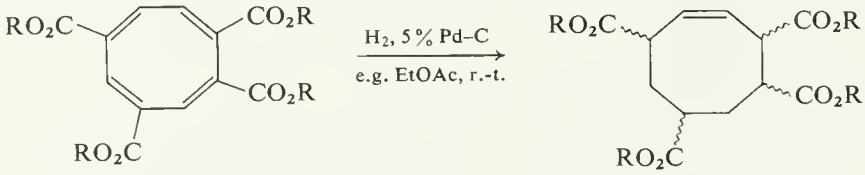
For alkali metal and electrochemical reductions of 1,3,5,7- and 1,3,6,8-tetraphenylcyclo-octatetraene, see refs. 80, 573; for the preparation of the dianion (**426***b*), see ref. 663.

The catalytic hydrogenation of 1,3,5,7-tetramethylcyclo-octatetraene affords four stereoisomers of the cyclo-octane (**427**).[664]



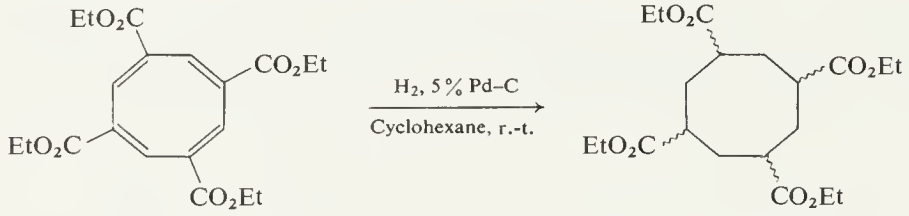
(**427**)

The catalytic hydrogenation of the 1,3,5,8-tetra-esters (**428**) may be controlled to yield cyclo-octenes, formulated as (**429**).[640] For this substitution



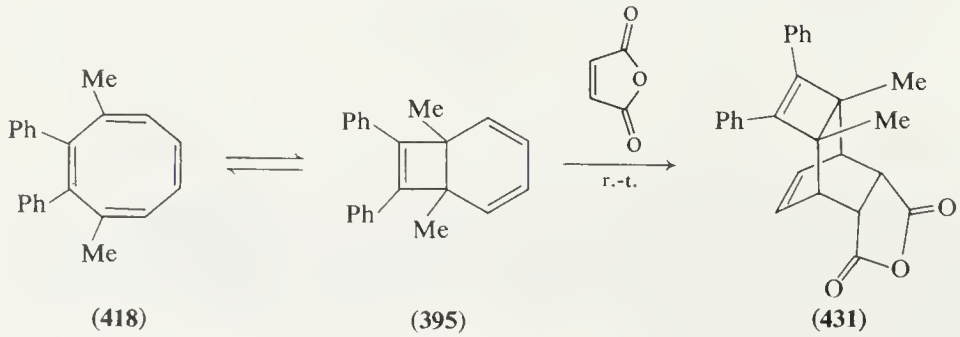
(**428**) R = Me, Et (**429**)

pattern, total saturation of the ring with this catalyst system requires a prolonged reaction time; in contrast, the complete hydrogenation of 1,3,5,7-tetraethoxycarbonylcyclo-octatetraene to (**430**) is rapid.[640]



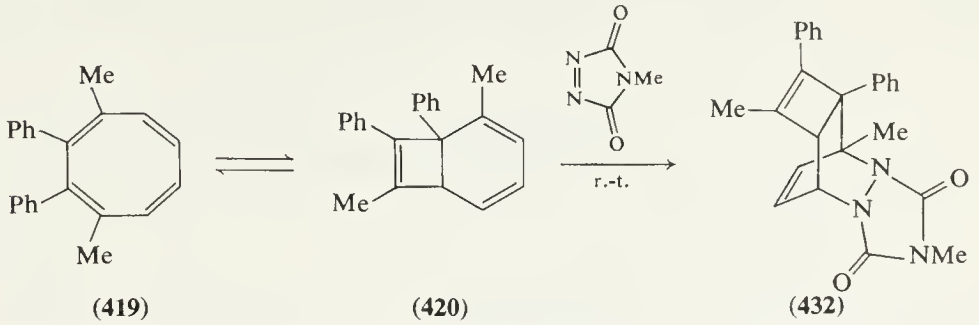
(**430**)

(*e*) *Cycloadditions.* The equilibrium mixture of (**418**) and (**395**) reacts with maleic anhydride to give the adduct (**431**).[651]



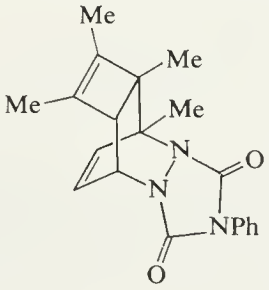
(**418**) (**395**) (**431**)

A similar adduct is obtained with *N*-methyltriazolinedione;[651] this also reacts with the equilibrium mixture of (**419**) and (**420**) to afford the adduct (**432**).[651]

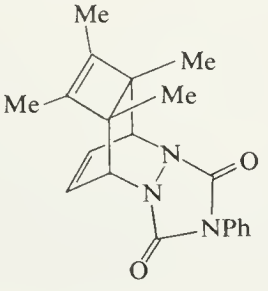


(**419**) (**420**) (**432**)

With *N*-phenyltriazolinedione, the 1,2,3,4- and 1,2,3,8-tetramethyl-compounds yield the adducts (**433**) and (**434**) respectively.[655]



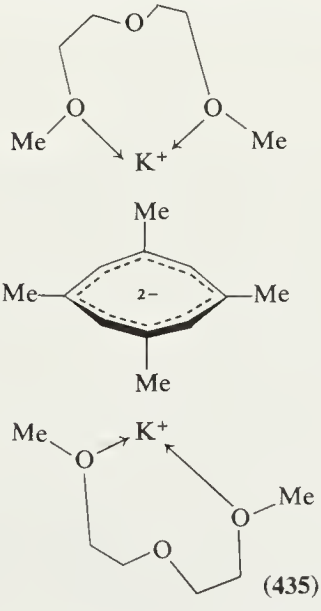
(**433**)



(**434**)

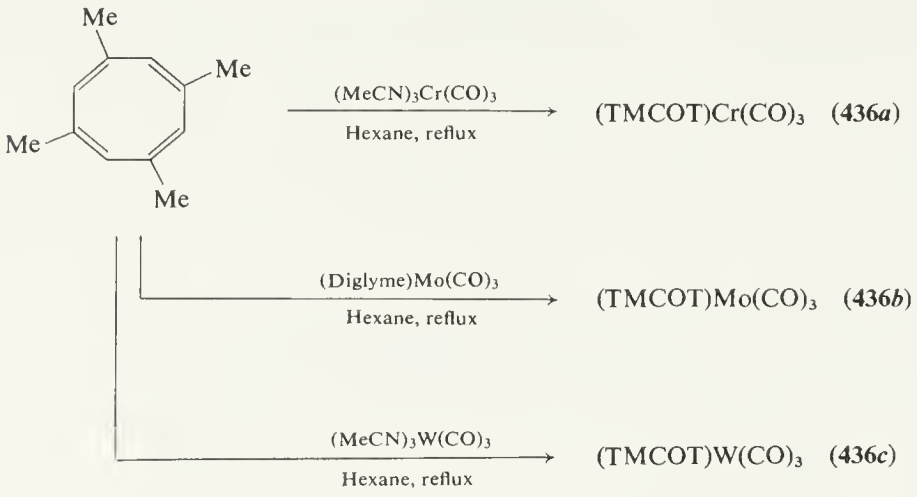
For the tetracyanoethylene adducts of 1,2,4,5-, 1,2,4,7- and 1,2,5,6-tetramethylcyclo-octatetraene, see ref. 652.

(*f*) *Formation of metal derivatives.* The 1,3,5,7-tetramethylcyclo-octatetraenide (**435**) incorporates a planar dianion, as shown by X-ray crystallography.[665]

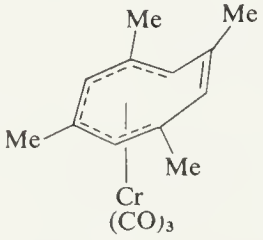


(**435**)

1,3,5,7-Tetramethylcyclo-octatetraene effects the following displacement reactions to afford the chromium (**436***a*) (60%),[648] molybdenum (**436***b*) (51%)[648, 666] and tungsten (**436***c*) (*ca.* 64%)[648] tricarbonyl complexes. The



structure of (TMCOT)$Cr(CO)_3$ (**436***a*)[667] resembles that of (COT)$Mo(CO)_3$ (**168***b*) (see p. 58). The ^1H [648, 666] and ^{13}C [432] spectra of these compounds reveal that they undergo a complex fluxional process in solution, involving 1,2-shifts of the metal atom.



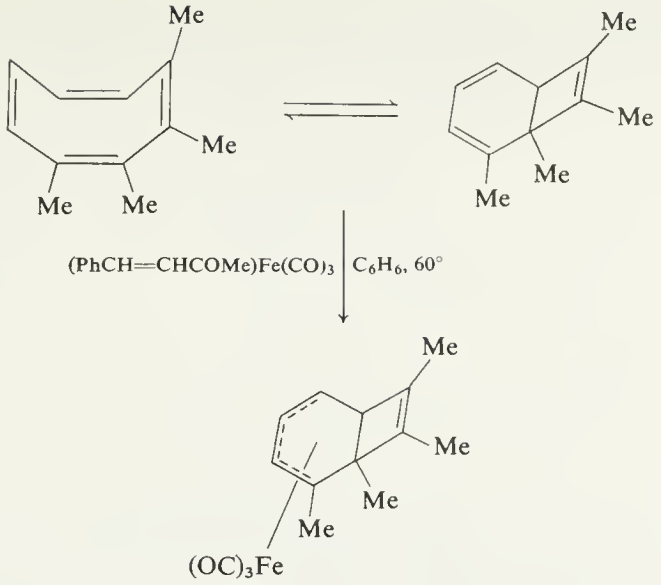
(**436***a*)

The equilibrium mixture of 1,2,3,4-tetramethylcyclo-octatetraene and its bicyclic valence tautomer reacts with (benzylidene–acetone)$Fe(CO)_3$ to give the complex (**437**) (79%).[655]

The 1,2,3,8-tetramethyl-compound is much less reactive, but with a large excess of the reagent yields the analogous product (**438**).[655]

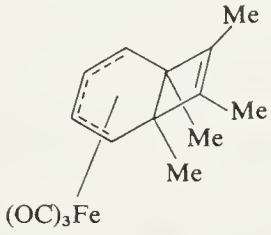
1,3,5,7-Tetramethylcyclo-octatetraene reacts with iron carbonyls to form a variety of complexes, some of which have no parallel amongst the complexes of COT itself.

With $Fe_3(CO)_{12}$, the main product is the tricarbonyl complex (**439**), containing a bicyclic ligand; in addition, the binuclear pentacarbonyl complex (**440**) is produced, together with an isomer (**441**) in which the ligand has apparently expericnced a 1,3-hydrogen shift.[668]



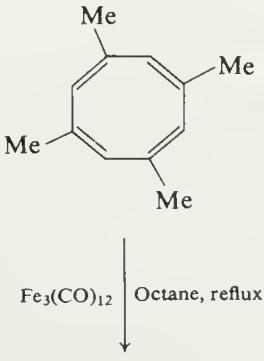
(437)

(Stereochemistry not certain)



(438)

(Stereochemistry not certain)

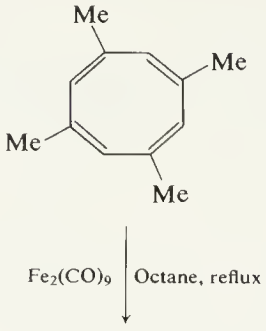


(1,3,5,7-Tetramethylbicyclo[4.2.0]octa-2,4,7-triene)$Fe(CO)_3$ **(439)**

\+ (TMCOT)$Fe_2(CO)_5$ **(440)**

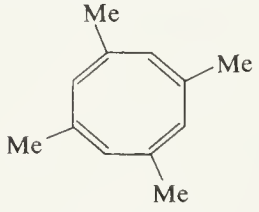
\+ (1,3,5-Trimethyl-7-methylenecyclo-octa-1,3,5-triene)$Fe_2(CO)_5$ **(441)**

Complex (**440**) is the main product when $Fe_2(CO)_9$ in refluxing octane is used, but the reaction also yields the isomer (**441**) and the '*trans*'-binuclear hexacarbonyl complex (**442**).[668]



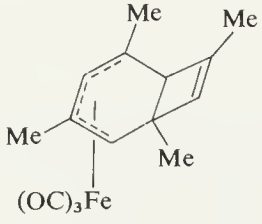
(TMCOT)$Fe_2(CO)_5$ (**440**)
+ (1,3,5-Trimethyl-7-methylenecyclo-octa-1,3,5-triene)$Fe_2(CO)_5$ (**441**)
+ '*trans*'-(TMCOT)$Fe_2(CO)_6$ (**442**)

In refluxing hexane, however, $Fe_2(CO)_9$ gives a minute yield of the '*cis*'-binuclear hexacarbonyl complex (**443**).[668]



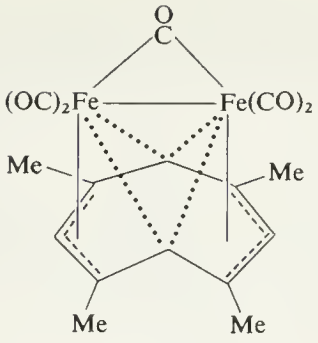
$\xrightarrow[\text{Hexane, reflux}]{Fe_2(CO)_9}$ '*cis*'-(TMCOT)$Fe_2(CO)_6$ (**443**)

Structure (**439**) is in accord with the spectral evidence.[668] The complex

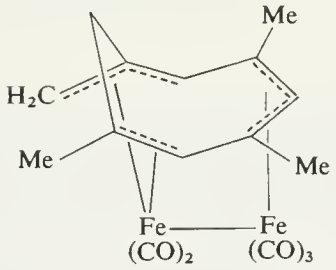


(**439**)
(Stereochemistry not certain)

(TMCOT)$Fe_2(CO)_5$ (**440**), which is fluxional, possesses a crystal structure analogous with that of (COT)$Fe_2(CO)_5$[669] (see p. 199). In compound (**441**), which contains an Fe–Fe bond, an $Fe(CO)_3$ grouping is bonded to a π-allyl system in the ring, while the remaining $Fe(CO)_2$ is attached to another allylic system involving an exocyclic methylene group, and also to an endocyclic double bond.[670] The complexes (**442**) and (**443**) are apparently analogues of

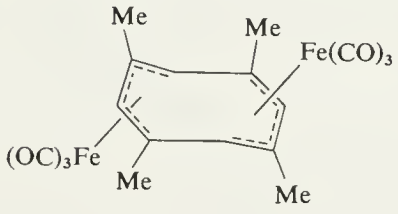


(440)

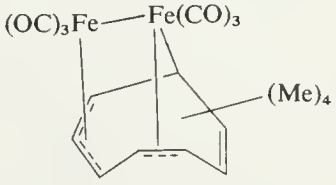


(441)

'*trans*'- and '*cis*'-$(COT)Fe_2(CO)_6$ respectively (see pp. 63, 65).[668]



(442)

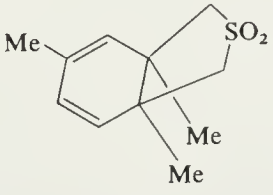


(443)

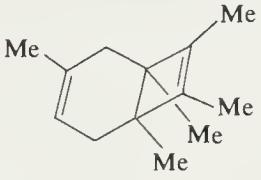
6. Pentasubstituted derivatives

Formation

1,2,3,4,6- and 1,2,3,5,8-pentamethylcyclo-octatetraene are formed from the sulphone (**444**) and the diene (**445**) respectively, using reaction sequences similar to those employed for the 1,2,3,4- and 1,2,3,8-tetramethyl-compounds[671] (see p. 140).

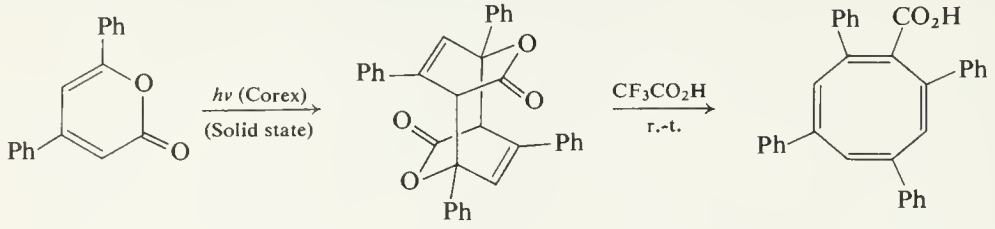


(444)



(445)

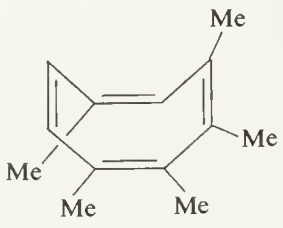
2,4,6,8-Tetraphenylcyclo-octatetraene-1-carboxylic acid is obtained (50%) when 4,6-diphenyl-2-pyrone photodimer (**446**) is treated with trifluoroacetic acid.[672]



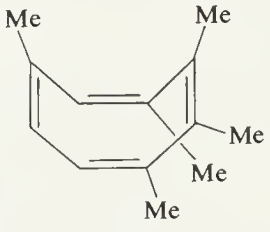
(446)

Structure

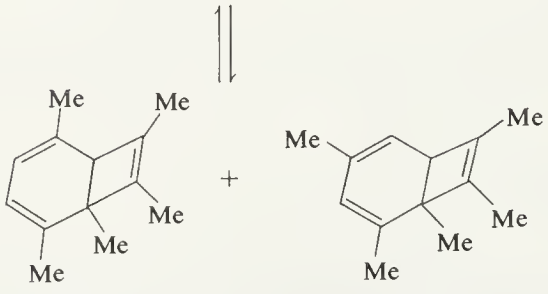
Like the 1,2,3,4- and 1,2,3,8-tetramethyl-derivatives (see p. 142), the pentamethyl-compounds (**447*a***) and (**447*b***) are isolable bond-shift isomers; (**447*a***) equilibrates with the bicyclic valence tautomers (**448**) and (**449**), but (**447*b***) is seemingly homogeneous.[671]



(447*a*)



(447*b*)



(448) **(449)**

7. Hexa- and heptasubstituted derivatives

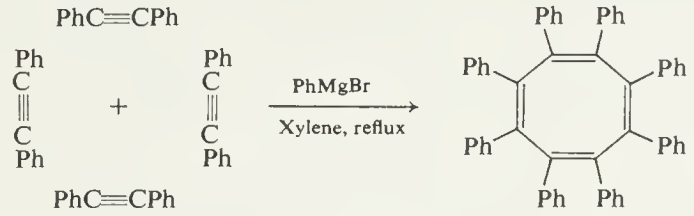
These are apparently unknown.

8. Octasubstituted derivatives

Formation

(*a*) *Cyclotetramerisation of disubstituted acetylenes.* The cyclotetramerisation

of diphenylacetylene may be achieved (up to 7.5% yield) in the presence of certain ether-free organomagnesium compounds, of which phenylmagnesium bromide is the most efficient.[673,674]

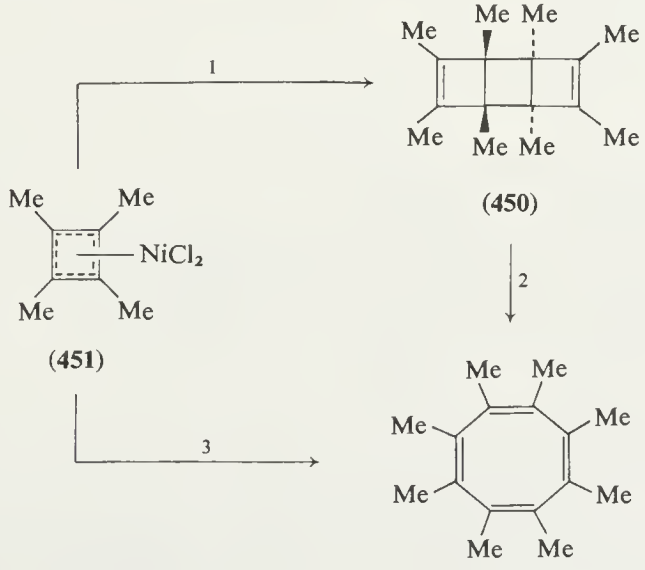


A minute yield (0.06%) of octaphenylcyclo-octatetraene is formed by u.v. irradiation of diphenylacetylene.[675]

(*b*) *Syntheses involving skeletal transformations.* The dimerisation of tetrasubstituted cyclobutadienes results in octasubstituted tricyclo[4.2.0.$0^{2,5}$]-octa-3,7-dienes, which undergo thermal rearrangement to yield octasubstituted COTs (see pp. 137–9); in some cases the cyclobutadiene dimers rearrange under the reaction conditions of their formation.

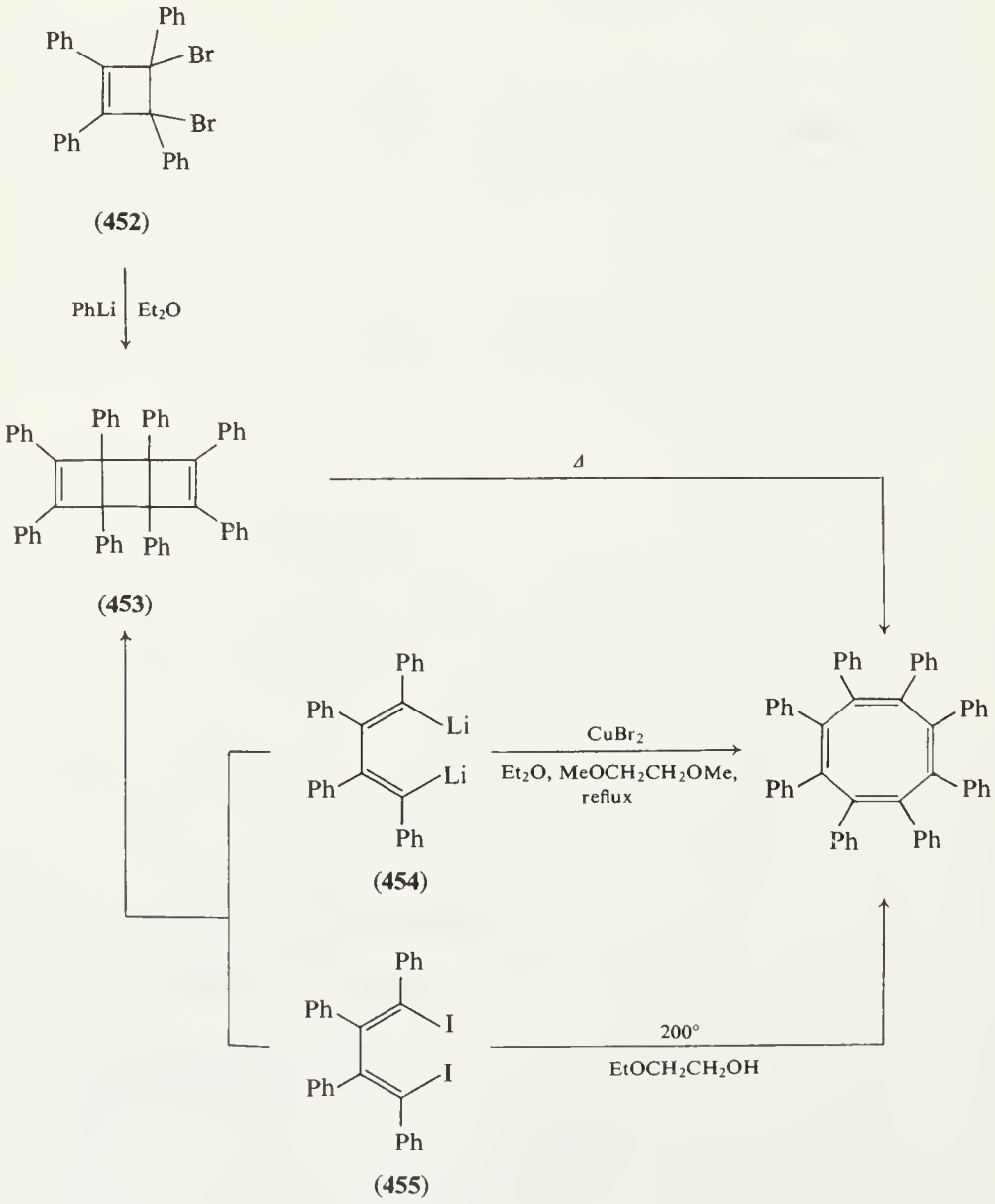
The tetramethylcyclobutadiene dimer (**450**) (shown to possess *anti*-stereochemistry) may be obtained by heating the nickel(II) chloride complex (**451**) at 120°; at higher temperatures octamethylcyclo-octatetraene is formed (scheme 63). The low yields of octamethylcyclo-octatetraene obtained by these procedures result from its thermal rearrangement (see p. 160).

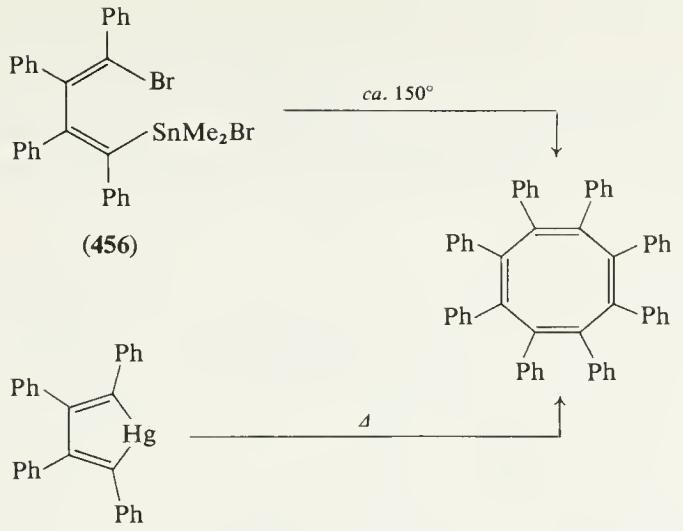
Scheme 63



Reaction	Conditions	Yield (%)	Ref.
1	120°, H_2O	63–65	676
2	300°/3 mm	10	220
3	185–200°/0.001 mm	7–21	677

The cyclobutene (**452**), on treatment with phenyl-lithium, forms a debrominated product which may be the cyclobutadiene dimer (**453**) (80%); the same compound results (40%) from a reaction between the dilithio- and di-iodobutadienes (**454**) and (**455**).[678] This product slowly rearranges to octaphenylcyclo-octatetraene (even in the solid state) at room temperature.[678] Octaphenylcyclo-octatetraene is also formed by thermolysis of the di-iodobutadiene (**455**) (5%), and by treatment of the dilithio-compound (**454**) with copper(II) bromide (15%).[679] Homolytic extrusion of dimethyltin bromide from the compound (**456**) affords octaphenylcyclo-octatetraene in high yield (85%);[680] thermolysis of tetraphenylmercurole (**457**) gives the same product.[679]

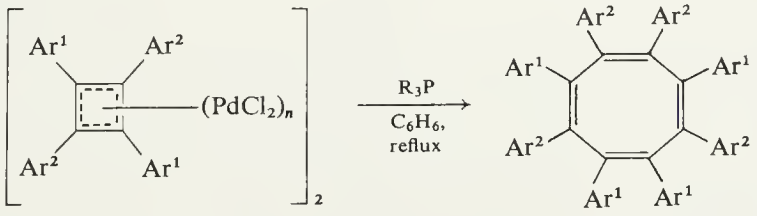




(456)

(457)

The dimeric (tetra-arylcyclobutadiene)palladium(II) chloride complexes (**458**) form octa-arylcyclo-octatetraenes (**459**) on treatment with triphenylphosphine or (preferably[681]) tributylphosphine (table 59).



(458)

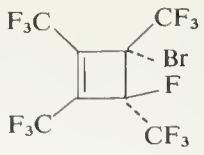
(459)

Table 59

Ar^1	Ar^2	*n*	R	Yield (%)	Ref.
Ph	Ph	1	Ph	*ca.* 70	682, (683)
p-Me.C_6H_4	*p*-Me.C_6H_4	3	Bu^n	38	681
p-Me.C_6H_4	*p*-MeO.C_6H_4	1	Ph	60	684
p-MeO.C_6H_4	*p*-MeO.C_6H_4	3	Bu^n	94	681
p-Cl.C_6H_4	*p*-Cl.C_6H_4	2	Bu^n	73	685

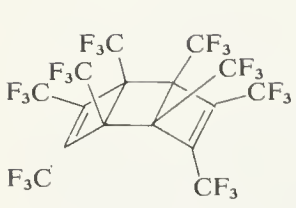
Treatment of the cyclobutene (**460**) with methyl-lithium gives a mixture of products, chiefly (**461**) (37%), (**462**) (22%) and (**463**) (36%); isomerisation of (**462**) to (**461**) and of (**463**) to (**464**) is effected by caesium fluoride, and at 300° these products rearrange to octakis(trifluoromethyl)cyclo-octatetraene in quantitative yield.[686]

The isolable tetrasubstituted cyclobutadiene (**465**), when heated at 110°, yields the octasubstituted COT (**466**) (70%).[687]

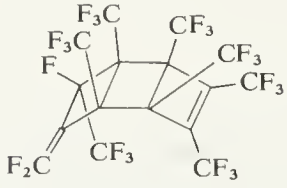


(460)

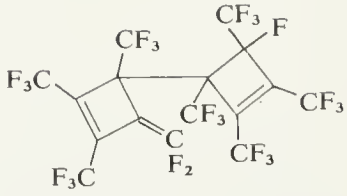
MeLi | Et_2O, −125°



+



+

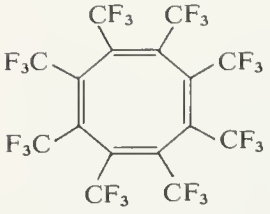


(461) **(462)** **(463)**

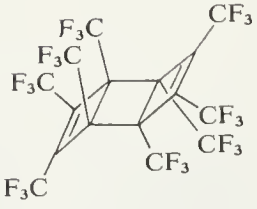
CsF

300°

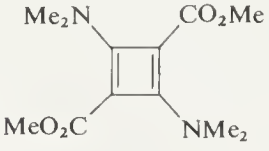
CsF



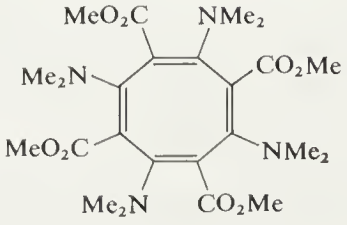
300°



(464)



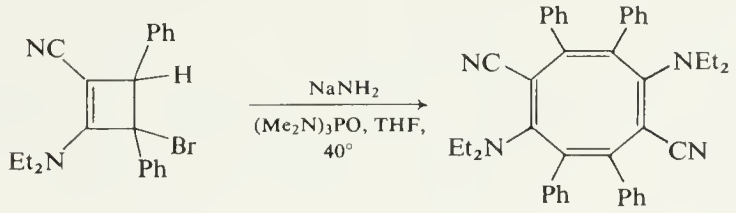
110°



(465) **(466)**

Dehydrobromination of the cyclobutene (**467**) gives the octasubstituted COT (**468**) in low yield (5%).[688]

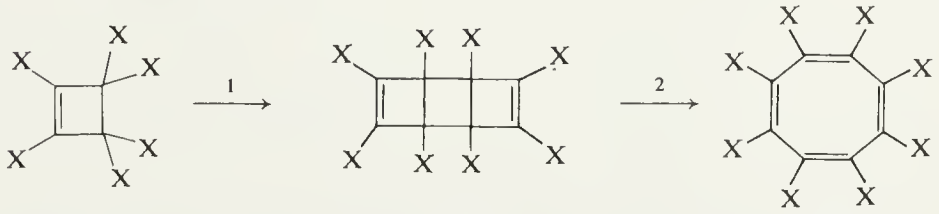
Dehalogenation of the cyclobutenes (**469**) affords the cyclobutadiene dimers (**470**), which are readily converted into the related octahalocyclo-octatetraenes (**471**) (scheme 64).[689] The octachloro-diene (**470**; X = Cl) is also formed



(**467**) (**468**)

on photolysis of the ozonide (**472**) derived from the 'Dewar-benzene' (**473**) (*ca.* 22% overall yield).[689]

Scheme 64

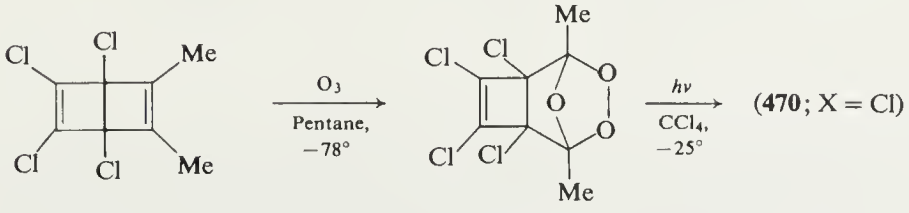


(**469**) (**470**) (**471**)

X = Cl, Br

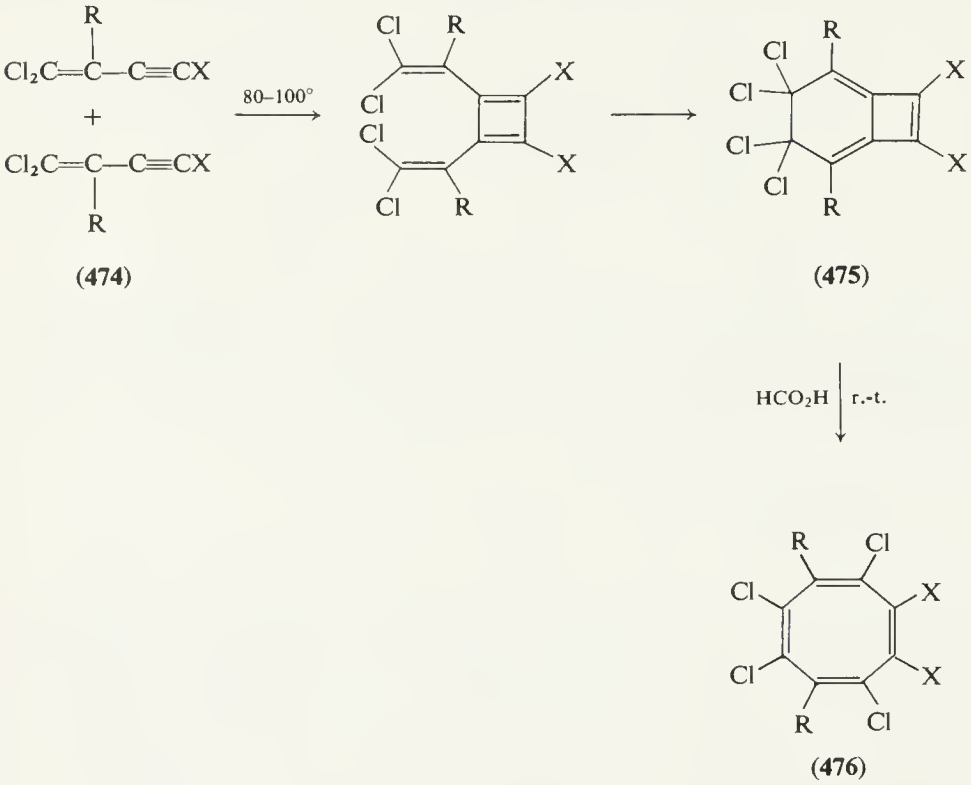
Reaction	X	Conditions	Yield (%)
1	Cl	Li–Hg, Et_2O, r.-t.	14–22
1	Br	Li–Hg, Et_2O, r.-t.	27–40
2	Cl[a]	$Cl_2C{=}CCl_2$, reflux	75
2	Br	*o*-Dichlorobenzene, reflux	58

[a] See also ref. 690.



(**473**) (**472**)

A special preparative method for halocyclo-octatetraenes involves thermal dimerisation of the enynes (**474**), which results in dimers of structure (**475**); acid-catalysed rearrangement then leads to the octasubstituted COTs (**476**) (table 60).[691–694]

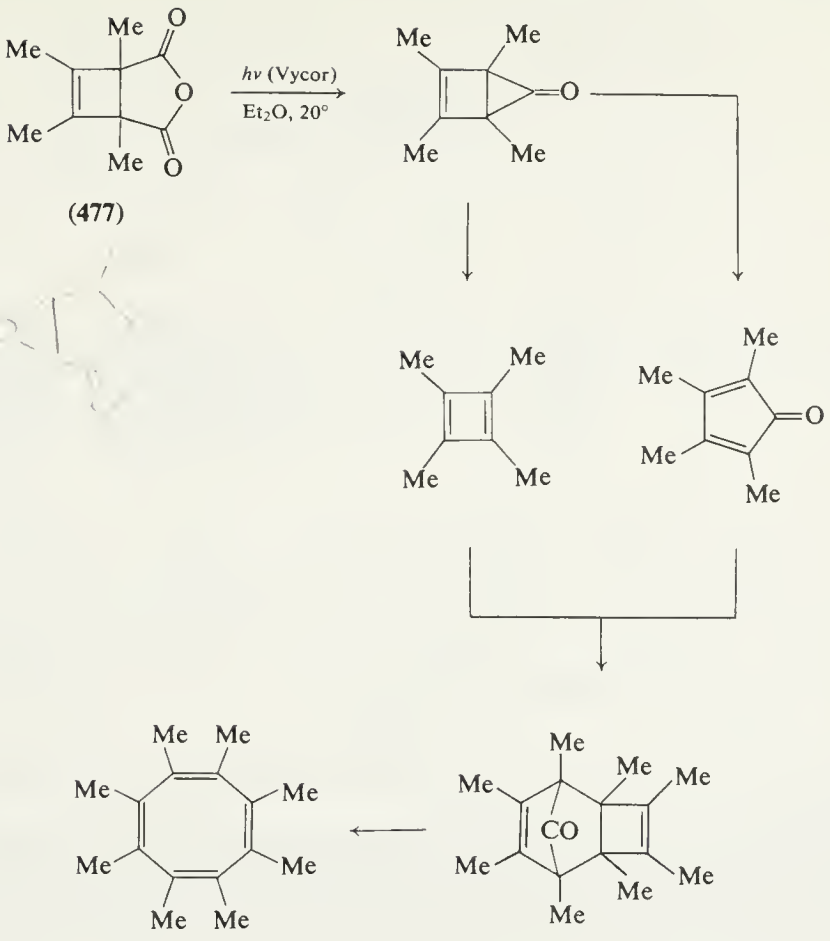


(**474**) (**475**) (**476**)

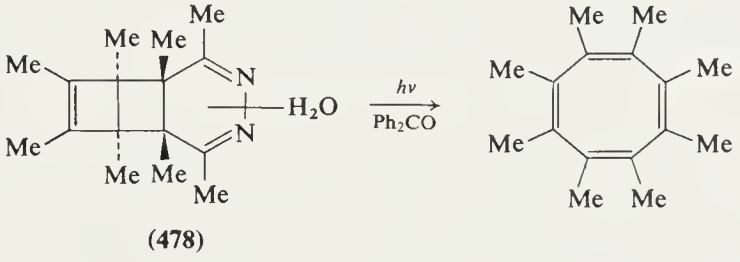
Table 60

Product	R	X	Yield (%)	Ref.
(**475**)	Me	Cl	7	694
	Cl	Cl	35	695
	Cl	Br	33–37	693
	Br	Cl	39	694
(**476**)	Me	Cl	60 (crude)	694
	Cl	Cl	35	695
	Cl	Br	83	693, (696)
	Br	Cl	33	694

U.v. irradiation of the anhydride (**477**) gives multifarious products, one of which is octamethylcyclo-octatetraene (5.3%); the reaction sequence involved in its formation may be as shown.[697]



The sensitised photolysis of the heterocycle (**478**) affords octamethylcyclo-octatetraene almost exclusively.[698]



Structure

The crystal structures of octamethyl- and octaphenylcyclo-octatetraene* have been determined, with the results (for the COT ring) listed in table 61.

* The structure of the compound now known[699–701] to be octaphenylcyclo-octatetraene was for some time in doubt.[678, 680, 683, 702]

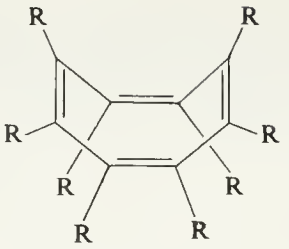
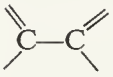


Table 61

R	Bond	Length (Å)	Ref.
Me	C=C	1.326	116
Ph	C=C	(1.35), 1.342	(700), 701
Me	C—C	1.483	116
Ph	C—C	(1.51), 1.493	(700), 701
Me	Angle 	122°	116
Ph	Angle 	(120°), 122°	(700), 701
Me	Torsion angle around 	67°	116

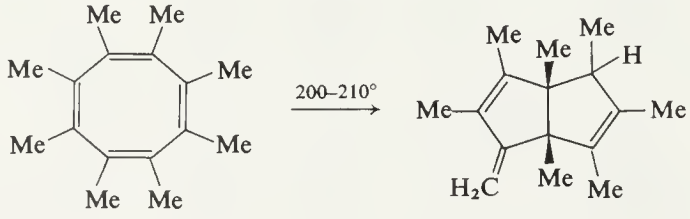
For X-ray confirmation of the structure of octachlorocyclo-octatetraene, see ref. 703.

It is evident that the presence of eight substituent groups produces a significant flattening of the COT ring (see pp. 9, 93, 115, 142).

For the calculated barrier to ring-inversion of octamethylcyclo-octatetraene, see ref. 127.

Reactions

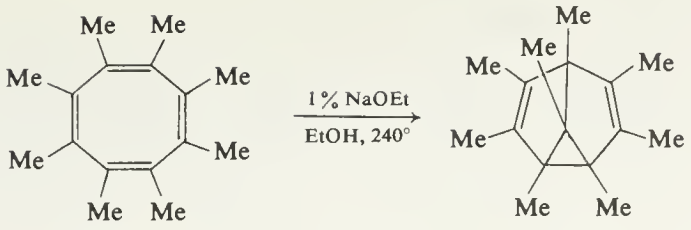
(*a*) *Thermal isomerisation.* Octamethylcyclo-octatetraene rearranges at 200–210°,[677] giving a product now formulated as (**479**).[220] (Thus thermolysis of the



(**479**)

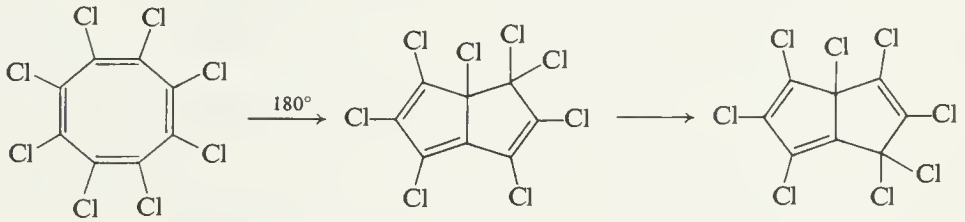
syn-[704] or *anti*-[220,676] dimers of tetramethylcyclo-butadiene (see p. 153) gives (**479**) as the main product (*ca.* 80%)).

In the presence of sodium ethoxide, however, thermal isomerisation of octamethylcyclo-octatetraene leads to the semibullvalene (**480**) (*ca.* 37%).[705,706]



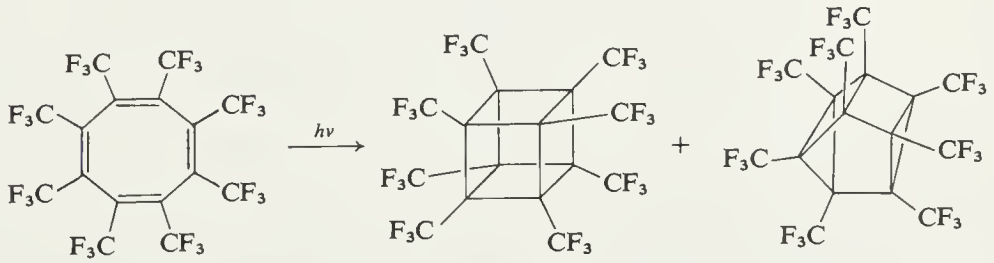
(480)

Octachlorocyclo-octatetraene, when kept at 180° for a short time, affords the bicyclic isomer (**481**) (41 %); prolonged heating effects further rearrangement to give a second isomer (**482**) (58 %).[707]



(481) (482)

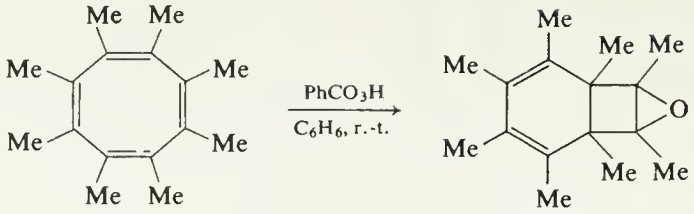
(*b*) *Photo-isomerisation.* Light-induced isomerisation of octakis(trifluoromethyl)cyclo-octatetraene leads to the formation of the cubane (**483**) and cuneane (**484**) as end-products.[686]



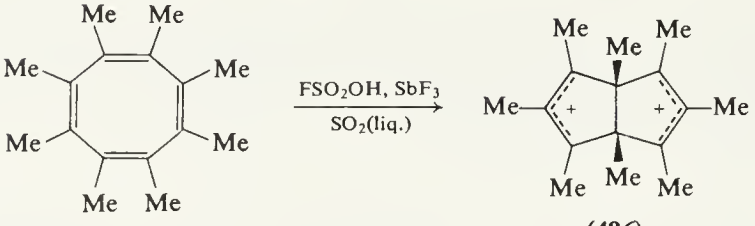
(483) (484)

(*c*) *Oxidation, and reactions with electrophiles.* With perbenzoic acid, octamethylcyclo-octatetraene gives a product formulated as (**485**) (96 %);[708] this structure may need correction (see refs. 220, 706).

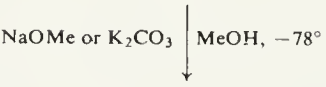
Treatment of octamethylcyclo-octatetraene with fluorosulphonic acid–antimony(III) fluoride produces a species formulated as the bicyclic dication (**486**), probably *via* protonation followed by hydride abstraction; proton abstraction by base then affords the $C_{16}H_{22}$ hydrocarbon (**487**).[220]

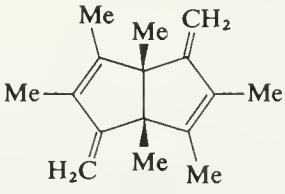


(485)

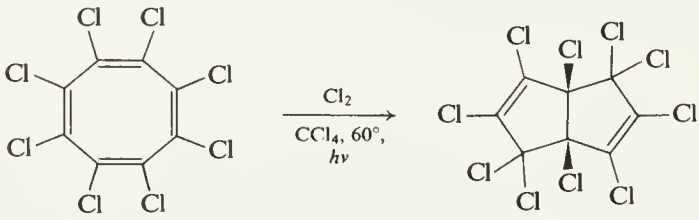


(486)

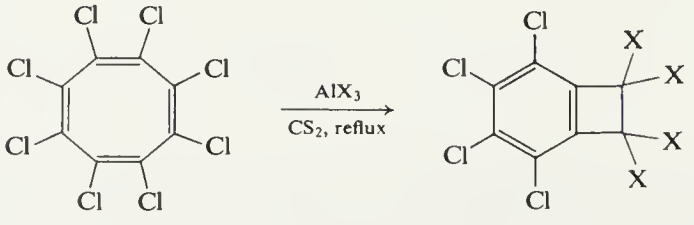




(487)



(488)



(489)

Table 62

X	Yield (%)
Cl	100
Br	90

Chlorination of octachlorocyclo-octatetraene yields the bicyclic decachloro-derivative (**488**) (81 %).[707]

With aluminium halides, octachlorocyclo-octatetraene affords the benzo-cyclobutenes (**489**)[709] (table 62).

(*d*) *Cycloadditions.* See appendix.

3

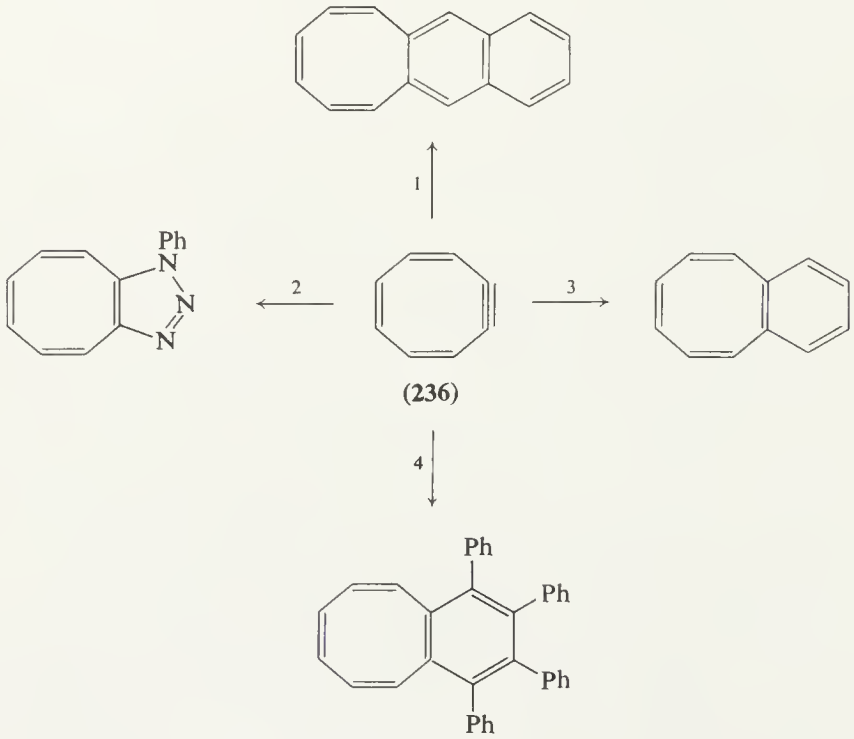
Further reactions of compounds derived from cyclo-octatetraenes

1. 1,2-Didehydrocyclo-octatetraene

1,2-Didehydrocyclo-octatetraene (**236**) may be generated by dehydrobromination of bromocyclo-octatetraene (see pp. 83–4).

Reactions. The preparation of some monosubstituted COTs and annulated derivatives from (**236**) has already been described (see pp. 83–4, 124–5); other reactions are outlined in scheme 65.

Scheme 65



(236)

Reaction	Reagents and conditions	Yield (%)	Ref.
1	THF, r.-t.	10	624
2	Phenyl azide, Et_2O, r.-t.	38	624
3	1-(*N*,*N*-Diethylamino)buta-1,3-diene, Et_2O, r.-t.	5	624
4	Tetracyclone, Et_2O, r.-t.	(72), 91	(624), 710

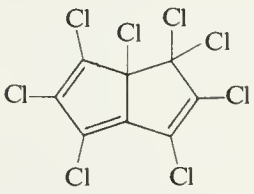
2. Bicyclo[4.2.0]octa-2,4,7-trienes

These valence tautomers of COTs have been discussed in the sections dealing with the parent compounds.

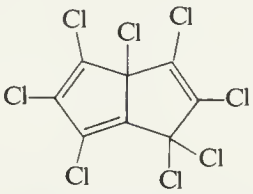
For the (low-temperature) preparation of bicyclo[4.2.0]octa-2,4,7-triene, see pp. 245, 354.

3. Bicyclo[3.3.0]octa-2,6-dienes, bicyclo[3.3.0]octa-1,3,6-trienes and bicyclo[3.3.0]octa-1,3,7-trienes

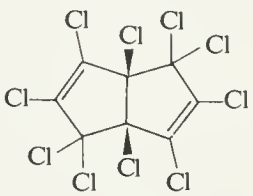
The perchloro-compounds (**481**), (**482**) and (**488**) are available from octachlorocyclo-octatetraene (see pp. 161–3).



(**481**)

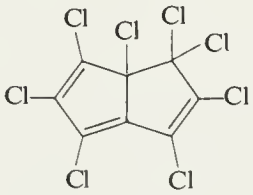


(**482**)

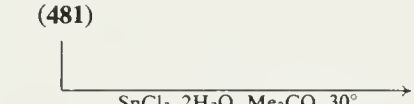


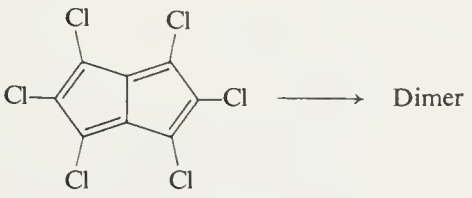
(**488**)

Reactions. Most of the known[707] chemistry of these systems is summarised in schemes 66 and 67. In addition, dechlorination of compounds (**481**) or (**482**) with tin(II) chloride affords a dimer of hexachloropentalene (**490**) (78–86%).[707]

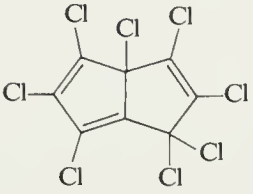


(**481**)



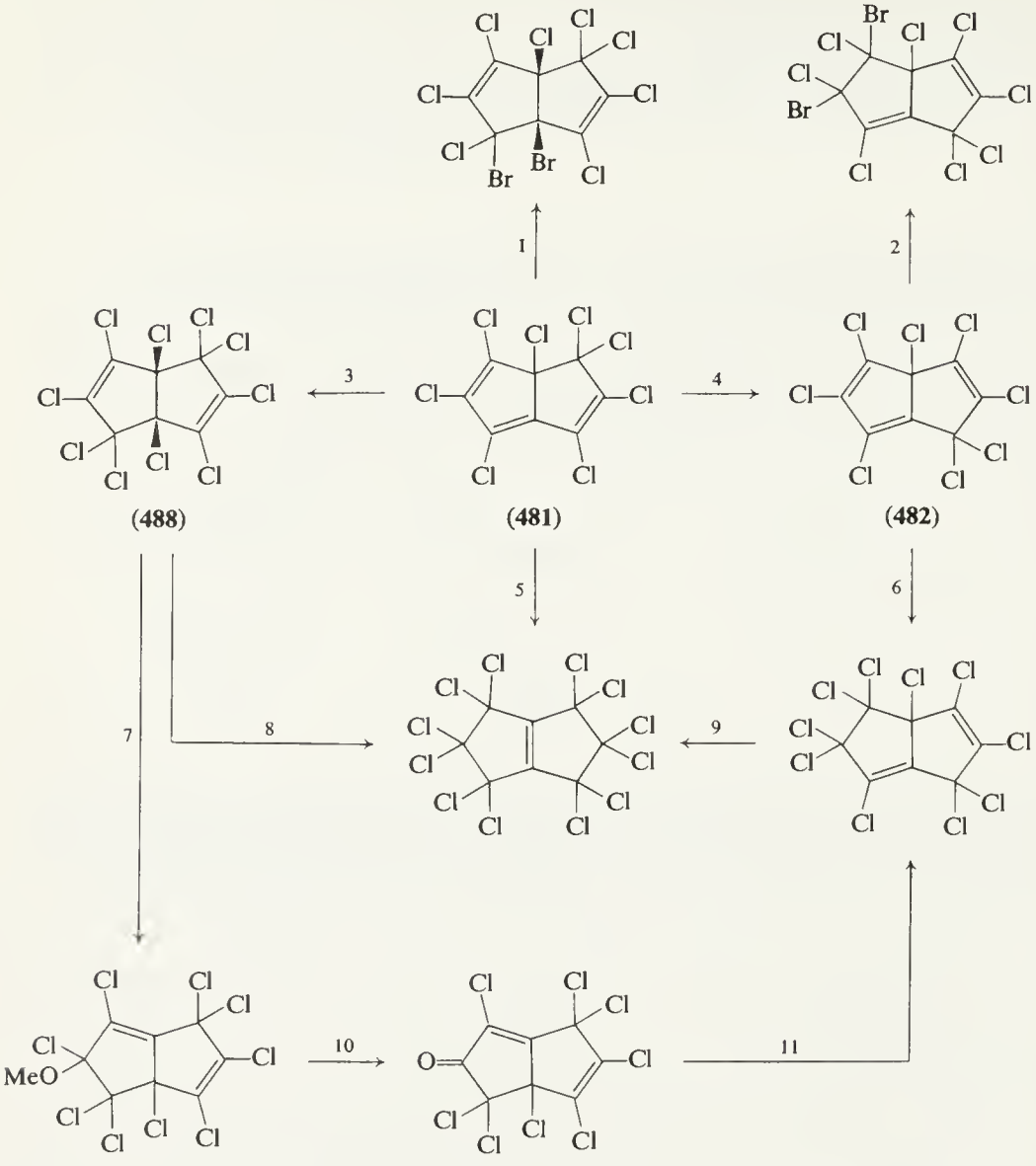


(**490**)



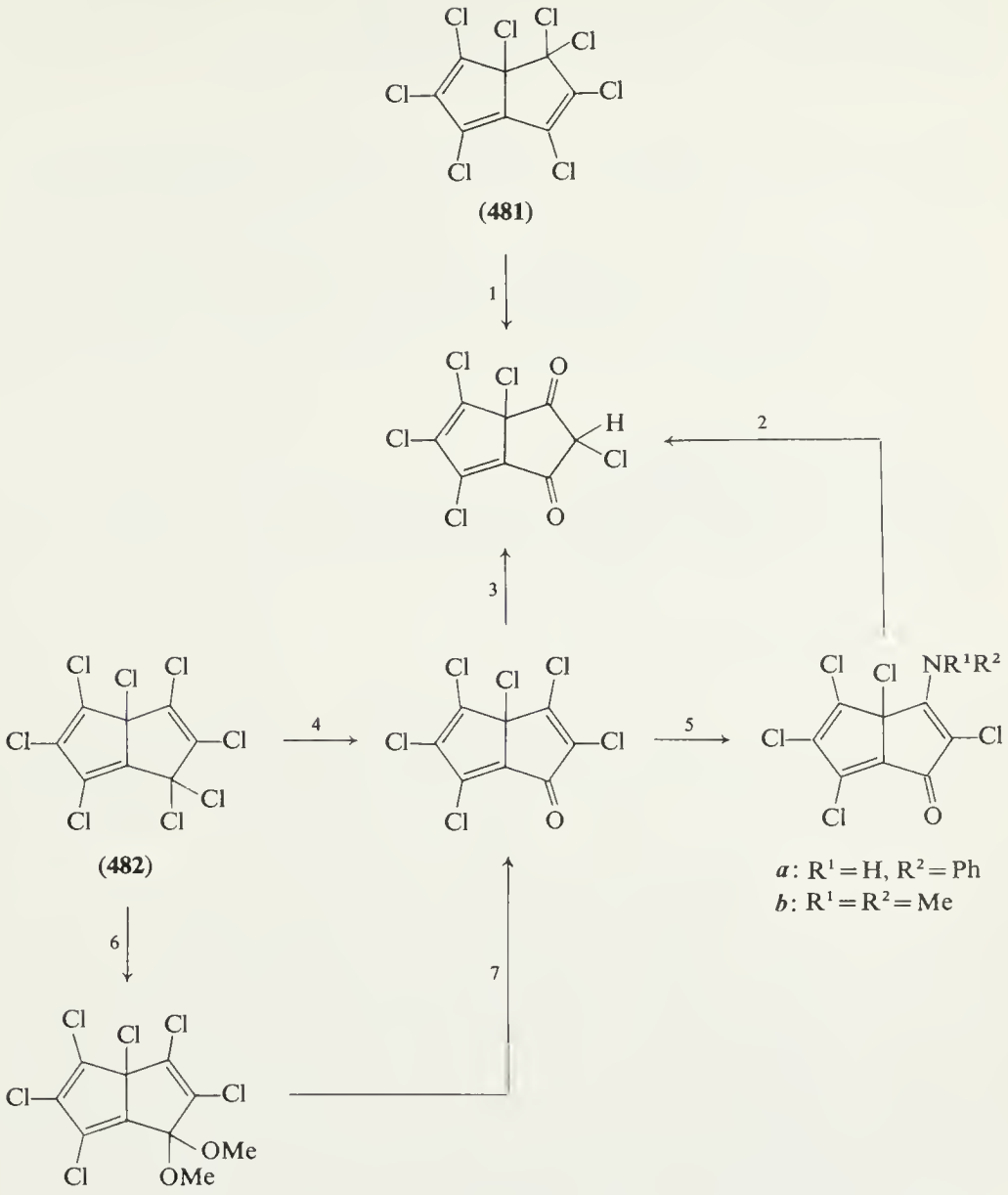
(**482**)

Scheme 66



Reaction	Conditions	Yield (%)
1	Br_2, r.-t.	77
2	Br_2, r.-t.	88
3	Cl_2, CCl_4, 40°, *hv*	68
4	$AlCl_3$, CS_2, r.-t.	100
5	Cl_2, CCl_4, 60°, *hv*	88
6	Cl_2, CCl_4, 40°, *hv*	27
7	NaOH, MeOH, reflux	60
8	Cl_2, CCl_4, 60°, *hv*	88–95
9	Cl_2, CCl_4, 60°, *hv*	88–95
10	Conc. H_2SO_4, r.-t.	72
11	PCl_5, 180°	78

Scheme 67

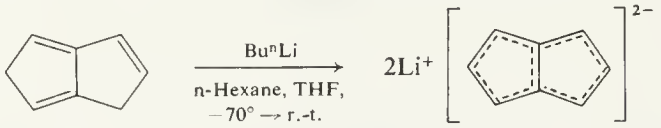


Reaction	Conditions	Yield (%)
1	Conc. H_2SO_4, r.-t.	77
2	Conc. H_2SO_4, r.-t.	52–68
3	HCO_2H, 80°	72
4	HCO_2H, r.-t.	65
	or $Ag(OCOCF_3)$, C_6H_6, r.-t.	74
5	(*a*) $PhNH_2$, Et_2O, r.-t.	81
	(*b*) Me_2NH(aq.), Et_2O, r.-t.	76
6	MeOH, reflux	53
7	Conc. H_2SO_4, r.-t.	72

4. Bicyclo[3.3.0]octa-1,4,6-triene

The dihydropentalene (**24**) may be prepared by the thermal isomerisation of COT (see p. 18).

Reactions. Proton-abstraction with n-butyl-lithium generates the 'aromatic' pentalenyl dianion, isolable as the crystalline dilithium salt.[711,712]

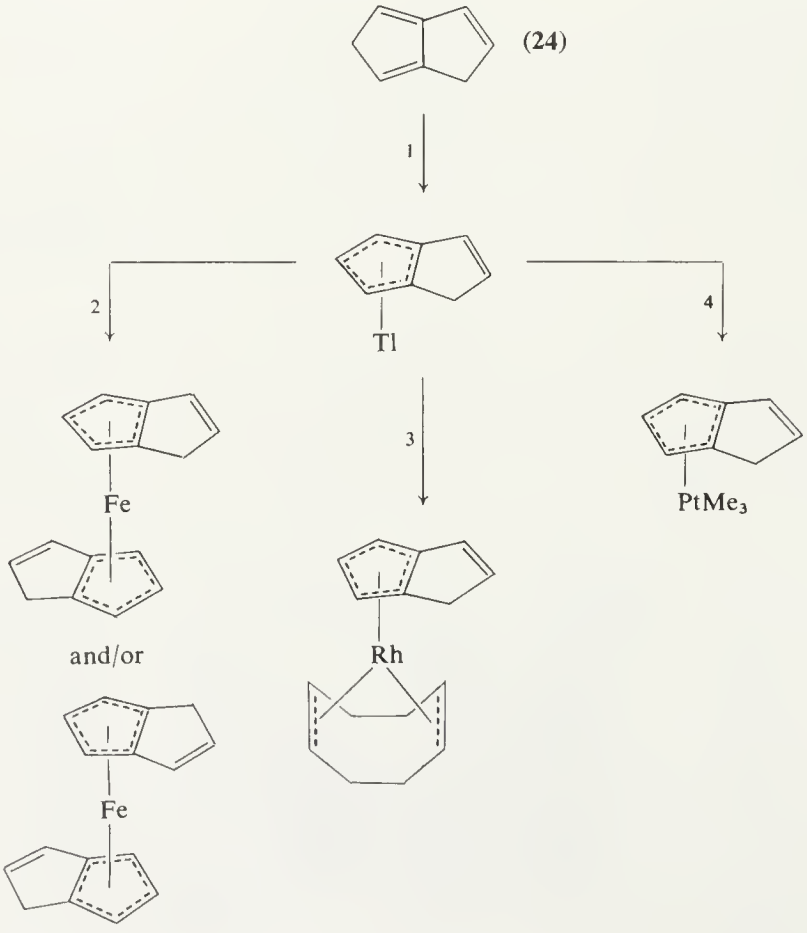


(**24**)

The dihydropentalene (**24**) reacts with maleic anhydride to form an adduct[712] (no structural evidence available).

The dihydropentalene (**24**) forms a thallium derivative from which other metal derivatives may be obtained[713] (scheme 68).

Scheme 68

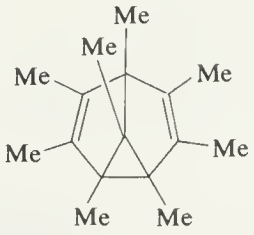


Reaction	Reagents and conditions	Yield (%)
1	Tl_2SO_4, NaOH(aq.), r.-t.	100
2	$FeCl_2$, THF, r.-t.	49
3	$[(COD)RhCl]_2$, THF, r.-t.	76
4	Me_3PtI, THF, r.-t.	43

5. Semibullvalenes

Semibullvalene (**18**) is formed directly from COT by u.v. irradiation (see p. 18), but a more satisfactory preparative procedure, which may also be used for substituted derivatives, is the indirect route *via* 9,10-diazatricyclo[4.2.2.$0^{2,5}$]-deca-3,7-dienes (see pp. 353, 355). The octamethyl-compound (**480**) is available from octamethylcyclo-octatetraene (see pp. 160–1).

(**18**)



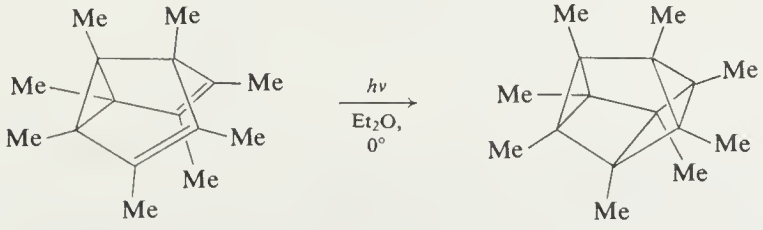
(**480**)

The semibullvalene structure undergoes an extremely rapid fluxional process *via* a degenerate Cope rearrangement.[44,714]

For other leading references on semibullvalene, see ref. 635.
For studies with substituted semibullvalenes, see refs. 715, 716.

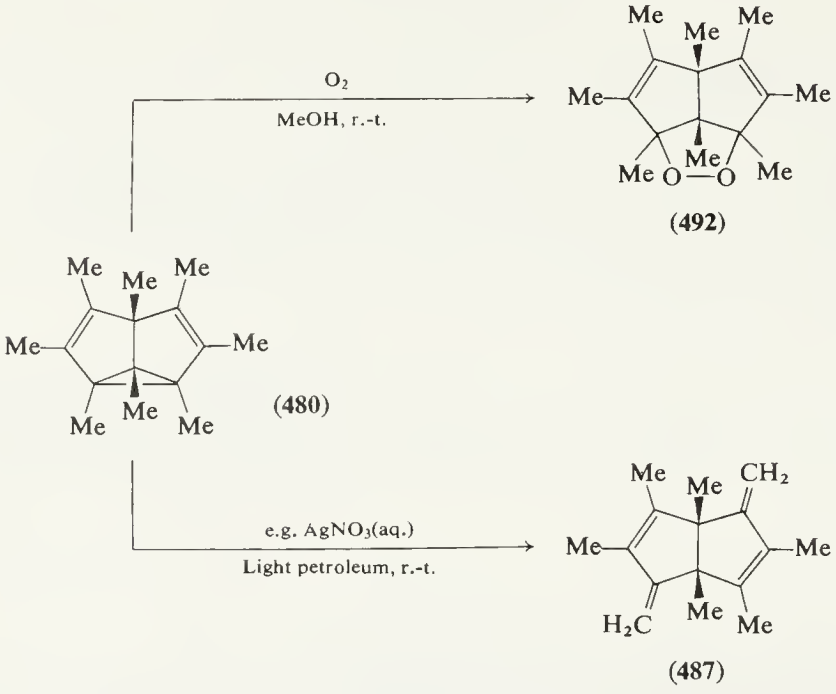
Reactions. The gas-phase thermolysis of semibullvalene leads to COT (see p. 4); u.v. irradiation also induces equilibration with COT (see p. 18).

Photo-isomerisation of octamethylsemibullvalene yields the cuneane (**491**) (10–20%).[706]



(**480**) (**491**)

The octamethyl-compound readily absorbs oxygen to form the peroxide (**492**) (75%),[705, 706] and is easily dehydrogenated to give the dimethylene compound (**487**) (up to 80%)[705, 706] (for a possible mechanism, see ref. 635).

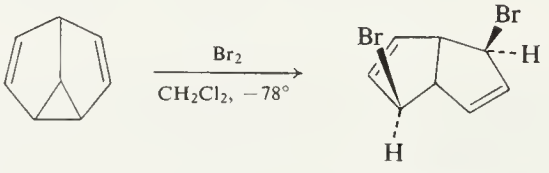


(**492**)

(**480**)

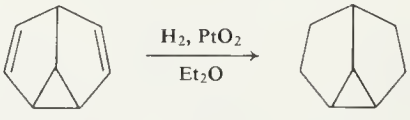
(**487**)

Semibullvalene adds bromine in a stereoselective manner to afford the *cis*, *exo*-dibromide (**493**) (67%).[717]



(**493**)

Catalytic hydrogenation of semibullvalene gives the tetrahydro-derivative (**494**).[714]

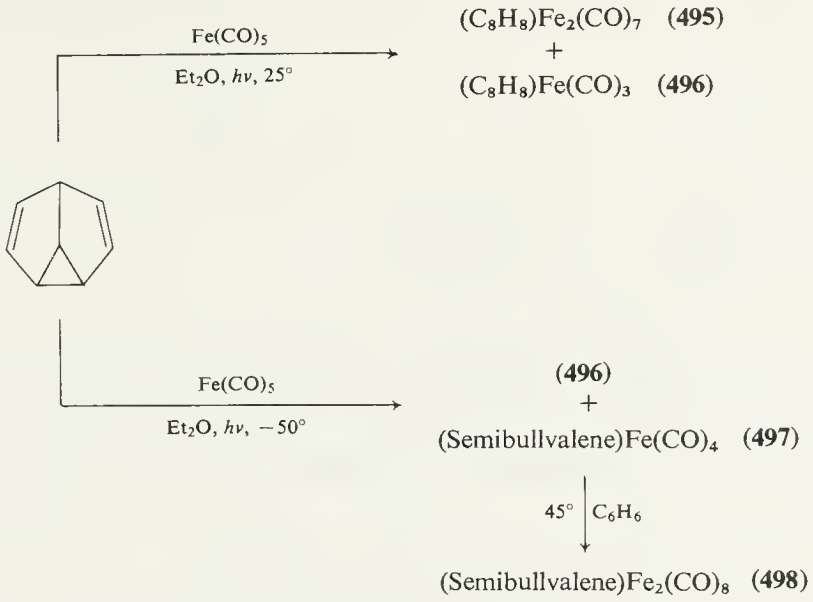


(**494**)

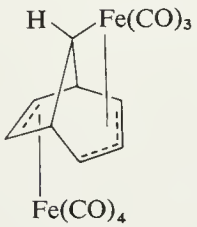
Octamethylsemibullvalene forms adducts with tetracyanoethylene and diethyl azodicarboxylate[705, 706] (see appendix).

Silver and tungsten complexes of semibullvalene are known[718] (for the silver-catalysed rearrangement of semibullvalene to COT, see p. 4).

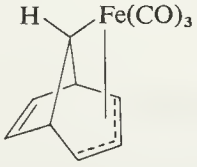
U.v. irradiation at 25° in the presence of $Fe(CO)_5$ affords the complexes (**495**) and (**496**); at −50° the products are (**496**) and (**497**), the latter disproportionating at 45° to semibullvalene and (**498**).[719] Spectral evidence indicates



that the C_8H_8 ligand in the complexes (**495**) and (**496**) is bonded as shown.[720]

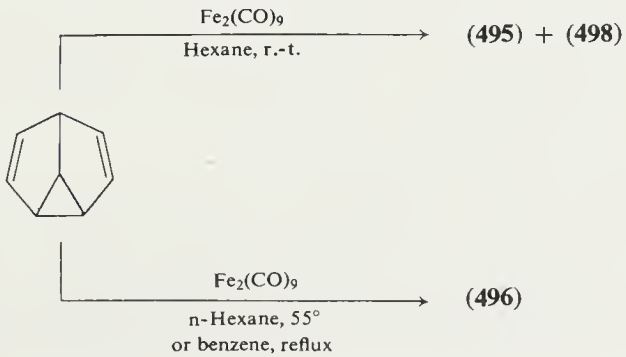


(**495**)

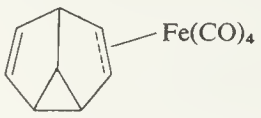


(**496**)

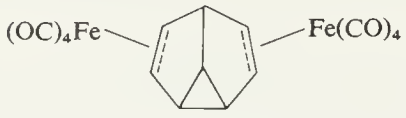
Thermal reactions occur with $Fe_2(CO)_9$; at room-temperature the main products are the binuclear species (**495**) and (**498**);[720] on heating, however, the



mononuclear tricarbonyl complex (**496**) is obtained (70%).[721,722] The complexes (**497**) and (**498**), containing the semibullvalene ligand, are formulated as follows.[719,720]



(**497**)

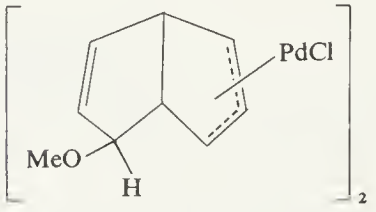


(**498**)

Semibullvalene reacts with methanolic potassium tetrachloropalladate, giving the dimeric complex (**499**) (75%).[723]

$\xrightarrow[MeOH]{K_2PdCl_4}$ $[(MeO.C_8H_8)PdCl]_2$ (**499**)

The suggested structure of the product is given below.



(**499**)

6. Metal derivatives

(*a*) *Lithium, sodium and potassium derivatives*

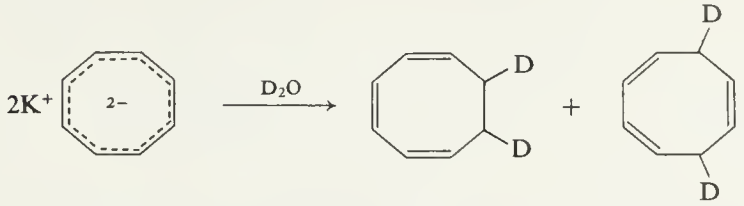
Donation of two electrons from an alkali metal to the COT ring leads to the dianion (**60**) (see pp. 28, 48–9).

Reactions. The cyclo-octatetraenyl dianion (**60**) is capable of transferring electrons to other species in several different ways.

Anion radicals may be generated from neutral substrates, e.g. COT (see p. 28), 6,6-diphenylfulvene,[724] phenanthraquinone,[725] dicyanodiphenylethylenes,[724] nitrosobenzene,[726] nitrobenzene,[726] *m*-dinitrobenzene,[727] nitrostilbenes,[728,729] benzofurazan,[730] benzothiadiazoles,[731] etc. With benzonitrile, electron-transfer induces trimerisation.[378]

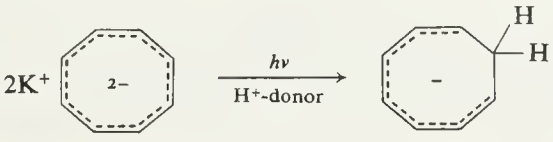
The ability of COT^{2-} to function as a reducing agent is illustrated by its reactions with benzil,[725] azobenzene,[732] azoxybenzene,[732] *N*-nitrosodiphenylamine,[378] sulphur dichloride,[380] benzenesulphenate esters,[733] metal halides[378] (see also below), and by its reductive dimerisation of the tropylium ion,[734] the 2,4,6-trimethylpyrylium ion[735] and *p*-nitroso-*N*,*N*-dimethylaniline.[378]

The dianion (**60**) naturally acts as a proton-acceptor, and with water or alcohols yields mixtures of cyclo-octa-1,3,5-triene and cyclo-octa-1,3,6-triene (see p. 28). The use of deuterium oxide leads to the dideuterio-derivatives (**500**) (80%) and (**501**) (20%).[736]



(**60**) (**500**) (**501**)

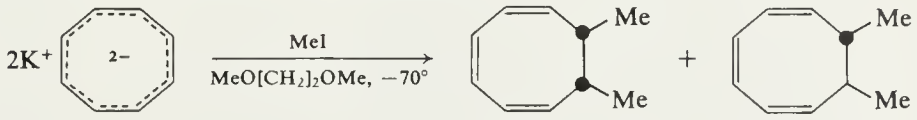
The basicity of COT^{2-} is enhanced in the excited state, and u.v. irradiation in the presence of weakly acidic proton-donors, e.g. amines, acetylenes, gives the cyclo-octatrienyl anion (**502**); this is eventually protonated further to yield cyclo-octatrienes (which then give their photo-products (see p. 216)], or is deprotonated to regenerate COT^{2-}.[737]



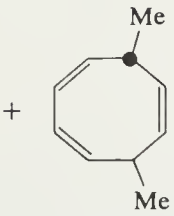
(**502**)

The most important synthetic applications of COT^{2-} result from its reactivity as a dicarbanion.

With alkyl halides, alkylation of COT^{2-} occurs with the formation of dialkylcyclo-octatrienes.[738,739] The products formed from methyl iodide apparently consist of a *ca.* 4:1 mixture of the *cis*- and *trans*-dimethylcyclo-octa-1,3,5-trienes, (**503**) and (**504**), together with the *trans*-dimethylcyclo-octa-1,3,6-triene (**505**) (total yield 84%).[379]

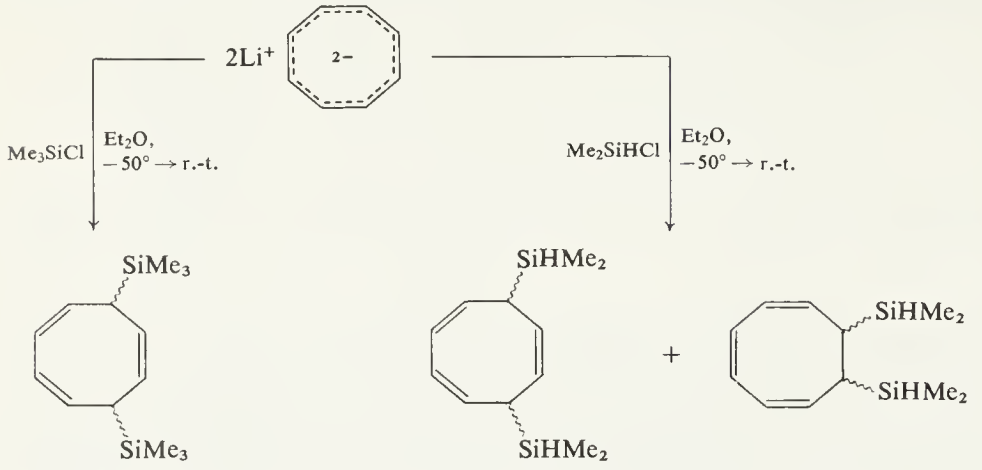


(**503**) (**504**)



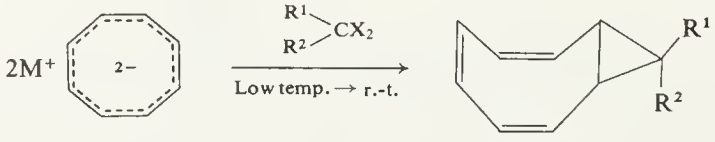
(**505**)

Silylation with chlorotrimethylsilane gives the cyclo-octa-1,3,6-triene-derivative (**506**)[740] (*cf.* ref. 741); chlorodimethylsilane, however, yields a mixture of (**507**) and (**508**) (*ca.* 2:1) (35%).[742]



(506) (507) (508)

Reaction of COT^{2-} with *gem*-dihalides affords the bicyclo[6.1.0]nona-2,4,6-triene system (**82**), possibly by generation of a carbenoid which then adds to COT.[307,743] The known reactions of this type are listed in table 63 (the use of dilithium cyclo-octatetraenide in liquid ammonia is recommended[744]). For



(82)

Table 63

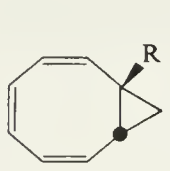
M	R^1	R^2	X	Solvent	Yield (%)	Ref.
K	H	H	Cl	THF	45	743, (745)
Li	H	Me	Cl	THF	20	307
—	H	Bu^t	Cl	NH_3	—	746
Li	H	OMe	Cl	Me_2O	—[a]	747
—	H	CN	Br	THF	—	748
K	H	Br	Br	THF	*ca.* 15	749
K	OMe	H	Cl	THF	Up to 49	743, 745
—	CN	H	Br	THF	—	748
Li	F	H	Cl	Et_2O	—[b]	747
Li or K	Cl	H	Cl	THF	Up to 52	743, 745
Li	Me	Me	Cl	NH_3	88	744
K	Cl[c]	Me[c]	Cl	THF	(Very low)	307
K	Cl	Cl	Cl	THF	19	743

[a] At −80°, the *syn*-isomer is the predominant product, but epimerises (90%) even at room-temperature to give the *anti*-isomer.

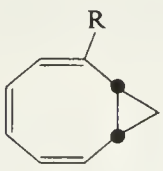
[b] At −78°, the product is a mixture of *syn*- and *anti*-isomers (25:75); at 0° the ratio is 13:87.

[c] Stereochemistry uncertain.

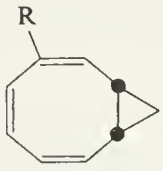
similar reactions with monosubstituted COT^{2-} species, leading to the products (**509**)–(**512**), see ref. 578.



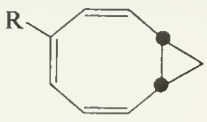
(**509**)



(**510**)



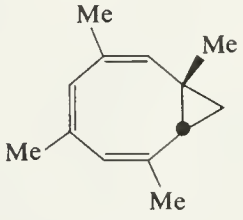
(**511**)



(**512**)

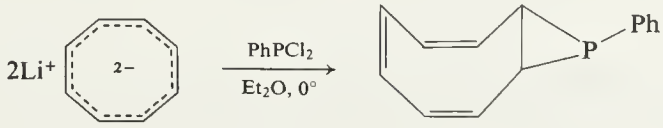
R = Me, OMe*

Dilithium 1,3,5,7-tetramethylcyclo-octatetraenide reacts with dichloromethane to afford the product (**513**) (83%).[578]



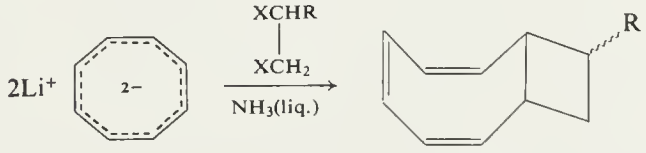
(**513**)

With dichlorophenylphosphine, COT^{2-} gives the 9-phosphabicyclo[6.1.0]-nona-2,4,6-triene (**514**) (64%).[380,750]



(**514**)

Treatment of COT^{2-} with 1,2-dibromoethane yields bicyclo[6.2.0]deca-2,4,6-triene (**515*a***), and an analogous reaction occurs with 1,2,3-trichloropropane (table 64).



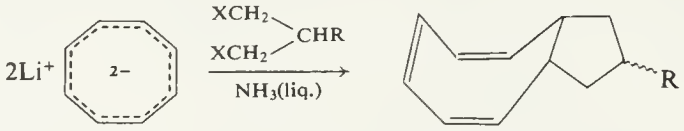
(**515**)

Table 64

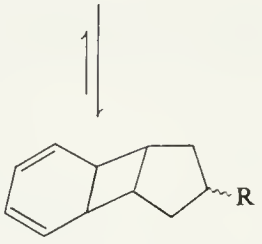
	R	X	Yield (%)	Ref.
a	H	Br	52	751
b	CH_2Cl	Cl	54	382

* Only one isomer (structure (**512**; R = OMe)) isolated in a pure state.

Reaction with 1,3-dibromopropane affords a mixture of bicyclo[6.3.0]-undeca-2,4,6-triene (**516*a***) and its tricyclic valence isomer (**517*a***) (ratio *ca.* 3:7); with 1,3-dichloro-2-tetrahydropyranyloxypropane, the isolated product has structure (**517*b***) (table 65).



(516)

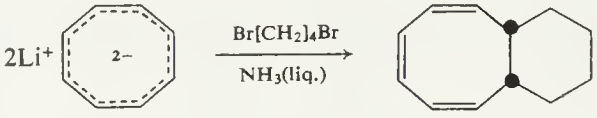


(517)

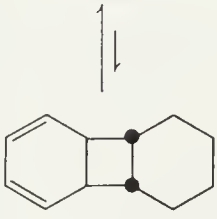
Table 65

	R	X	Yield (%)	Ref.
a	H	Br	48.5	(752), 753
b	2-Tetrahydropyranyloxy	Cl	64	382

1,4-Dibromobutane gives a mixture of bicyclo[6.4.0]dodeca-2,4,6-triene (**518**) and its tricyclic valence tautomer (**519**) (ratio *ca.* 7:3, total yield 35%).[752,753]

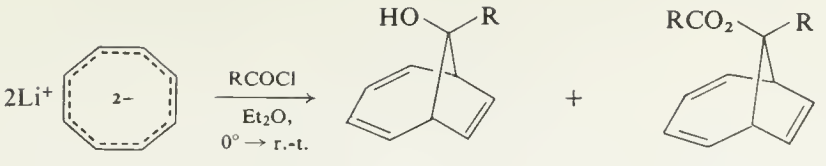


(518)

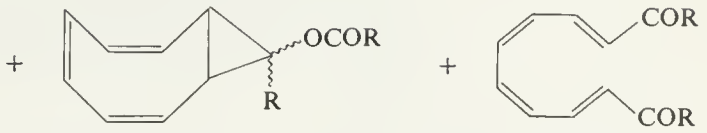


(519)

The acylation of COT^{2-} with acid chlorides may lead to various products including bicyclo[4.2.1]nonatrienes (**520**) and (**521**), bicyclo[6.1.0]nonatrienes (**522**), and acyclic tetraenes (**523**) (table 66) (*cf.* refs. 738, 739, 754). With



(520) (521)

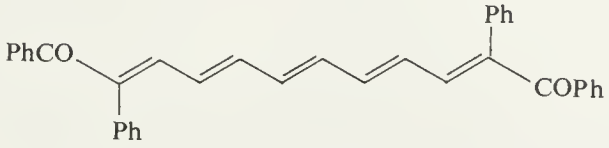


(522) (523)

Table 66

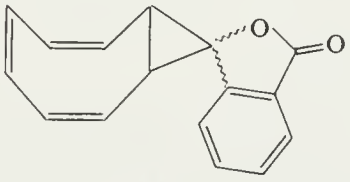
R	Yield (%) (520)	(521)	(522)	(523)	Ref.
Me[a]	18–19	12–13	19–22	7–8	377
$PhCH_2$	60	—	—	—	378
Ph[a, b]	—	58–62	—	6–7	377
p-Br.C_6H_4[a]	—	44	—	5	377

[a] $2Li^+COT^{2-}$ added to the acid chloride.
[b] Using $2K^+COT^{2-}$ in THF, the products are (**521**) (38%) and the all-*E*-pentaene (**524**) (0.3%).



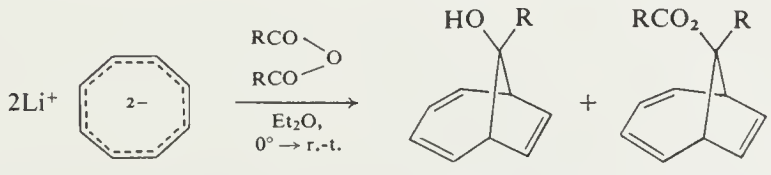
(524)

phthaloyl chloride, the bicyclo[6.1.0]nonatriene-lactone (**525**) is produced (28%).[377]



(525)

Analogous reactions[378] with acid anhydrides are listed in table 67. Phthalic

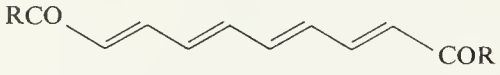


(520) (521)

Table 67

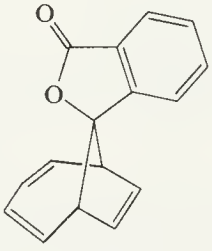
R	Yield (%) (520)	(521)
Me	22.5	39
Ph[a, b]	52	—

[a] If the reaction mixture is refluxed, the exclusive product is (**521**) (51%).
[b] Reaction at −60° produces (**520**) (43%), together with the tetraene (**526**; R = Ph) (4.2%).



(**526**)

anhydride yields the bicyclo[4.2.1]nonatriene-lactone (**527**) (48%).[378]



(**527**)

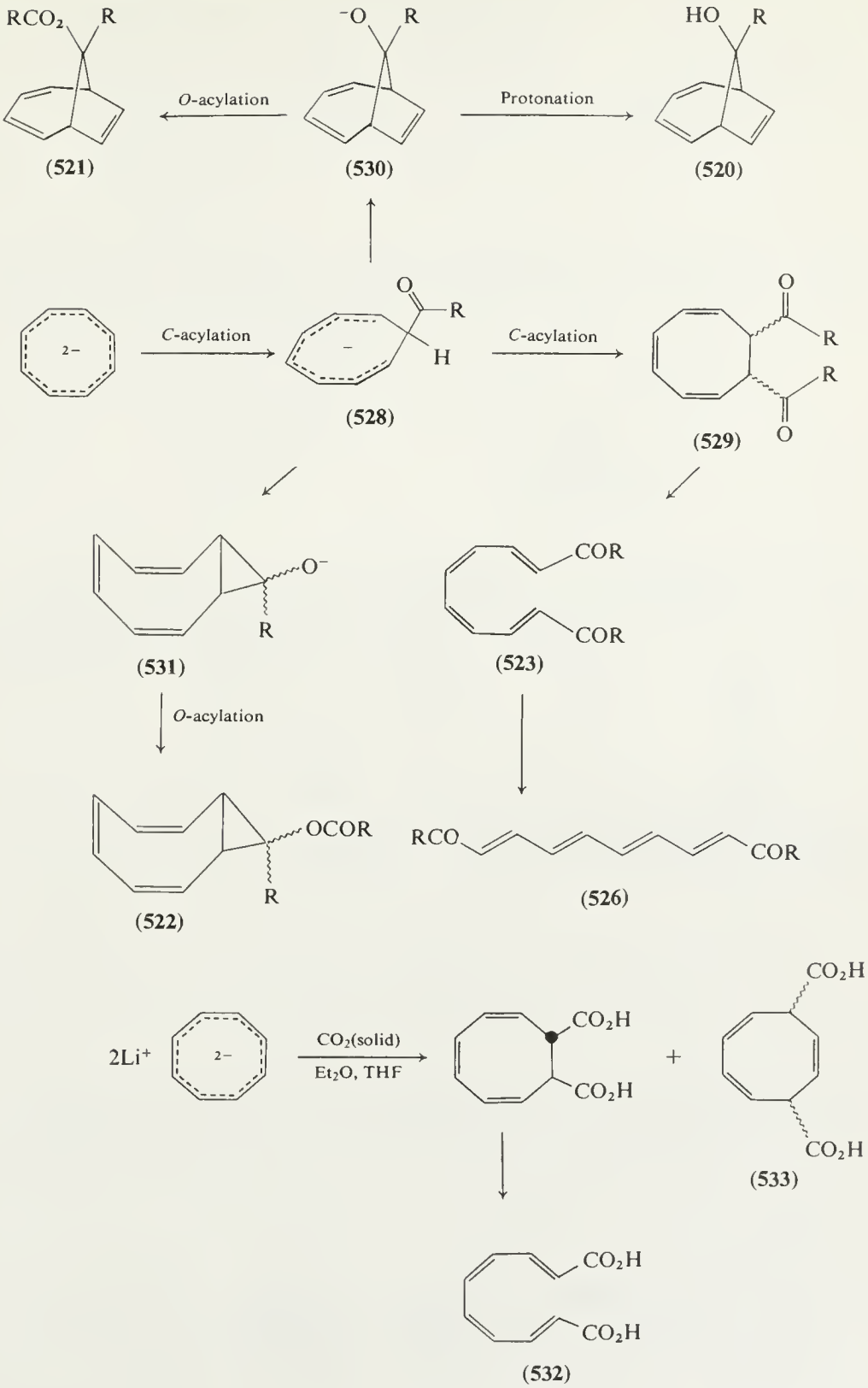
The manifold acylation products of COT^{2-} may arise as outlined in scheme 69. The initially formed acylcyclo-octatrienyl anion (**528**) may not only undergo further (vicinal) *C*-acylation to give the precursor (**529**) of acyclic tetraenes, but also give rise to the bicyclic [4.2.1] and [6.1.0] systems (**530**) and (**531**), each of which may be *O*-acylated.

Carboxylation of COT^{2-} with carbon dioxide gives mainly the acyclic tetraene dicarboxylic acid (**532**) (50–65%), together with small amounts (2–3%) of the cyclic isomer (**533**)[755,756] (*cf.* ref. 11) (but see appendix).

Aldehydes and ketones also yield, initially, mixtures of disubstituted cyclo-octa-1,3,5-trienes and cyclo-octa-1,3,6-trienes; however, the former products isomerise to bicyclo[4.2.0]octa-2,4-dienes or open-chain tetraenes[725] (table 68) (*cf.* refs. 259, 738, 739, 754). Phthalaldehyde gives a low yield (3.6%) of the tetracyclic diol (**537**).[725] Fluorenone affords the cyclo-octa-1,3,6-triene derivative (**534**; R^1R^2 = fluorenyl) (42%).[725]

In general, the reaction of esters with COT^{2-} furnishes the bicyclo[4.2.1]-nonatrienes (**520**)[378] (table 69). Ethyl formate (at −60°), however, affords the

Scheme 69


RCO2
R
O-acylation
-O
R
Protonation
HO
R
(521)
(530)
(520)
2-
C-acylation
O
R
H
C-acylation
O
R
R
O
(528)
(529)
O-
R
COR
COR
(531)
(523)
O-acylation
OCOR
R
RCO
COR
(522)
(526)
2Li+
2-
CO2(solid)
Et2O, THF
CO2H
CO2H
+
CO2H
CO2H
(533)
CO2H
CO2H
(532)

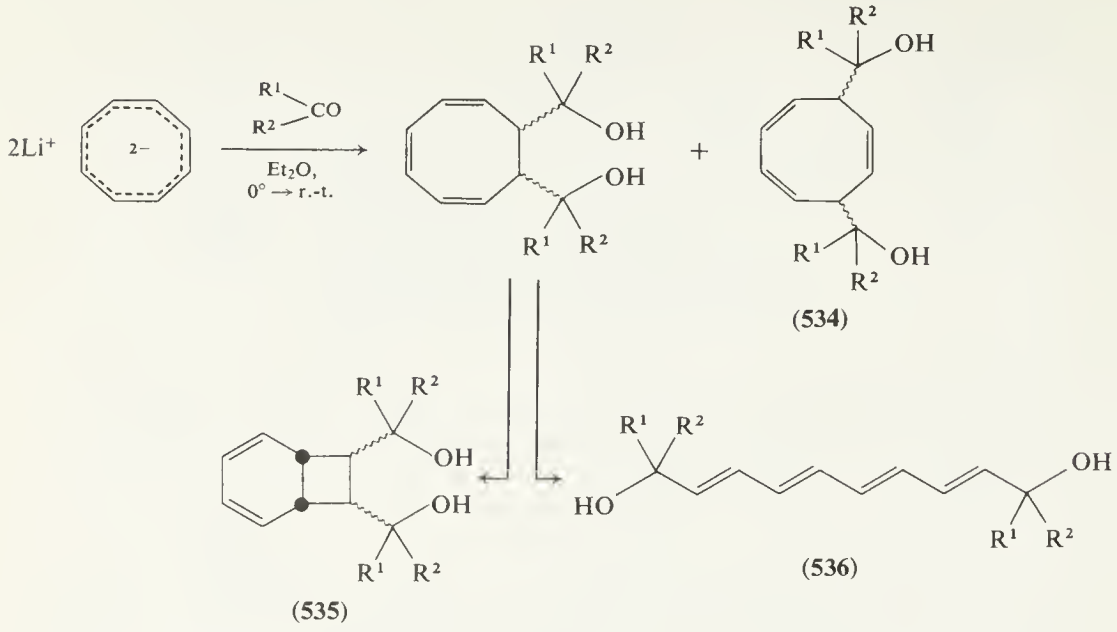
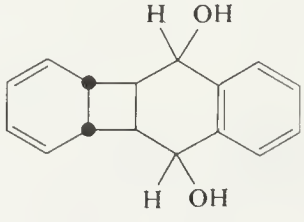


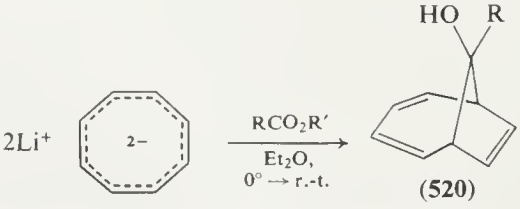
Table 68[a]

	R[1]	R[2]	Yield (%) (534)	(535)	(536)
a	Me	H	*ca.* 31	*ca.* 10	—
b	Ph	H	66	15	—
c	Me	Me		96[b]	—
d	Ph	Ph	64	—	28

[a] $2Li^+COT^{2-}$ added to aldehyde or ketone.
[b] Mixture of products not separated; ratio (**534**):(**535**) = 38:62.



(537)



(520)

Table 69

R	R′	Yield (%)	Ref.
Me	Et	77[a]	378
Ph	Me	74, (46)	378, (757)
p-MeO.C_6H_4	Me	48	757

[a] Reduced to 31% if $2Li^+COT^{2-}$ is added to the ester, rather than the reverse.

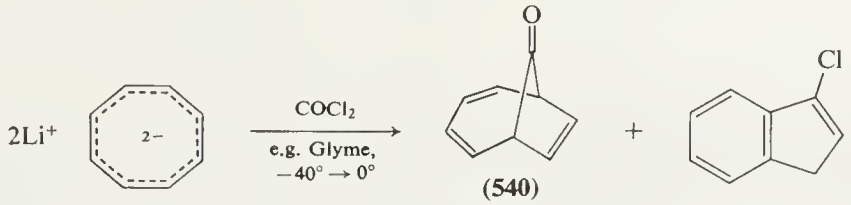
tetraene-dialdehyde (**538**) (mixture of geometrical isomers) (25%), and diethyl oxalate and methyl chloroformate give the tetraene-diesters (**539*a***) (12%) and (**539*b***) (28%) respectively; diethyl phthalate gives the bicyclo[6.1.0] nonatriene-lactone (**525**) (15%).[378]

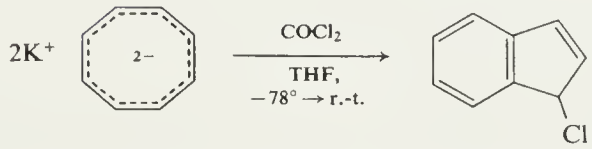
$OHC[CH{=}CH]_4CHO$ (**538**)

$RO_2C[CH{=}CH]_4CO_2R$ (**539**)

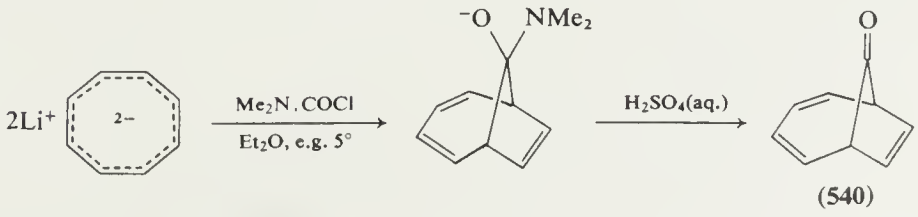
a: R = Et
b: R = Me

Reaction with phosgene leads to a mixture of 9-oxobicyclo[4.2.1]nona-2,4,7-triene (**540**) (17–20%) and 3-chloroindene (22–25%),[758] or, under slightly different conditions, 1-chloroindene (33%).[759]

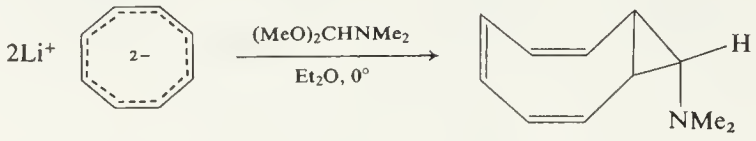




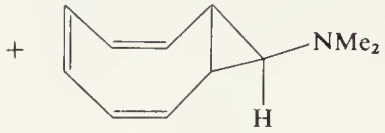
The reaction of COT^{2-} with dimethylcarbamoyl chloride provides a high-yield (up to 76%) synthesis of the carbonyl-bridged triene (**540**).[52,757]



1,1-Dimethoxytrimethylamine gives a mixture of *syn*- and *anti*-9-dimethylaminobicyclo[6.1.0]nonatrienes, (**541**) and (**542**) (3:2)[747] (*cf. gem*-dihalides, p. 174).

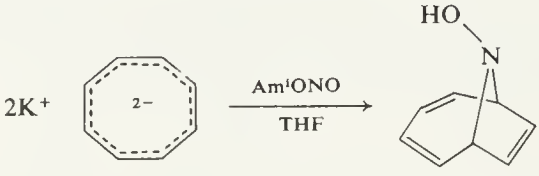


(**541**)



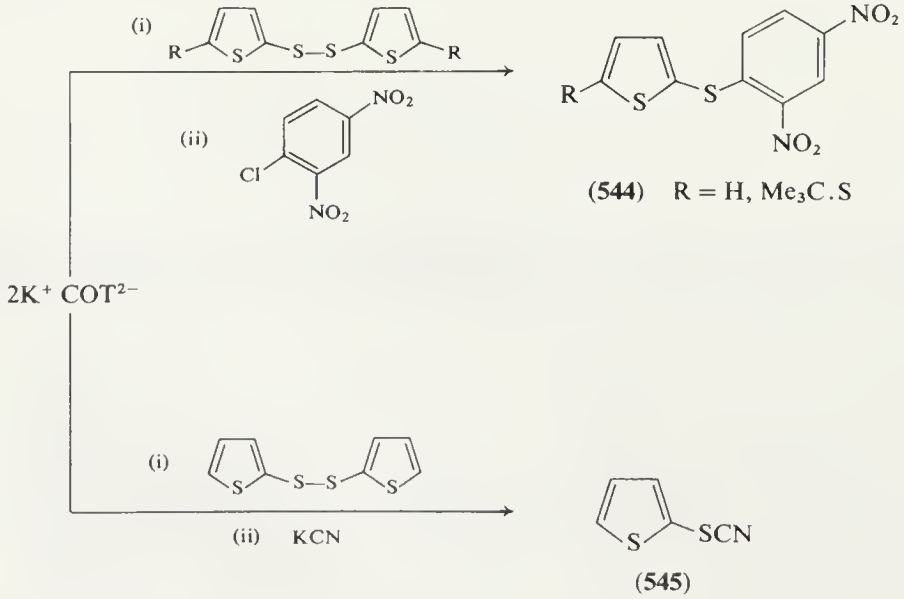
(**542**)

An efficient preparation (74%) of the 9-azabicyclo[4.2.1]nonatriene system (**543**) results from the use of isoamyl nitrite.[320]



(**543**)

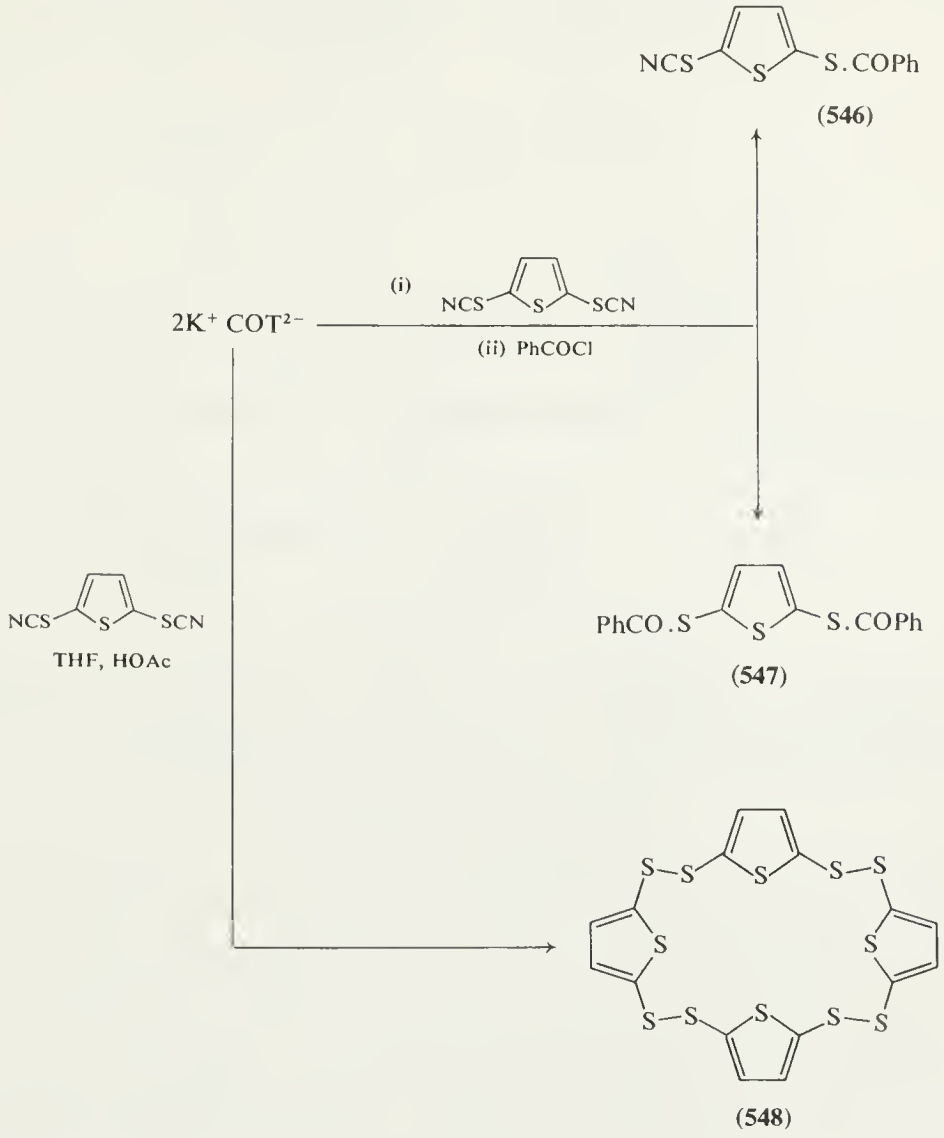
Treatment of thiophene disulphides with COT^{2-}, followed by 2,4-dinitrochlorobenzene or potassium cyanide, gives the products (**544**) or (**545**)



(**544**) R = H, $Me_3C.S$

(**545**)

respectively.[760] 2,5-Dithiocyanatothiophene reacts with one equivalent of COT^{2-}, followed by benzoyl chloride, to give compound (**546**); using two equivalents of COT^{2-}, the product (**547**) is formed.[760] Reaction with COT^{2-} in the presence of acetic acid leads to the product (**548**).[760]



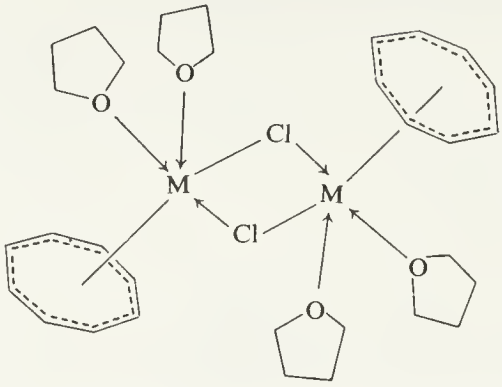
The cyclo-octatetraenyl dianion is the progenitor of numerous metal derivatives containing co-ordinated COT.

Reaction with various lanthanide metal(III) chlorides in tetrahydrofuran affords the solvated dimeric complexes (**549**) in high yield[761,762] (the best yields are obtained by the addition of $2K^+COT^{2-}$ to the metal chloride[762]).

$$2K^+COT^{2-} \xrightarrow[\text{THF, } -10° \rightarrow \text{r.t.}]{MCl_3} [(COT)MCl.2THF]_2 \quad (549)$$

M = Ce, Pr, Nd, Sm

(Complexes (COT)NdX.*n*THF (X = Br, I) have been reported[763].) The crystal structure of the cerium compound (**549**; M = Ce) is as shown.[761,764]



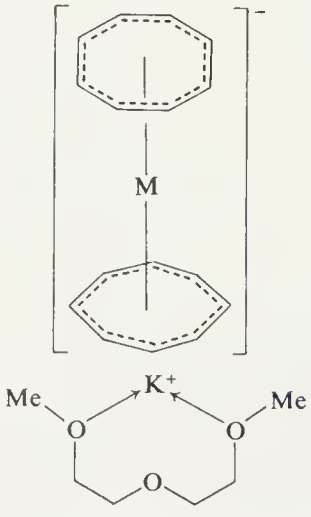
(**549**; M = Ce)

In the presence of COT, similar reactions produce the ionic complexes (**550**) (36–78%).[762,765]

$$2K^+COT^{2-} \xrightarrow[\text{THF, } ca.\ -10° \rightarrow \text{r.-t.}]{MCl_3,\ COT} K^+[(COT)_2M]^- \quad (\mathbf{550})$$

M = Y, La, Ce, Pr, Nd, Sm, Gd, Tb

The cerium complex (**550**; M = Ce), on treatment with cerium(III) chloride in tetrahydrofuran, gives (**549**; M = Ce) quantitatively.[762] The diglyme-solvated cerium complex (**550**; M = Ce) possesses the structure shown.[766]



(**550**; M = Ce) (diglyme-solvated)

With dipyridinium hexachlorocerate(IV), COT^{2-} yields the complex (**551**) (64%).[767]

$$2K^+COT^{2-} \xrightarrow[\text{THF, r.-t.}]{(PyH^+)_2[CeCl_6]^{2-}} (COT)_2Ce \quad (\mathbf{551})$$

(For the application of ligand field theory to this type of complex, see ref. 768.)

'Mixed' sandwich complexes of the type (**552**) result from the reaction of COT^{2-} with yttrium or lanthanide complexes $(CPD)MCl_2.3THF$; the products are desolvated by heating under reduced pressure, giving (**553**).[769]

$$2K^+COT^{2-} \xrightarrow[THF]{(CPD)MCl_2.3THF} (COT)M(CPD).THF \quad (552)$$

$$(552) \xrightarrow{50°/10^{-3}\ mm} (COT)M(CPD) \quad (553)$$

M = Y, Ho, Er

Treatment of COT^{2-} with actinide metal(IV) chlorides gives complexes of structure (**155**) (see p. 186) (table 70). For the i.r. spectra of (**155**; M = Th, U),

$$2K^+COT^{2-} \xrightarrow[\text{THF, e.g. } -20° \rightarrow \text{r.-t.}]{MCl_4} (COT)_2M \quad (155)$$

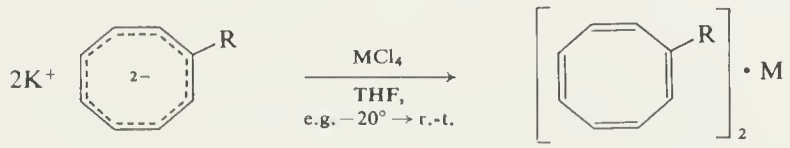
M = Th, Pa, U, Np, Pu

Table 70

M	Yield (%)	Ref.
Th	60	(770), 771
Pa	1	772, (773)
U	60–80	381, (774)
Np	—	775
Pu[a]	—	775

[a] Complex prepared using $(Et_4N)_2PuCl_6$.

see ref. 409. For a 'wide-line' n.m.r. study of (**155**; M = U), see ref. 776. Analogous preparations using monosubstituted dianions (**275**) result in the



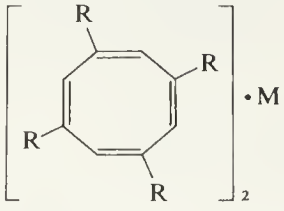
(**275**) (**554**)

Table 71

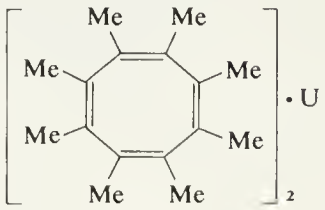
R	M	Yield (%)	Ref.
Et	U	92	777, (778)
Bu^n	U	90	777, (778)
Ph	U	87	777
$CH{=}CH_2$	U	97	777
Cyclopropyl	U	88	777
Et	Np	—	778
Bu^n	Np	—	778
Et	Pu[a]	—	778
Bu^n	Pu[a]	—	778

[a] Complex prepared using $(Et_4N)_2\ PuCl_6$.

complexes (**554**) (table 71). The 1,3,5,7-tetrasubstituted compounds (**555*a***) (53%),[777,779] (**555*b***)[779] and (**555*c***) (64%)[663] may be obtained in similar fashion, and likewise the octamethylcyclo-octatetraene complex (**556**).[780] The



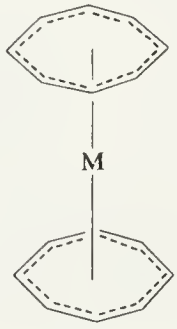
(555)



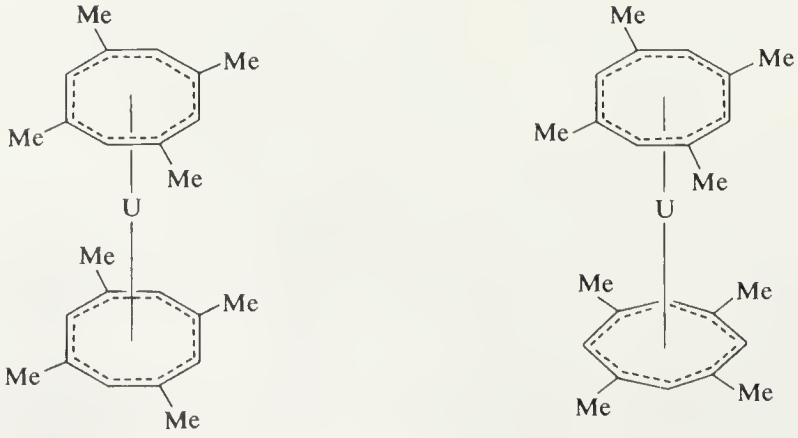
(556)

a: R = Me, M = U
b: R = Me, M = Np
c: R = Ph, M = U

complexes of this type are known to have sandwich structures, and have been dubbed 'uranocene' etc. The ligands in $(COT)_2M$ (**155**; M = Th, U) are arranged as shown,[781,782] while in $(TMCOT)_2U$ (**555*a***) two crystallographically independent molecules exist in the unit cell, one with eclipsed and the other with staggered methyl groups.[783,784] In these compounds the question



(155)



(555*a*)

of f-orbital participation in the metal–ligand bonding is of great interest (see

e.g. refs. 381, 779, 780, 785; for a review, see ref. 786). For the application of ligand field theory, see ref. 768.

Complexes (**557**) may be obtained from actinide metal(III) bromides.[787]

$$2K^+COT^{2-} \xrightarrow[\text{THF, } -10° \text{ to } -20° \rightarrow \text{r.-t.}]{MBr_3} K^+[(COT)_2M]^-.THF \quad (\mathbf{557})$$

M = Np, Pu

Dipyridinium pentachlorothallate(III) reacts with COT^{2-} to afford the thallium(III) complex (**558**) (65%).[788]

$$2K^+COT^{2-} \xrightarrow[\text{THF, r.-t.} \rightarrow \text{reflux}]{(PyH^+)_2[TlCl_5]^{2-}} (COT)TlCl \quad (\mathbf{558})$$

Titanium(IV) chloride reacts with COT^{2-} to give the product (**159**) (see p. 54) (53%).[416]

$$2Na^+COT^{2-} \xrightarrow[C_6H_6,\ 70°]{TiCl_4} (COT)_2Ti \quad (\mathbf{159})$$

The 'mixed' sandwich complex (**165**) (see pp. 56–7) may be prepared (60%) by treatment of COT^{2-} with a mixture of titanium(IV) chloride and sodium cyclopentadienide.[789]

$$2K^+COT^{2-} \xrightarrow[\text{Toluene, reflux}]{TiCl_4,\ Na(CPD)} (COT)Ti(CPD) \quad (\mathbf{165})$$

The same product results (in lower yields) from the use of $(CPD)TiCl_3$ or $(CPD)_2TiCl_2$;[789] an analogous complex (**559**) (50–60%) is formed from the sodio-derivative of indene.[790]

(COT)Ti(indenyl) (**559**)

With titanium(III) chloride there is obtained the dimeric complex (**560**) (*cf.* (**157*a***), p. 54) (64%),[791] which in ether forms the tetrameric (**561**).[792]

$$2K^+COT^{2-} \xrightarrow[\text{THF, reflux}]{TiCl_3} [(COT)TiCl.THF]_2 \quad (\mathbf{560})$$

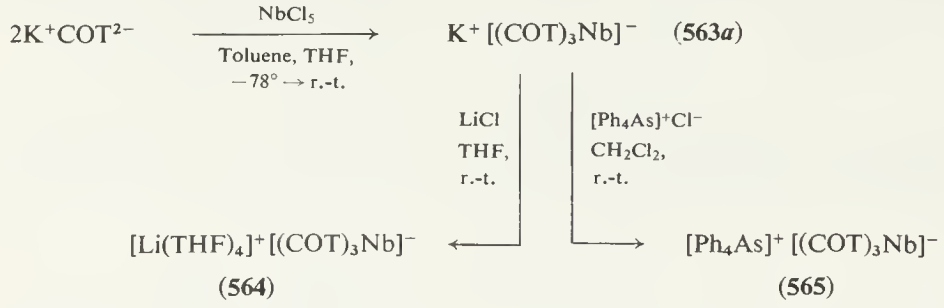
$$[(COT)TiCl.THF]_2 \xrightarrow[\text{r.-t.}]{Et_2O} [(COT)TiCl]_4 \quad (\mathbf{561})$$

Reaction of COT^{2-} with hafnium(IV) chloride results in the complex (**562**) (70–80%).[793]

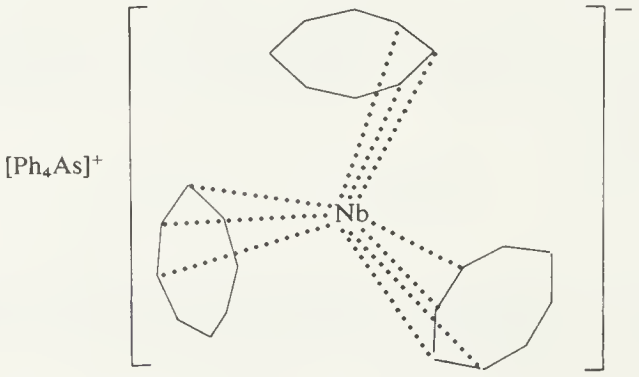
$$2Na^+COT^{2-} \xrightarrow[\text{Xylene, } 120°]{HfCl_4} (COT)_2Hf \quad (\mathbf{562})$$

The vanadium complex $(COT)_2V$ may be prepared from COT^{2-}.[409,416] (For the e.p.r. spectrum, see ref. 420.)

Niobium(v) chloride affords the ionic complex (**563***a*) (70%), from which the other salts (**564**) (85%) and (**565**) are readily obtained[423] (see p. 57). In the



salt (**565**), which is fluxional, two of the COT rings are η^3-bonded to the niobium, while the third ring is apparently η^4-bonded.[423]



(**565**)

(The exact nature of the bonding within the rings is not clear)

Complexes $(COT)_3M_2$ (M = Cr, Mo, W) are obtainable from COT^{2-}.[416]

The 'mixed' ruthenium complex (**566**) is obtained (20–30%) by reaction of COT^{2-} with the polymeric norbornadiene complex $[(NBD)RuCl_2]_n$; the cyclo-octa-1,3,5-triene complex (**567**) is a co-product (4%).[794]

$$2K^+COT^{2-} \xrightarrow[THF]{[(NBD)RuCl_2]_n} (COT)Ru(NBD) \quad (566)$$

$$+ \text{(Cyclo-octa-1,3,5-triene)Ru(NBD)} \quad (567)$$

If a similar reaction is carried out using potassium dissolving in COT, a low yield of the binuclear product (**568**) is obtained in place of complex (**566**).[794]

$$(COT)Ru_2(NBD)_2 \quad (568)$$

Reaction of COT^{2-} with the cyclo-octa-1,5-diene complex $[(COD)RuCl_2]_n$

gives an ill-defined product of formula $C_{16}H_{20}Ru$ (10%), the cyclo-octa-1,3,5-triene complex (**569**) (10%), and a small amount (*ca.* 1%) of a binuclear product $C_{24}H_{32}Ru_2$.[794]

$$2K^+COT^{2-} \xrightarrow{[(COD)RuCl]_n} C_{16}H_{20}Ru + \text{(Cyclo-octa-1,3,5-triene)Ru(COD)} \quad (569) + C_{24}H_{32}Ru_2$$

With the reagents $(PPh_3)_4RuCl_3$ and $[(PPhMe_2)_6Ru_2Cl_3]^+Cl^-$, COT^{2-} affords the complexes (**570**) (50%) and (**571**) (20%) respectively.[794]

$$2K^+COT^{2-} \xrightarrow{(PPh_3)_4RuCl_3} (COT)Ru(PPh_3)_2 \quad (570)$$

$$2K^+COT^{2-} \xrightarrow{[(PPhMe_2)_6Ru_2Cl_3)^+Cl^-} (COT)Ru(PPhMe_2)_3 \quad (571)$$

Treatment of COT^{2-} with the osmium complex $[(COD)OsCl_2]_n$ results in the 'mixed' products (**572**) (*ca.* 25%) and (**573**) (1–2%).[794]

$$2K^+COT^{2-} \xrightarrow{[(COD)OsCl_2]_n} (COT)Os(COD) \quad (572) + \text{(Cyclo-octa-1,3,5-triene)Os(COD)} \quad (573)$$

The complexes (COT)M (M = Co, Ni) may be obtained from COT^{2-}.[416]

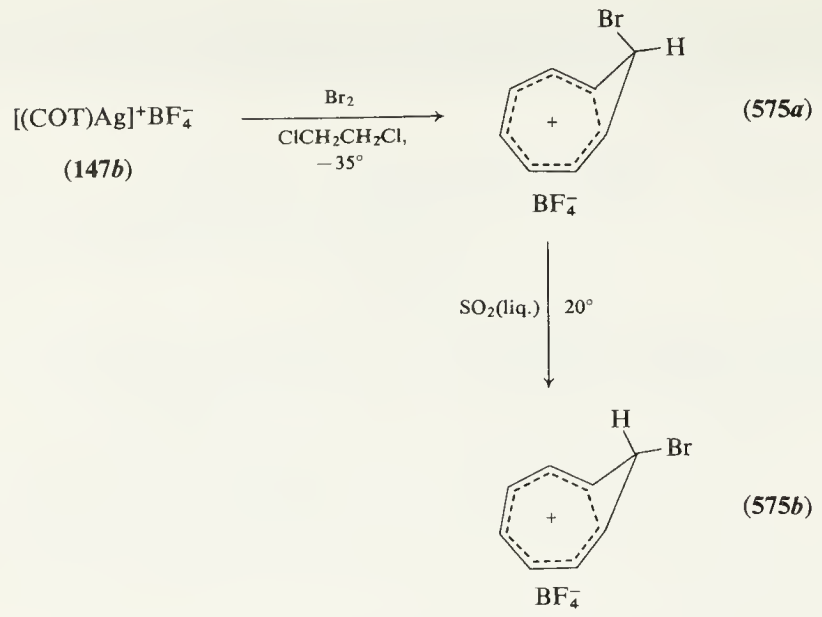
Reaction of COT^{2-} with $(COD)PtCl_2$ in the presence of cyclo-octa-1,5-diene affords the product (**574**) (30–50%).[795]

$$2Li^+COT^{2-} \xrightarrow[Et_2O,\ -20°]{(COD)PtCl_2,\ COD} (COD)_2Pt \quad (574)$$

(*b*) *Silver derivatives*

For preparation from COT, see pp. 51–2.

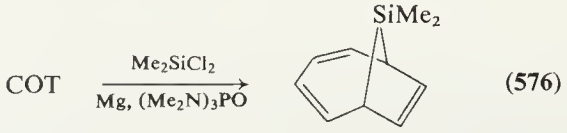
Reactions. Treatment of the silver complex (**147*b***) (see p. 51) with bromine at low temperature affords the salt (**575*a***), containing the *endo*-bromohomotropylium ion; at 20° in sulphur dioxide conversion to the *exo*-form (**575*b***) occurs.[230]



(*c*) *Magnesium derivative*

For preparation from COT, see p. 52.

Reactions. Treatment of COT in hexamethylphosphoramide with dichlorodimethylsilane in the presence of magnesium gives the 9-silabicyclo[4.2.1]nonatriene (**576**) (*ca.* 20%);[796] the reaction may involve COT^{2-} (see p. 174, but *cf.* ref. 797).



The thorium and uranium complexes (**155**; M = Th, U) (see pp. 185–6) are produced (in very low yield) by heating magnesium cyclo-octatetraenide with the metal(IV) fluoride.[773]

(*d*) *Yttrium and lanthanide derivatives*

For preparation from COT, see pp. 52–3; from COT^{2-}, see pp. 183–5.

Reactions. The lanthanide complexes $[(COT)MCl.2THF]_2$ (see p. 183) react with sodium cyclopentadienide to give the 'mixed' sandwich complexes (**552**) (see p. 185).[769]

$$[(COT)MCl.2THF]_2 \xrightarrow[THF]{(CPD)Na} (COT)M(CPD).THF$$

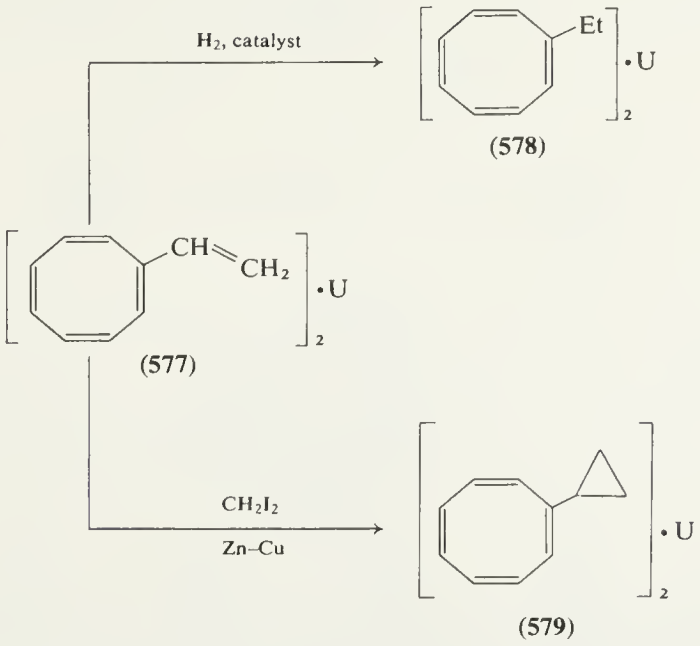
(**549**) (**552**)

M = Y, Nd

(*e*) *Actinide derivatives*

For preparation from COT, see p. 53; from COT^{2-}, see pp. 185–7.

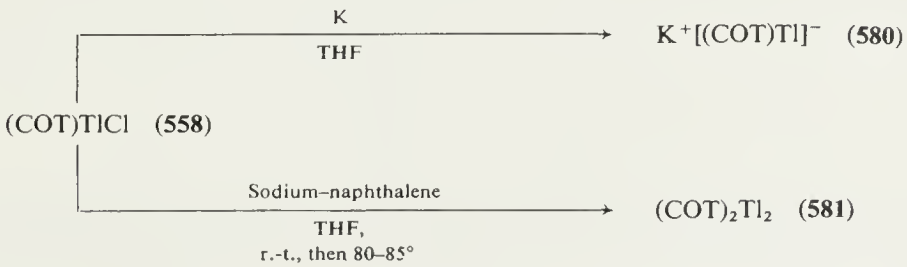
Reactions. The 'uranocene' (**577**) undergoes catalytic hydrogenation, and cyclopropanation, affording the ethyl- and cyclopropyl-derivatives, (**578**) and (**579**).[777]



(*f*) *Thallium derivatives*

For preparation from COT^{2-}, see p. 187.

Reactions. Treatment of the thallium(III) complex (**558**) (see p. 187) with potassium yields the thallium(I) complex (**580**) (46%);[788] reaction with sodium–naphthalene, however, gives the product (**581**) (40%).[798]



(*g*) *Titanium and hafnium derivatives*

For preparation from COT, see pp. 53–7; from COT^{2-}, see p. 187.

Reactions. The titanium complex (**560**) (see p. 187) reacts with allyl Grignard reagents in ether to form the π-allyl complexes (**582**); in tetrahydrofuran, the isolated products are the solvated derivatives (**583**) (table 72). With hydrogen chloride, these compounds give the tetrameric complex (**561**)[799] (see p. 187).

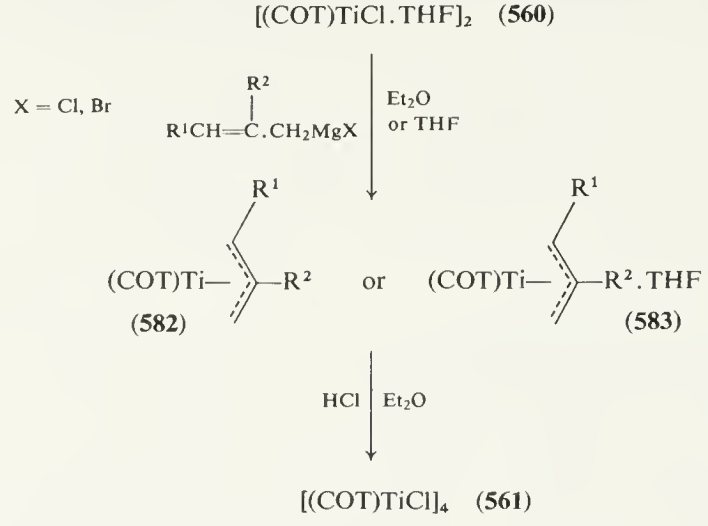


Table 72

		Yield (%)		
R^1	R^2	(**582**)	(**583**)	Ref.
H	H	57	44	799
H	Me	40	63	799
Me	H	(50), 70	34	(791), 799

With sodium cyclopentadienides, products (**584**) are obtained[800] (table 73).

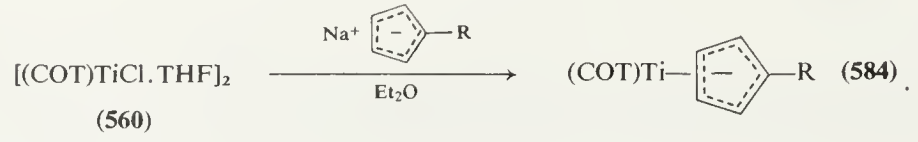


Table 73

R	Yield (%)
Me	60
Bu^t	61
$SiMe_3$	63

Indenyl and fluorenyl derivatives may be prepared similarly (77% and 63% respectively).[800] (For e.p.r. spectral studies on the indenyl complex, see ref. 801.)

Reactions with the sodium salts of carborane dianions afford mixed-ligand titanacarboranes (**585**), which may be isolated as the tetra-ethylammonium salts, and oxidised to the neutral species (**586**).[802]

$$[(COT)TiCl]_2 \xrightarrow[THF]{Na_2C_2B_nH_{n+2}} Na^+[(COT)Ti(C_2B_nH_{n+2})]^- \quad (585)$$

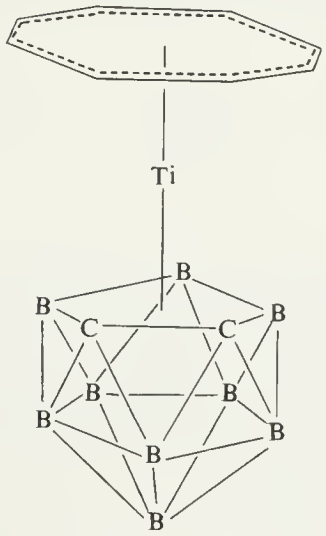
(158)

H_2O_2 ↓

$n = 9$ or 10

$(COT)Ti(C_2B_nH_{n+2})$ (586)

The proposed structure for (**586**, $n = 9$) is as shown.



(586)

(H atoms omitted)

The titanium complex (**165**) (see pp. 56–7) reacts quantitatively with iodine to give either the mono- or the tri-iodide (**587**) or (**588**), depending on the relative proportions of the reactants.[803]

$$(COT)Ti(CPD) \xrightarrow[Et_2O,\ r.\text{-}t.]{I_2} (COT)TiI(CPD) \text{ or } (COT)TiI_3(CPD)$$

(165) (587) (588)

Treatment of the hafnium complex (**562**) (see p. 187) with hydrogen chloride in tetrahydrofuran affords the solvated product (**589**) (*ca.* 80%); removal of the solvent may be effected (quantitatively) to give complex (**590**), which with allylmagnesium halides yields the bis(π-allyl)-compound (**591**) (60%).[793] For

$$(COT)_2Hf \xrightarrow[THF]{HCl} (COT)HfCl_2.THF \quad (589)$$

(562)

70° ↓ High vacuum

$$(COT)Hf \xleftarrow[Et_2O,\ -35°]{CH_2{=}CH.CH_2MgX} (COT)HfCl_2 \quad (590)$$

(591)

analogous reactions of $(COT)_2Zr$ (**160**) (see p. 55), and additional transformations, see ref. 417.

(h) Niobium and tantalum derivatives

For preparation from COT, see p. 57; from COT^{2-}, see p. 188.

Reactions. The COT ligands in the complexes (**563**) (see p. 188) are displaced by carbon monoxide with the formation of the products (**592**).[423]

$$K^+[(COT)_3M]^- \xrightarrow[\text{THF, } 110°,\ 50\ \text{atm}]{CO} K^+[M(CO)_6]^-$$

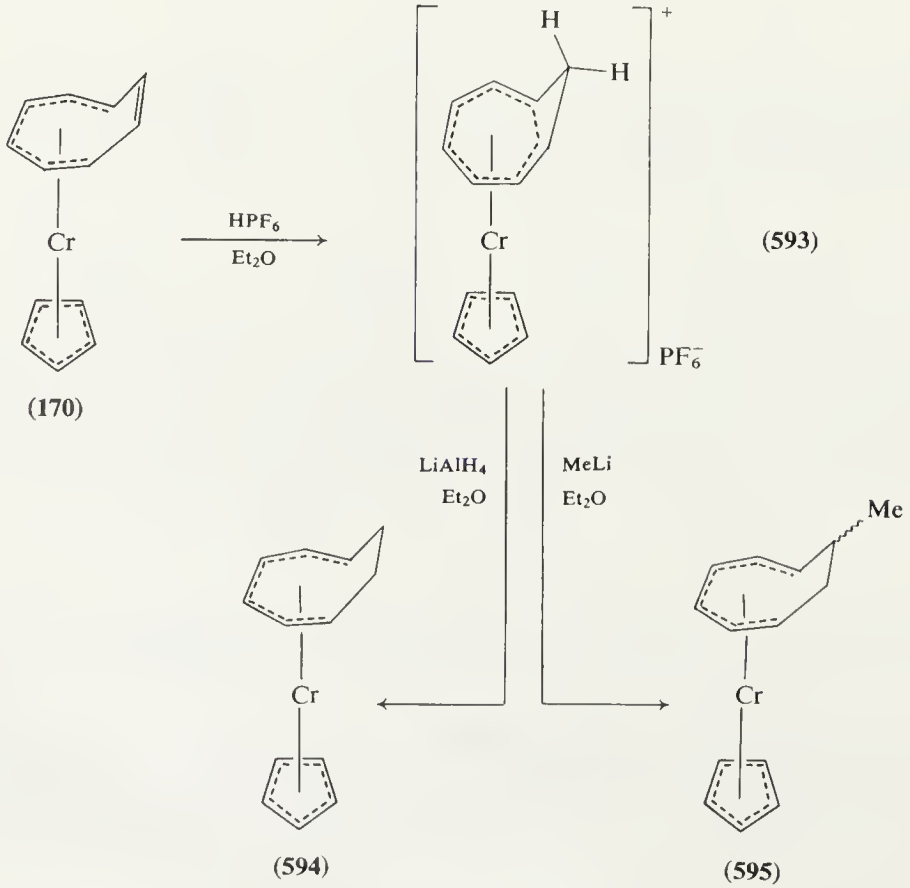
(**563**) (**592**)

M = Nb, Ta

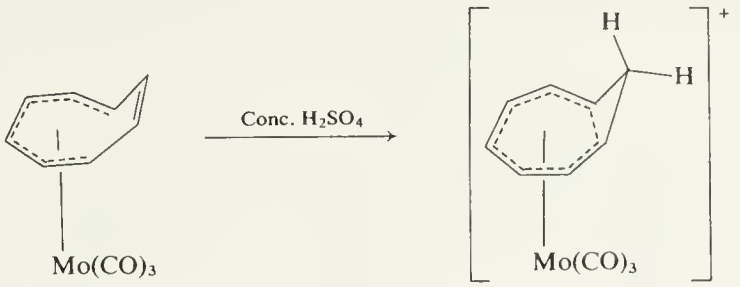
(i) Chromium, molybdenum and tungsten derivatives

For preparation from COT, see pp. 57–9; from COT^{2-}, see p. 188.

Reactions. The chromium complex (**170**) (see p. 59) is protonated by HPF_6 to give the salt (**593**) (*ca.* 35%); reaction with lithium aluminium hydride then gives (**594**) (*ca.* 90%), while methyl-lithium affords (**595**).[434]

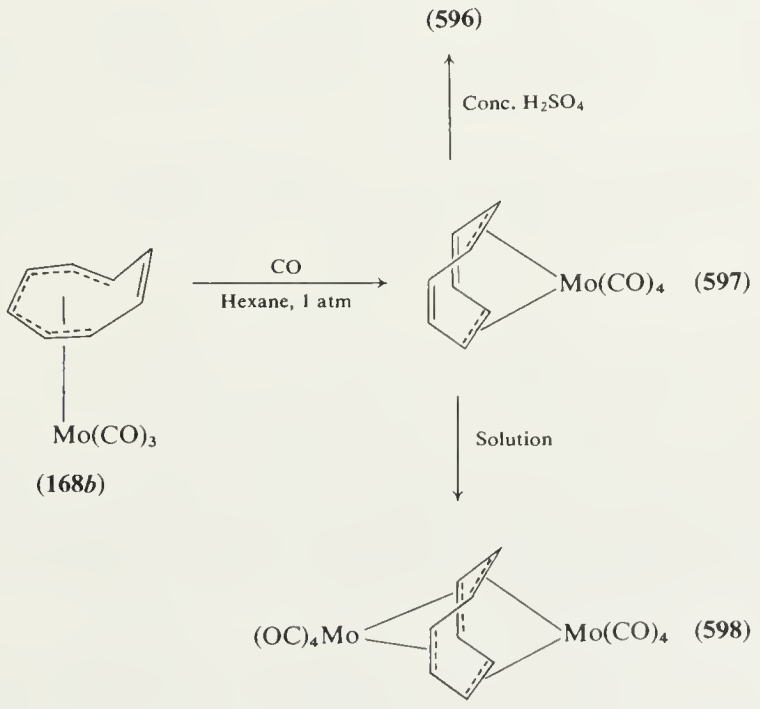


Protonation of the molybdenum tricarbonyl complex (**168***b*) (see pp. 57–8) affords the homotropylium derivative (**596**), the incoming proton occupying the *exo*-position.[214] The tricarbonyl complex (**168***b*) readily takes up carbon



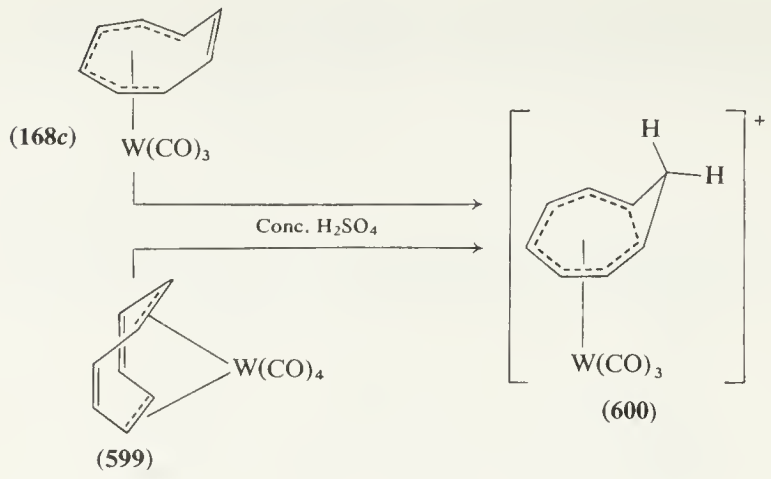
(**168***b*) (**596**)

monoxide to give the tetracarbonyl compound (**597**) (65%), which in solution rapidly forms the product (**598**); protonation of the tetracarbonyl (**597**) is accompanied by loss of carbon monoxide and the formation of the homotropylium tricarbonyl complex (**596**).[804]



(**168***b*)

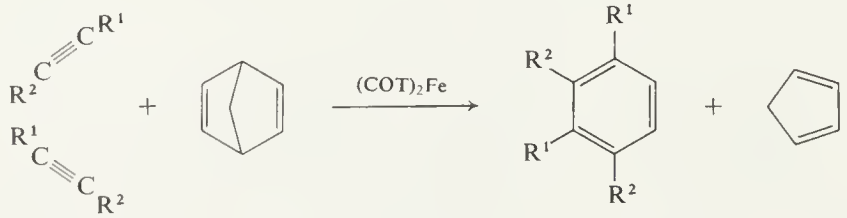
Protonation of the tungsten tricarbonyl and tetracarbonyl complexes (**168***c*) (see p. 57) and (**599**) is analogous to that of the molybdenum compounds, and the resulting cation has the homotropylium structure (**600**) (incoming proton *exo*).[805]



(*j*) *Iron, ruthenium and osmium derivatives*

For preparation from COT, see pp. 60–71; from COT^{2-}, see pp. 188–9.

Reactions. The iron(0) complex $(COT)_2Fe$ (**176**) (see pp. 60–1) catalyses the cyclotrimerisation of disubstituted acetylenes,[806] and the reaction of mono- and disubstituted acetylenes with norbornadiene, which gives rise to cyclopentadiene and 1,3-disubstituted or 1,2,3,4-tetrasubstituted benzenes (20–40%).[807]



$R^1 = H$; $R^2 = Me, Ph$ or $R^1 = R^2 = Me, Ph$

The [4 + 2] cycloaddition of buta-1,3-diene to but-2-yne proceeds at 18° (55% yield) in the presence of $(COT)_2Fe$.[806] This also acts as a selective oligomerisation catalyst for buta-1,3-diene, which affords the trimer (**601**) as the main product, and it promotes the reaction of ethylene with buta-1,3-diene to give *Z*-hexa-1,4-diene (**602**).[808]

$CH_2{=}CH.CH{=}CH.CH_2.CH{=}CH.[CH_2]_2.CH{=}CH.CH_3$ (**601**)

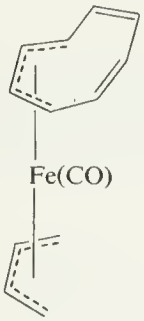
$CH_2{=}CH.CH_2.CH\overset{Z}{=}CH.CH_3$ (**602**)

Reaction of $(COT)_2Fe$ (**176**) at 0° with buta-1,3-diene followed by carbon monoxide gives the complex (**603**) (*ca.* 25%).[809]

$$(COT)_2Fe \xrightarrow[\text{(ii) CO, 0°, 2 atm}]{\text{(i) Butadiene, hexane, 0°}} (COT)(\text{butadiene})Fe(CO) \quad (603)$$

(176)

The structure of (**603**) is shown.[810] (For the ^{57}Fe Mössbauer spectrum, see ref. 448.)



(**603**)

With carbon monoxide alone, $(COT)_2Fe$ forms the tricarbonyl complex (**177**) (see p. 62) (50%).[808]

$$(COT)_2Fe \xrightarrow[20°,\ 1\ atm]{CO} (COT)Fe(CO)_3 \quad (177)$$

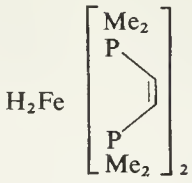
Reaction with hydrogen in the presence of phosphorus(III) ligands results in complexes of the type (**604**)[442] (table 74). A similar reaction with the bidentate

$$(COT)_2Fe \xrightarrow[H_2,\ \text{pressure}\\ \text{toluene},\ \Delta]{R^1\!-\!P(R^2)\!-\!R^3} H_2Fe\left[P(R^1)(R^2)(R^3)\right]_4 \quad (604)$$

Table 74

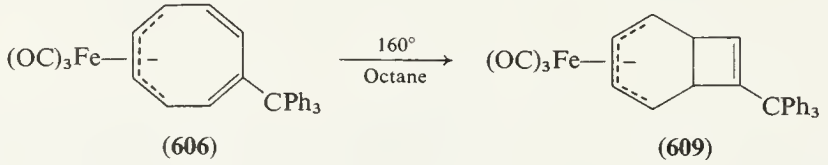
R^1	R^2	R^3	Pressure (atm)	Temp. (°C)
Ph	OMe	OMe	100	80
OPr^i	OPr^i	OPr^i	100	75
OPh	OPh	OPh	1000	70
O(*o*-tolyl)	O(*o*-tolyl)	O(*o*-tolyl)	1000	70
	$[OCH_2]_3CEt$		100	150
F	F	F	200	160[a]

[a] The initial product was $Fe(PF_3)_5$, which was hydrogenated in a second stage.

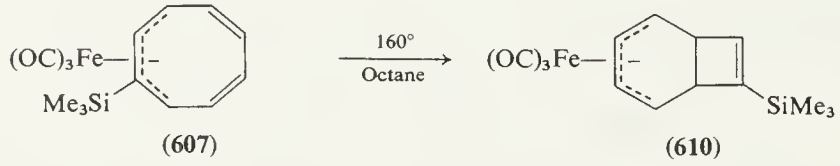


(605)

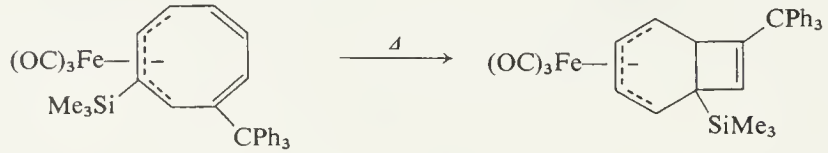
The iron tricarbonyl complex (**177**) decomposes at *ca.* 160°, but the substituted COT ligands in (**606**)–(**608**) (see pp. 106–8, 204) rearrange to give complexes of bicyclo[4.2.0]octa-2,4,7-trienes (**609**)–(**611**).[811]



(606) (609)

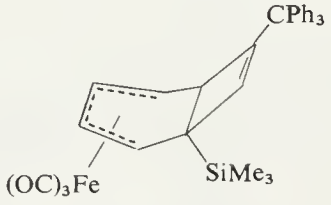


(607) (610)



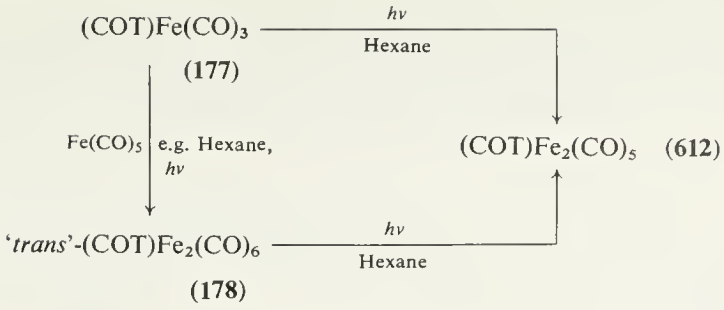
(608) (611)

Structure (**611**) is based on X-ray studies.[811]

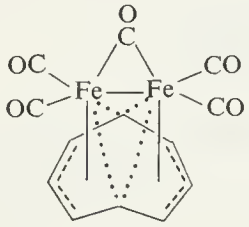


(611)

U.v. irradiation of the iron tricarbonyl complex (**177**), or the '*trans*'-hexacarbonyl (**178**), affords the pentacarbonyl (**612**) in good yield;[812] the hexacarbonyl (**178**) results (70%) from the light-induced reaction of the tricarbonyl (**177**) with $Fe(CO)_5$.[453]



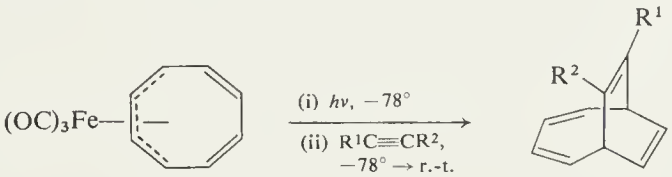
The molecule of $(COT)Fe_2(CO)_5$ (**612**) incorporates two π-allyl systems, a formal four-centre four-electron bonding system, and a bridging carbonyl group.[813] This structure is fluxional in solution,[454] and a rapid rotation of the



(612)

ring (relative to the Fe–Fe bond) is invoked as an explanation.[813] (For 'wide-line' n.m.r. studies on the solid, see refs. 455, 460.)

If $(COT)Fe(CO)_3$ is irradiated at low temperature, and then a disubstituted acetylene is added, the system (**613**) is produced[814] (table 75) (see p. 206).



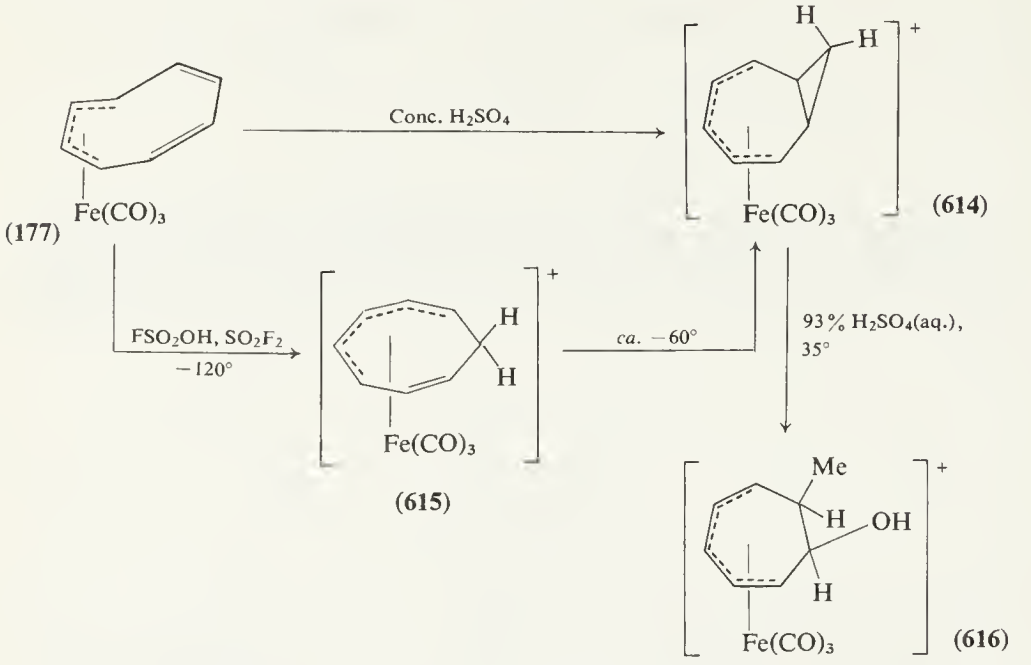
(613)

Table 75

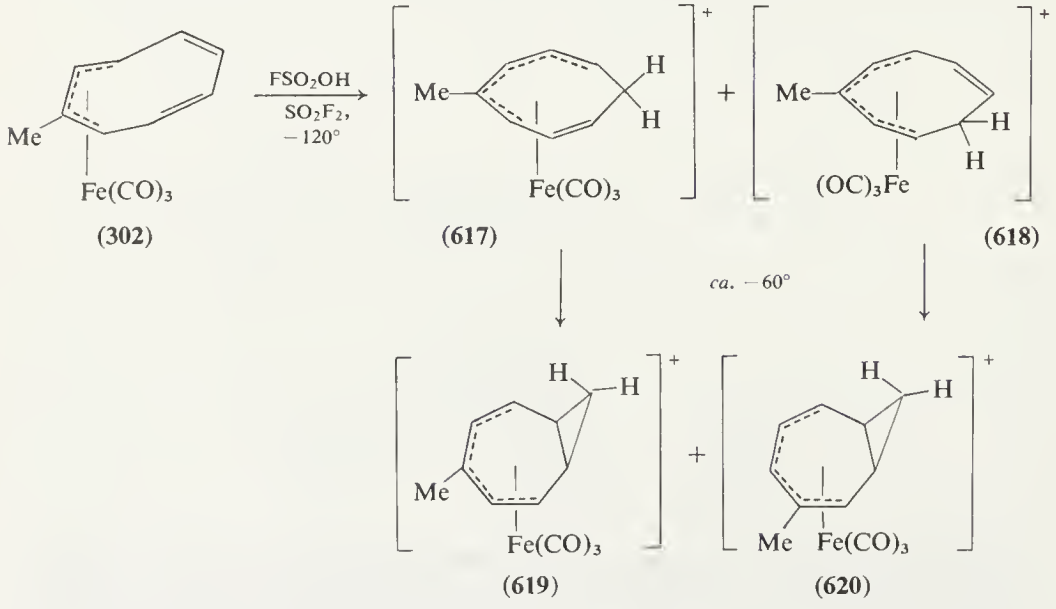
R^1	R^2	Yield (%)
Ph	Ph	*ca.* 20
CO_2Me	CO_2Me	*ca.* 20

The iron tricarbonyl complex (**177**) undergoes protonation in e.g. concentrated sulphuric acid to give the bicyclic cation (**614**) (incoming proton *endo*).[474,815,816] However, using e.g. fluorosulphonic acid-sulphuryl fluoride at −120°, it may be shown that the initial product is the monocyclic species

(**615**), which at −60° is converted into the bicyclic product (**614**).[584,817] In 93% aqueous sulphuric acid, cleavage of the cyclopropane ring occurs with the formation of a species tentatively formulated as (**616**).[584] Similar protonation

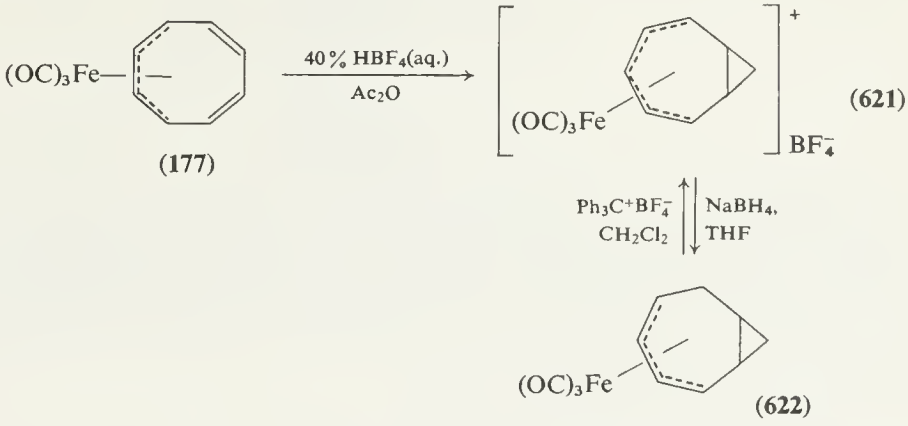


of the methylcyclo-octatetraene complex (**302**) (see p. 107) affords the initial products (**617**) and (**618**) (ratio *ca.* 2:1), which rearrange to give the species (**619**) and (**620**) respectively.[818]



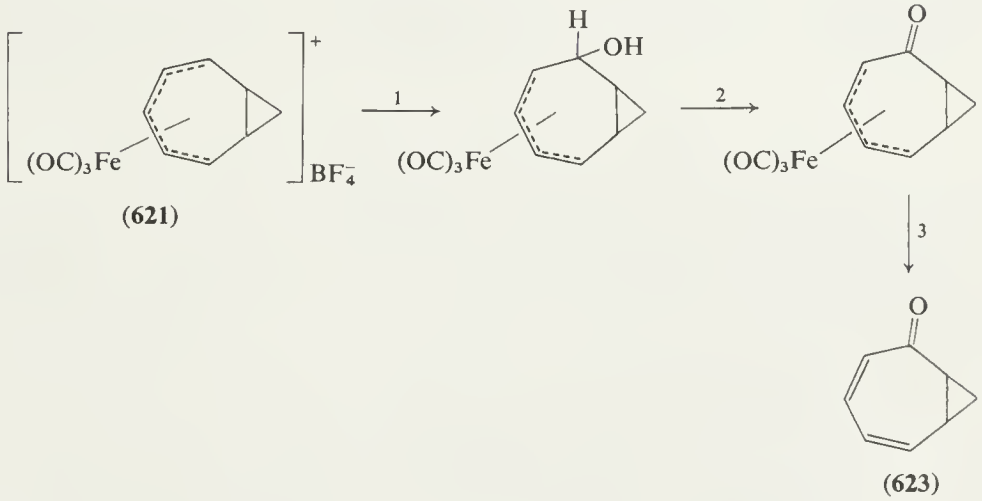
The bicyclic cationic complex (**614**) may be isolated in the form of the crystalline tetrafluoroborate (**621**);[474,815,816] treatment of the salt with sodium boro-

hydride then gives the bicyclo[5.1.0]octa-2,4-diene complex (**622**) (16%), which may be reconverted into the original tetrafluoroborate by hydride-abstraction with triphenylmethyl tetrafluoroborate.[474,815,819]



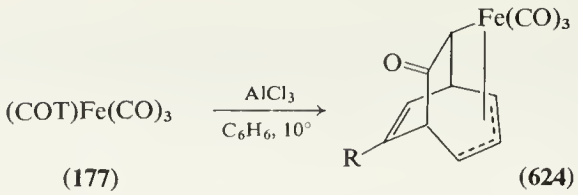
By the steps outlined in scheme 70, the tetrafluoroborate (**621**) may be transformed into 2,3-homotropone (**623**).[820]

Scheme 70



Reaction	Reagents and conditions
1	NaOH, Me_2CO(aq.), low temp.
2	CrO_3, pyridine
3	$Ce(NO_3)_4.2NH_4NO_3$

The iron tricarbonyl complex (**177**) reacts with aluminium chloride to give the carbonyl insertion product (**624*a***) (*ca.* 40%), which on treatment with carbon monoxide liberates barbaralone (90%).[821]



(177) **(624)**

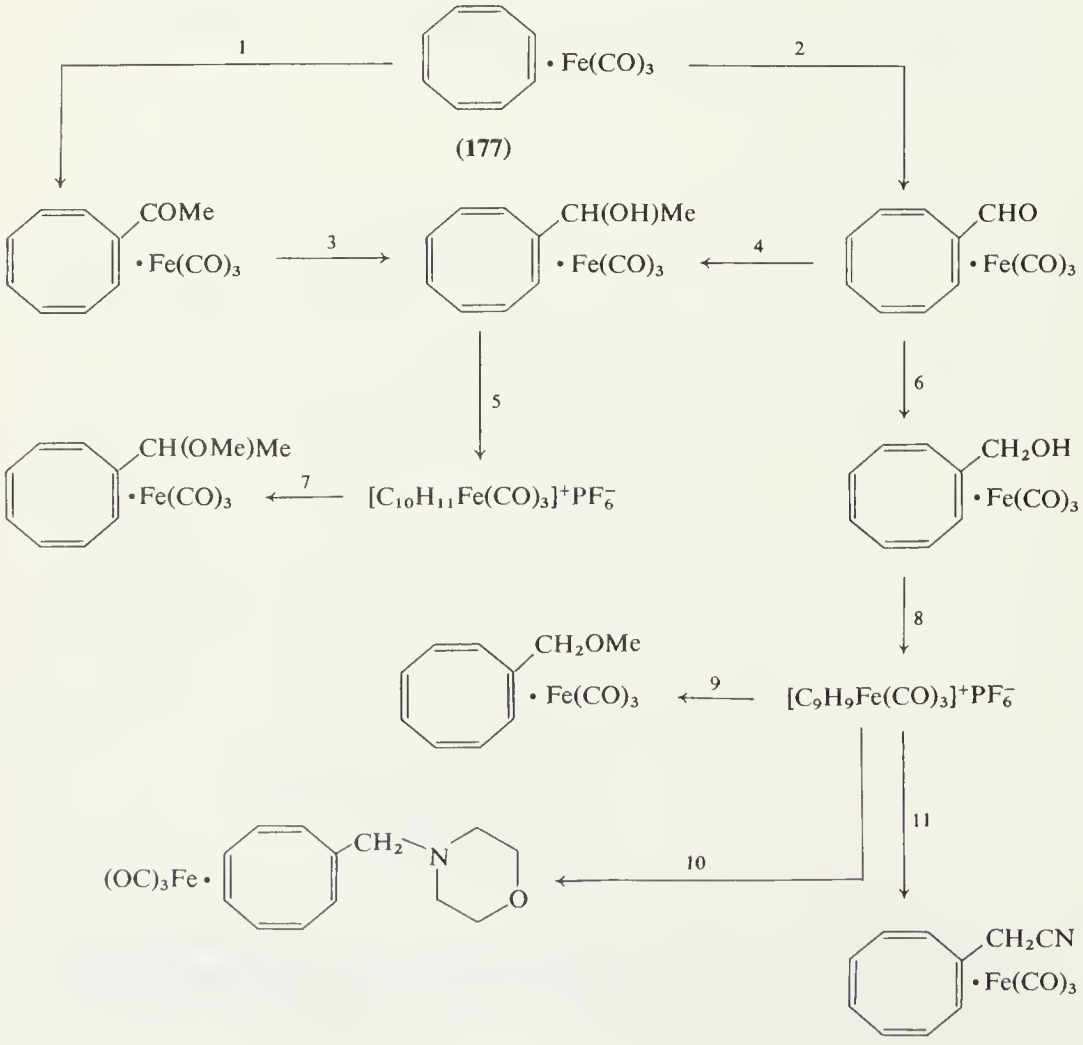
a: R = H

b: R = Me

A similar reaction with (methylcyclo-octatetraene)$Fe(CO)_3$ (**302**) gives the complex (**624*b***).[821]

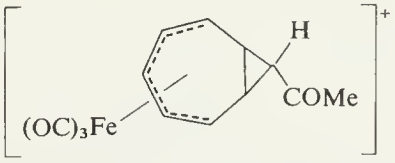
Under certain conditions the iron tricarbonyl complex (**177**) may be substituted by electrophilic reagents. The use of this property in the preparation of monosubstituted COTs has been described (see pp. 82–3); scheme 71 outlines other transformations.[552, 822]

Scheme 71



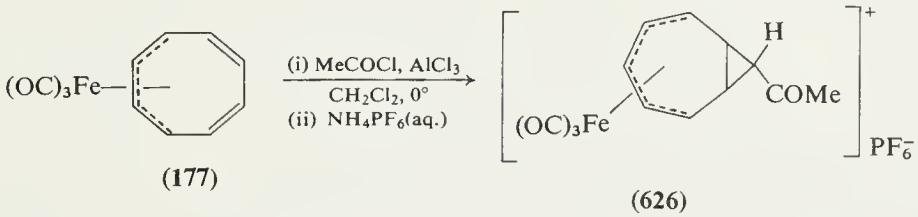
Reaction	Reagents and conditions	Yield (%)
1[a]	$MeCOCl$, $AlCl_3$, CH_2Cl_2, 0°	5
2	$HCONMe_2$, $POCl_3$, 4°	60
3	$NaBH_4$, EtOH, 0°	85
4	MeMgX	—
5	65% HPF_6(aq.), Et_2O, 20°	90
6	$NaBH_4$, EtOH, 0°	93
7	MeOH, r.-t.	83
8	65% HPF_6(aq.), Et_2O, 20°	89
9	MeOH, r.-t.	89
10	Morpholine, Et_2O, r.-t.	—
11	NaCN, Me_2CO(aq.), r.-t.	—

[a] A diacetyl-derivative may also be isolated (0.9% yield). The main acetylation product appears to be the cation (**625**), isolable as the hexafluorophosphate (see below).

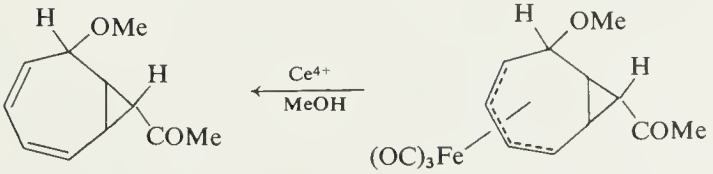


(**625**)

With acetyl chloride in the presence of aluminium chloride, followed by ammonium hexafluorophosphate, the iron tricarbonyl complex (**177**) affords the salt (**626**) (28%), which with sodium methoxide gives the methoxy-derivative (**627**); removal of the metal then gives the free bicyclic diene (**628**).[552]

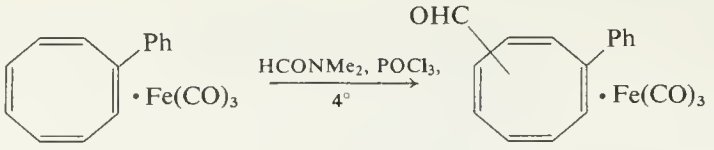


(**177**) (**626**)



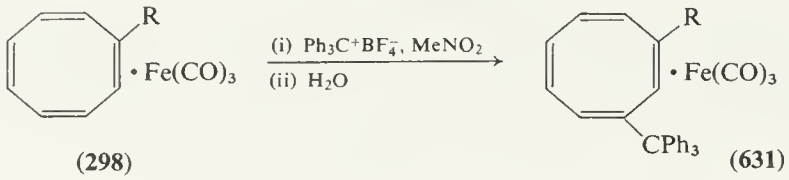
(**628**) (**627**)

Using the same reaction conditions as for $(COT)Fe(CO)_3$ (see above), the phenylcyclo-octatetraene complex (**629**) may be converted into the formyl-derivative (**630**) (60%).[590]



(629) (630)

The complexes (**298**) (p. 106) react with trityl tetrafluoroborate to give salts which on hydrolysis yield the products (**631**)[551] (table 76).



(298) (631)

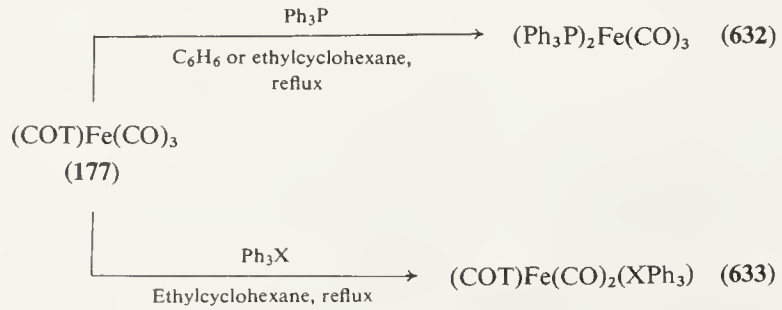
Table 76

R	Yield (%)
Ph	11[a]
$SiMe_3$	15
$GeMe_3$	12

[a] Position of trityl group uncertain.

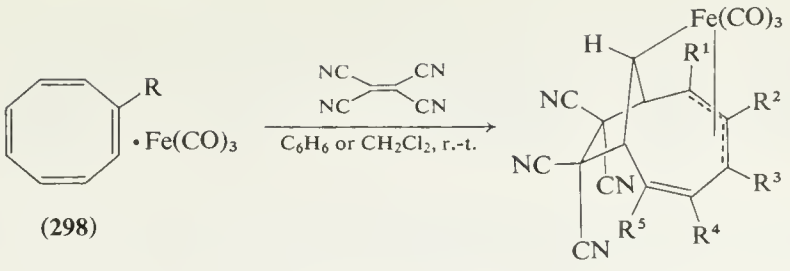
The electrochemical reduction of $(COT)Fe(CO)_3$ is mentioned in ref. 823.

Displacement of COT from the iron tricarbonyl complex (**177**) is effected by carbon monoxide at 100° and high pressure.[824] Triphenylphosphine in refluxing benzene[824] or ethylcyclohexane[450] also displaces COT, giving the product (**632**) (for the kinetics of this type of displacement, see ref. 825). Triphenylarsine and triphenylstibene, however, displace carbon monoxide to afford complexes of the type (**633**) (80% and 50% respectively.)[450]



X = As, Sb

The iron tricarbonyl complexes of COTs (**298**) undergo cycloaddition reactions with e.g. tetracyanoethylene, forming products now known to possess structure (**634**)[587,826] (table 77). Demetallation of the adduct (**634*a***; R = H)



(298)

(634)

a: $R^1 = R$ ($R^2 = R^3 = R^4 = R^5 = H$)

b: $R^2 = R$ ($R^1 = R^3 = R^4 = R^5 = H$)

c: $R^3 = R$ ($R^1 = R^2 = R^4 = R^5 = H$)

d: $R^4 = R$ ($R^1 = R^2 = R^3 = R^5 = H$)

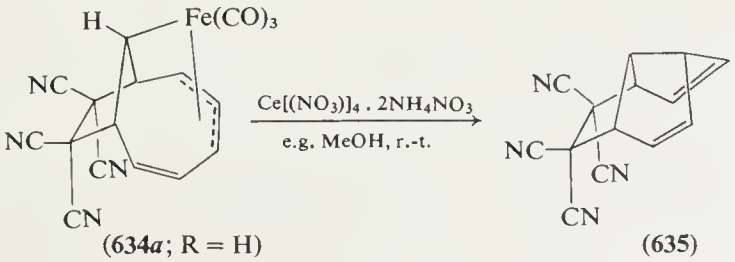
e: $R^5 = R$ ($R^1 = R^2 = R^3 = R^4 = H$)

Table 77

R	Yield (%) (634*a*)	(634*b*)	(634*c*)	(634*d*)	(634*e*)	Ref.
H			96			(474), 826, 827
Me	71	21.5	—	—	—	(587), 588
Ph_3C			75[a]			587
Ph	16	23	—	39	—	(587), 588
CO_2Me	—	—	—	64	23	588
OMe	—	—	31.5	—	—	588
Br			81[a]			587

[a] Only one isomer reported.

gives the dihydroquinacene (**635**) (84 %),[826, 827] starting material for a projected synthesis of the dodecahedrane system.[828, 829] For demetallation of substituted derivatives (**634**), see ref. 588.



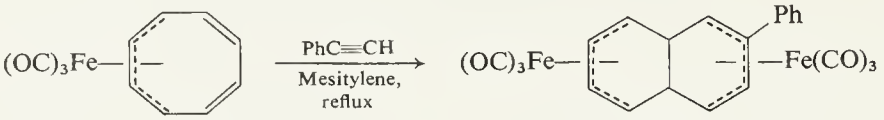
(634*a*; R = H) (635)

Similar cycloadditions occur with 1,1-dicyano-2,2-bis(trifluoromethyl)-ethylene (table 78); the structures of the products, originally formulated as 1,2-cycloadducts, are probably analogous to the tetracyanoethylene-derivatives (**634**).

Table 78

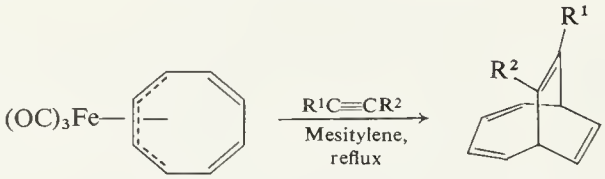
	R	Conditions	Yield (%)	Ref.
(298)	H	Hexane, r.-t.	95	(830), 831
	Ph_3C	Hexane, r.-t.	25	587

Reaction of the iron tricarbonyl complex (**177**) with phenylacetylene affords a product formulated as (**636**).[832]



(**177**) (**636**)

With disubstituted acetylenes, however, the metal is displaced to give the bicyclo[4.2.2]decatetraenes (**613**)[832] (table 79) (see p. 199).

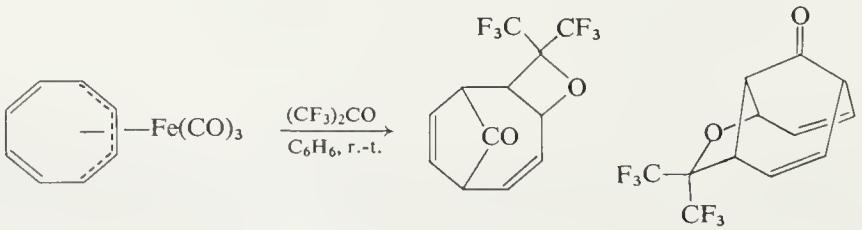


(**177**) (**613**)

Table 79

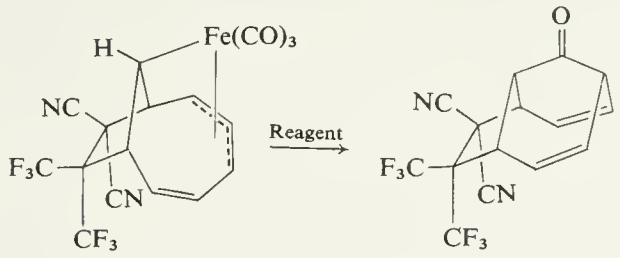
R^1	R^2	Yield (%)
Ph	Ph	Up to 35
Ph	CO_2Me	15
Ph	$SiMe_3$	*ca.* 10

Hexafluoroacetone reacts with the iron complex (**177**) to give '*trans*'-$(COT)Fe_2(CO)_6$ (**178**) and a metal-free product (12%), tentatively assigned structure (**637**);[831] in view of the proved structure (**634***a*; R = H) for the tetracyanoethylene-adduct, it is likely that the hexafluoroacetone-adduct possesses structure (**638**) (*cf.* the reaction of tetracyanoethylene with (benzocyclo-octatetraene)$Fe(CO)_3$, followed by demetallation[588]).



(**177**) (**637**) (**638**)

A similar structure (**639**) probably results from the reaction of the 1,1-dicyano-2,2-bis(trifluoromethyl)ethylene-adduct (presumably (**640**)) with carbon monoxide, nitric oxide, or 1,2-bis(diphenylphosphino)ethane[831] (table 80).

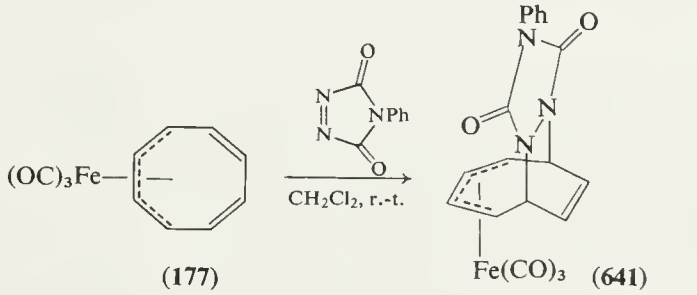


(**640**) (**639**)

Table 80

Reagents and conditions	Yield (%)
CO (100 atm), CH_2Cl_2, 80°	53
or NO, CH_2Cl_2, r.-t.	46
or $Ph_2PCH_2.CH_2PPh_2$, CH_2Cl_2, r.-t.	54

In contrast with the 1,3-cycloaddition of tetracyanoethylene etc., 4-phenyl-1,2,4-triazoline-3,5-dione reacts with $(COT)Fe(CO)_3$ to afford a product (**641**) (29%) resulting from 1,4-cycloaddition to the ligand.[831]



(**177**) (**641**)

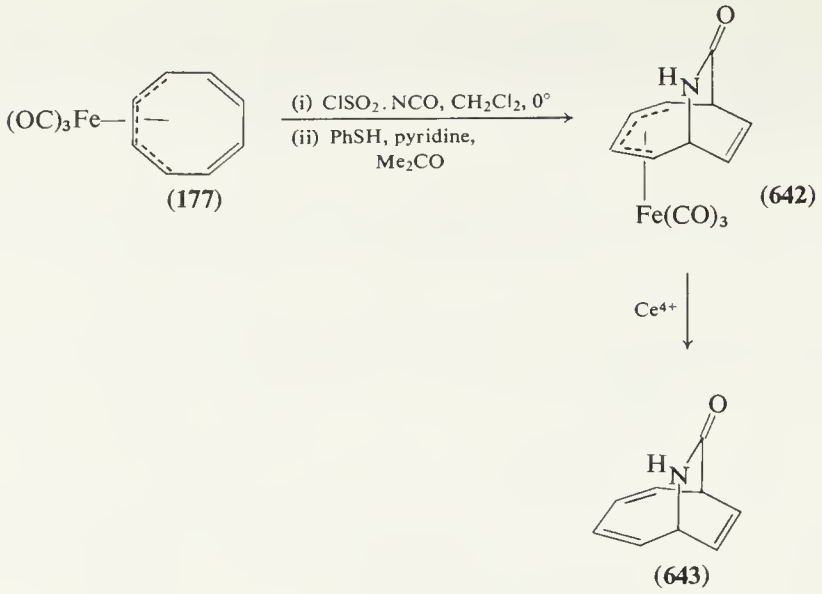
(Stereochemistry not certain)

1,4-Attack on the complex (**177**) is also adopted by chlorosulphonyl isocyanate; the product obtained (80%) after dechlorosulphonylation has structure (**642**), and on demetallation yields the free ligand (**643**).[826]

Light-induced reactions of $(COT)Fe(CO)_3$ with COT, giving derivatives of COT dimers, have already been mentioned (see p. 63).

In the presence of tetrafluorobenzyne, $(COT)Fe(CO)_3$ is apparently converted into '*trans*'-$(COT)Fe_2(CO)_6$ (**178**) (25%).[833]

Highly efficient (95%) demetallation of $(COT)Fe(CO)_3$ is effected by trimethylamine *N*-oxide in refluxing benzene.[834]

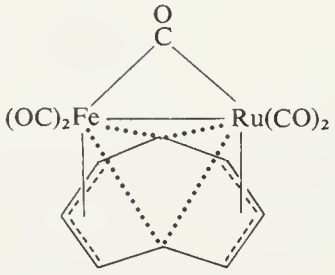


(177) (642) (643)

Reaction of $(COT)Fe(CO)_3$ with $Ru_3(CO)_{12}$ results in the 'mixed' binuclear complex (**644**).[835]

$$(COT)Fe(CO)_3 \xrightarrow[\text{Xylene, reflux}]{Ru_3(CO)_{12}} (COT)FeRu(CO)_5 \quad \textbf{(644)}$$

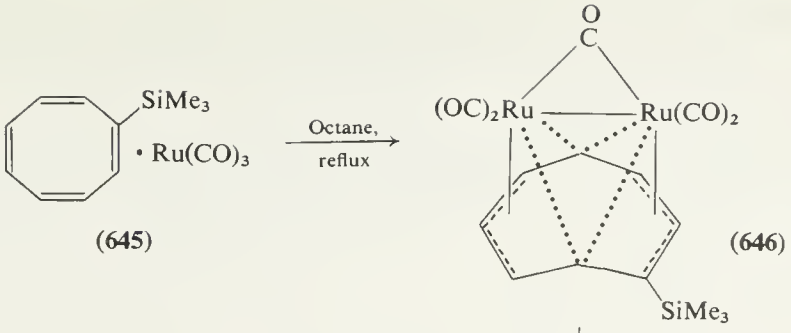
From the spectroscopic evidence, the structure of this fluxional product is as shown (*cf.* (**612**), p. 199).



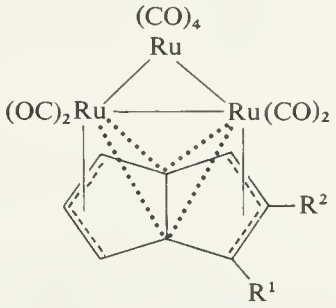
(644)

The ruthenium complex (**645**), in refluxing octane, is transformed into the binuclear compound (**646**), which at higher temperatures forms the pentalene complex (**304**) (mixture of isomers)[811] (see p. 108). Thermolysis of (trityl-cyclo-octatetraene)$Ru(CO)_3$ also affords a polynuclear species.[811]

Protonation of $(COT)Ru(CO)_3$ (**184**) (p. 65) initially leads to the bicyclic cation (**647**), isolable as the tetrafluoroborate; on standing in solution, however, this bicyclic cation isomerises to a monocyclic species best formulated as (**648**)[836] (*cf.* the protonation of $(COT)Fe(CO)_3$ (**177**), pp. 199–200). Treatment



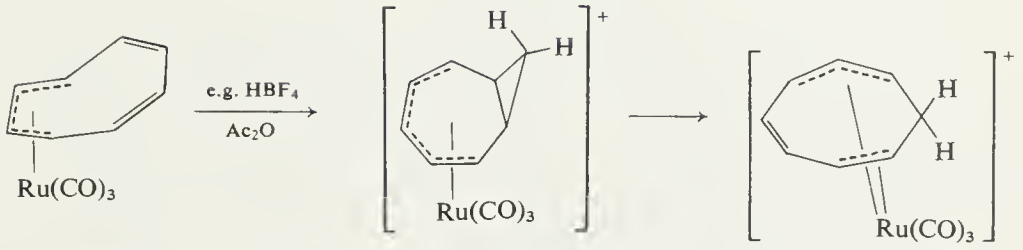
(645) (646)



(304)

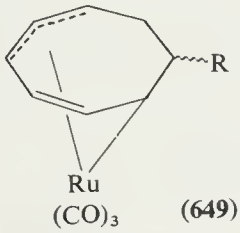
$R^1 = SiMe_3$, $R^2 = H$

$R^1 = H$, $R^2 = SiMe_3$



(184) (647) (648)

of the salts of (**648**) with cyanide ions, or nitromethane in the presence of sodium carbonate, gives the neutral complexes (**649*a***) or (**649*b***).[836]



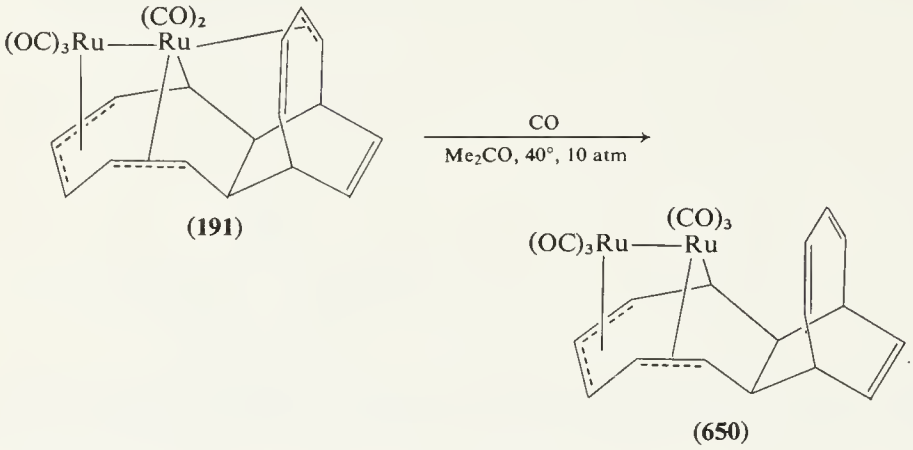
(**649**)

a: R = CN

b: R = CH_2NO_2

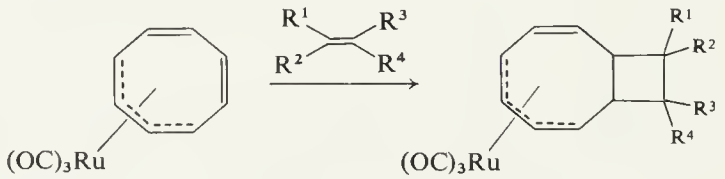
COT is displaced from (COT)Ru(CO)$_3$ (**184**) by e.g. triphenylphosphine, iodine, mercury(II) chloride;[479] for kinetics of the reactions with tertiary phosphines, see ref. 837.

The pentacarbonyl complex (**191**) of dimeric COT (see pp. 65–7) reacts with carbon monoxide to give a hexacarbonyl species, probably (**650**), which is fluxional.[484]



(**191**) (**650**)

The ruthenium tricarbonyl complex (**184**) reacts with tetracyanoethylene and related compounds to form 1:1 adducts[831] (table 81); the original formulation of the products as 1,2-cycloadducts (**651**) is questionable (see the corresponding iron compounds, pp. 204–5, 207).

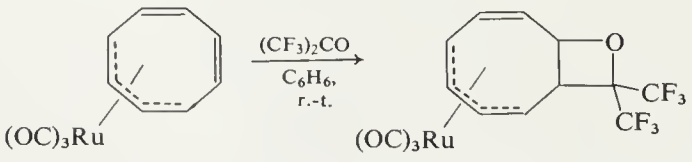


(**184**) (**651**)

Table 81

R^1	R^2	R^3	R^4	Conditions	Yield (%)
CN	CN	CN	CN	CH_2Cl_2, r.-t.	18
CN	CN	CF_3	CF_3	C_6H_6, r.-t.	16
CN	CF_3	CN	CF_3	CH_2Cl_2, r.-t.	44

Reaction of hexafluoroacetone with the complex (**184**) affords an adduct (14%) with the suggested structure (**652**)[831] (but see p. 206).



(**184**) (**652**)

The ruthenium complex (**183**) (see p. 64) reacts with allylmagnesium chloride to give the bis-allyl-derivative (**653**).[838]

$$\underset{(\mathbf{183})}{[(COT)RuCl_2]_n} \xrightarrow[Et_2O,\ r.\text{-}t.]{CH_2{=}CH.CH_2MgCl} (COT)Ru(allyl)_2 \quad (\mathbf{653})$$

Protonation of α-(COT)Os(CO)$_3$ (**202**) (see p. 70) is similar to that of (COT)Ru(CO)$_3$ (**184**)[836] (see pp. 208–9). For the displacement of COT by trimethyl phosphite, see ref. 496.

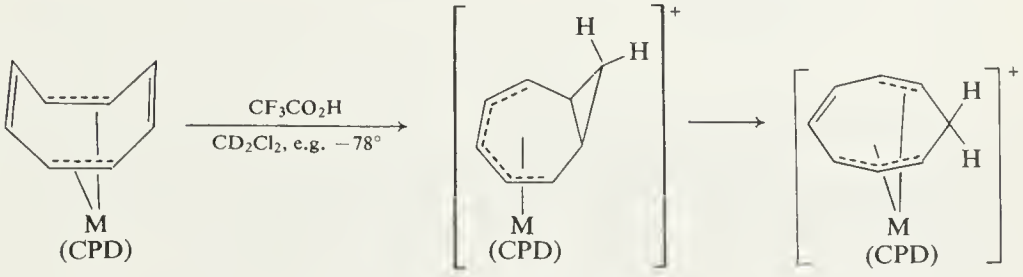
(*k*) *Cobalt, rhodium and iridium derivatives*

For catalytic and displacement reactions of complex (**203**) (see p. 71), see ref. 498.

The 'mixed' cobalt complex (**205**) (see pp. 71–2) is transformed by the action of heat into the product (**206**).[839]

$$\underset{(\mathbf{205})}{(COT)Co(CPD)} \xrightarrow{133°} \underset{(\mathbf{206})}{(COT)Co_2(CPD)_2}$$

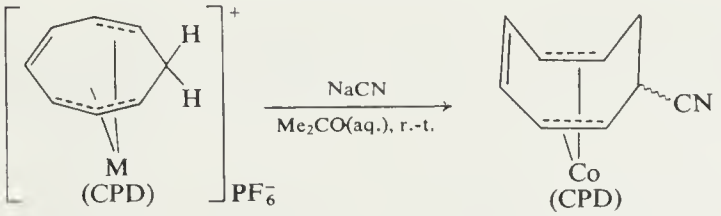
Protonation of the 'mixed' complexes (**654***a*) and (**654***b*) may be effected by trifluoroacetic acid to give, initially, the bicyclic cations (**655**), which subsequently isomerise to the monocyclic form (**656**)[840] (*cf.* ruthenium, pp. 208–9).



(**654**) (**655**) (**656**)

a: M = Co *b*: M = Rh *c*: M = Ir

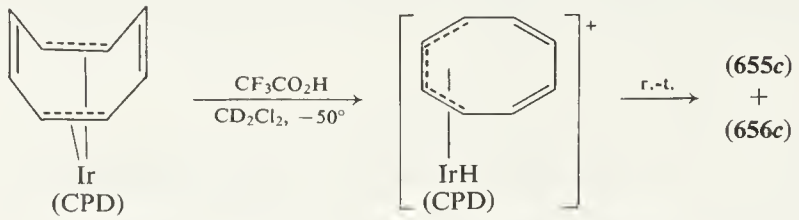
With aqueous HPF_6, the cobalt and iridium complexes (**654***a*) and (**654***c*) afford the salts (**657**); the cobalt salt (**657**; M = Co) with sodium cyanide yields the cyano-derivative (**658**) (63%).[840] The rhodium complex (**654***b*),



(**657**) (**658**)

however, reacts with HPF_6 to form a hexafluorophosphate salt of the bicyclic cation (**655**).[840]

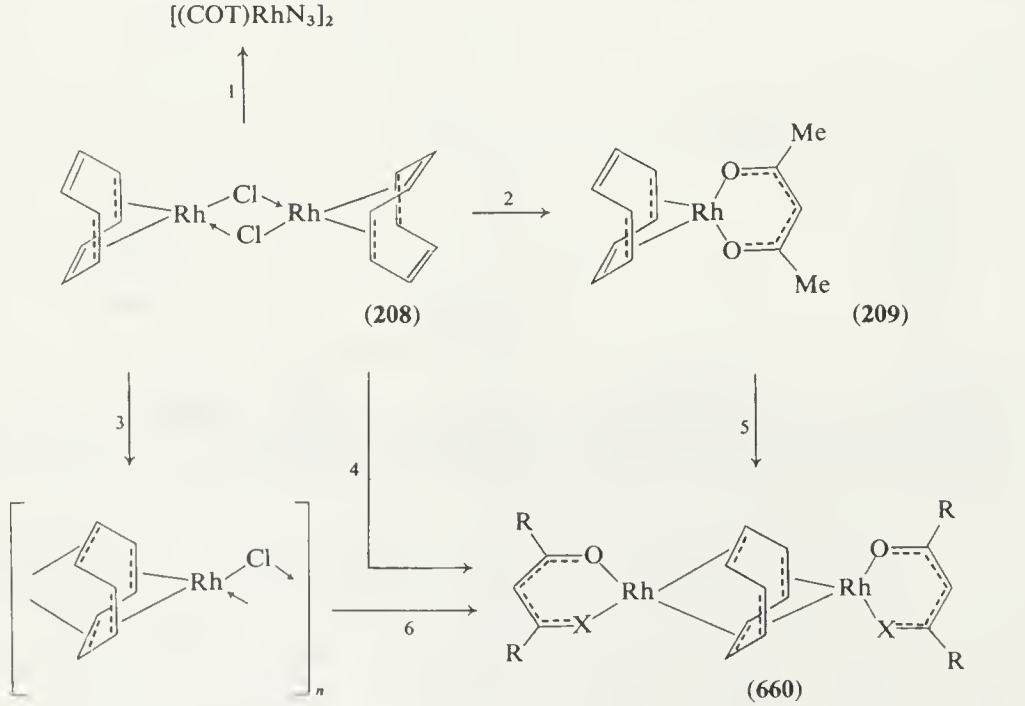
At low temperatures, metal-protonation of the iridium complex (**654***c*) occurs to give the hydrido-species (**659**), which at room-temperature affords a mixture of (**655***c*) and (**656***c*).[840]



(**654***c*) (**659**)

Some transformations of the dimeric rhodium complex (**208**) (see p. 73) are outlined in scheme 72. (For the dipole moments of (COT)Rh(acac) (**209**) and $(COT)Rh_2(acac)_2$ (**660***b*), see ref. 843.)

Scheme 72



a: R = Ph, X = S

b: R = Me, X = O

Reaction	Reagents and conditions	Yield (%)	Ref.
1	NaN_3, MeOH, r.-t.	*ca.* 100	841
2	$CH_3COCH_2COCH_3$, K_2CO_3, light petroleum (b.p. 60–80°), r.-t.	80	507
3	$CHCl_3$ or CS_2, r.-t.	*ca.* 65	507
4	$PhCOCH_2CSPh$, K_2CO_3, petroleum, r.-t.	48[a]	842
5	130°	77[b]	510
6	(As for reaction 2)	65[b]	507

[a] Product (**660***a*). [b] Product (**660***b*).

COT is displaced from the rhodium complex (**208**) by e.g. triphenyl phosphite; for heats of reaction, see ref. 509.

The 'mixed' complex (**661**) results from the reaction of $[(COT)IrHCl_2]_n$ (**217**) (see p. 75) with sodium cyclopentadienide; treatment with iodine then leads to $(CPD)IrI_2$ (**662**).[515]

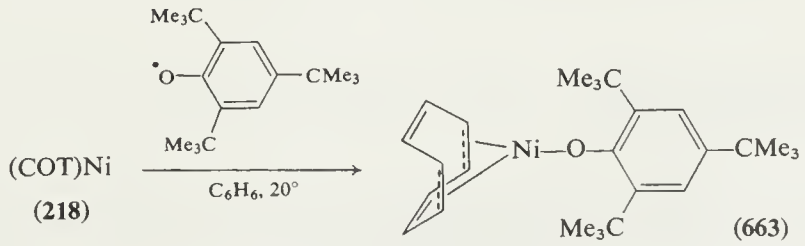
$$[(COT)IrHCl_2]_n \text{ (217)} \xrightarrow[THF]{(CPD)Na} (COT)Ir(CPD) \text{ (661)} \xrightarrow[r.\text{-}t.]{I_2,\ CH_2Cl_2} (CPD)IrI_2 \text{ (662)}$$

(*l*) *Nickel and platinum derivatives*

For preparation from COT, see pp. 75–8.

Reactions. COT is displaced from (COT)Ni(duroquinone) (**220**) (p. 76) by tertiary phosphines and phosphites; for kinetics, see ref. 844.

The nickel(0) complex (**218**) (pp. 75–6) reacts with 2,4,6-tri-t-butylphenoxy radicals to yield the product (**663**) (66%).[845]



The platinum complex (**226***b*) (pp. 77–8) reacts with Grignard reagents to give products of the types (**664**)–(**666**)[846,847] (table 82). (For the ^1H n.m.r. spectrum of (**665**; R = Me), see ref. 530).

$$(COT)PtI_2 \text{ (226}b\text{)} \xrightarrow[Et_2O,\ C_6H_6,\ r.\text{-}t.]{RMgI} \begin{cases} (COT)PtRI & (664) \\ \text{or } (COT)PtR_2 & (665) \\ \text{and/or } (COT)Pt_2R_4 & (666) \end{cases}$$

Table 82

R	Yield (%) (664)	(665)	(666)
Me	—	5	36
Et	4	—	—
Ph	—	—	70
o-Me.C_6H_4	—	64	—
p-Me.C_6H_4	—	29	—
1-Naphthyl	—	65	—

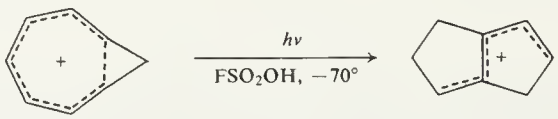
7. Homotropylium species

These are produced by protonation of COTs (see pp. 21–2, 99), or from 7,8-dichlorocyclo-octa-1,3,5-trienes by treatment with proton or Lewis acids (see p. 236).

For the ^{13}C n.m.r. spectrum of the homotropylium cation (**35**), see refs. 848, 849.

Ring-inversion of the *endo*-8-chloro-derivative (see p. 23) is catalysed by *cis*-7,8-dichlorocyclo-octa-1,3,5-triene.[850]

Reactions. U.v. irradiation of the homotropylium ion (**35**) leads to a species identified as the bicyclic cation (**667**).[851,852]



(**35**) (**667**)

For the electrochemical reduction of (**35**), see ref. 267.

8. Cyclo-octa-1,3,5-triene, bicyclo[4.2.0]octa-2,4-diene and cyclo-octa-1,3,6-triene

Cyclo-octa-1,3,5-triene (**62**) and cyclo-octa-1,3,6-triene (**63**) are produced from COT by various reduction processes (see pp. 28–30); they may be purified *via* their silver nitrate complexes.[63,264]

At moderate temperatures cyclo-octa-1,3,5-triene equilibrates with bicyclo-[4.2.0]octa-2,4-diene (**64**) (see table 83), and pure bicyclo[4.2.0]octa-2,4-diene may be obtained by slow fractional distillation of the mixture;[853] if pure cyclo-octa-1,3,5-triene is required, the bicyclic valence tautomer may be removed by treatment with maleic anhydride (in the cold).[260]

Cyclo-octa-1,3,5-triene also equilibrates (slowly) with the 1,3,6-triene (*via* 1,5-hydrogen shifts[736,854]), but the equilibrium mixture contains only

ca. 0.5–1 % of the 1,3,6-triene at 100–129°.[855] This almost complete conversion of the 1,3,6-triene into the 1,3,5-triene can be catalysed by potassium t-butoxide in t-butanol,[63] or potassium hydroxide in ethanol.[264] (For the conformations of (**62**) and (**63**), see ref. 857.)

(**64**) (**62**) (**63**)

Table 83

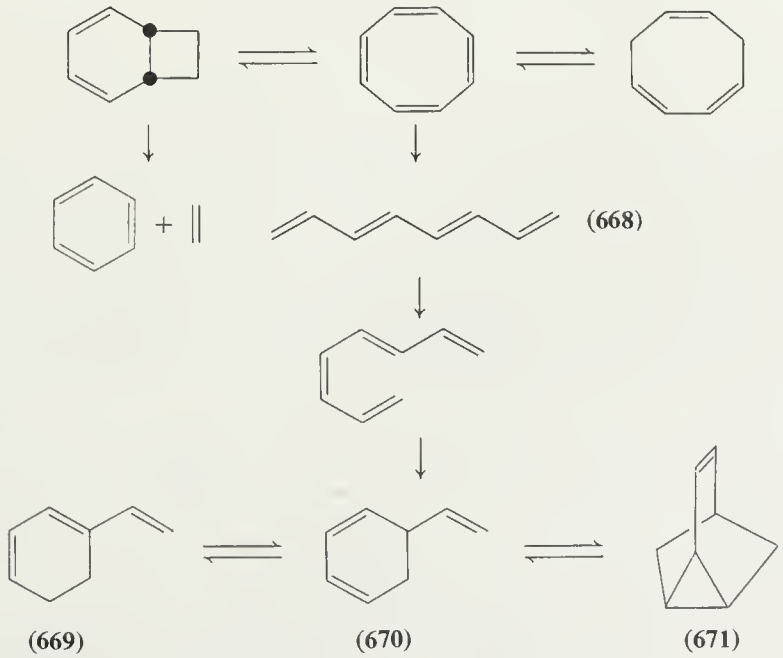
Temp. (°C)	Proportion of (**64**) (%)	Ref.
20	9	856
60	10.8	136
80–100	15	260

Reactions. The chemistry of the cyclo-octatrienes (up to 1963) has been reviewed[265] (see also ref. 858); some of this early work would appear to need reinvestigation.

Thermal dimerisation. See p. 225.

Thermolysis. At temperatures above *ca.* 225°, cyclo-octa-1,3,5-triene gives a complex mixture of hydrocarbons from which the following constituents may be isolated:[853,859] benzene, *E,E*-octa-1,3,5,7-tetraene (**668**), 1-vinylcyclohexa-1,3-diene (**669**), 5-vinylcyclohexa-1,3-diene (**670**), and tricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**671**). The reaction sequence of scheme 73 is suggested.[853]

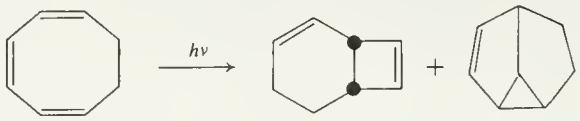
Scheme 73



(**668**)

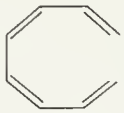
(**669**) (**670**) (**671**)

Photolysis. U.v. irradiation of cyclo-octa-1,3,5-triene yields the photo-isomers (**672**) and (**673**).[853,860,861]



(**672**) (**673**)

Z,Z-Octa-1,3,5,7-tetraene (**674**) has been detected as a transient intermediate in this reaction,[862,863] and under certain conditions the *E,E*-tetraene (**668**) may be isolated.[853]

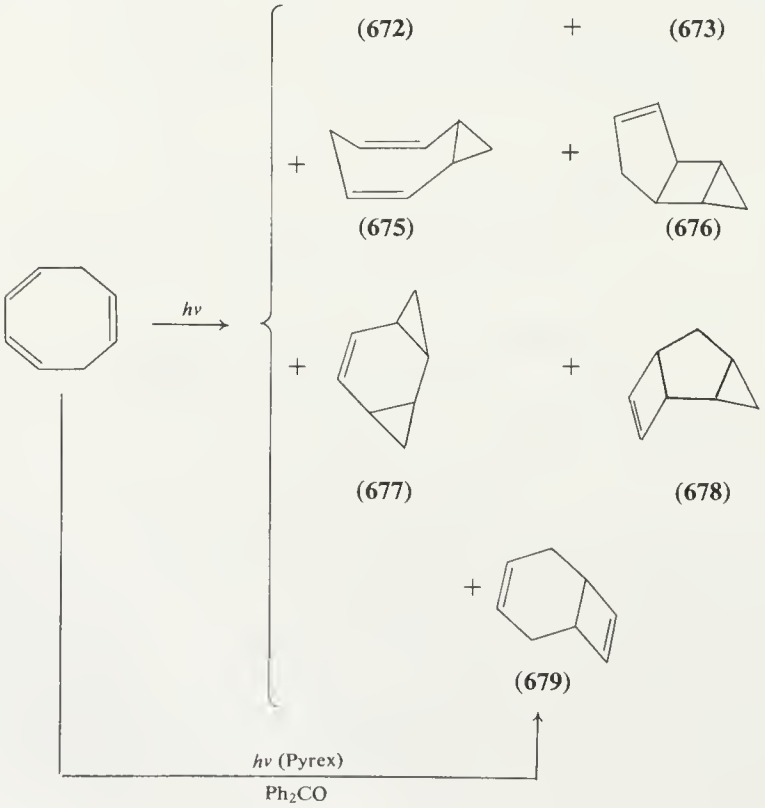


(**674**)

Photolysis of bicyclo[4.2.0]octa-2,4-diene yields cyclo-octa-1,3,5-triene, together with benzene and ethylene.[853]

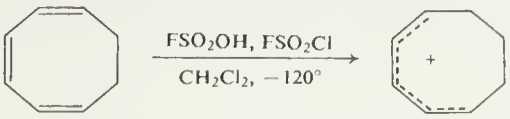
The photoproducts (**672**) and (**673**) are also obtained from cyclo-octa-1,3,6-triene, but in addition, five other isomers formulated as (**675**)–(**679**) may be isolated;[853,860] the benzophenone-sensitised photo-reaction, however, leads to isomer (**679**) exclusively[853] (scheme 74).

Scheme 74



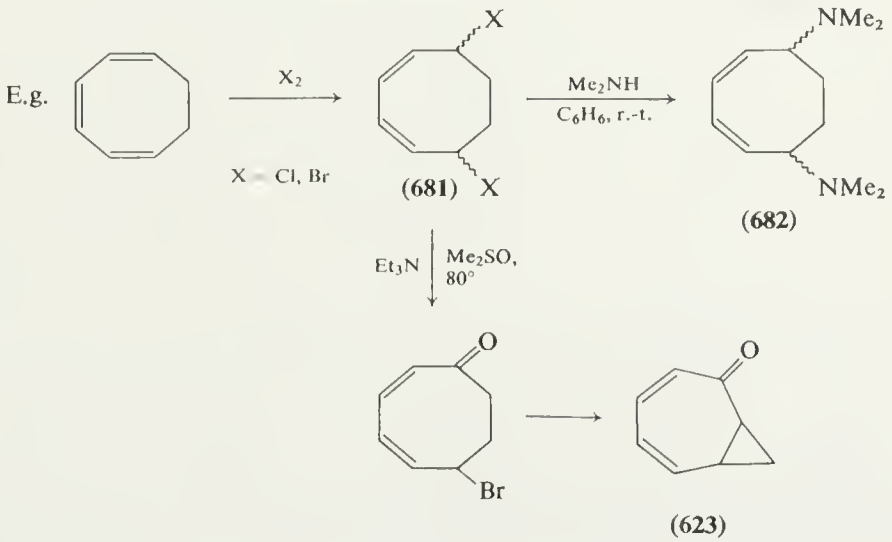
Oxidation, and reactions with electrophiles. For oxidation reactions, see ref. 265.

The cation (**680**) may be generated from cyclo-octa-1,3,5-triene in a 'super-acid' medium.[864]



(**680**)

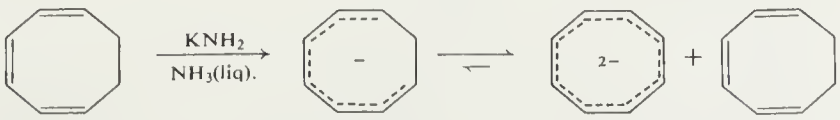
Reaction of the 1,3,5- or the 1,3,6-triene with chlorine or bromine yields the dihalo-derivative (**681**);[265,865] further reaction then affords tetra- and hexa-halides.[264,265] The dibromide (**681**; X = Br)[3,865] with dimethylamine gives the bis(dimethylamino)-derivative (**682**) (47%);[3] with triethylamine in dimethyl sulphoxide, 2,3-homotropone (**623**) is formed.[866] (For reactions of (**681**; X = Cl), see ref. 265.)



For reactions with hydrogen chloride and hydrogen bromide, see ref. 265.

Reduction, and proton-abstraction. For catalytic hydrogenation of cyclo-octa-1,3,5-triene, see e.g. refs. 3, 264; of cyclo-octa-1,3,6-triene, see e.g. ref. 63.

Potassium amide in liquid ammonia abstracts a proton from cyclo-octa-1,3,5-triene to generate the cyclo-octatrienyl anion (**683**), which disproportionates into COT^{2-} and cyclo-octa-1,3,5-triene.[867]



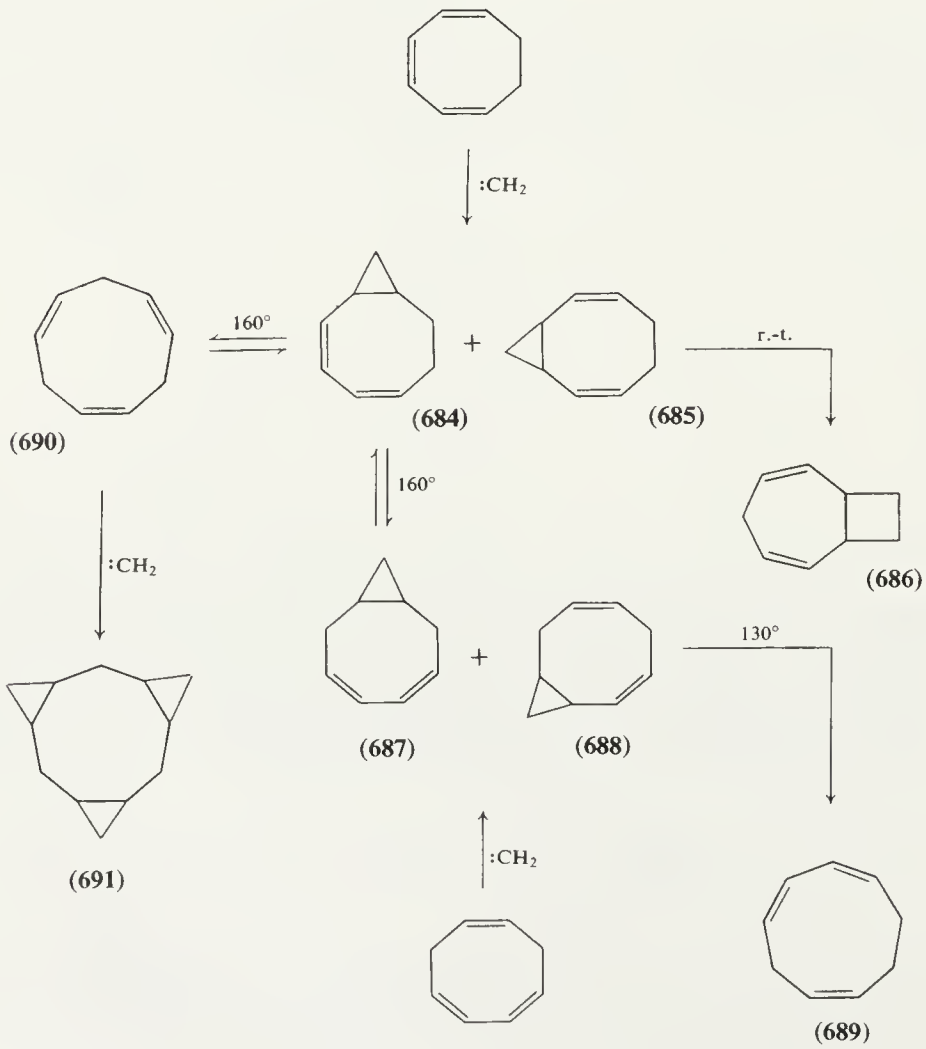
(**683**)

In the presence of $KOCPr^n_3$–Pr^n_3COD, cyclo-octa-1,3,5-triene catalyses H–D exchange in COT (see p. 31).

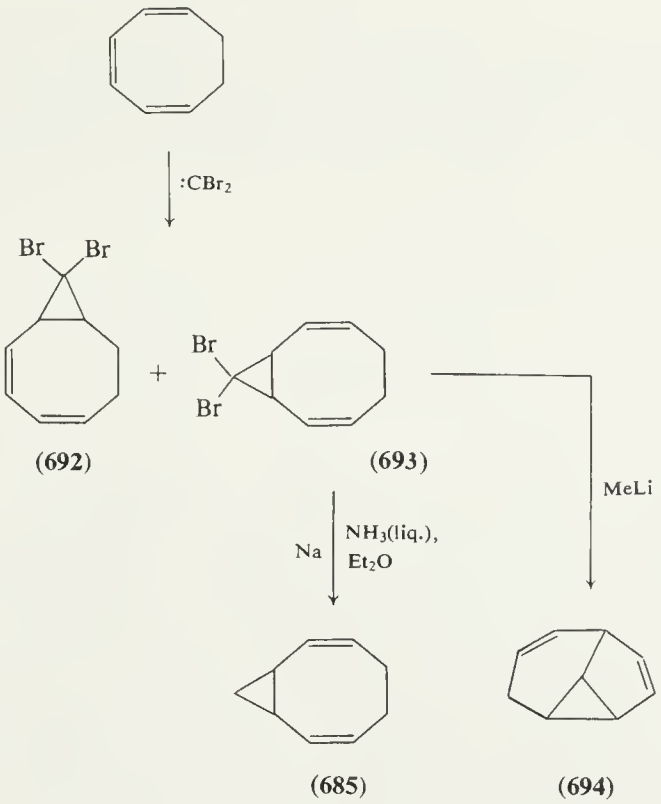
Cycloadditions. Carbene-addition to cyclo-octa-1,3,5-triene, using di-iodomethane and a zinc–copper couple,[868] or diazomethane in the presence of copper(I) chloride,[869] affords the isomeric products (**684**) and (**685**) (combined yield 42%; ratio 4.5:1[869]) (the initially formed adduct (**685**) is very susceptible to Cope rearrangement, and at 25° changes into (**686**) with a half-life of *ca.* 1 day[870]) (scheme 75).

Similar cyclopropanation[868,869] of cyclo-octa-1,3,6-triene yields a mixture of the products (**687**) (51%) and (**688**) (37%).[869] At 130°, the bicyclic diene (**688**) undergoes a 1,5-homodienyl hydrogen shift to form *Z,Z,Z*-cyclonona-1,3,6-triene (**689**).[869] Reversible 1,5-hydrogen shifts in the products (**684**) and (**687**) result in an equilibrium mixture at 160°, a third component being 'trishomobenzene' (**690**),[868,869] cyclopropanation of which gives 'hexahomobenzene' (**691**).[871]

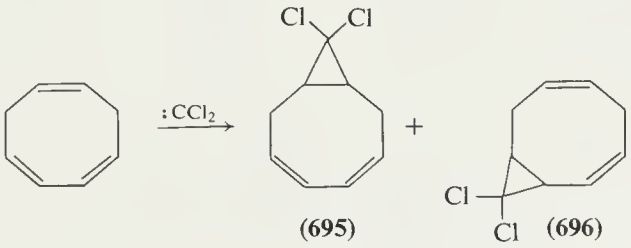
Scheme 75



The addition of dibromocarbene to cyclo-octa-1,3,5-triene leads to the monoadducts (**692**) (36%) and (**693**) (10.5%), together with two bis-adducts.[870] Reduction of the product (**693**) using sodium in liquid ammonia gives the labile system (**685**) (see above), and reaction with methyl-lithium yields the tricyclic diene (**694**).[870]



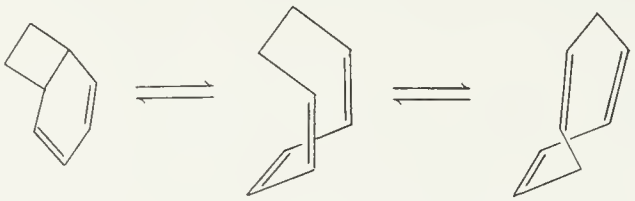
With cyclo-octa-1,3,6-triene, dichlorocarbene gives the adducts (**695**) and (**696**) (in a ratio of 1 : 1)[872] (an erroneous structure for the product was originally proposed[265, 858]).



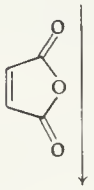
[2 + 2] Cycloadditions with chlorosulphonyl isocyanate are mentioned later (see p. 222).

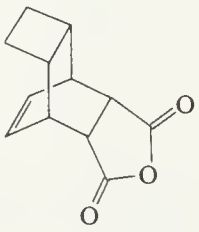
The addition of dienophiles such as maleic anhydride to the cyclo-octatrienes occurs *via* bicyclo[4.2.0]octa-2,4-diene (**64**), so that both the 1,3,5- and the 1,3,6-triene yield the same adduct (**697**);[264, 265, 858] this is identical with the

product obtained by selective semihydrogenation of the cyclo-octatetraene–maleic anhydride adduct.[260] Similarly, structures (**698**) and (**699**) result from acetylenedicarboxylic and azodicarboxylic esters respectively. The known reactions of this type are listed in table 84.

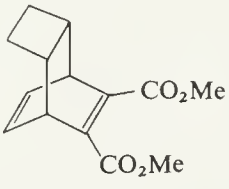


(**64**)

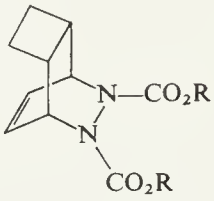




(**697**)



(**698**)



(**699**)

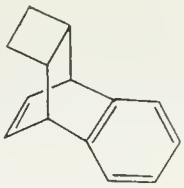
Table 84

Dienophile	Reaction conditions	Product	Yield (%)	Ref.
Maleic anhydride	C_6H_6, reflux	(**697**)	86[a], (64)	259, (873)
Dimethyl acetylene-dicarboxylate	C_6H_6, reflux	(**698**)	77	260
'Azodicarboxylic ester'	—	(**699**)	—	858
Dimethyl azodicarboxylate	—	(**699**; R = Me)	—	874

[a] Reaction temperature 100°.

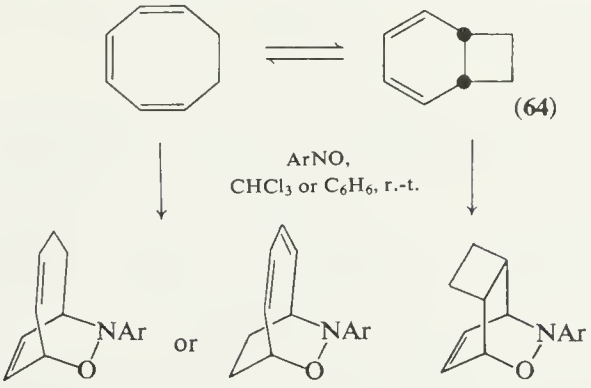
Thermolysis of compound (**698**) provides a route to cyclobutene (see p. 352); for further reactions of (**699**; R = Me), see ref. 874.

Reaction of cyclo-octa-1,3,5-triene with benzyne (from the decomposition of benzenediazonium-2-carboxylate in dichloromethane at 50°) also occurs *via* the valence tautomer (**64**), affording the adduct (**700**) (35%) exclusively.[875]



(700)

Nitrosobenzenes, however, also add to cyclo-octa-1,3,5-triene itself, and products of types (**701**)–(**703**) may be isolated[876] (see table 85). In refluxing ethanol, products of structure (**701**) isomerise to the conjugated system (**702**).[876]



(64)

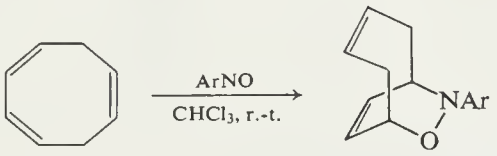
(701) (702) (703)

Table 85

	Ar	Yield (%) (701)	(702)	(703)
a	Ph	—	26	15
b	*p*-Cl.C_6H_4	—	42	17
c	*p*-NO_2.C_6H_4		66[a]	
d	2,4-$(NO_2)_2$.C_6H_3	56	—	3

[a] Total yield; only (**702***c*) was obtained pure. With purified cyclo-octa-1,3,5-triene, (**701***c*) (25%) is isolable.

Cyclo-octa-1,3,6-triene reacts to form [4 + 2] adducts (**704**)[876] (table 86).



(704)

Table 86

Ar	Yield (%)
p-NO_2.C_6H_4	50
2,4-$(NO_2)_2$.C_6H_3	58

In polar solvents, chlorosulphonyl isocyanate reacts with cyclo-octa-1,3,5-triene to give the adducts (**705**)–(**707**) (characterised as the parent lactams) in varying proportions (see table 87) *via* the dipolar intermediate (**708**), adduct (**707**) being the ultimate product of thermodynamic control.[877] No reaction

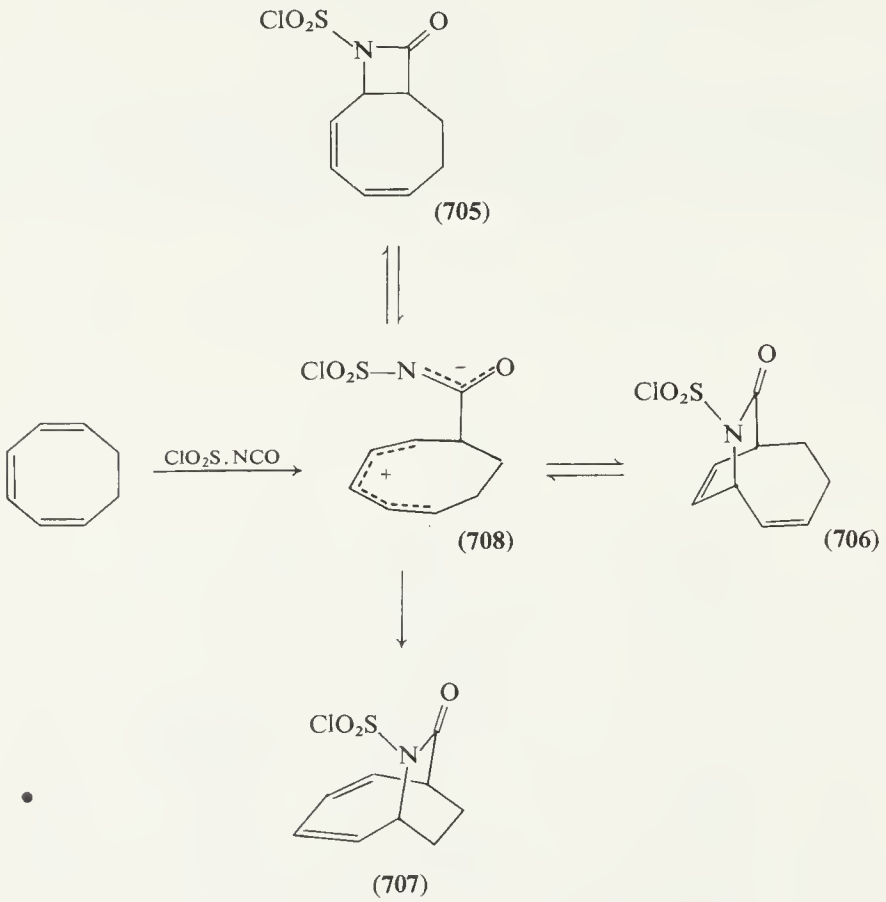


Table 87

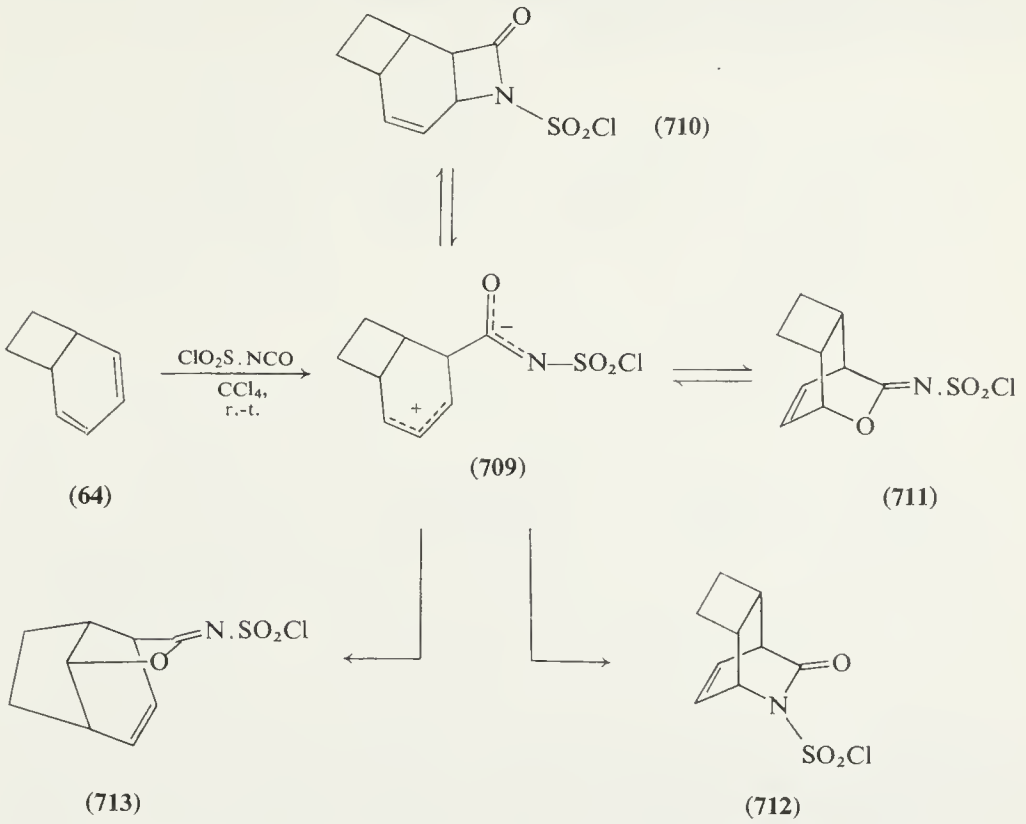
Solvent	Temp. (°C)	Time (h)	Product ratio (**706**):(**707**)[a]	Total yield (%)
CH_2Cl_2	25	4	86:14	(Incomplete reaction)[b]
CH_2Cl_2	25	36	71:29	63
CH_2Cl_2	25	200	63:37	64
$MeNO_2$	85	4	50:50	61
$MeNO_2$	85	24	28:72	65

[a] Determined for parent lactams.
[b] Adduct (**705**) isolated as the lactam (2%).

occurs in cold non-polar solvents; on heating, adducts derived from bicyclo-[4.2.0]octa-2,4-diene are obtained (see below).

With bicyclo[4.2.0]octa-2,4-diene (**64**), the dipolar intermediate (**709**) cyclises not only through nitrogen, but also through oxygen; after 1 h in

carbon tetrachloride, the products are the adducts (**710**) (41% (as lactam)) and (**711**) (37%), but after 5 days these are completely transformed into the isomers (**712**) (30% (as lactam)) and (**713**) (25%).[878]



With electron-deficient dienes, cyclo-octa-1,3,5-triene reacts *via* the valence tautomer (**64**) acting as a dienophile. Thus hexachlorocyclopentadiene and its derivatives give adducts of structure (**714**)[879] (table 88).

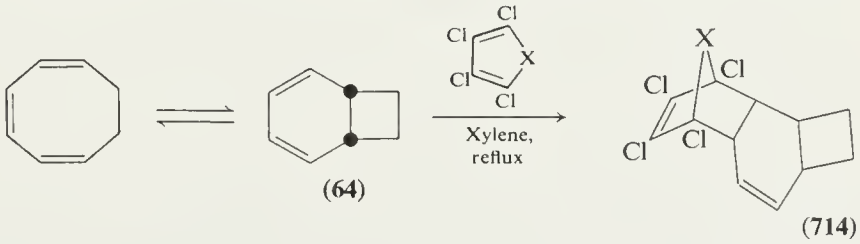


Table 88

X	Yield (%)
CCl_2	60
$C(OMe)_2$	60
	58

Similar additions take place with tetracyclone and 2,5-dimethyl-3,4-diphenylcyclopentadienone, although the initial reaction is followed by Cope rearrangement to give products of structure (**715**); some direct addition to cyclo-octa-1,3,5-triene itself may also occur, since hexa-1,3-dienylbenzenes (**716**) are co-products[879] (table 89).

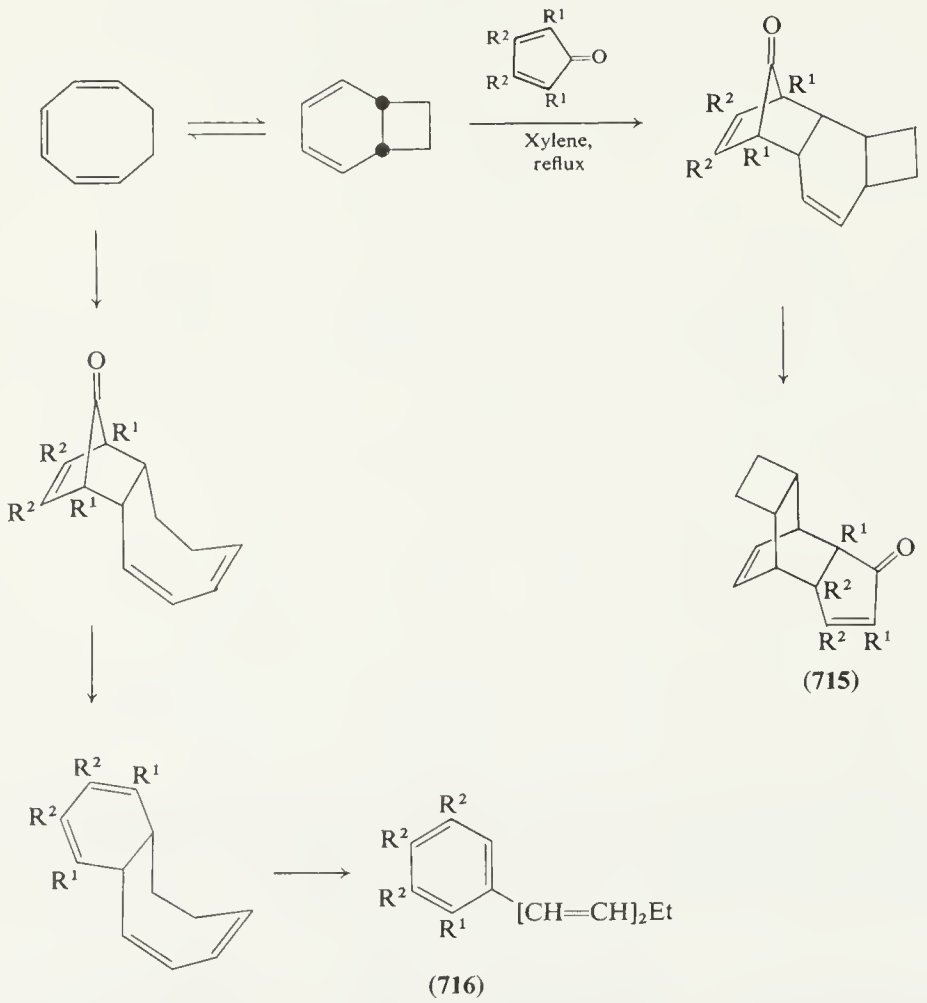
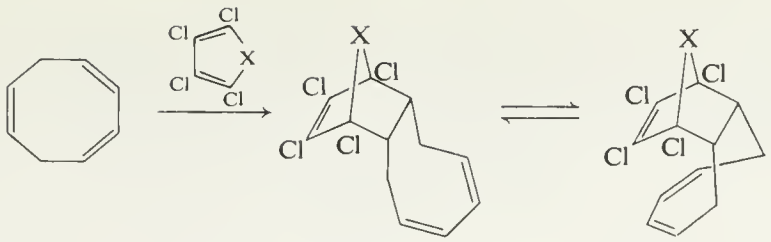
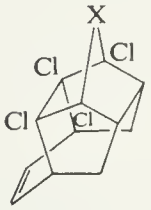


Table 89

		Yield (%)	
R^1	R^2	(**715**)	(**716**)
Me	Ph	34	(Very low)
Ph	Ph	36	28

Electron-deficient dienes also add to cyclo-octa-1,3,6-triene. With e.g. hexachlorocyclopentadiene, the isolated product has the cage-like structure (**717**), evidently formed by initial addition to the 6,7-double bond of the 1,3,6-triene, followed by an intramolecular Diels–Alder reaction[880] (table 90).



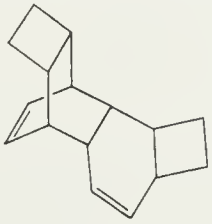


(717)

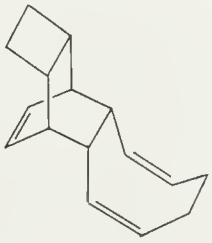
Table 90

X	Conditions	Yield (%)	Ref.
CCl_2	Toluene, *ca.* 100°	10	880
	Toluene, *ca.* 100°	68	880
CO.CCl=CCl	Xylene, reflux	33	881

Cyclo-octa-1,3,5-triene undergoes dimerisation *via* Diels–Alder addition. If either of the cyclo-octatrienes is subjected to prolonged heating in the presence of e.g. potassium t-butoxide, dimer (**718**) is produced; however, in the absence of base a different product, allegedly of structure (**719**), is formed.[858]

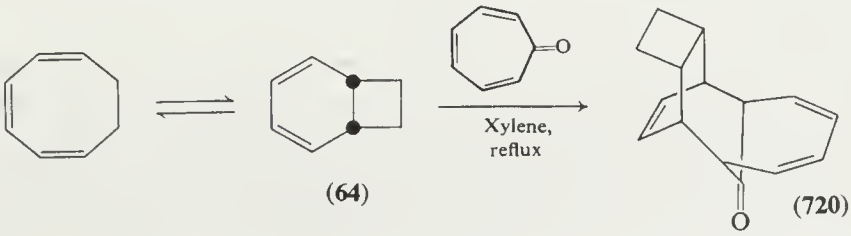


(718)



(719)

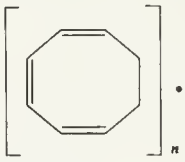
Tropone reacts with cyclo-octa-1,3,5-triene to give the [6 + 4] adduct (**720**) (21%) of the valence tautomer (**64**).[882]



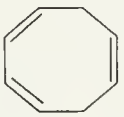
(64)

(720)

Reactions with metal derivatives. With 50% aqueous silver nitrate, cyclo-octa-1,3,5-triene gives an immediate precipitate of the complex (**721***a*);[63,264] with silver tetrafluoroborate, however, the 2:1 product (**721***b*) is formed.[396] Cyclo-octa-1,3,6-triene with ethanolic silver nitrate gives the 1:3 complex (**722**).[264]

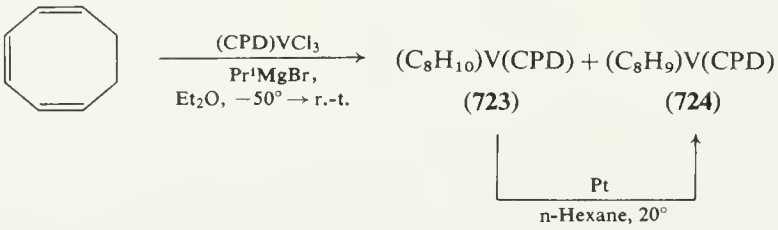


(**721**) *a*: X = NO_3, *n* = 1
b: X = BF_4, *n* = 2

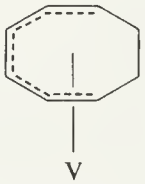


(**722**)

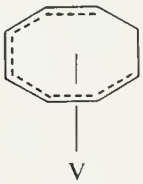
Reaction of cyclo-octa-1,3,5-triene with (CPD)VCl_3 in the presence of isopropylmagnesium bromide affords a mixture of the complexes (**723**) and (**724**) (total yield 34%), which may be converted quantitatively into the product (**724**) by platinum-catalysed dehydrogenation.[883]



The crude structures of (**723**) and (**724**) are presumably as shown.[883]



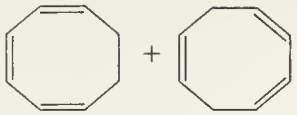
(**723**)



(**724**)

For ion-molecule reactions of (CPD)$V(CO)_4$ and cyclo-octa-1,3,5-triene, see ref. 422.

The cyclo-octatrienes (mixed isomers) react with the hexacarbonyls of chromium, molybdenum and tungsten to form complexes of types (**725**) and (**726**) (table 91).[884,885] The tricarbonyl complexes (**725**) also result from the action of (MeCN)$Cr(CO)_3$, (diglyme)$Mo(CO)_3$ and $(NH_3)_3W(CO)_3$ in dioxan or tetrahydrofuran.[886] The chromium complex (**725**; M = Cr) has the structure



$M(CO)_6$ | Hydrocarbon solvent, 125–145°

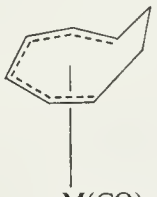
(Cyclo-octatriene)$M(CO)_3$ + (Cyclo-octatriene)$_2M(CO)_2$

(**725**) (**726**)

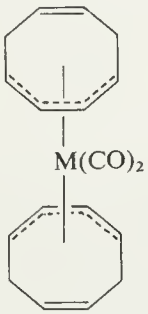
Table 91

Product	M	Yield (%)
(**725**)	Cr	13
	Mo	69
(**726**)	Mo	17
	W	16

shown,[887] but it is suggested that the dicarbonyl complexes (**726**; M = Mo, W) contain cyclo-octa-1,3,6-triene ligands.[885] (For the mass spectrum of (**725**; M = W), see ref. 433.)

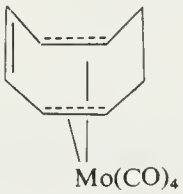


(**725**)



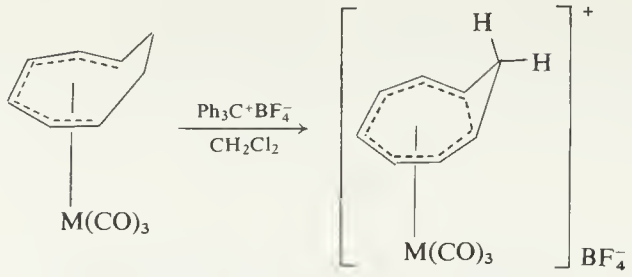
(**726**)

The molybdenum complex (**725**; M = Mo) absorbs carbon monoxide to form the product (**727**).[804]



(**727**)

With trityl tetrafluoroborate the complexes (**725**) undergo proton abstraction to give crystalline salts (**728**)[886] (table 92).

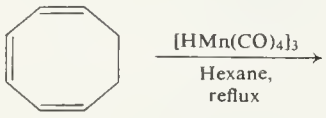


(725) (728)

Table 92

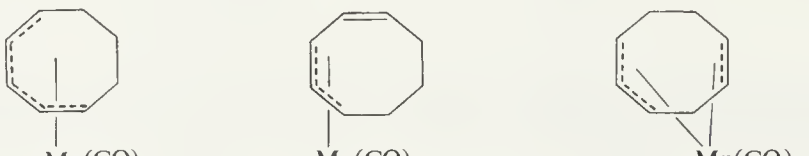
M	Yield (%)
Cr	73
Mo	72
W	62

Cyclo-octa-1,3,5-triene, on treatment with the hydridomanganese carbonyl $[HMn(CO)_4]_3$, gives cyclo-octadienyl complexes (**729**) and (**730**) in minute yield.[439]



(Cyclo-octadienyl)$Mn(CO)_3$ (**729**)
+ (Cyclo-octadienyl)$Mn(CO)_4$ (**730**)

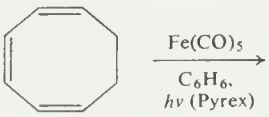
The proposed structures of these products are shown below; a third complex, isomeric with (**729**), is thought to possess structure (**731**) (possibly derived from cyclo-octa-1,3,6-triene present in the starting material).



(**729**) (**730**) (**731**)

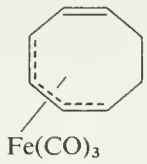
For ion-molecule reactions of $(CPD)Mn(CO)_3$ and cyclo-octa-1,3,5-triene, see ref. 422.

U.v. irradiation of cyclo-octa-1,3,5-triene in the presence of $Fe(CO)_5$[888,889] (or $Fe_2(CO)_9$[888]) yields the tricarbonyl complex (**732**) (up to 56%).



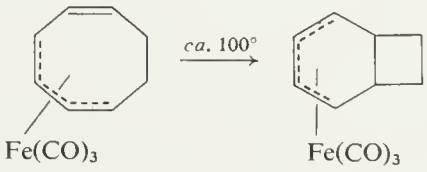
(Cyclo-octatriene)$Fe(CO)_3$ (**732**)

The structure of the complex (**732**) is formulated as shown.



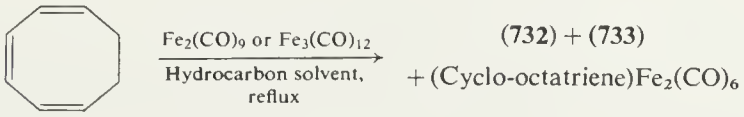
(**732**)

The cyclo-octatriene complex (**732**) is also formed thermally from iron carbonyls (up to 20% yield),[890,891] but when vigorous conditions or long reaction times are employed, the main product is the bicyclo[4.2.0]octa-2,4-diene complex (**733**).[450,885,888,891] The isomerisation (**732**) → (**733**) is essentially complete in 20–24 h at *ca.* 100°.[889]



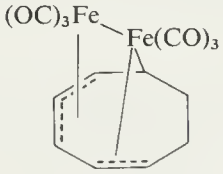
(**732**) (**733**)

(For evidence bearing on the stereochemistry of (**733**), see ref. 892.) Under certain conditions, the binuclear complex (**734**) may be produced in low yield (*ca.* 3%).[893,894]



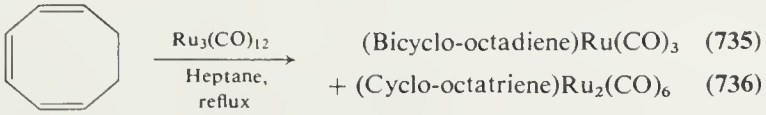
(**734**)

The structure of the (fluxional) binuclear complex (**734**) may be represented as shown[488,895] (*cf.* '*cis*'-(COT)$Ru_2(CO)_6$ (**186**) (see p. 65)); for ^{13}C n.m.r. spectral studies, see ref. 896.

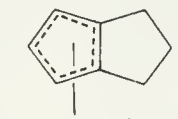


(**734**)

Cyclo-octa-1,3,5-triene reacts with $Ru_3(CO)_{12}$ to give the complexes (**735**) (38%) and (**736**) (11%), the ruthenium analogues of the iron complexes (**733**) and (**734**) respectively.[897]

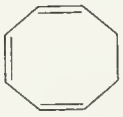


With $Ru(SiMe_3)_2(CO)_4$ or $[Ru(SiMe_3)(CO)_4]_2$, an additional product is the tetrahydropentalenyl complex (**737**) (*cf.* (**199**), p. 69); this type of product is also formed from $Ru(GeMe_3)_2(CO)_4$.[897]



$(OC)_2Ru(SiMe_3)$ (**737**)

The tricarbonyl complex (**735**) is produced (in high yield) by the displacement of cyclo-octa-1,5-diene from $(COD)Ru(CO)_3$.[492]



$\xrightarrow[C_6H_6,\ \text{reflux}]{(COD)Ru(CO)_3}$ (**735**)

Reaction of iron(III) or ruthenium(III) chlorides with isopropylmagnesium bromide in the presence of cyclo-octa-1,3,5-triene, under the influence of u.v. light, affords complexes of the type (**738**)[898] (table 93). The ruthenium com-

$\xrightarrow[Et_2O,\ h\nu]{MCl_3,\ Pr^iMgBr}$ (Cyclo-octatriene)M(bicyclo-octadiene)

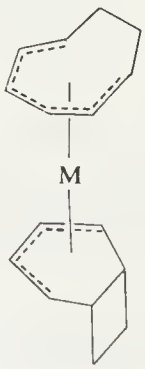
(**738**)

Table 93

M	Yield (%)
Fe	29
Ru	2.2

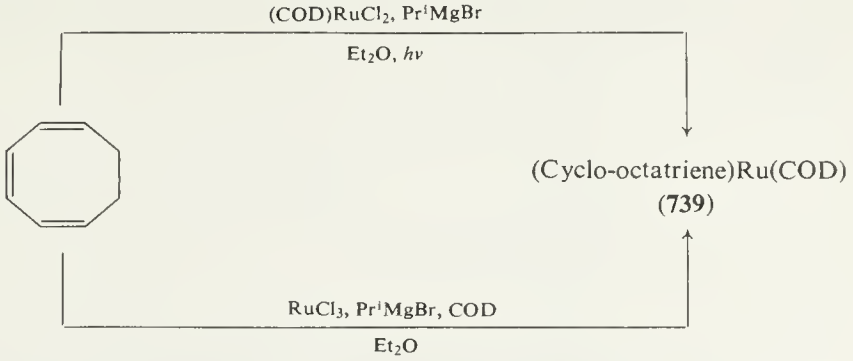
pound (**738**; M = Ru) may be obtained in higher yield (up to 19%) by using (norbornadiene)$RuCl_2$[898] or $[(benzene)RuCl_2]_n$[899] in place of $RuCl_3$.

Structure (**738**; M = Fe) for the iron complex is revealed by X-ray crystallography.[900]

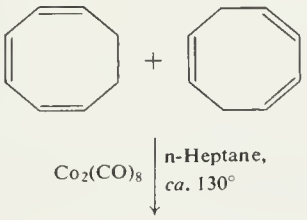


(**738**)

The 'mixed' complex (**739**) results from the use of $(COD)RuCl_2$ (yield 12%),[898] or $RuCl_3$ in the presence of cyclo-octa-1,5-diene (yield 6%).[901]

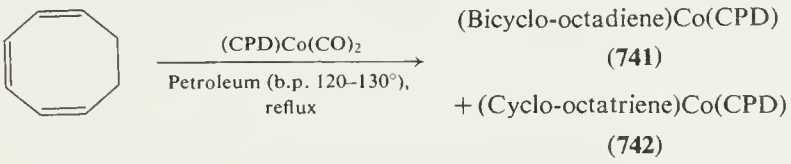


The cyclo-octatrienes (mixed isomers), on treatment with $Co_2(CO)_8$, yield the dimeric complex (**740**) (87%)[902] (the structure of the ligand is uncertain).

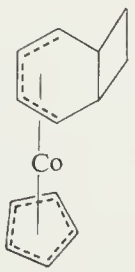


$[(Cyclo\text{-}octatriene)Co(CO)_2]_2$ (**740**)

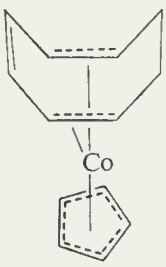
Cyclo-octa-1,3,5-triene reacts with $(CPD)Co(CO)_2$ to give the 'mixed' products (**741**) (8%) and (**742**) (11.5%).[903]



At higher temperatures only the latter (**742**) is isolated.[501,903,904] (*cf.* the iron complexes (**732**) and (**733**)). The proposed structures are as follows.



(**741**)

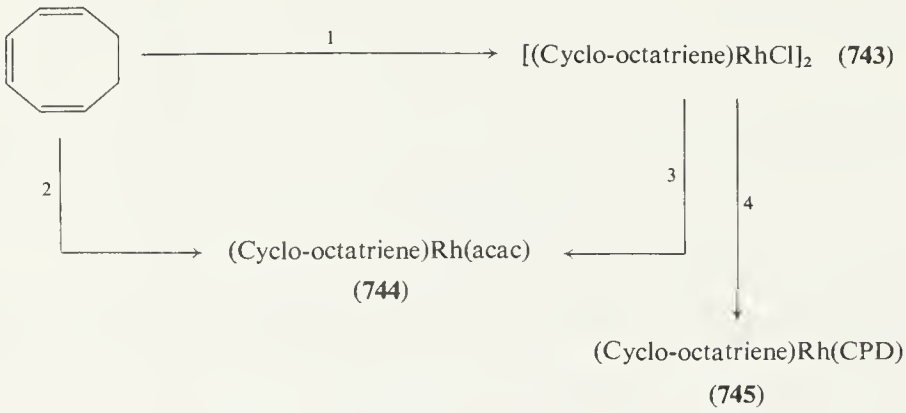


(**742**)

(For ion-molecule reactions of $(CPD)Co(CO)_2$ and cyclo-octa-1,3,5-triene, see ref. 422.)

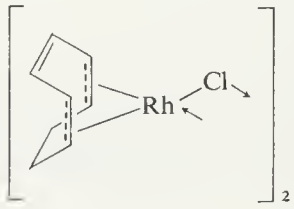
The rhodium complexes (**743**)–(**745**) may be prepared as shown in scheme 76.

Scheme 76

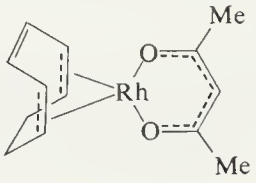


Reaction	Reagents and conditions	Yield (%)	Ref.
1	$[(CH_2{=}CH_2)_2RhCl]_2$, Et_2O, r.-t.	91	905
2	$(OC)_2Rh(acac)$, n-hexane, reflux	—	510
3	Tl(acac), CH_2Cl_2, r.-t.	51	905
4	(CPD)Tl, C_6H_6, r.-t.	87	905

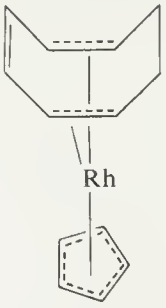
The species (**743**)–(**745**) are formulated as follows.[905]



(**743**)



(**744**)



(**745**)

The iridium complexes (**746**) and (**747**), analogues of (**743**) and (**745**) respectively, result from the following reactions.[905]

$\xrightarrow{Na_2IrCl_6}$ [(Cyclo-octatriene)IrCl]$_2$

(**746**)

$\downarrow$ (CPD)Tl, C_6H_6, r.-t.

(Cyclo-octatriene)Ir(CPD)

(**747**)

9. Substituted cyclo-octa-1,3,5-trienes, cyclo-octa-1,3,6-trienes and bicyclo[4.2.0]octa-2,4-dienes

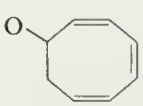
7-Bromocyclo-octa-1,3,5-triene, and 7,8-dichloro- or 7,8-dibromocyclo-octa-1,3,5-triene, result from the low-temperature addition of hydrogen bromide or halogens, respectively, to COT (see pp. 23–5); at higher temperatures equilibrium is established with the corresponding 7-substituted or 7,8-disubstituted bicyclo[4.2.0]octa-2,4-diene. The substituent halogen may of course be replaced by other groups, and the *trans*-7,8-diacetoxy-compound is available directly from COT and mercury(II) acetate (see p. 20).

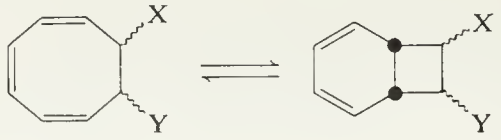
5,8-Disubstituted cyclo-octa-1,3,6-trienes are formed by free radical attack on COT (see pp. 32–3), and by reaction of COT^{2-} with aldehydes or ketones (see pp. 178–80). Dialkyl- and disilyl-derivatives of both cyclo-octa-1,3,5-triene and cyclo-octa-1,3,6-triene are also available from COT^{2-} (see pp. 173–4).

The position of the cyclo-octa-1,3,5-triene $\rightleftharpoons$ bicyclo[4.2.0]octa-2,4-diene equilibrium for various monosubstituted (**748**) and disubstituted (**749**) derivatives is shown in tables **94** and 95. (For energy-barriers to ring-inversion of (**749**; X = Y = D, Br), see refs. 231, 281, 564.)

(**748**)

Table **94**

X	Proportion of bicyclic form (%)	Temp. (°C)	Ref.
Br	30, (35)	30–35, (60)	233, 906, (136)
OAc	75, (53)	30–35, (60)	906, (136)
OH	90	30–35	906
	90	30–35	906



(749)

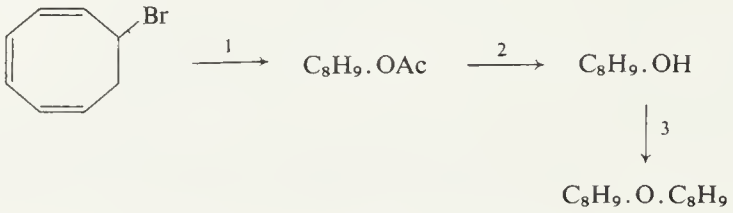
Table 95

X	Y	Relative stereochemistry of substituent groups	Proportion of bicyclic form (%)	Temp. (°C)	Ref.
Me	Me	*cis*	81	60	136
Me	Me	*trans*	94	60	136
OAc	OAc	*trans*	95	60	136
Br	Br	*trans*	100	20	231
Cl	Cl	*cis*	80	60	136
Cl	Cl	*trans*	99	−30	136

7-Substituted cyclo-octa-1,3,5-trienes

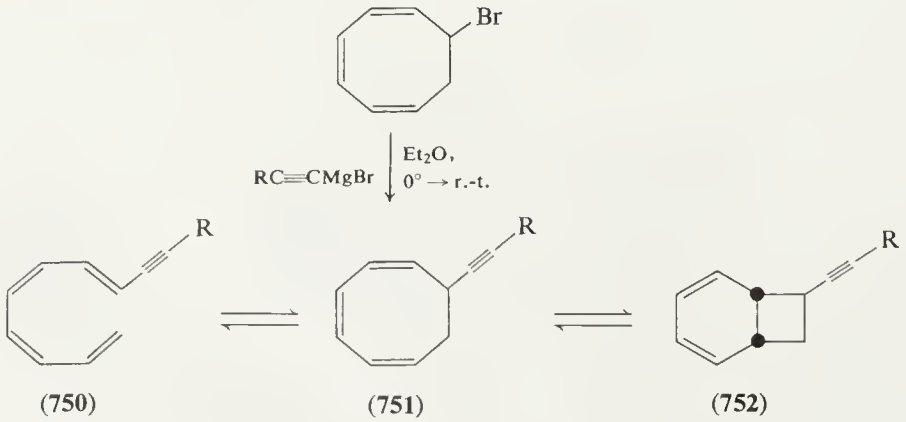
Some functional group transformations in this series are outlined in scheme 77.

Scheme 77



Reaction	Reagents and conditions	Yield (%)	Ref.
1	NaOAc, HOAc, 10–20°	47	906
2	$LiAlH_4$, Et_2O, −34° → 10°	54	906
3	50–70°/0.8 mm	—	906

Reaction of 7-bromocyclo-octa-1,3,5-triene with acetylenic Grignard reagents results in a valence tautomeric mixture of the open-chain, monocyclic and bicyclic derivatives, (**750**), (**751**) and (**752**)[907] (table 96).

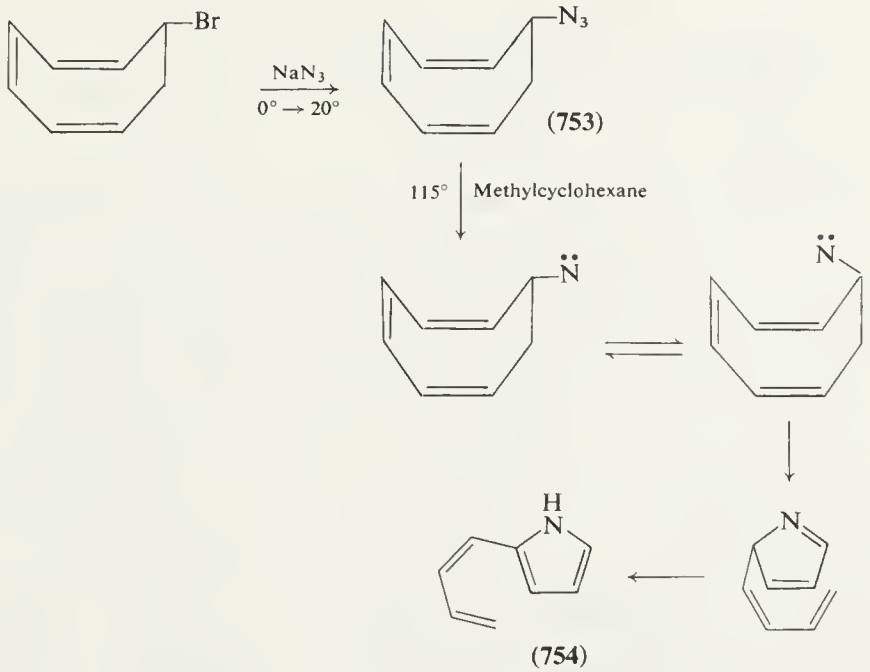


(750) (751) (752)

Table 96

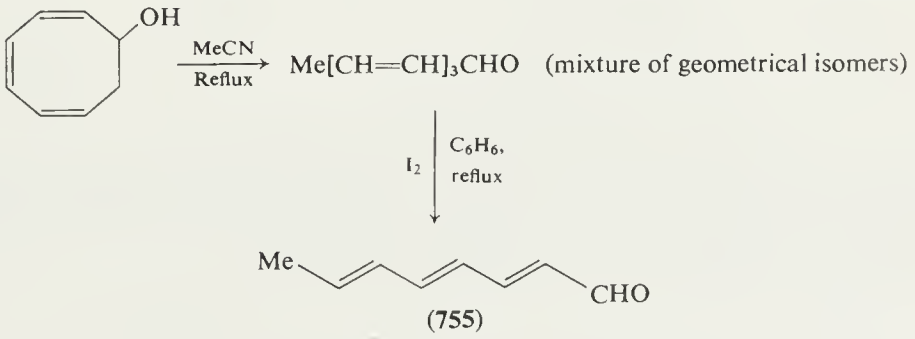
R	Total yield (%)
Bu^t	45
Ph	28

7-Bromocyclo-octa-1,3,5-triene (see p. 25) is converted by the action of sodium azide into the azido-compound (**753**) (55%), thermolysis of which affords the pyrrolylbutadiene (**754**) (43%).[233]



(754)

7-Hydroxycyclo-octa-1,3,5-triene (see p. 257) undergoes ring-opening at *ca.* 80° to give an acyclic triene-aldehyde (mixture of geometrical isomers) (87%), which on treatment with iodine is converted into the all-*E*-compound (**755**).[906]



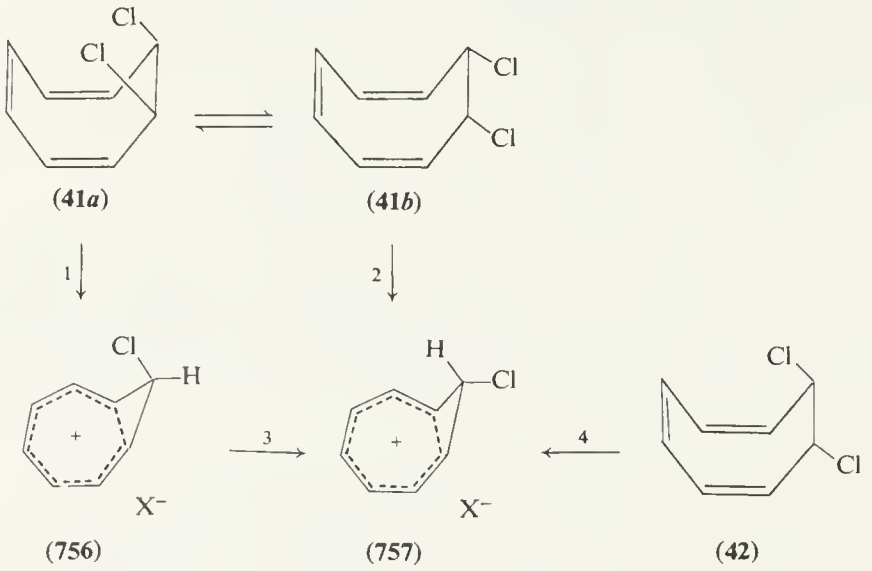
(755)

7,8-Disubstituted cyclo-octa-1,3,5-trienes

Thermal dimerisation of the dimethyl stereoisomers (**503**) and (**504**) (see p. 173) occurs *via* their respective valence isomers (see p. 254).

The generation of *endo*- and *exo*-8-chlorohomotropylium salts, (**756**) and (**757**) respectively, from the two isomers (**41**) and (**42**) of 7,8-dichlorocyclo-octa-1,3,5-triene (see p. 23), by the action of proton or Lewis acids, is summarised in scheme 78. For the mechanisms of these reactions, see ref. 909. The salt (**757**; X = $SbCl_6^-$) may be isolated as a crystalline solid.[908]

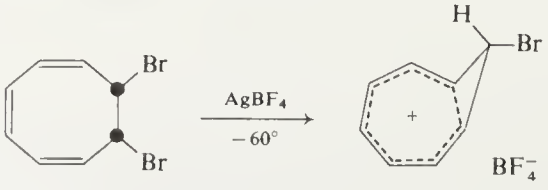
Scheme 78



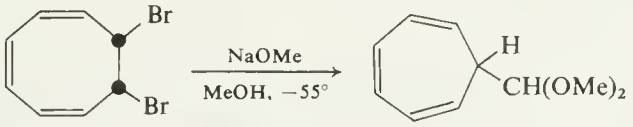
Reaction	Reagents and conditions	X	Ref.
1	FSO_2OH, 0°	FSO_2O^-	908
	$SbCl_5$, $CHCl_3$, −70°	$SbCl_6^-$	909
2	$AgBF_4$, $ClCH_2CH_2Cl$, −30°[a]	BF_4^-	909
	$SnCl_4$, CH_2Cl_2, −15°	$SnCl_5^-$	908
	$AgSbF_6$, SO_2 or CD_3NO_2, −15°	SbF_6^-	908
	$SbCl_5$ (SO_2 or CH_2Cl_2, −15° or $CHCl_3$, −70°)	$SbCl_6^-$	908 909
3	30°	FSO_2O^-	908
4	FSO_2OH, −20°	FSO_2O^-	908
	$SbCl_5$ (CH_2Cl_2, −20° or SO_2, −40° or $CHCl_3$, −70°)	$SbCl_6^-$	908 908 909

[a] $AgBF_4$ added to (**41***a*) ⇌ (**41***b*).

Treatment of the dibromo-derivative (**758**) with silver tetrafluoroborate results in the *exo*-8-bromohomotropylium salt (**759**).[230]



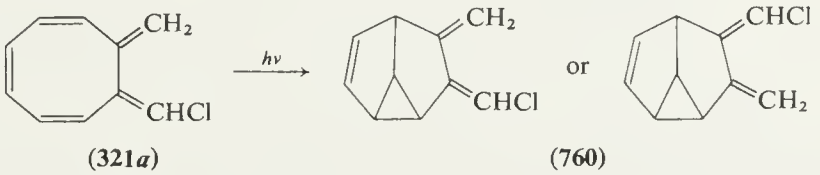
The low-temperature dehydrohalogenation of 7,8-dihalocyclo-octa-1,3,5-trienes with potassium t-butoxide in dichloromethane, which provides an excellent route to chloro- and bromocyclo-octatetraene, has already been described (see p. 83). With the dibromide (**758**) and sodium methoxide in methanol the reaction takes a different course, the main product being the cycloheptatriene derivative (**29**) (76%)[540] (see p. 20).



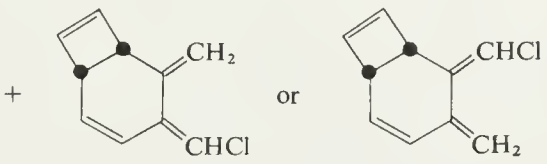
(**758**) (**29**)

7,8-Dimethylenecyclo-octa-1,3,5-trienes are available by dehydrogenation of suitable 1,2-di(halomethyl)cyclo-octatetraenes (see p. 117).

The use of 7,8-dimethylenecyclo-octa-1,3,5-trienes for the synthesis of annulated COTs has already been mentioned (see pp. 124–7). U.v. irradiation of the chloro-derivative (**321*a***) (see p. 117) gives rise to a mixture of the products (**760**) (*ca.* 10%) and (**761**) (*ca.* 3%).[910]



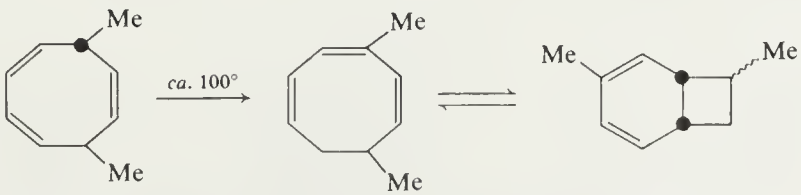
(**321*a***) (**760**)



(**761**)

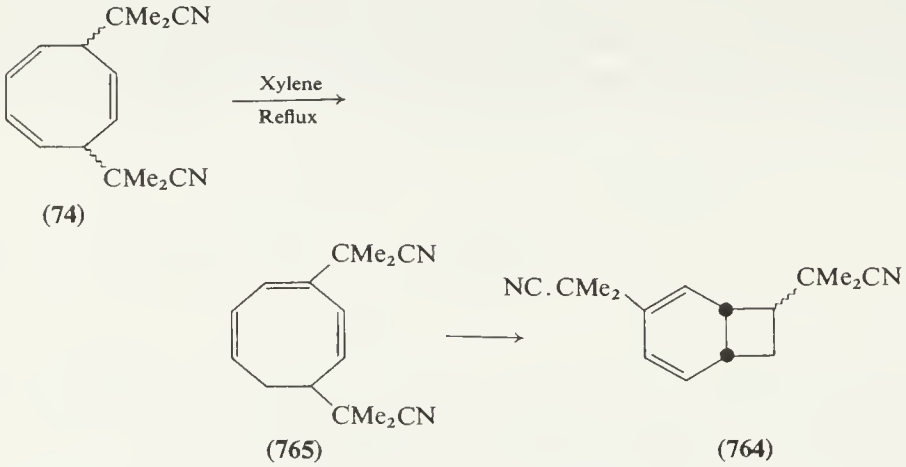
5,8-Disubstituted cyclo-octa-1,3,6-trienes

At *ca.* 100° the dimethyl-derivative (**505**) (see p. 173) undergoes a [1,5]-hydrogen shift to form the 1,3,5-triene (**762**), which then equilibrates with the bicyclo-[4.2.0]octadiene (**763**) (this fragments at *ca.* 225° to give toluene).[379]

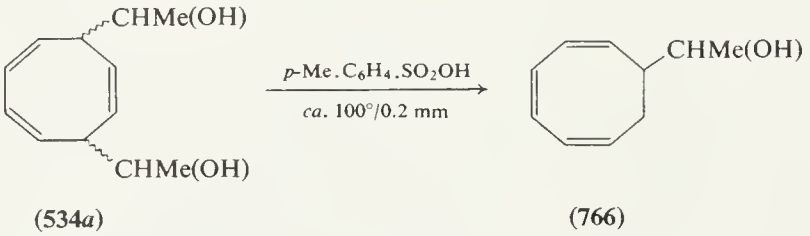


(**505**) (**762**) (**763**)

Similarly, compound (**74**) (see p. 33) rearranges in refluxing xylene to give the bicyclic product (**764**) (82%),[289] presumably *via* (**765**).



Treatment of the diol (**534*a***) (containing *ca.* 25% of the bicyclic isomer (**535*a***)) (see p. 180) with acid results in the product (**766**) (48%); a *retro*-aldol type condensation is apparently involved.[725]



Tertiary diols (**534**) (see p. 180), however, yield the tricyclic ethers (**767**)[725] (*cf.* refs. 739, 754) (table 97).

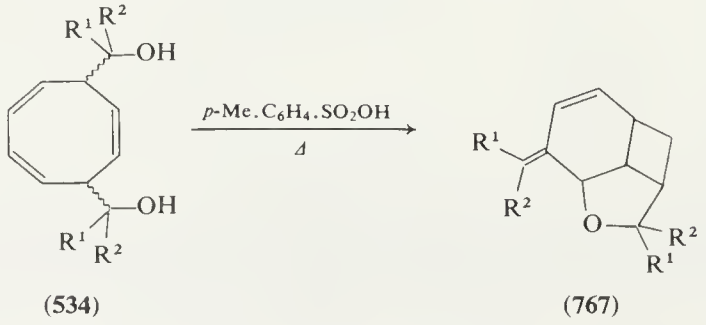
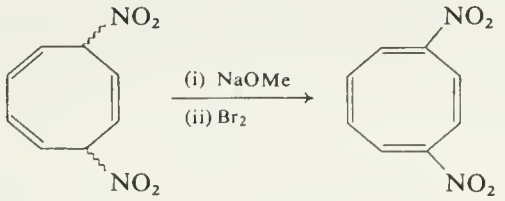


Table 97

R^1	R^2	Reaction conditions	Yield (%)
Me[a]	Me	Δ/1 mm	28
Ph	Ph	C_6H_6, reflux	45
Fluorenyl		C_6H_6, reflux	44

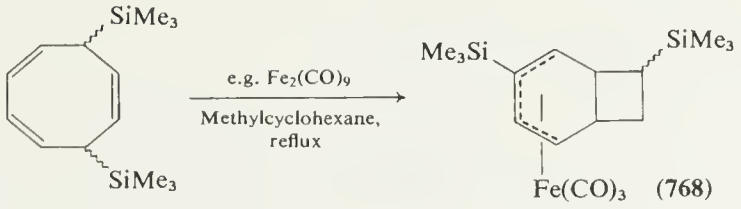
[a] Starting material contained 62% of (**535*c***).

The 5,8-dinitro-compound (**75**) (see p. 33), on treatment with sodium methoxide followed by bromine, affords 1,4-dinitrocyclo-octatetraene.[615]

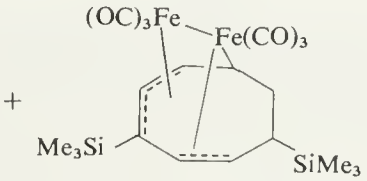


(**75**)

The 5,8-bis(trimethylsilyl)-compound (**506**) (see p. 174) reacts with $Fe_2(CO)_9$ (or $Fe_3(CO)_{12}$) to form the complexes (**768**) (8%) and (**769**) (0.5%).[911]

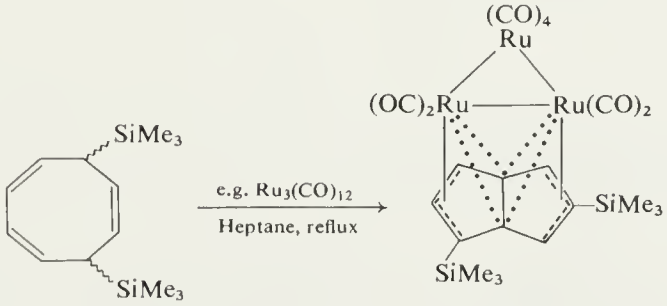


(**506**) (**768**)



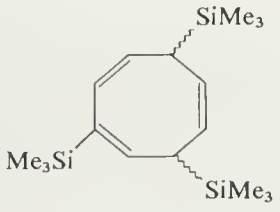
(**769**)

With $Ru_3(CO)_{12}$ or $[Ru(SiMe_3)(CO)_4]_2$, the complex (**770**) (6%) is formed.[912]



(**506**) (**770**)

A similar product is formed (15%) from the trisubstituted starting material (**771**).[912]

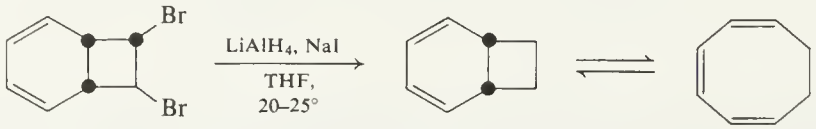


(**771**)

7,8-Disubstituted bicyclo[4.2.0]octa-2,4-dienes

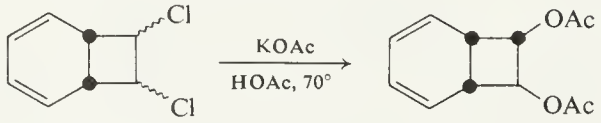
For thermal dimerisation, see p. 254.

In the dibromo-compound (**44**) (p. 24), replacement of halogen by hydrogen occurs with lithium aluminium hydride–sodium iodide, giving cyclo-octa-1,3,5-triene (32%).[260]



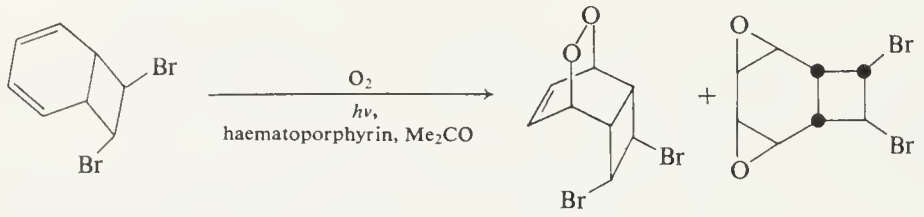
(**44**)

Reaction of the dichloride (**38**/**39**) (see p. 23) with potassium acetate gives the *trans*-diacetoxy-derivative (**28**) (39%).[11]



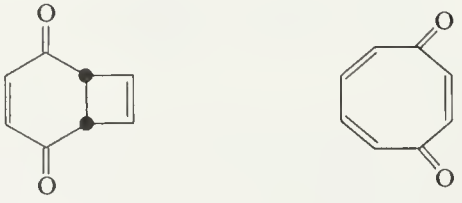
(**38**/**39**) (**28**)

Sensitised photoaddition of oxygen to the dibromide (**44**) leads to the peroxy-bridged product (**772**) (78% from COT), together with a diepoxide (**773**) (3.5%).[913]



(**44**) (**772**) (**773**)

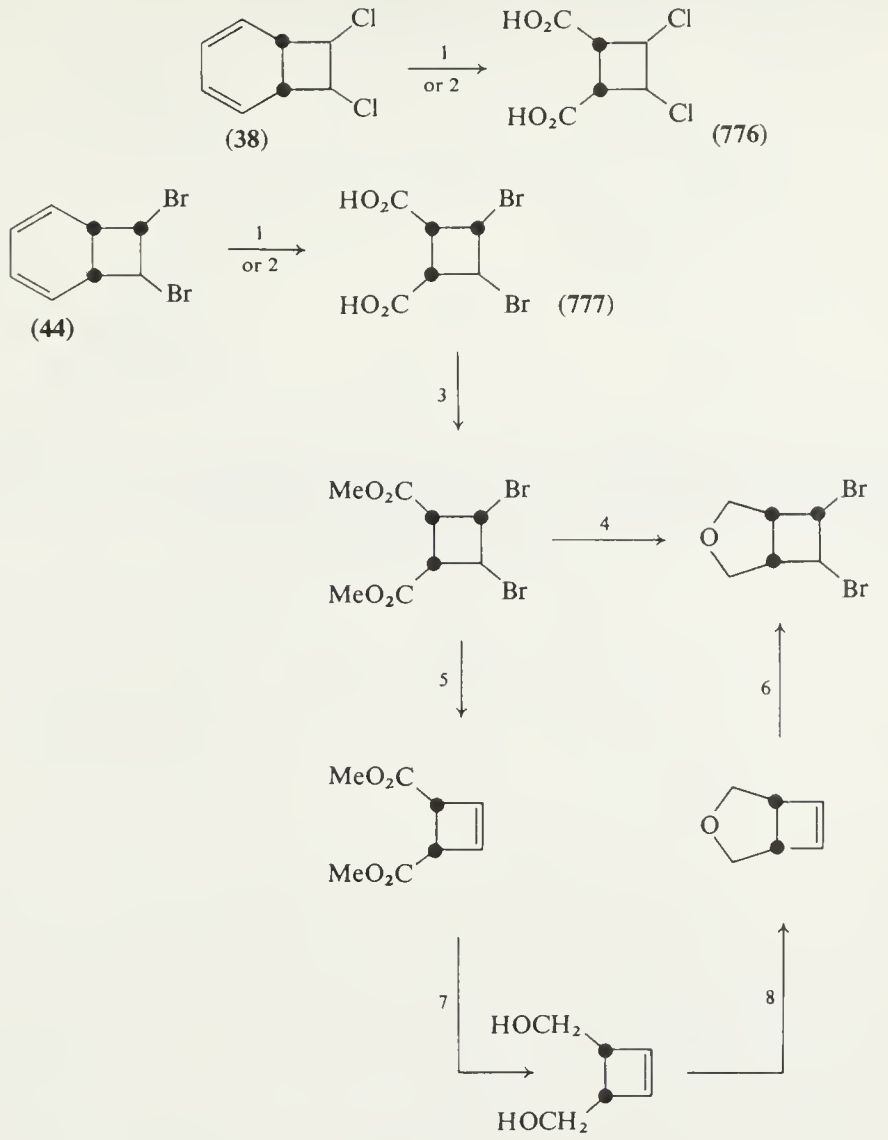
The peroxide (**772**) is a source of the bicyclic diendione (**774**)[913] and of cyclo-octa-2,5,7-trien-1,4-dione (**775**).[914]



(**774**) (**775**)

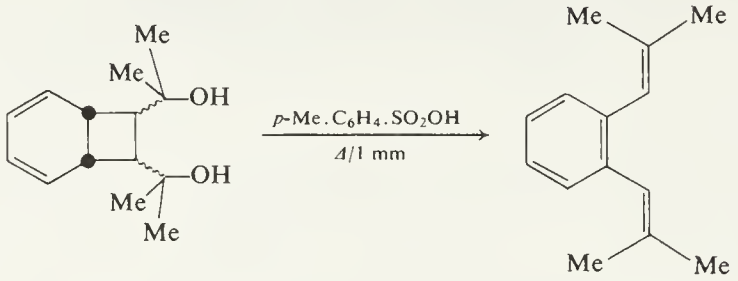
Oxidative cleavage of the cyclohexadiene ring in the *cis*-dichloro-compound (**38**) affords the dichlorocyclobutanedicarboxylic acid (**776**),[553] of proved stereochemistry.[915] Analogous oxidation of the dibromide (**44**) results in the *trans*-dibromo-derivative (**777**),[915,916] which provides a source of 3,4-disubstituted cyclobutenes (scheme 79).

Scheme 79



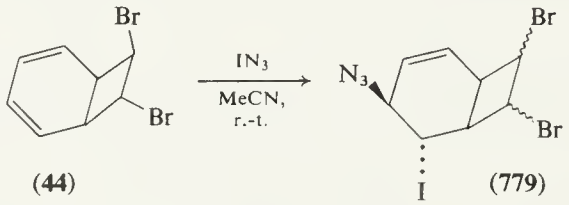
Reaction	Reagents and conditions	Yield (%)	Ref.
1	$KMnO_4$, Me_2CO(aq.), 3–5° then r.-t.	(Dichloride) 35 (Dibromide) (27), 43	553 (916), 917
2	O_3, EtOAc, −60°	(Dichloride) 35 (Dibromide) 67	553 916
3	CH_2N_2	97	916
4	(i) $LiAlH_4$, Et_2O (ii) Acid hydrolysis	58	918
5	Zn–Cu, MeOH, 75°	76	916
6	Br_2, CCl_4	70	918
7	(i) $LiAlH_4$ (ii) Na_2SO_4(aq.)	84	918
8	*p*-Me.C_6H_4.SO_2Cl, pyridine	—	918

Acid-catalysed dehydration of the diol (**535***c*) containing 38% of (**534***c*) (see p. 180) yields the 1,2-divinylbenzene (**778**) (36%).[725]

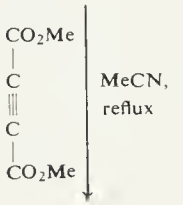


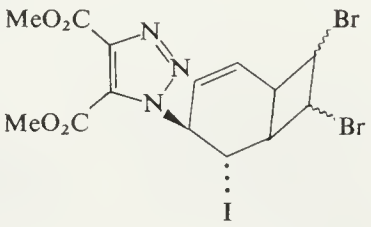
(**535***c*) (**778**)

Iodine azide (from sodium azide and iodine monochloride in acetonitrile at −20°) reacts with the dibromide (**44**) to afford the product (**779**), characterised as the acetylenedicarboxylic ester-adduct (**780**) (50%).[919]



(**44**) (**779**)



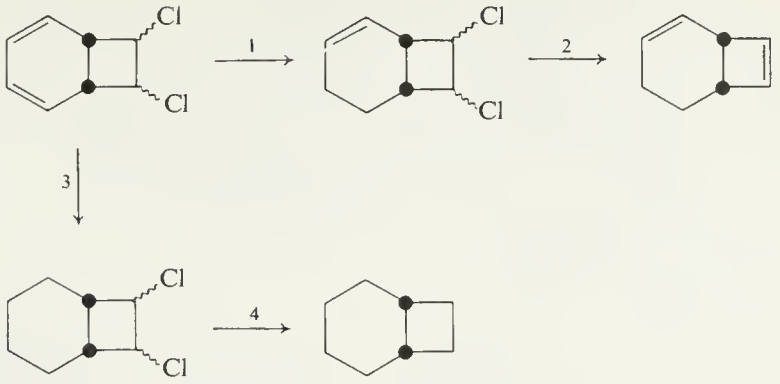


(**780**)

Schemes 80 and 81 show the products obtained on catalytic hydrogenation and subsequent dehalogenation of 7,8-dihalobicyclo[4.2.0]octa-2,4-dienes.

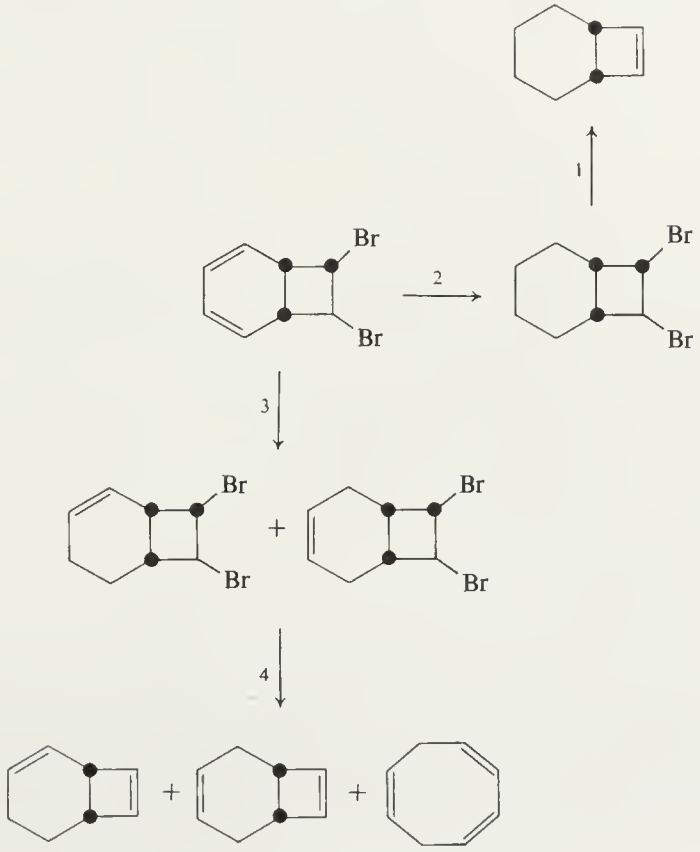
Catalytic hydrogenation of the diacetoxy-compound (**28**) affords the tetrahydro-derivative (**781**) (92%), which on acid-catalysed methanolysis gives the diol (**782**) (71%).[11,206]

Scheme 80



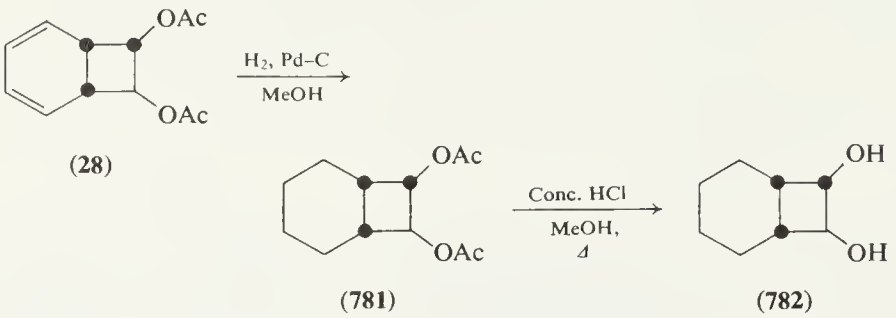
Reaction	Reagents and conditions	Yield (%)	Ref.
1	H_2, Pd–C, MeOH, EtOAc	73	(11), 920
2	Na, NH_3(liq.), Et_2O	83	920
3	H_2, Pd–$CaCO_3$, MeOH, −5° to 0°	—	11
	or H_2, Raney Ni, THF, 150 atm	—	11
4	H_2, Raney Ni, KOH(aq.), MeOH, 100°, 200 atm	75	11

Scheme 81

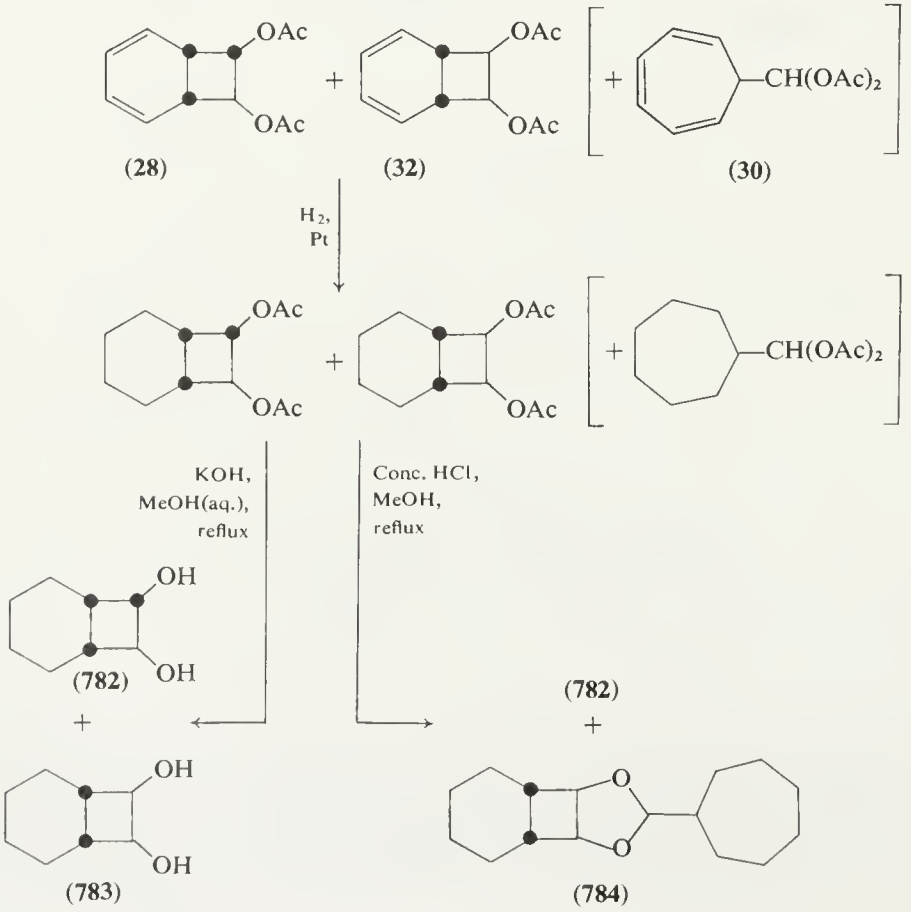


Reaction	Reagents and conditions	Yield (%)	Ref.
1	Mg	—	921
2	H_2, Pd–$CaCO_3$ or Pd–$BaSO_4$, MeOH, *ca.* 0°	—	11, 921
3	H_2, Pd	—	853
4[a]	Zn, EtOH	—	853

[a] The reaction products were subjected to g.l.c. at 100°.

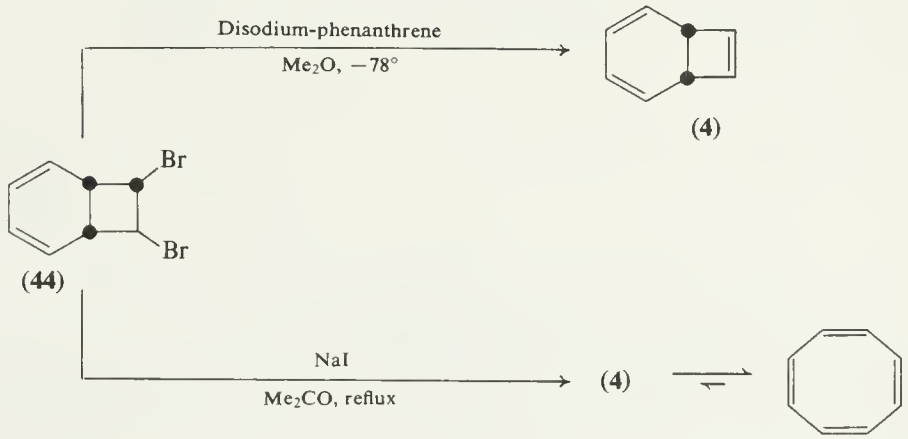


The mixture of diacetoxy-derivatives, presumably (**28**) and (**32**), obtained by electrolysis of COT in acetic acid using a carbon anode (see p. 21), may be hydrogenated to give a product which on alkaline hydrolysis yields the diols

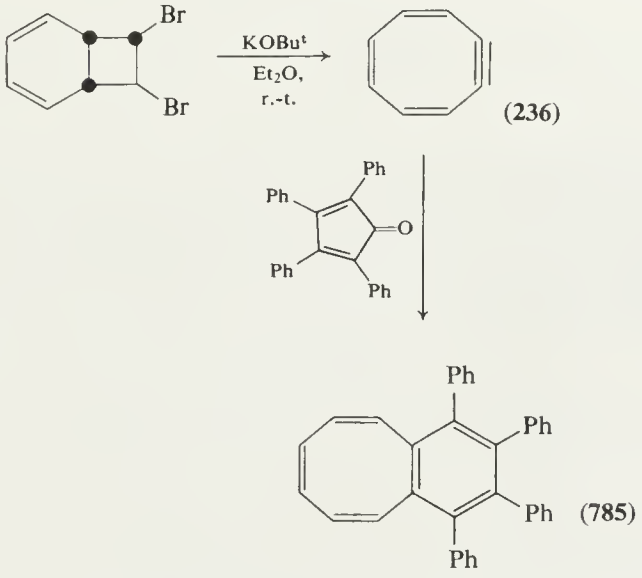


(**782**) and (**783**) (29 % and 20 % respectively); in acid, however, a mixture of the *trans*-diol (**782**) (30 %) and the acetal (**784**) (62 %) is obtained.[922]

The low-temperature debromination of the dibromide (**44**) with disodium-phenanthrene generates bicyclo[4.2.0]octa-2,4,7-triene (**4**) (half-life 14 min at 0°);[32] with sodium iodide in refluxing acetone the product is COT.[39]

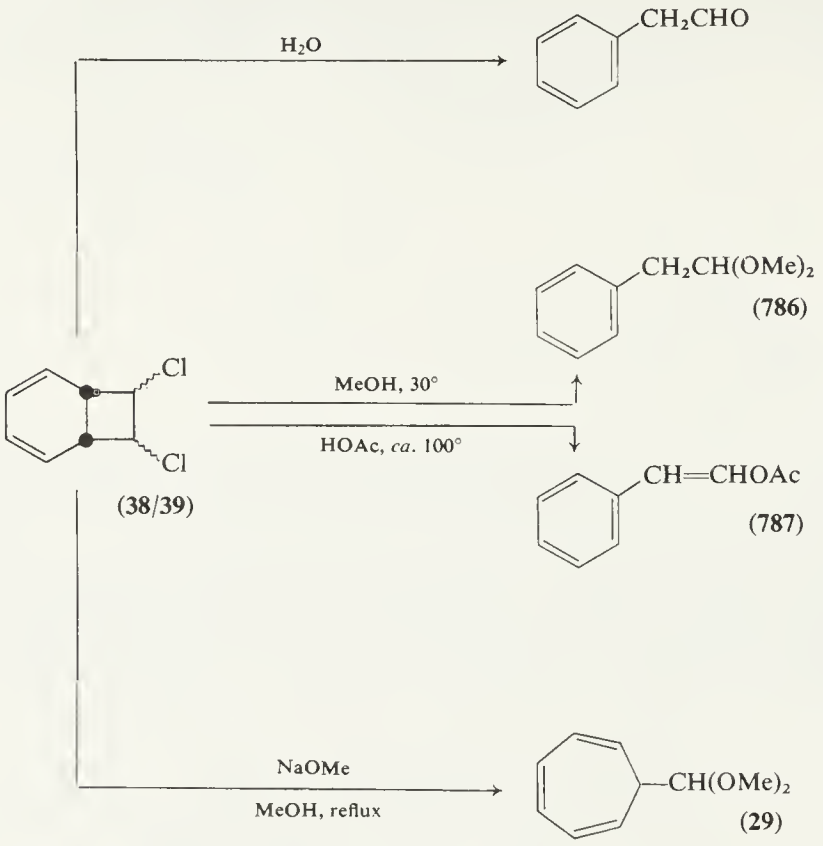


Dehydrobromination with potassium t-butoxide affords 1,2-didehydro-cyclo-octatetraene (**236**), which may be trapped with tetracyclone to give the adduct (**785**) (21 %)[624] (this process is not as efficient as with bromocyclo-octatetraene; see pp. 83–4, 164).



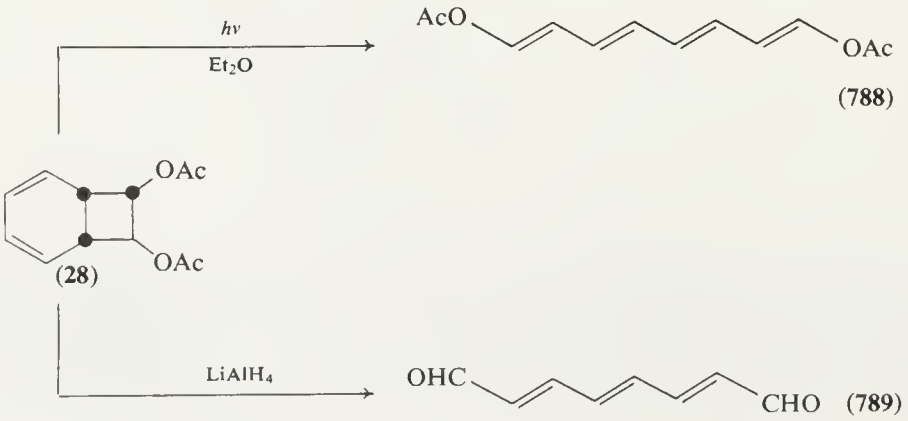
In general the 7,8-dihalobicyclo[4.2.0]octa-2,4-dienes are very susceptible to rearrangement. Hydrolysis of the dichloro-compound (**38**/**39**) (in water) furnishes phenylacetaldehyde,[923] methanolysis the dimethyl acetal (**786**),[923] and acetolysis the enol acetate (**787**);[923] in the presence of sodium methoxide, however, treatment with methanol gives the cycloheptatrienal derivative

(**29**).[206] (For possible rearrangement mechanisms, see ref. 923.) The diacetoxy-compound (**28**) also rearranges on treatment with aqueous acid, giving phenylacetaldehyde.[206]

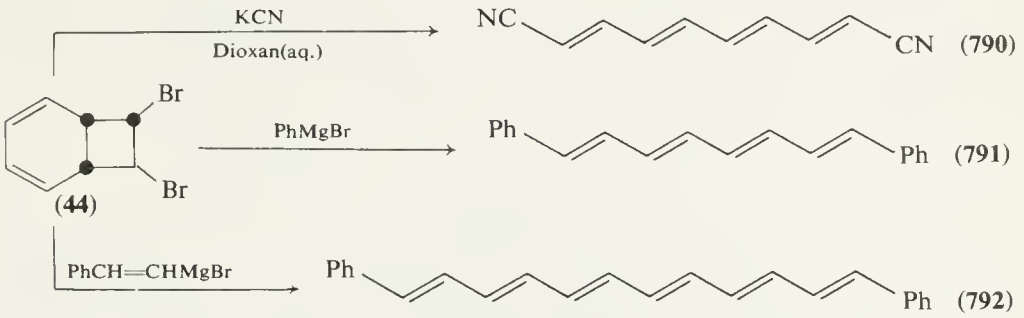


In addition to these rearrangements, a number of ring-cleavage reactions, resulting in acyclic polyenes, are known.

U.v. irradiation of the diacetoxy-compound (**28**) yields the diacetoxy-tetraene (**788**),[924] and reaction with lithium aluminium hydride gives the triene-dialdehyde (**789**) (50–60%).[925]



With potassium cyanide, the dibromide (**44**) is converted into the tetraene-dinitrile (**790**) (27%),[926] and phenylmagnesium bromide affords the tetraene (**791**);[927] extension of the polyene chain can be effected by the use of styryl-magnesium bromide, which gives the hexaene (**792**)[927] (see also below). Treatment with acetylenic Grignard reagents yields tetraene-diynes (**793**) in which the



two central double bonds generally have the *Z*-configuration (table 98); the proposed mechanism involves an initial coupling reaction of the monocyclic valence tautomer (**794**), and subsequent conrotatory ring-opening of the

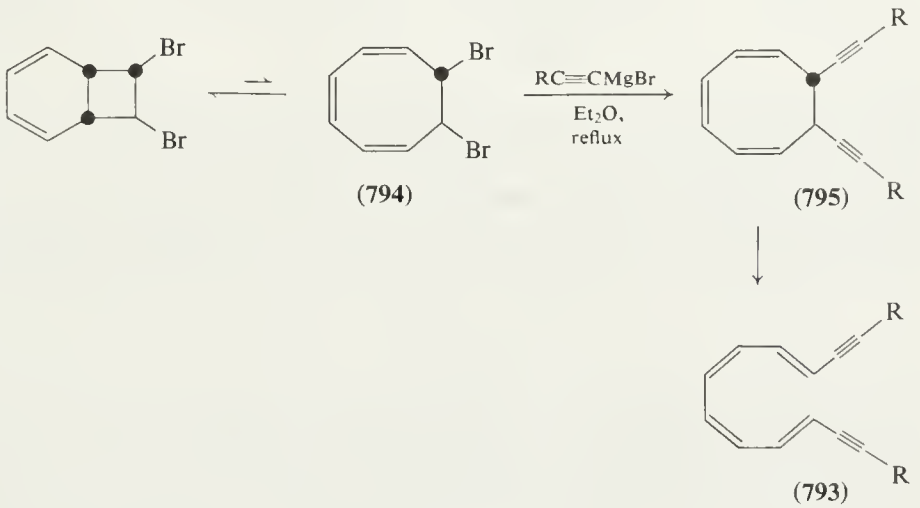


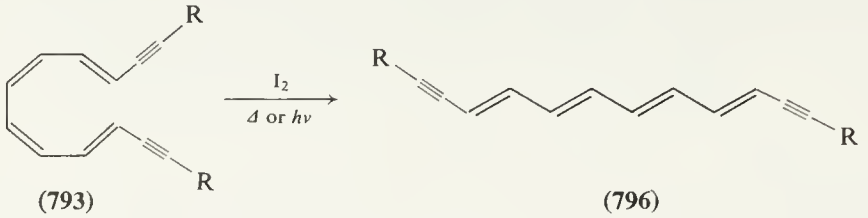
Table 98

R	Yield (%)
H[a]	—
Me	16
Bu^t	30[b]
CMe=CH$_2$	24
Ph	50
p-Me.C$_6$H$_4$	53
2,4,6-Me$_3$.C$_6$H$_2$	30
p-Br.C$_6$H$_4$	57

[a] Reaction in THF at r.-t.; product characterised by spectra only.

[b] The isolated product was the all-*E*-compound.

resulting *trans*-7,8-disubstituted cyclo-octa-1,3,5-triene (**795**).[928] The *E,Z,Z,E*-products (**793**) are converted into the all-*E*-isomers (**796**) by the action of heat or light in the presence of iodine[928] (table 99). Partial hydrogenation



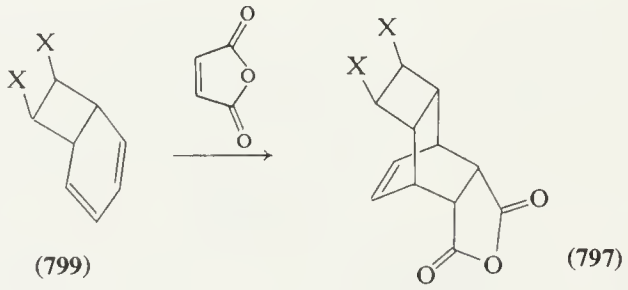
(**793**) (**796**)

Table 99

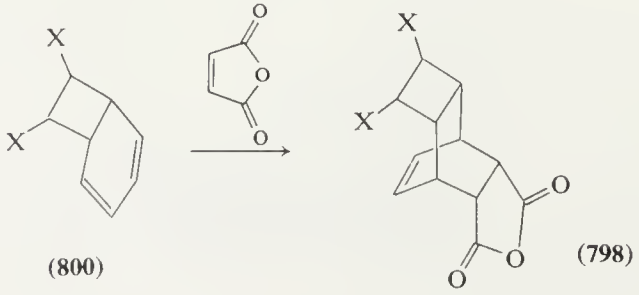
R	Reaction conditions	Yield (%)
Me	Light petroleum (b.p. 60–80°), C_6H_6, Me_2CO, *hν*	50
$CMe{=}CH_2$	C_6H_6, *hν*	10
p-Me.C_6H_4	C_6H_6, *hν*	38
Ph	C_6H_6, *hν*	75
2,4,6-Me_3.C_6H_2	C_6H_6, *hν*	20
	Xylene, reflux	10–20
p-Br.C_6H_4	C_6H_6, *hν*	85

(Lindlar catalyst) of these tetraene-diynes furnishes hexaenes;[927] complete hydrogenation (Pd–$CaCO_3$) gives long-chain alkanes.[928]

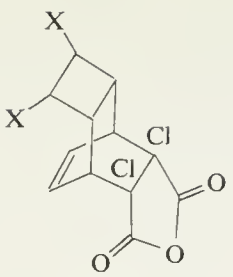
With e.g. maleic anhydride, stereoisomeric [4 + 2] cycloadducts (**797**) and (**798**) are produced from the *cis*- and *trans*-compounds (**799**) and (**800**) respectively; similar reactions with other dienophiles lead to structures (**801**)–(**808**)



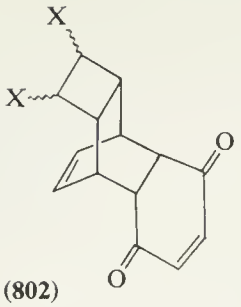
(**799**) (**797**)



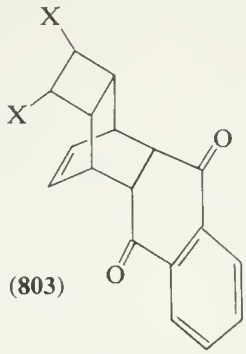
(**800**) (**798**)



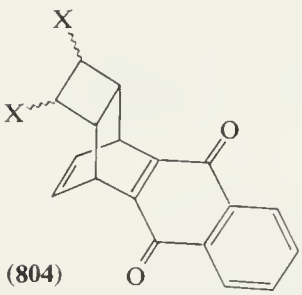
(801)



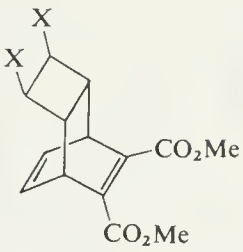
(802)



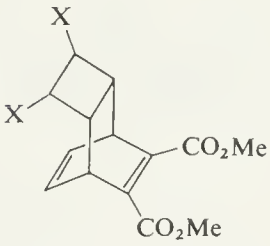
(803)



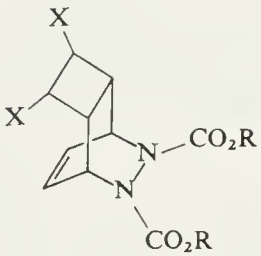
(804)



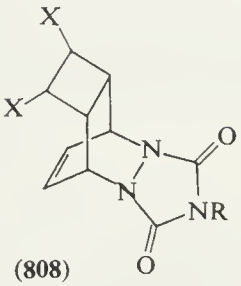
(805)



(806)



(807)

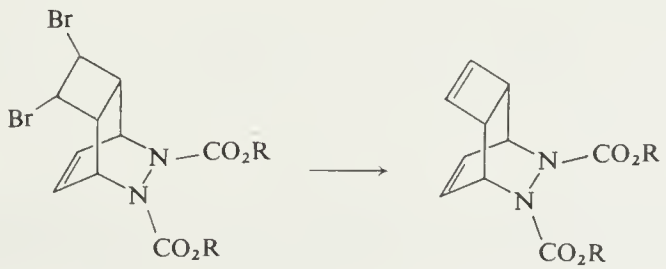


(808)

a: X = Cl
b: X = Br
c: X = OAc

(table 100). For the adduct of (**799**/**800**; X = Cl) and acrylonitrile, see ref. 39. For the adduct of (**800**; X = CO_2Me) (obtained from the dimethyl ester of (**532**) (see p. 179)) and *N*-phenylmaleimide, see ref. 756. For the adducts of the annulated derivatives (**111**) (see p. 40) with maleic anhydride and dimethyl acetylenedicarboxylate, see ref. 331.

Debromination of the adducts (**807***b*) and (**808***b*) leads to the products (**809**) and (**125**) (see p. 46) respectively (tables 101 and 102).



(807*b*) (809)

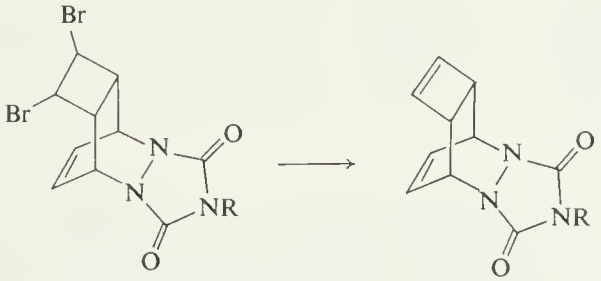
Table 100

X	Stereochemistry	Dienophile	Conditions	Product	Yield (%)	Ref.
Cl	*cis* + *trans*	Maleic anhydride	C_6H_6, reflux	(797*a*) + (798*a*)[a]	37 + 40	11
Cl	*cis* + *trans*	*p*-Benzoquinone	C_6H_6, reflux	(802*a*)[b]	41	11
Cl	*cis* + *trans*	1,4-Naphthoquinone	C_6H_6, reflux	(803*a*)[c]	65	11
Cl	*cis* + *trans*	Dimethyl acetylenedicarboxylate	C_6H_6, reflux	(806*a*)	51	11
			CCl_4, reflux	(805*a*) + (806*a*)[d]	75 (total)	228, (929)
Br	*trans*	Maleic anhydride	C_6H_6, reflux	(798*b*)	93	11
			CH_2Cl_2, r.-t.		88	11
Br	*trans*	Dichloromaleic anhydride	Toluene, reflux	(801*b*)	—	372
Br	*trans*	Dimethyl acetylenedicarboxylate	C_6H_6, reflux	(806*b*)	55	11
Br	*trans*	Dimethyl azodicarboxylate	C_6H_6, 70°	(807*b*; R = Me)	86	40
Br	*trans*	Diethyl azodicarboxylate	C_6H_6, 70°	(807*b*; R = Et)	94	40
Br	*trans*	Dibenzyl azodicarboxylate	C_6H_6, 70°	(807*b*; R = CH_2Ph)	95	40
Br	*trans*	4-Methyl-1,2,4-triazoline-2,5-dione	Me_2CO, −70° to −50° → r.-t.	(808*b*; R = Me)	81	930
Br	*trans*	4-Phenyl-1,2,4-triazoline-3,5-dione	CH_2Cl_2, −78° → r.-t.	(808*b*; R = Ph)	87	583, (931)
OAc	*trans*	Maleic anhydride	C_6H_6, reflux	(798*c*)	100	11
OAc	*trans*	1,4-Naphthoquinone	C_6H_6, reflux	(803*c*)	84	11
OAc	*trans*	Dimethyl acetylenedicarboxylate	C_6H_6, reflux	(806*c*)	52	11, (207)

[a] Both isomers are isolable, but it is not certain which is which.
[b] The stereochemistry of the chlorine atoms is not certain.
[c] The isolated product is the dehydro-derivative (**804**) (stereochemistry of the chlorine atoms uncertain).
[d] The two isomers are separable.

Table 101 (see p. 249)

R	Reagents and conditions	Yield (%)	Ref.
Et	Zn–Cu, THF, reflux	68	40
	Li–Hg, THF, r.-t.	72	40
	Zn, DMF, reflux	92	932

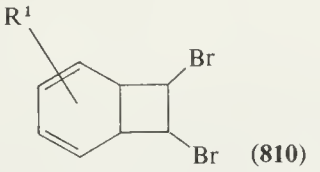


(**808***b*) (**125**)

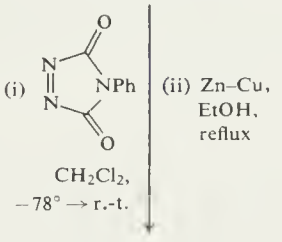
Table 102

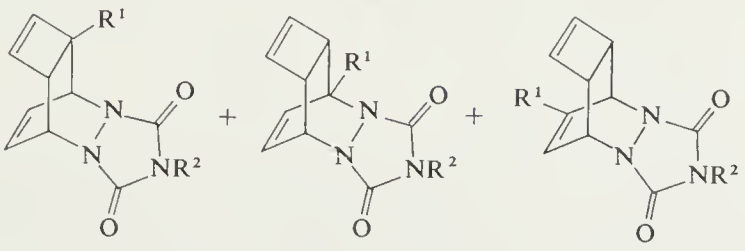
R	Reagents and conditions	Yield (%)	Ref.
Me	Zn–Cu, EtOH, reflux	77	930
Ph	Zn–Cu, DMF, reflux	99	569, (931)

The bicyclic dibromides (**810**) derived from monosubstituted COTs react with *N*-phenyltriazolinedione to give adducts which may be debrominated to afford the products (**288**)–(**290**)[569] (table 103). (For the photochemical trans-



(**810**) (Stereochemistry unspecified)





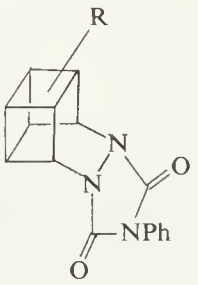
(**288**) (**289**) (**290**)

R^2 = Ph

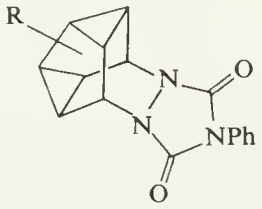
Table 103

	Yield (%)		
R^1	(**288**)	(**289**)	(**290**)
Me	30	—	—
Ph	6	—	9
CH_2OMe	23	32	—
CH_2OAc	10	35	10
CN	12	9	49
CO_2Me	—	31	—
F	90	—	—
Br	—	—	28

formation of compounds (**288**)–(**290**) into the 9,10-diazabasketanes (**811**), which by silver-catalysed rearrangement yield 9,10-diazasnoutanes (**812**), see pp. 355–6; subsequent conversion into monosubstituted semibullvalenes is described in ref. 716.)

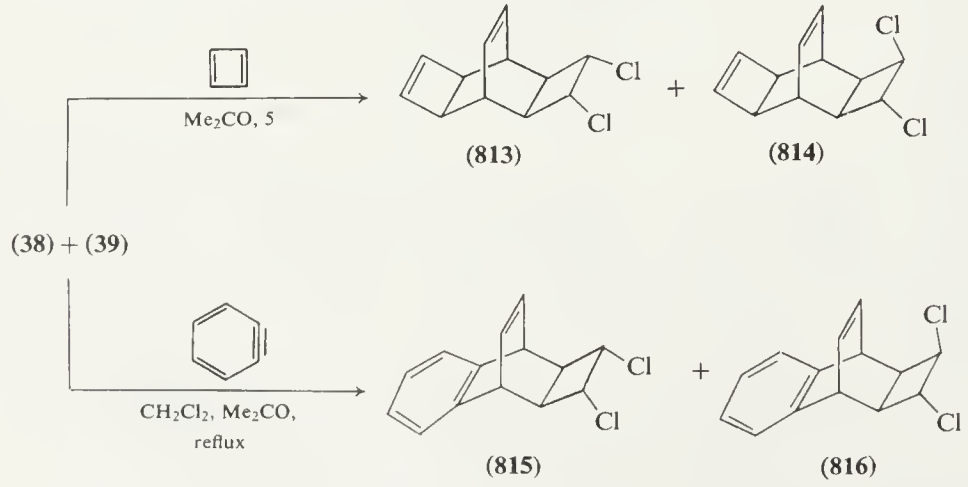


(**811**)

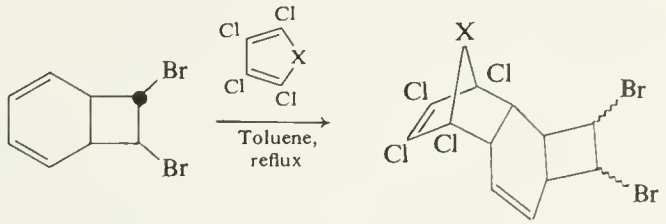


(**812**)

Cyclobutadiene (generated from its iron tricarbonyl complex by means of cerium(IV) ions) reacts with a mixture of the *cis*- and *trans*-dichloro-compounds (**38**) and (**39**) to give a mixture of the adducts (**813**) and (**814**) (52%).[933] (For further transformations, see ref. 933.) Similarly, benzyne (generated from anthranilic acid and isoamyl nitrite) gives the adducts (**815**) and (**816**) (40%)[934] (for further transformations, see ref. 934).

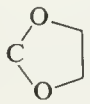


Cycloadditions in which the dibromo-compound (**44**) plays a dienophilic role result from the action of hexachlorocyclopentadiene or tetrachlorocyclopentadienone ketals, affording adducts of structure (**817**)[372] (table 104).

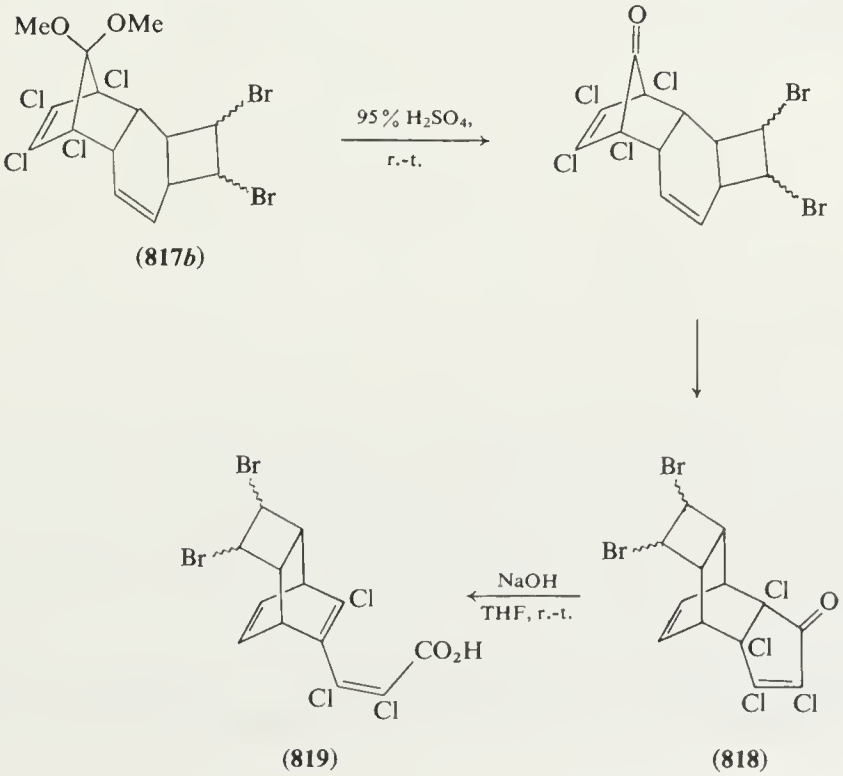


(**44**) (**817**)

Table 104

	X	Yield (%)
a	CCl_2	77
b	$C(OMe)_2$	34
c		65

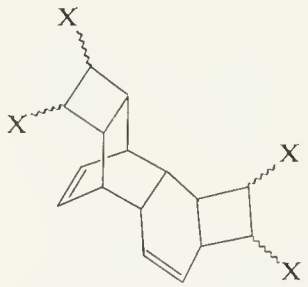
Hydrolysis of the ketal group in the adduct (**817***b*) leads to the Cope-rearranged ketone (**818**) (90%),[372] which with sodium hydroxide in tetrahydrofuran gives the carboxylic acid (**819**) (63%).[881]



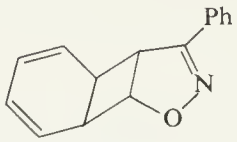
(**817***b*)

(**819**) (**818**)

Diels–Alder dimerisation of 7,8-disubstituted bicyclo[4.2.0]octa-2,4-dienes occurs on heating (or even on storage at room-temperature) to yield products



(820)

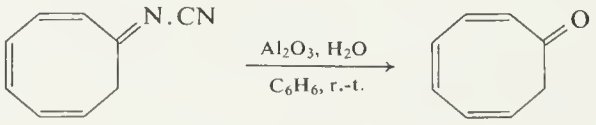


(111*c*)

of structure (**820**).[11,379] An analogous product is formed from the annulated derivative (**111*c***), although fragmentation also occurs.[330,332]

10. Cyclo-octa-2,4,6-trienones

Cyclo-octa-2,4,6-trienone (**821**) is produced from the epoxide (**27**) of COT by base-catalysed isomerisation (see p. 314); it is also formed (63%) from compound (**94**) (see pp. 41–2) by treatment with moist neutral alumina.[317]

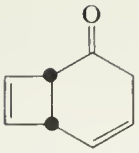


(94) **(821)**

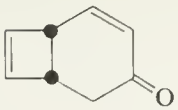
(See also pp. 96 and 143–4.)

The trienone (**821**) shows little tendency to enolise;[200,935] for ring-inversion studies, using variable-temperature n.m.r. spectroscopy, see ref. 935. It exists in equilibrium with the bicyclic isomer (**822**) (see scheme 82) (at 20°, *ca.* 5% of the bicyclic form is present;[200,856] at 60°, 6.6%[136]); the cyclobutenes (**823**) and (**824**), previously considered as valence tautomers,[936] may now be recognised as thermally forbidden cyclisation products.

Thermolysis. At 300°, the trienone (**821**) affords a 1:1:1 mixture of benzene, *o*-vinylphenol (**825**) and *o*-vinylphenyl acetate (**826**); scheme 82 is suggested.[936]

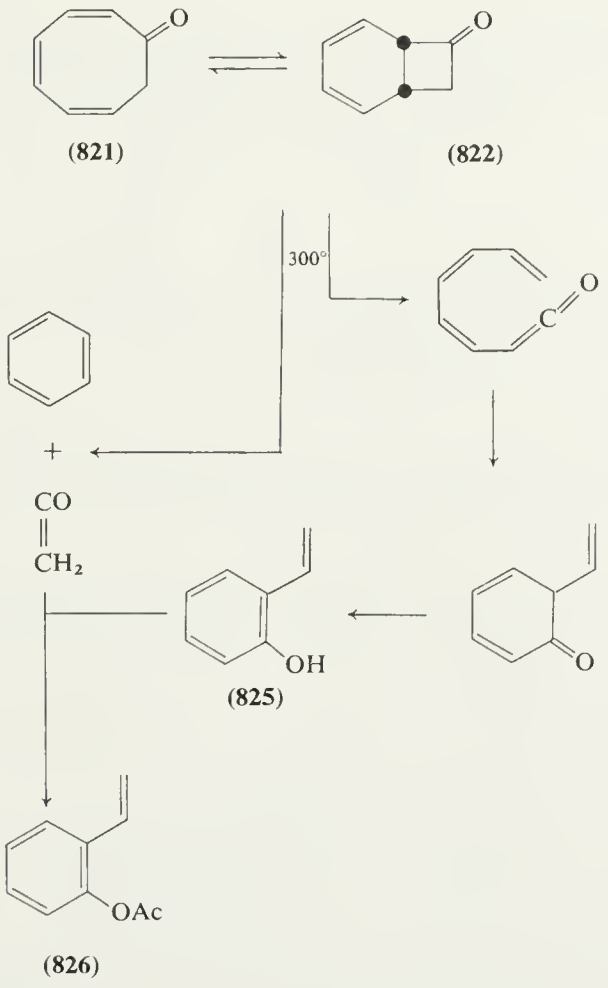


(823)

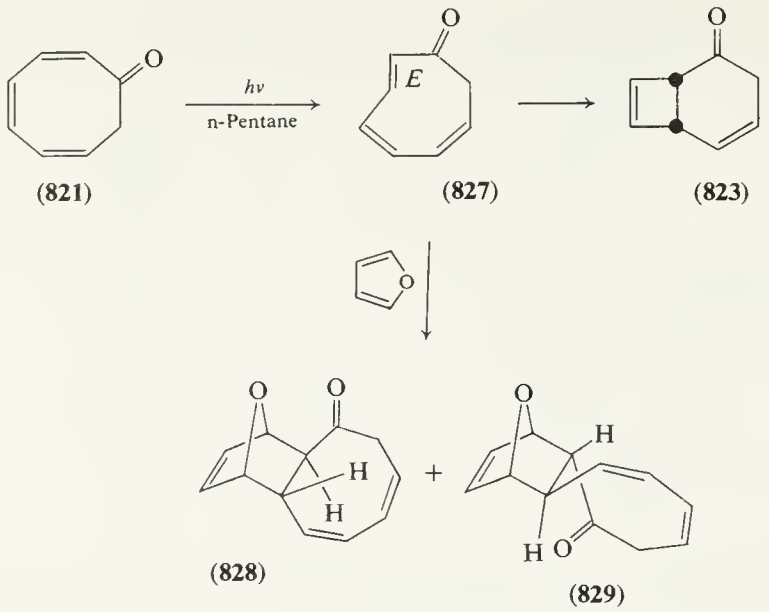


(824)

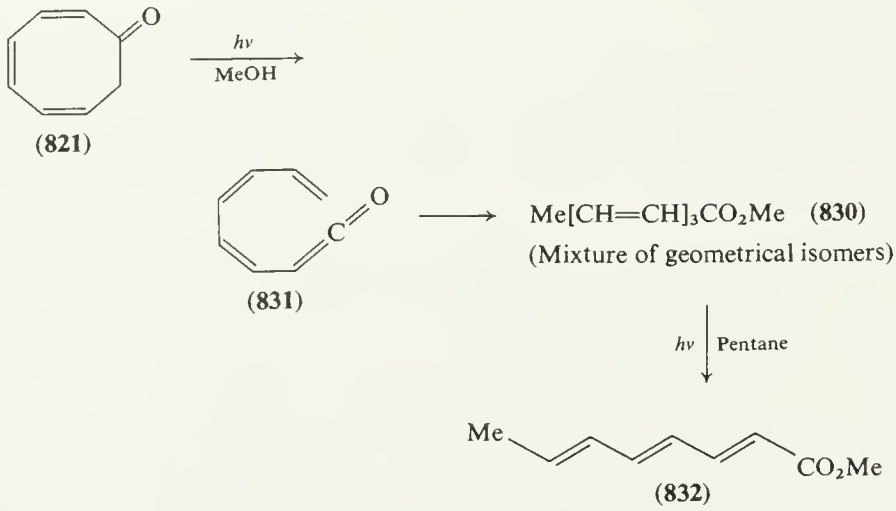
Scheme 82



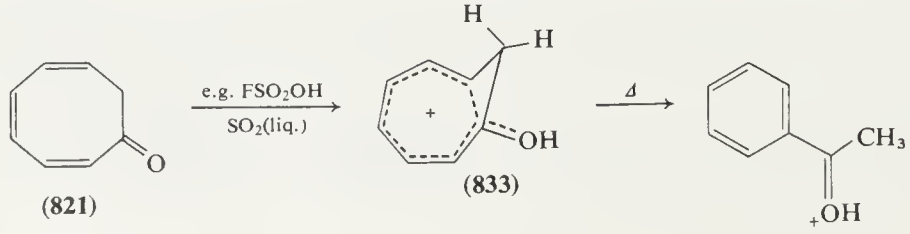
Photolysis. U.v. irradiation of the trienone (**821**) in pentane converts it into the thermally labile valence tautomer (**823**) (31 %), which reverts to the parent trienone on heating.[936] The photo-isomerisation occurs *via* the *E,Z,Z*-trienone (**827**), which may be trapped with furan to give the adducts (**828**) and (**829**).[937] Irradiation of the trienone (**821**) in methanol, however, yields a mixture of acyclic triene esters (geometrical isomers) (**830**) (31 %),[936] formed *via* the



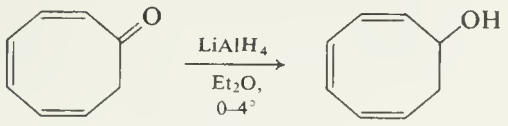
ketene (**831**).[936] On further irradiation in pentane, the mixture (**830**) is converted into the all-*E*-compound (**832**) (30%).[936]



Protonation. Low-temperature protonation of cyclo-octatrienone in strongly acid media generates the hydroxyhomotropylium ion (**833**), which decomposes on warming to give the conjugate acid of acetophenone.[938]

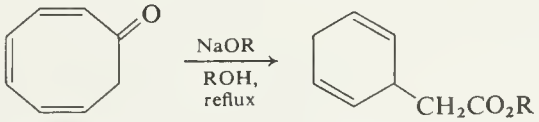


Reduction. Reduction of the trienone (**821**) with lithium aluminium hydride gives a low yield (**23**%) of impure trienol (**834**).[906]



(**821**) (**834**)

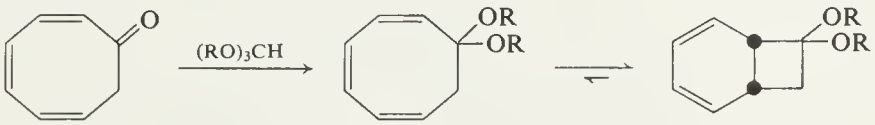
Reactions with nucleophiles. Refluxing the trienone (**821**) with sodium hydroxide in water, or sodium alkoxide in the corresponding alcohol, gives low yields (up to 24%) of cyclohexa-1,4-diene derivatives (**835**).[939]



(**821**) (**835**)

R = H, Me, Et, $CHMe_2$

The trienone (**821**) reacts with orthoformic esters to yield the ketals (**836**), which exist predominantly in the bicyclic form (**837**) (see ref. 136) (table 105).

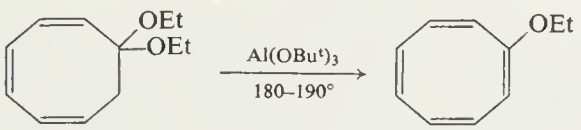


(**821**) (**836**) (**837**)

Table 105

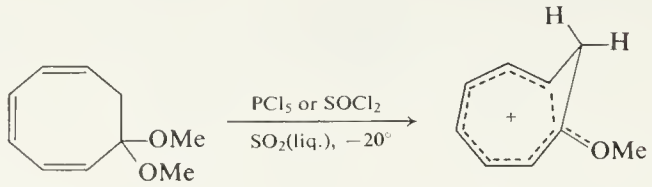
	R	Reaction conditions	Yield (%)	Ref.
a	Me	*p*-Me.C_6H_4.SO_2OH, MeOH, CH_2Cl_2	—	940
b	Et	$FeCl_3$, EtOH, r.-t.	69	941

Heating the diethyl ketal (**836***b*) with aluminium t-butoxide gives ethoxycyclo-octatetraene (37%).[941]



(**836***b*)

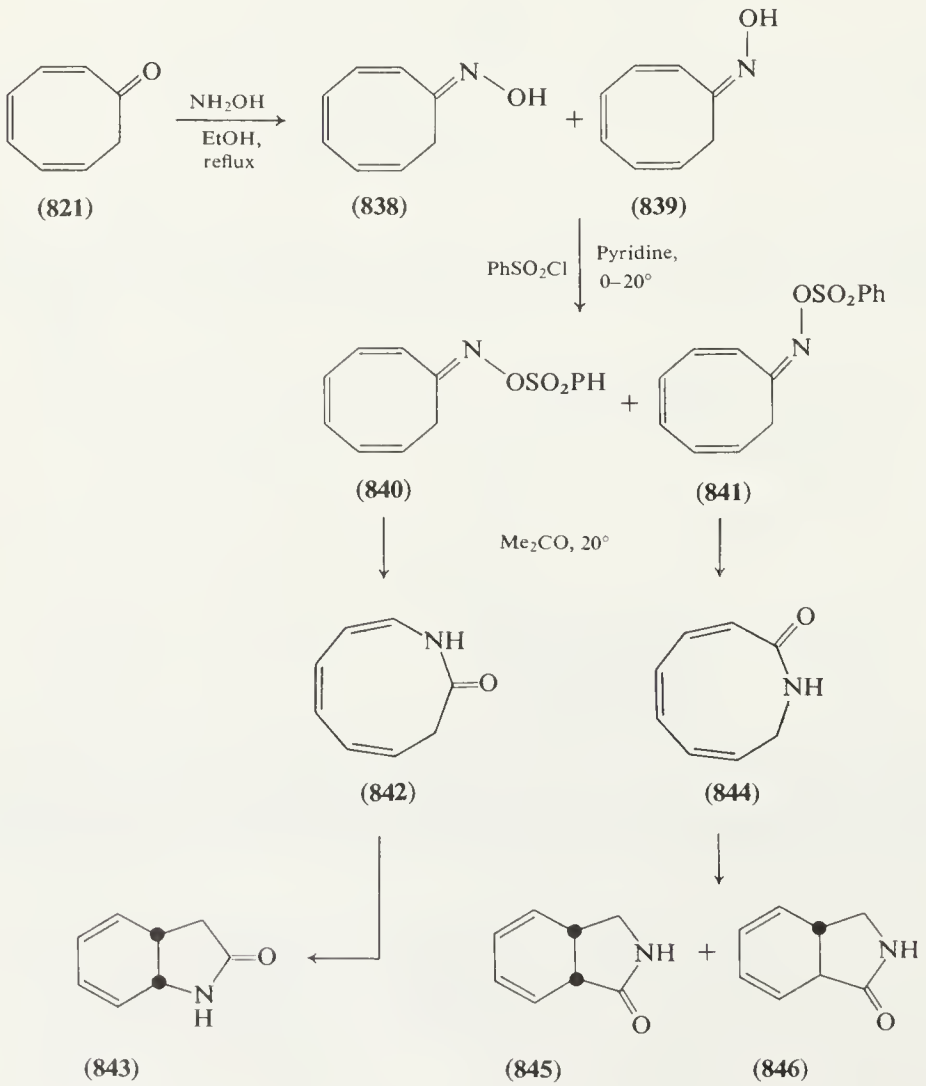
With phosphorus pentachloride or thionyl chloride in liquid sulphur dioxide, the dimethyl ketal (**836***a*) affords the methoxyhomotropylium cation (**271**)[940] (see p. 99).



(**836***a*) (**271**)

The trienone (**821**) reacts with hydroxylamine to form a mixture of the stereoisomeric oximes (**838**) and (**839**);[200,233] if these are converted into the benzenesulphonate derivatives (91%), one pure isomer (**840**) may be

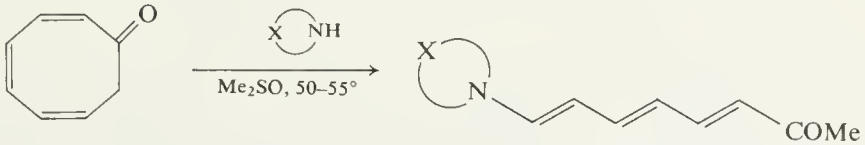
Scheme 83



(**821**) (**838**) (**839**) (**840**) (**841**) (**842**) (**844**) (**843**) (**845**) (**846**)

isolated.[233] Beckmann rearrangement of the benzenesulphonates (**840**) and (**841**) occurs in aqueous acetone; of the resulting lactams, (**842**) gives the *cis*-dihydro-oxindole (**843**), but (**844**) affords a mixture of the *cis*- and *trans*-dihydrophthalimidines (**845**) and (**846**)[233] (scheme 83).

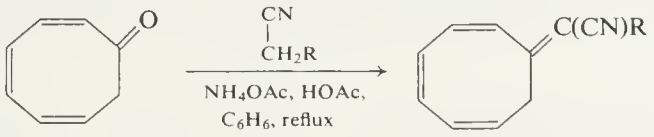
With cyclic secondary amines in dimethyl sulphoxide, the trienone (**821**) gives the acyclic products (**847**) in almost quantitative yields.[942]



(**821**) (**847**)

X = $[CH_2]_4$, $[CH_2]_5$, $[CH_2]_2O[CH_2]_2$

Reaction of the trienone (**821**) with cyanoacetic esters or malononitrile affords the condensation products (**848**) (table 106). (For the photochemical conversion of (**848**) into (**849**), see ref. 943.)



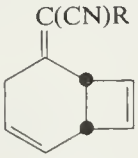
(**821**) (**848**)

Table 106

R	Yield (%)	Ref.
CO_2Me	86[a]	943
CO_2Et	10[b]	941
CN	76	943

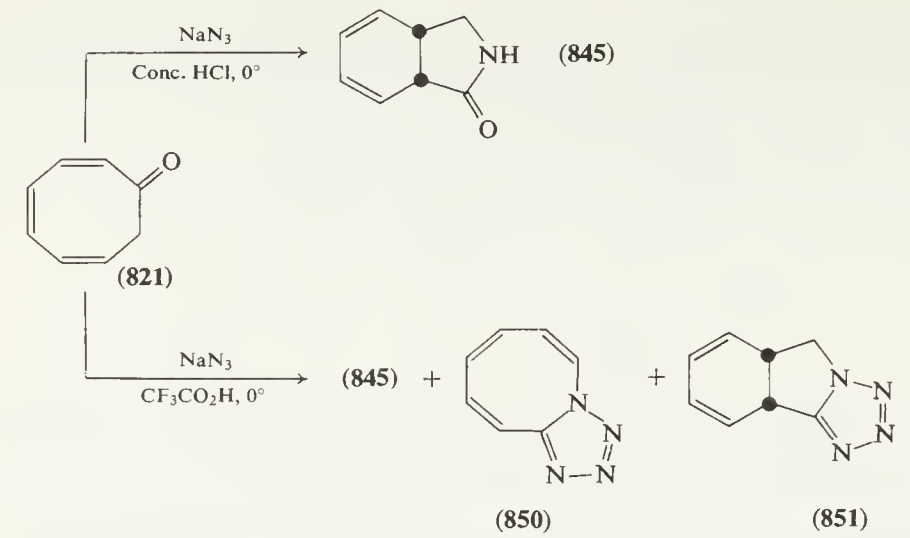
[a] A (separable) mixture of two geometrical isomers is formed.

[b] Only one geometrical isomer isolated from the mixture of products.

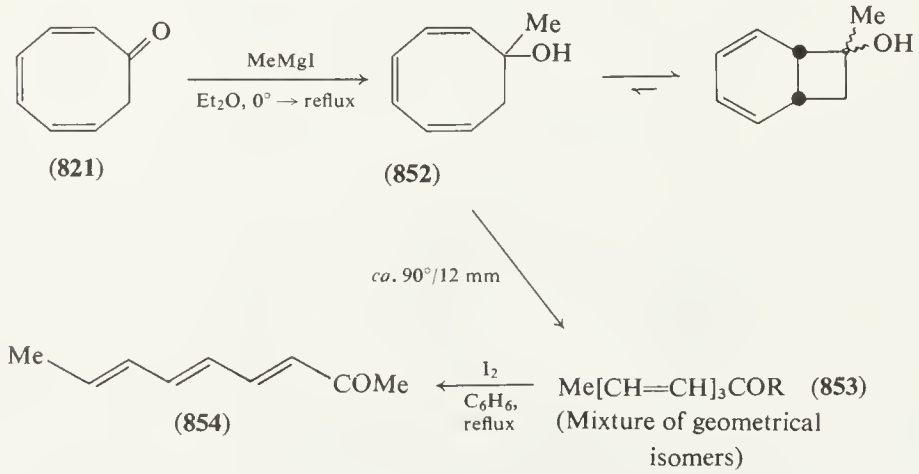


(**849**)

The Schmidt reaction of the trienone (**821**) with sodium azide in concentrated hydrochloric acid at 0° yields the *cis*-dihydrophthalimidine (**845**) (66%); the same reaction in trifluoroacetic acid, however, produces the tetrazoles (**850**) and (**851**) as the main products (19% and 6% respectively).[944]



Methylmagnesium iodide reacts with the trienone (**821**) to give the product (**852**) (23%) but ring-opening readily occurs with the formation of the acyclic trienone (**853**; R = Me) (mixture of geometrical isomers); conversion to the all-*E*-compound (**854**) (82%) is catalysed by iodine.[906] With ethyl- or phenyl-



magnesium bromide the initial product is not isolated, the open-chain ketone (**853**) being obtained directly (table 107). Similar results are obtained with

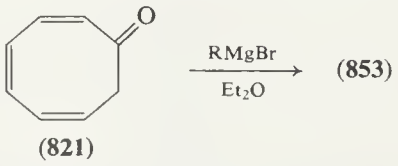
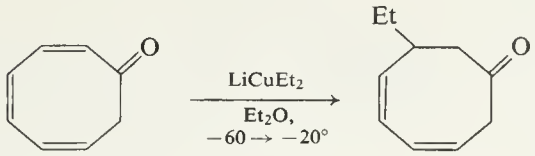


Table 107

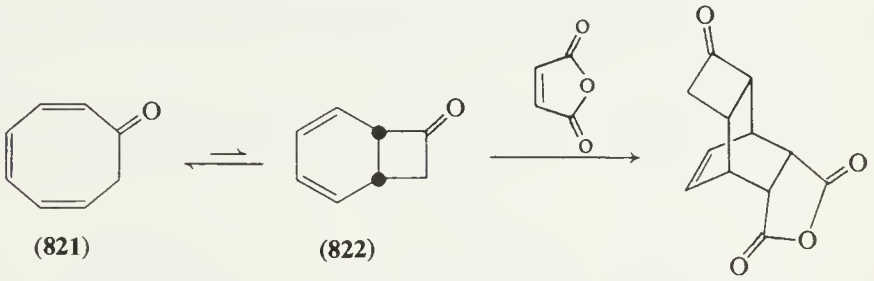
R	Yield (%)	Ref.
Et	52	945
Ph	92	906

ethyl-lithium or triethylaluminium, but with lithium 'diethylcuprate' 1,4-addition occurs to give the cyclo-octadienone (**855**) (65.5%).[945]



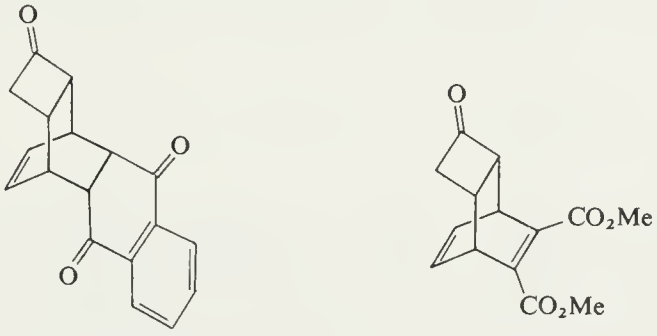
(**821**) (**855**)

Cycloadditions. Cyclo-octa-2,4,6-trienone readily forms Diels–Alder adducts with e.g. maleic anhydride, *via* the bicyclic valence tautomer (**822**); 1,4-



(**821**) (**822**) (**856**)

naphthoquinone and dimethyl acetylenedicarboxylate afford the adducts (**857**) and (**858**) respectively[941] (table 108).

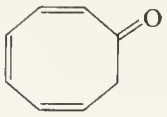


(**857**) (**858**)

Table 108

Dienophile	Conditions	Product	Yield (%)
Maleic anhydride	C_6H_6, 60°	(**856**)	84
1,4-Naphthoquinone	C_6H_6, reflux	(**857**)	80
Dimethyl acetylenedicarboxylate	50–90°	(**858**)	76

Reactions with metal derivatives. The trienone (**821**) reacts with $Fe_3(CO)_{12}$ (or $Fe_2(CO)_9$) to give the complexes (**300**) (13%) and (**301**) (2.4%)[893] (see p. 107).



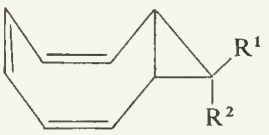
(**821**)

$\xrightarrow[C_6H_6,\ \text{reflux}]{Fe_3(CO)_{12}}$ (Cyclo-octatrienone)$Fe(CO)_3$ (**300**) + (Cyclo-octatrienone)$Fe_2(CO)_6$ (**301**)

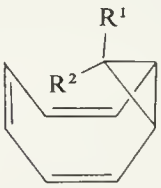
11. Bicyclo[6.1.0]nona-2,4,6-trienes

Bicyclo[6.1.0]nonatrienes (**82**) result from the addition of carbenes to COT (see pp. 35–6); they may also be generated from COT^{2-} and *gem*-dihalides etc. (see pp. 174–8).

For n.m.r. evidence for the 'extended' conformation (**82A**), see ref. 314.



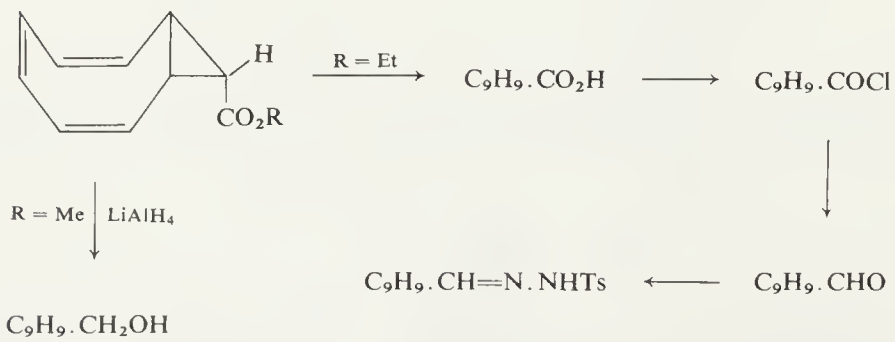
(**82A**)



(**82B**)

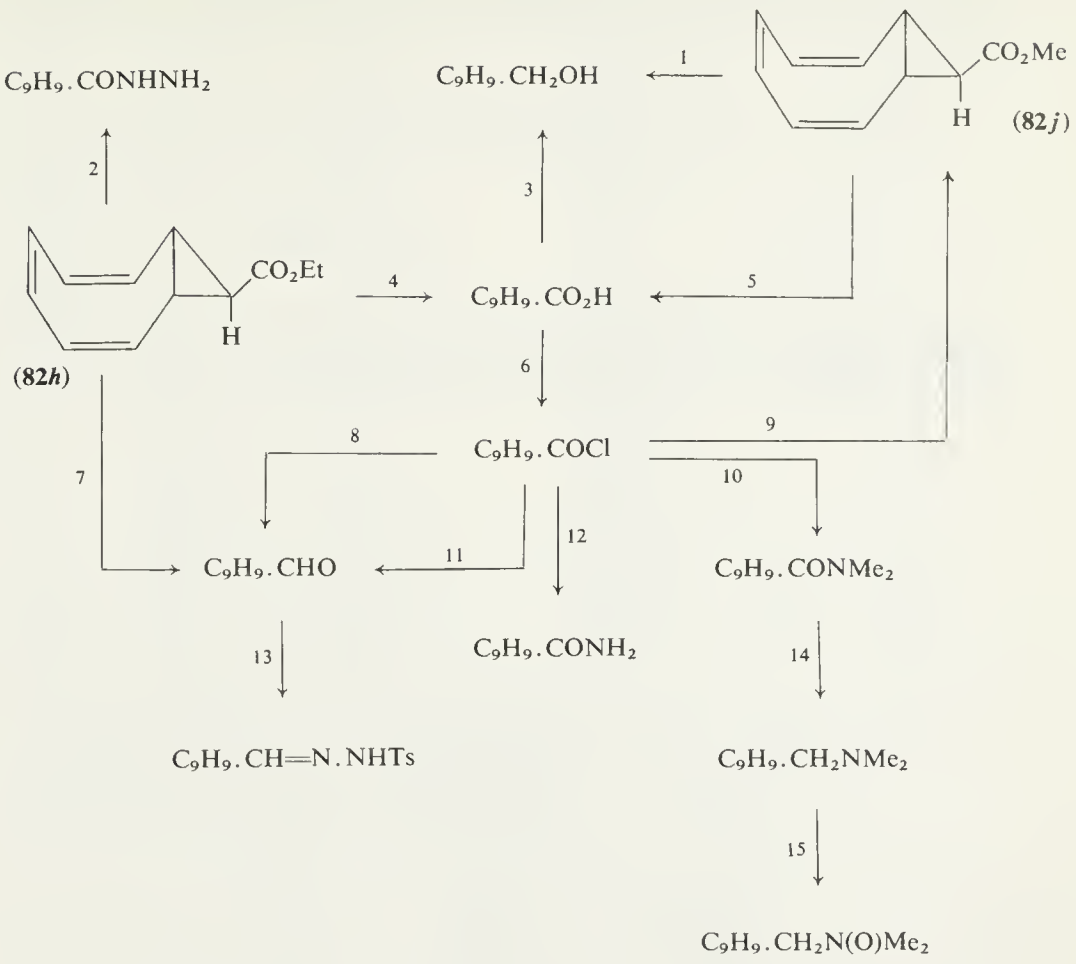
Functional group transformations. Transformations of the *syn-* and *anti*-9-alkoxycarbonyl-derivatives (see pp. 35–6) are outlined in schemes 84 and 85.

Scheme 84*



* No other experimental details are available, except spectral data for the alcohol,[314] and the m.ps. of the carboxylic acid[312] and the tosylhydrazone,[946] but see scheme 85 for analogous reactions.

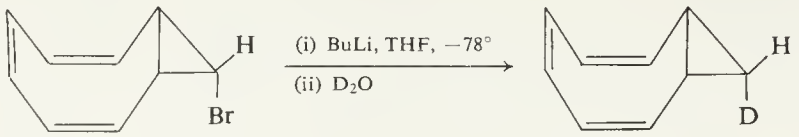
Scheme 85



Reaction	Reagents and conditions	Yield (%)	Ref.
1	$LiAlH_4$	—	314
2	NH_2NH_2	—	310
3	$LiAlH_4$, Et_2O, r.-t.	100[a]	947
4	NaOH(aq.), 80–90°	45	309, (311)
5	NaOH(aq.), reflux	88	948
6	$SOCl_2$, reflux	88	(311), 948
7	(i) $LiAlH_4$, Et_2O, reflux; (ii) CrO_3, pyridine, r.-t.	30	948
8	$LiAlH(OBu^t)_3$, diglyme, −65°	39	948
9	MeOH	85[b]	311
10	Me_2NH, Et_2O	—	949
11	(i) Aziridine, Et_3N, Et_2O, 0°; (ii) $LiAlH_4$, Et_2O, 0°	24	948
12	NH_3	80[b]	311
13	$H_2N.NHTs$, EtOH, 60°	61	948
14	$LiAlH_4$	—	949
15	30% H_2O_2, MeOH	—	949

[a] Product not purified. [b] Overall yield from the carboxylic acid.

The bromo-derivative (**82*l***) may be converted into the deuterio-derivative (**82*m***) (*ca.* 90%) by the action of butyl-lithium, followed by deuterium oxide.[749]



(**82*l***) (**82*m***)

Thermal epimerisation. The *syn*-9-substituted derivatives (**82**; $R^1 = H$) undergo thermal equilibration with the corresponding *anti*-isomers (**82**; $R^2 = H$) (table 109) (for mechanistic discussions, see refs. 313, 747, 749).

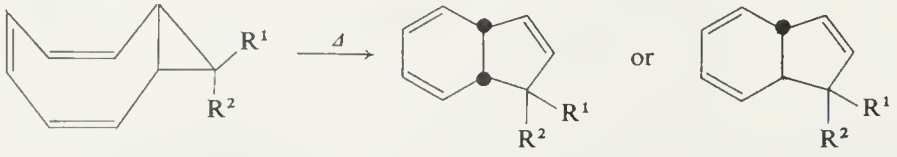
(**82**) ($R^1 = H$) (**82**) ($R^2 = H$)

Table 109

R	Temp. (°C)	Ref.
D	30	749
CO_2Me	100	313
CO_2Et	100	313
CN	139	748
OMe	r.-t.	747
F	0	747

Thermolysis. The thermal rearrangements of the system (**82**) have been studied intensively.

The products obtained from the hydrocarbons (**82**; $R^1 = H$ or alkyl, $R^2 = H$ or alkyl) and certain other derivatives are the *cis*- or *trans*-dihydroindenes (**859**) or (**860**) (mixtures of epimers) (table 110). (For kinetic data on the

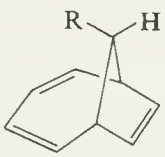


(**82**) (**859**) (**860**)

Table 110

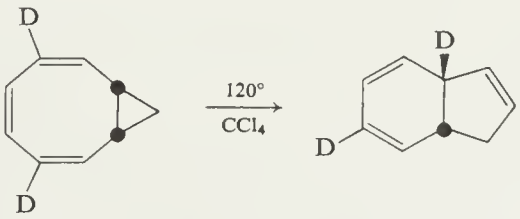
R^1 (*anti*)	R^2 (*syn*)	Temp. (°C)	Predominant product[a]	Ref.
H (D)	H (D)	90	(**859**)	297, 299, (950), 951
Me	H	110–199	(**859**)	952, (953), 954
Bu^t	H	179	(**859**)	746
CH_2OH	H	120, [150]	(**859**)	947, [955]
CO_2H	H	150	(**859**)	955
CO_2Me	H	130, [160]	(**859**)	[299], [311], 313
CO_2Et	H	130, [160–180]	(**859**)	[311], 313, (955)
CN	H	139	(**859**)	748
NMe_2	H	70	(**859**)[b]	747
Cl	H (D)	70, [75]	(**859**)	743, 956, [957]
H	Me	110–200	(**859**)[c]	952, (953), 954
H	Bu^t	179	(**860**)	746
H	CO_2Me	130	(**859**)[d]	313
H	CO_2Et	130	(**859**)[d]	313
H	CN	139	(**859**)[d]	748
H	OMe	58	(**859**)[d]	747
H	F	35	—[d, e]	747
Me	Me	151	(**860**)	744
Me	Et	170	(**860**)	958
Et	Me	170	(**860**)	958

[a] Usually >90%, ignoring secondary products.
[b] The major product is the bicyclo[4.2.1]nonatriene (**861**; R = NMe_2) (see p. 269).
[c] Ratio (**859**):(**860**) = *ca.* 7:3. Epimerisation at C-9 may be involved.[313, 749]
[d] Epimerisation at C-9 precedes rearrangement.
[e] The products are indene and the bicyclo[4.2.1]nonatriene (**861**; R = F).



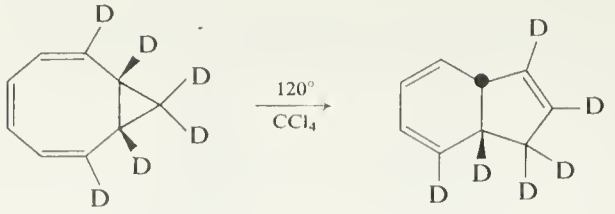
(**861**)

rearrangement of (**82**; R^1 = H, Ph, CO_2Me, CN, OMe, Cl; R^2 = H), see ref. 959.) Thermolysis of the deuterium-labelled species (**862**) and (**863**) affords the

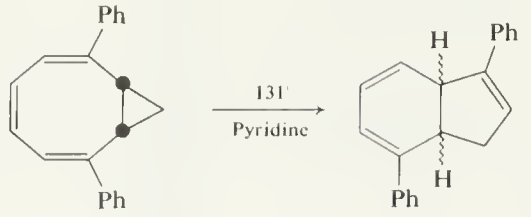


(**862**) (**864**)

products (**864**) and (**865**) respectively.[960] The diphenyl-derivative (**866**) gives the product (**867**).[961, 962]



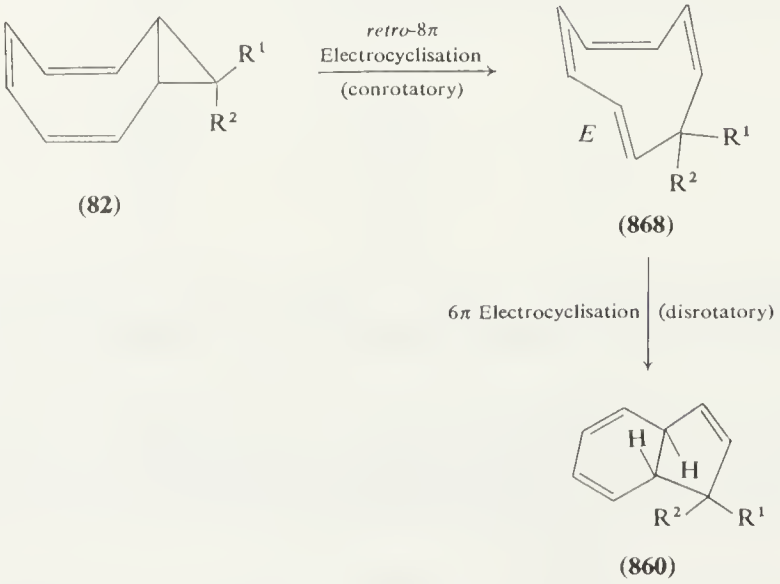
(863) **(865)**



(866) **(867)**

The rearrangements resulting in *trans*-products (**860**) may proceed by ring-opening to give the *Z,Z,Z,E*-cyclononatetraene (**868**), followed by a 6π electrocyclisation (scheme 86), both of the proposed steps being unexceptional from the viewpoint of orbital symmetry.

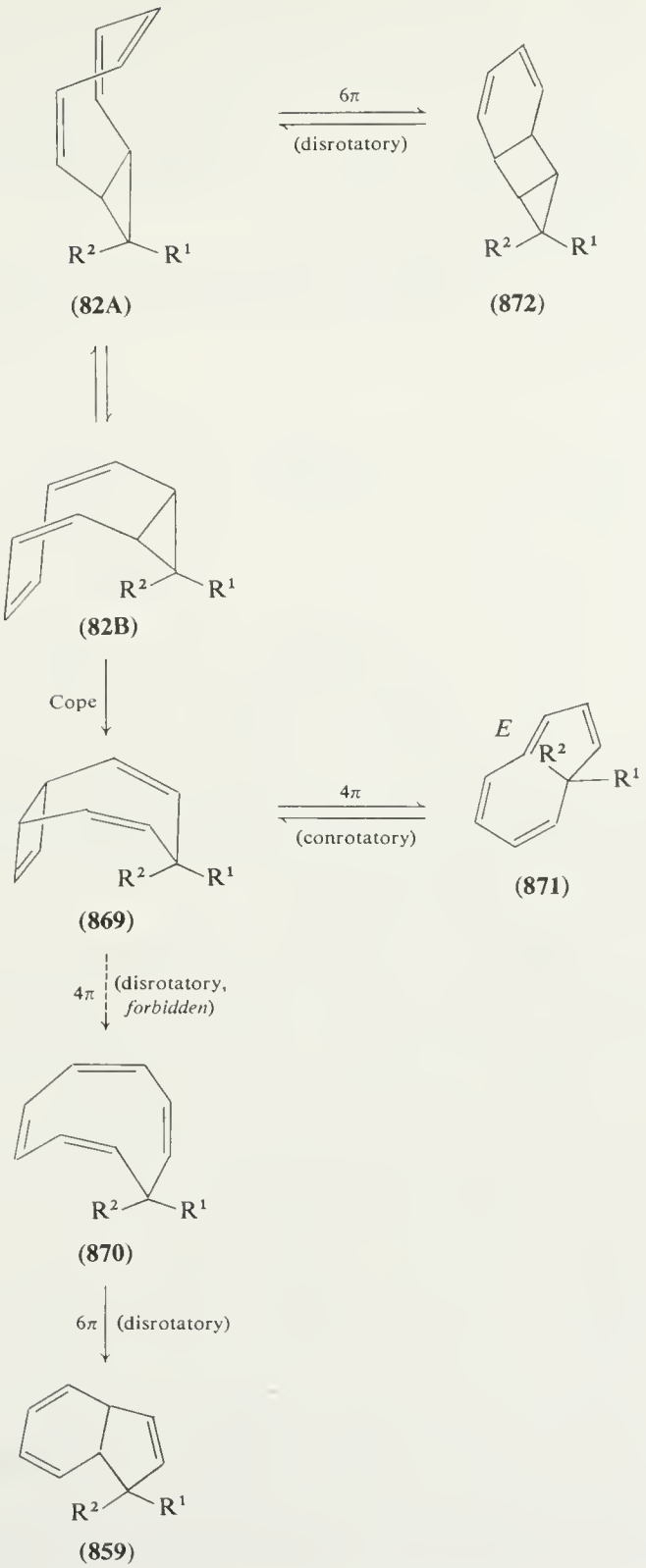
Scheme 86



(82) **(868)** **(860)**

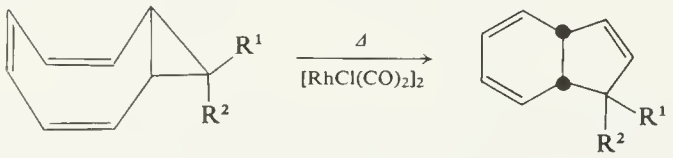
However, the formation of *cis*-products (**859**), which would seem to involve a thermally 'forbidden' step, is *kinetically preferred*, the 'allowed' pathway being followed only when the starting material (**82**) contains a bulky *syn*-9-substituent (R^2). This indicates that the adoption of the more congested conformation (**82B**) (scheme 87) is the initial step in the bond reorganisation leading

Scheme 87


6π
(disrotatory)
R²
R¹
(82A)
(872)
(82B)
Cope
4π
(conrotatory)
E
(871)
(869)
4π
(disrotatory,
forbidden)
(870)
6π
(disrotatory)
(859)

to *cis*-products (**859**). The next step may be a Cope rearrangement, for which the conformer (**82B**) is an essential precursor, leading to the bicyclo[5.2.0]nonatriene system (**869**). The subsequent steps are more controversial. The all-*Z*-cyclononatetraenes (**870**) could be the immediate source of the observed products (**859**), but trapping experiments provide evidence only for the presence of the *Z*,*Z*,*E*,*Z*-system (**871**) (see pp. 286–7), and the tricyclic diene (**872**) (see p. 282). (The problem has been reviewed by Staley;[963] for later papers see e.g. refs. 313, 746, 749, 953, 954, 960, 964.)

The rearrangement (**82**) → (**859**) is catalysed by $[RhCl(CO)_2]_2$ (table 111); under these conditions the 9,9-dimethyl-compound (**82*n***) also gives a *cis*-fused product[965] (*cf.* table 110).

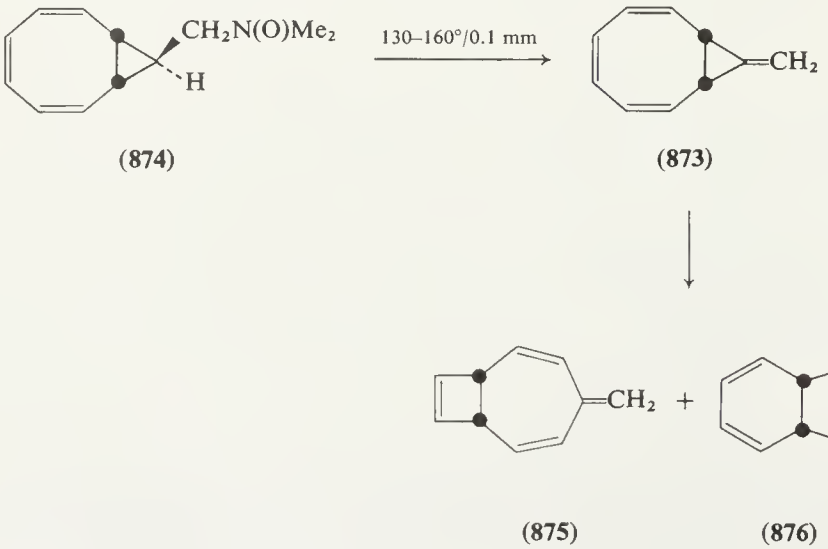


(**82**) (**859**)

Table 111

	R^1	R^2	Temp. (°C)	Yield (%)
a	H	H	35	>99.5
n	Me	Me	140	80

Generation of the 9-methylene-derivative (**873**) by thermolysis of the amine-*N*-oxide (**874**) is followed by rearrangement to the Cope product (**875**) (21 %) and the *cis*-dihydroindene (**876**) (31 %).[949]

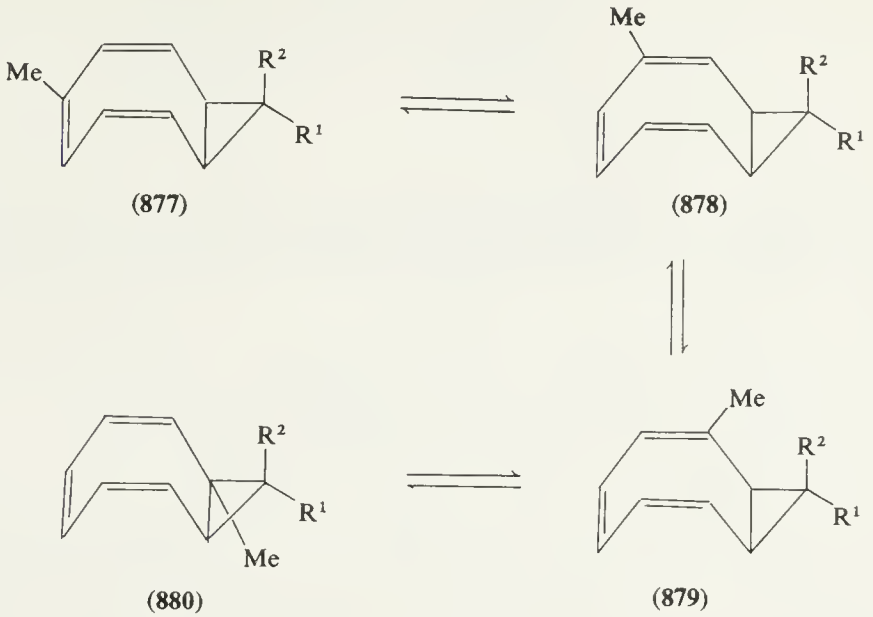


(**874**) (**873**)

(**875**) (**876**)

A degenerate rearrangement may be detected in the systems (**877**)–(**880**), complete equilibration of the isomers occurring at 102.5°; migration of C-9

(with inversion) around the C_8 ring takes place *via* a series of symmetry-controlled [1,7] sigmatropic shifts.[966]



R^1 = Me, R^2 = CN
or R^1 = CN, R^2 = Me

At 180–190°, however, the 9-cyano-compounds (**82***d*), (**82***o*) and (**82***p*) undergo rearrangement to bicyclo[4.2.1]nonatrienes (**881**) (the reaction is not completely stereospecific) (table 112). The same type of rearrangement occurs

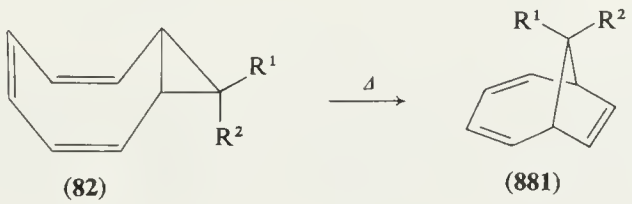
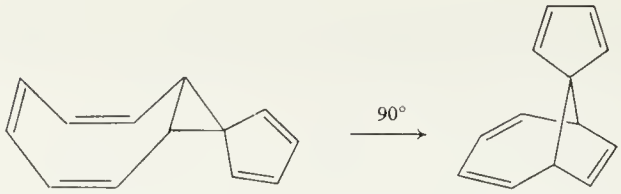


Table 112

	R^1	R^2	Temp. (°C)	Yield (%)	Ref.
o	Me	CN	180	—	967
p	CN	Me	180	—	967
d	CN	CN	190	72	304, 305

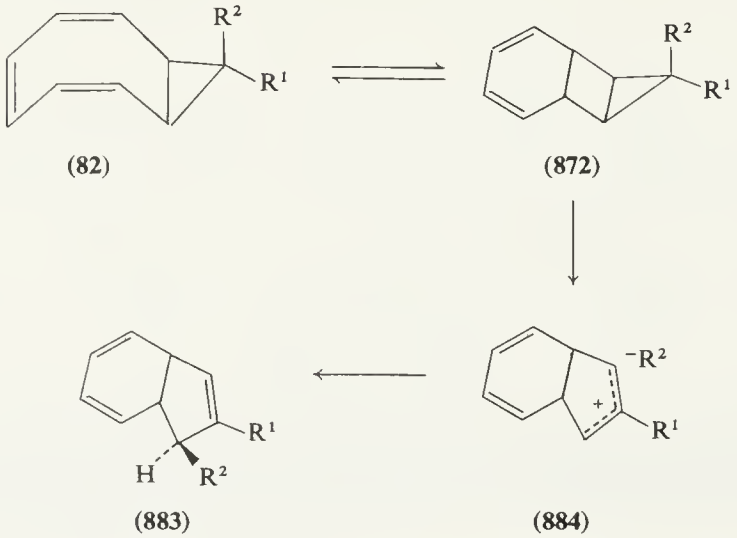
with the *spiro*-cyclopentadiene (**88***a*), which gives the system (**882**) (25–30%);[315] the related *spiro*-fluorene behaves similarly.[968]

The *syn*-9-halo-derivatives (**82***b*), (**82***c*) and (**82***e*) rearrange to the *cis*-dihydroindenes (**883**) (table 113), migration of halogen being involved (*cf.* the *anti*-9-chloro-compound (table 110)). It is suggested that ionisation of the



(**88***a*) (**882**)

tricyclic valence tautomer (**872**) is followed by rapid disrotatory ring-opening to give an allylic cation (**884**) which recaptures the halide ion on the same face.[957]



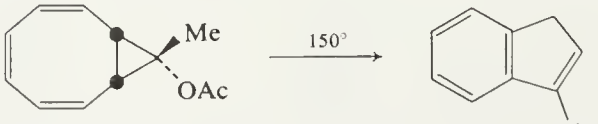
(**82**) (**872**)

(**883**) (**884**)

Table 113

	R^1	R^2	Temp. (°C)	Yield (%)	Ref.
b	Cl	Cl	80–90	*ca.* 100	(956), 957
c	Br	Br	80–90	*ca.* 100	297
e	H	Cl	(70), 75	(80)	(956), 957

Thermolysis of the 9-acetoxy-9-methyl-compound (**522**; R = Me) results in the elimination of acetic acid and the formation of 3-methylindene (79%).[377]

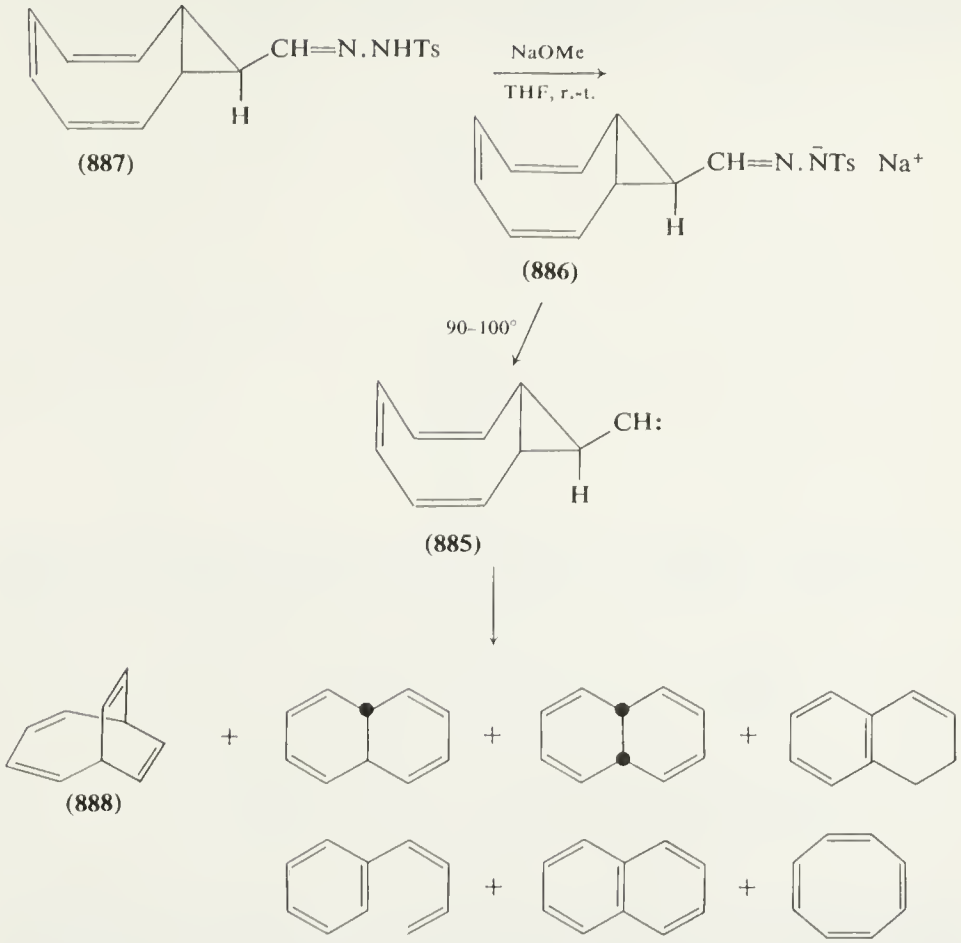


(**522**; R = Me)

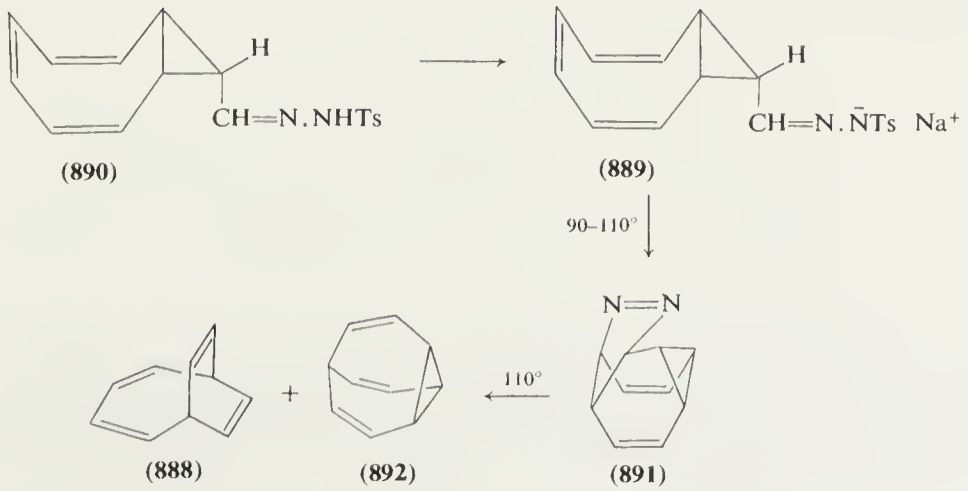
(Stereochemistry not certain)

Generation of the carbene (**885**) by thermolysis of the sodium salt (**886**) of the *anti*-tosylhydrazone (**887**) leads to a variety of products, of which the bi-

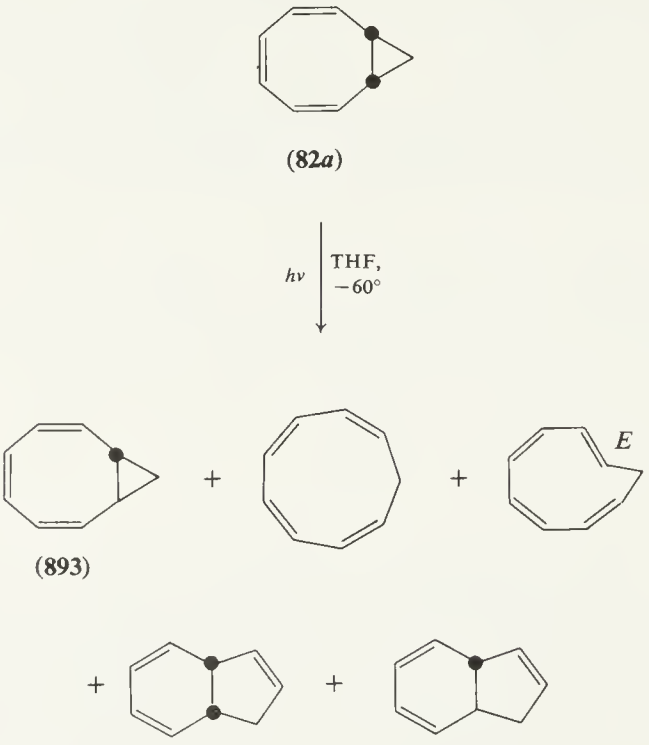
cyclic tetraene (**888**) is the most abundant (38%)[948,969] (*cf.* the *syn*-isomer below).



Similar thermal decomposition of the sodium salt (**889**) of the *syn*-tosylhydrazone (**890**) leads to the pyrazoline (**891**), which in turn thermolyses to give the bicyclic product (**888**) (53%) and bullvalene (**892**) (46%).[946]



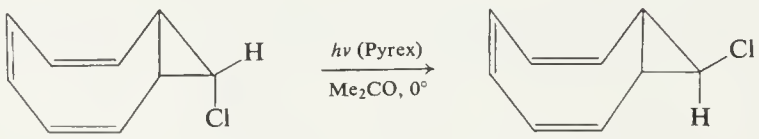
Photolysis. U.v. irradiation of *cis*-bicyclo[6.1.0]nonatriene (**82*a***) at −60° gives rise to a stationary state in which the starting material and a number of its isomers are in equilibrium.[970] The *trans*-fused isomer (**893**)[971] is obtainable in up to 11% yield in methanol at 23°.[972]



(**82*a***)

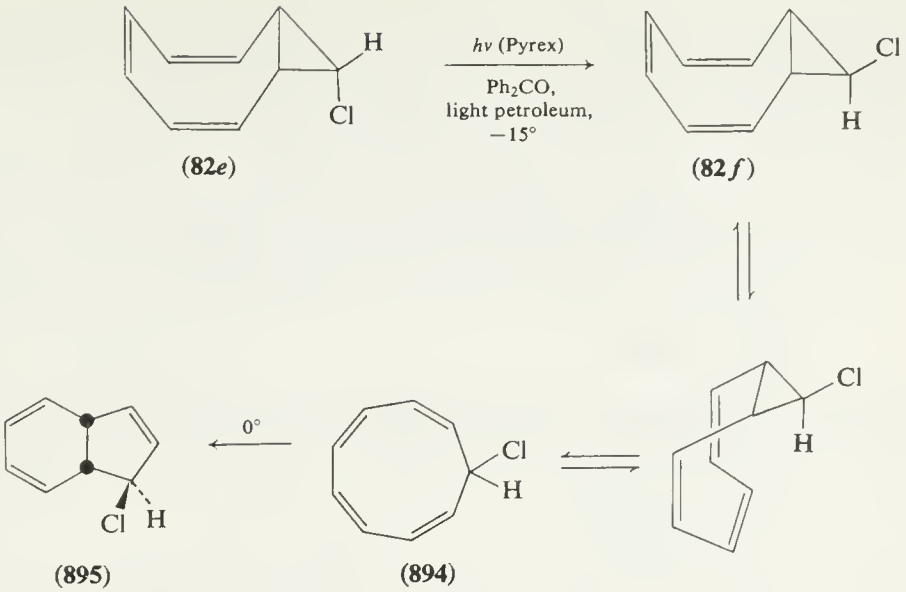
(**893**)

Irradiation of *syn*-9-substituted derivatives of the parent hydrocarbon (**82*a***) effects their transformation into the *anti*-stereomers;[746,953,973] for example, photo-isomerisation of the *syn*-9-chloro-compound (**82*e***) affords the *anti*-9-chloro-derivative (**82*f***) (up to 85%).[973]



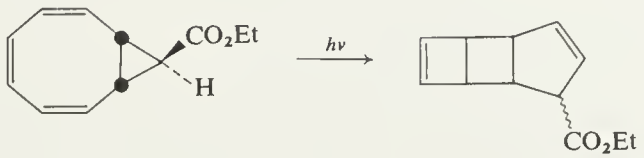
(**82*e***) (**82*f***)

At −15° in the presence of benzophenone as sensitiser, the chlorocyclononatetraene (**894**) is produced from either of the 9-chloro-stereomers (**82*e***) or (**82*f***); at 0°, thermal rearrangement of the cyclononatetraene (**894**) results in the *cis*-dihydroindene (**895**).[973]



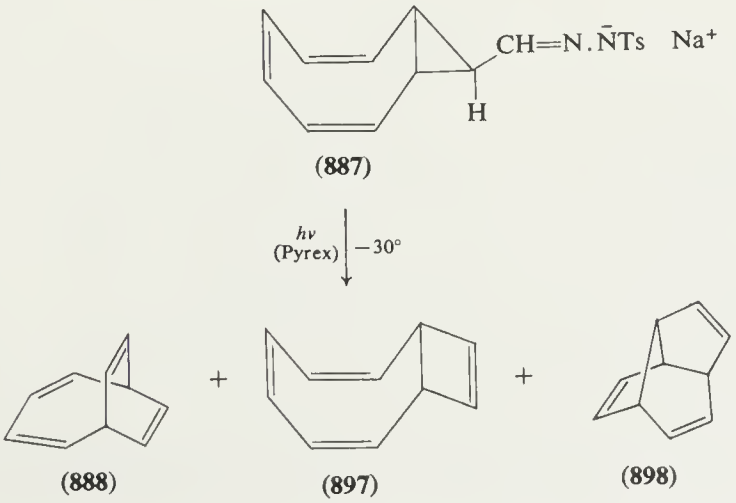
(82*e*) (82*f*) (895) (894)

U.v. irradiation of the ester (**82*h***) yields a tricyclic product formulated as (**896**).[955]



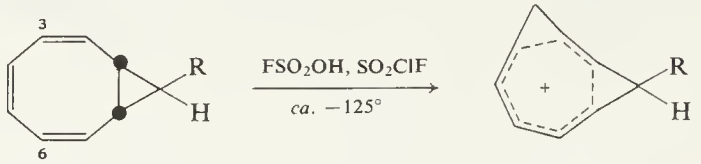
(82*h*) (896)

Photolysis of the sodium salt of the *anti*-tosylhydrazone (**887**) results (after low-temperature work-up) in a mixture of the $C_{10}H_{10}$ hydrocarbons (**888**), (**897**) (major product) and (**898**)[312,946] (*cf.* thermolysis, p. 271). (For photolysis of the pyrazoline (**891**), see ref. 946.)



(887) (888) (897) (898)

Reactions with electrophiles. Protonation of bicyclo[6.1.0]nonatriene (**82***a*) or its *anti*-9-methyl-derivative (**82***q*) in a 'super-acid' medium occurs at C-3 (≡ C-6) to afford a 1,3-bis(homotropylium) ion (**899**).[848, 864, 974]



(**82***a*) (R = H)
(**82***q*) (R = Me)

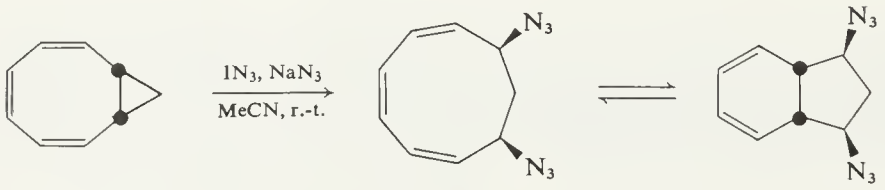
(**899**)

The relative stereochemistry of the methylene bridges (*syn* (**899***a*) or *anti* (**899***b*)) in this species is uncertain. (For ^{13}C n.m.r. spectra, refs. 848, 849.)

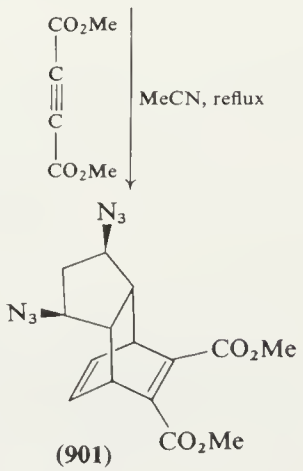
(**899***a*) (**899***b*)

The *syn*-9-methyl- and 9,9-dimethyl-derivatives fail to give bis(homotropylium) ions on protonation.[848]

Reaction of the bicyclic triene (**82***a*) with iodine azide (from an excess of sodium azide and iodine monochloride) yields the monocyclic triazide (**900**) (80–90%), characterised as the acetylenedicarboxylic ester-adduct (**901**) (40%).[975, 976]



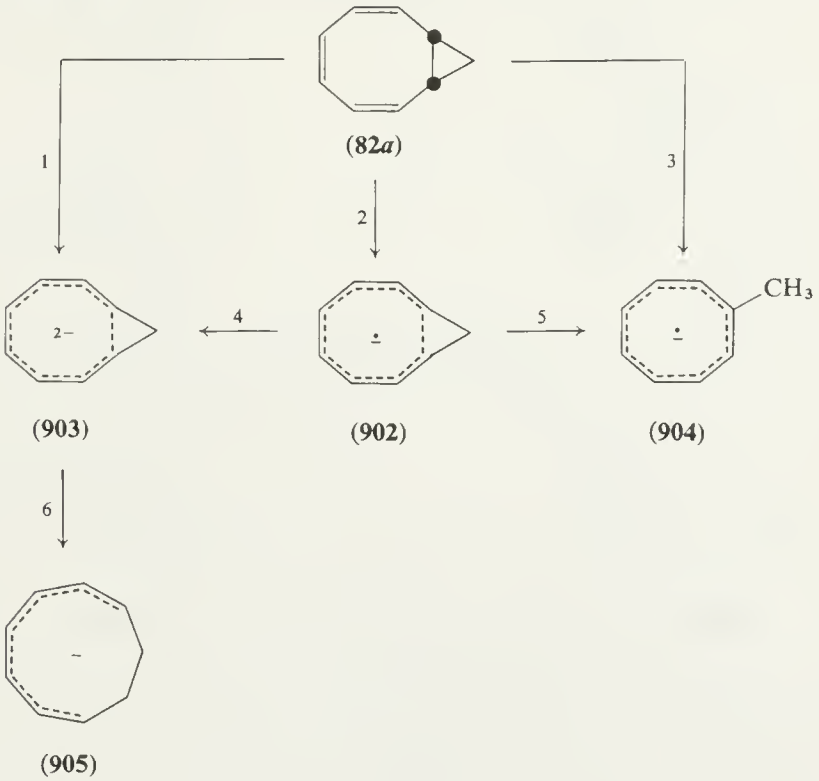
(**82***a*) (**900**)



(**901**)

Reduction, and reactions with nucleophiles. The addition of an electron to bicyclo[6.1.0]nonatriene (**82***a*), using an alkali metal in e.g. tetrahydrofuran, or by means of electrolysis in liquid ammonia, generates the non-classical anion-radical (**902**), which accepts a further electron to form the dianion (**903**). With alkali metals in liquid ammonia, the anion-radical (**904**) of methylcyclo-octatetraene is produced. The preparations of these species are summarised in scheme 88. (For a polarographic study of the electrochemical reduction of (**82***a*), see ref. 986. For a theoretical discussion of (**902**), see ref. 987.)

Scheme 88

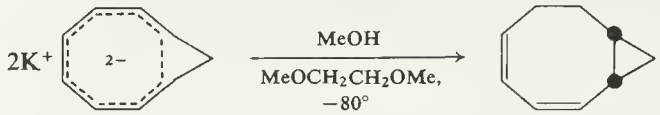


Reaction	Reagents and conditions	Ref.
1	2M, NH_3(liq.), −78° [a]	977
	or 2Na, HMPA, THF, −30° [a]	977
	or 2K, $MeOCH_2.CH_2OMe$	978, 979
2	1M, THF, −80°	972, 980, 981
	or electrolysis, NH_3(liq.), $Me_4N^+Cl^-$	982
3	1M, NH_3(liq.)	983
4	1K, THF, −80°	984
5	Electrolysis, NH_3(liq.), $Me_4N^+Cl^-$	982
6	NH_3(liq.), or HMPA	977, 985

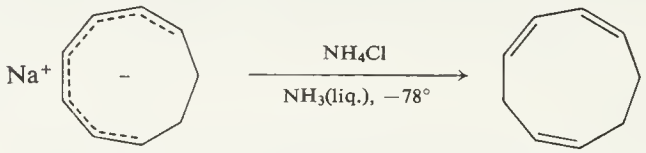
[a] Protonation of (**903**) by the solvent results in (**905**) (see reaction 6).

Protonation of the dianion (**903**) (dipotassium salt in 1,2-dimethoxyethane) with methanol affords the bicyclic diene (**906**) (85%),[978] whereas addition of

solid ammonium chloride to the monoanion (**905**) (sodium salt in liquid ammonia) gives the monocyclic triene (**689**) (67%).[977]

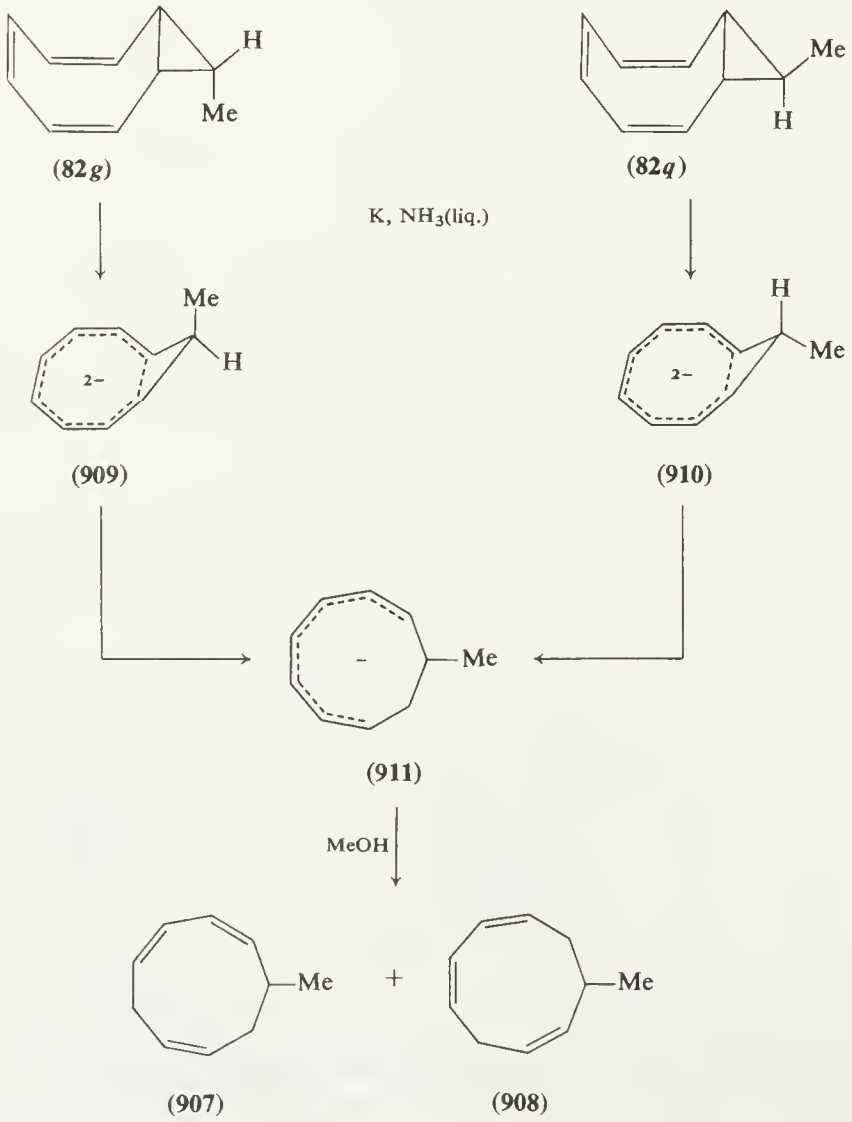


(**903**) (**906**)



(**905**) (**689**)

Scheme 89



(**82***g*) (**82***q*)

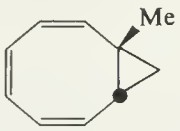
(**909**) (**910**)

(**911**)

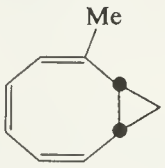
(**907**) (**908**)

(For the reaction of (**903**) with carbon tetrachloride, see ref. 979. For the reactions of (**905**) with oxygen, potassium permanganate and methyl iodide, see refs. 985, 988.)

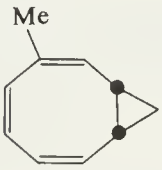
Reduction of the *syn*- or *anti*-9-methyl-derivative (**82*g***) or (**82*q***) with potassium in liquid ammonia, followed by quenching with methanol, yields a mixture of the isomeric cyclononatrienes (**907**) and (**908**), *via* stereochemically distinct dianions (**909**) and (**910**), but a common intermediate monoanion (**911**)[985] (scheme 89). (For the analogous reduction of the 1-, 2-, 3- and 4-methyl-compounds (**912**)–(**915**), see ref. 985; of the 9,9-dimethyl-derivative (**82*n***), see refs. 977, 985.)



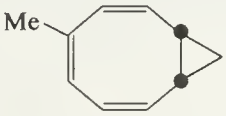
(**912**)



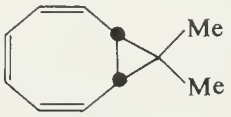
(**913**)



(**914**)



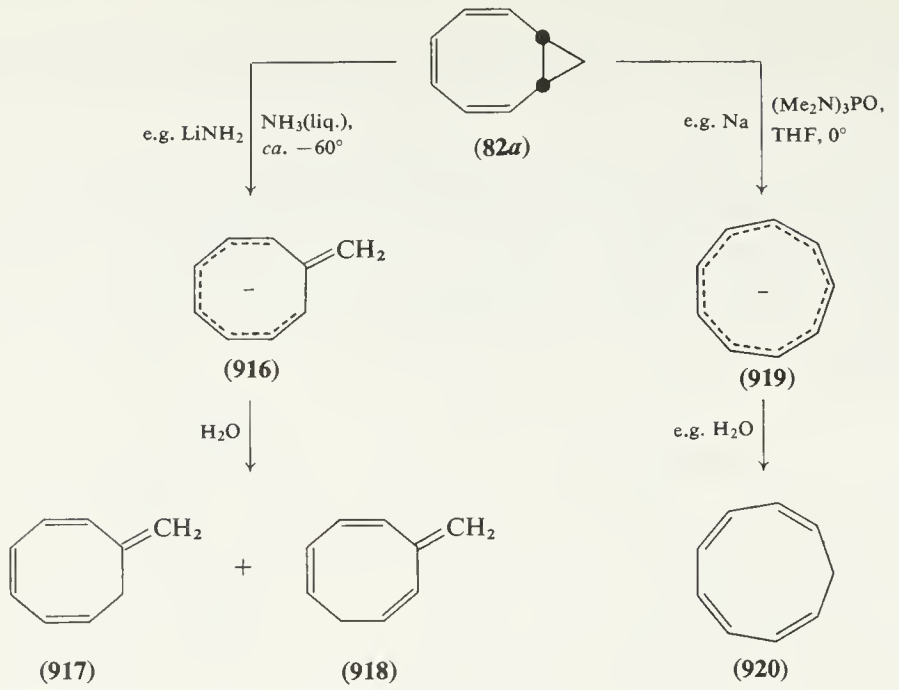
(**915**)



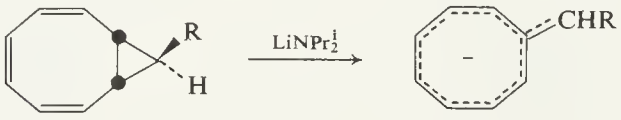
(**82*n***)

For catalytic hydrogenation of the bicyclo[6.1.0]nonatriene system, see e.g. refs. 309, 310, 377.

Anions can also be generated from bicyclo[6.1.0]nonatriene by proton-abstraction. Thus reaction with e.g. lithium amide in liquid ammonia gives rise to the methylenecyclo-octatrienyl anion (**916**), which with water yields (mainly) a mixture of the methylenecyclo-octatrienes (**917**) and (**918**).[989] (For reaction of (**82*a***) with potassium t-butoxide, see pp. 84–5.) Treatment with one equivalent of sodium in hexamethylphosphoramide-tetrahydrofuran,[977] or sodium hydride in dimethyl sulphoxide,[958] generates the cyclononatetraenyl anion (**919**); this gives all-*Z*-cyclononatetraene (**920**) (half-life 50 min. at 23°[990]) when it is quenched with water,[990] methanol,[991] or dilute acetic acid.[992]



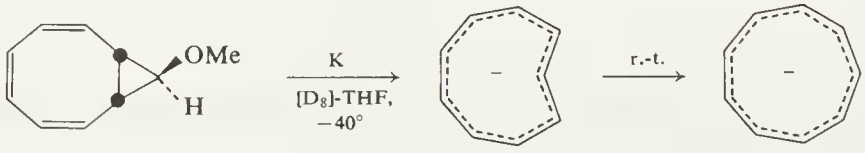
The *anti*-9-substituted derivatives (**82***j*) and (**82***r*) are deprotonated by lithium di-isopropylamide to form anions represented as (**921**).[993]



(**82***j*) (R = CO_2Me)
(**82***r*) (R = CN)

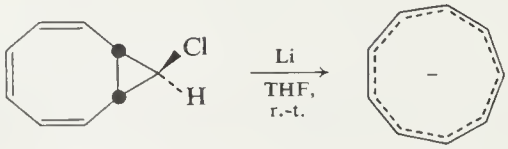
(**921**)

The *anti*-9-methoxy-compound (**82***s*), on treatment with potassium at −40°, gives the anion (**922**) of *Z*,*Z*,*Z*,*E*-cyclononatetraene; at room-temperature this is completely converted into the all-*Z*-cyclononatetraenyl anion (**923**).[994]



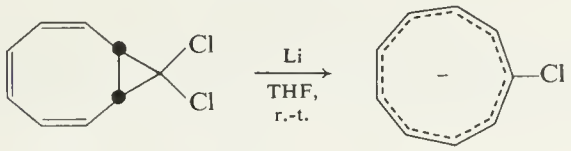
(**82***s*) (**922**) (**923**)

The anion (**923**) is also produced from the *anti*-9-chloro-compound (**82***f*),[743] or from a mixture of the *syn*- and *anti*-isomers,[956] by reaction with lithium in tetrahydrofuran; the yields are 60–65%.[956]



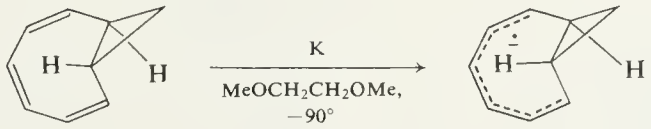
(**82***f*) (**923**)

Similarly, the chlorocyclononatetraenyl anion (**924**) may be prepared (*ca.* 50%) from 9,9-dichlorobicyclo[6.1.0]nonatriene (**82*b***).[956]



(**82*b***) (**924**)

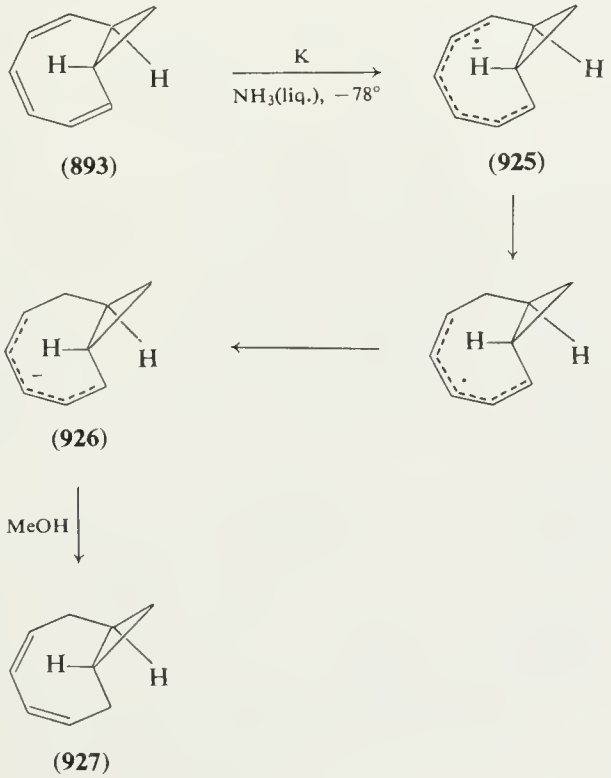
In contrast with the non-classical radical anion (**902**) obtained by the addition of an electron to *cis*-bicyclo[6.1.0]nonatriene (**82*a***), the radical anion similarly derived from the *trans*-fused isomer (**893**) has the classical structure (**925**).[995]



(**893**) (**925**)

In liquid ammonia the radical anion (**925**) apparently suffers protonation followed by further reduction to the monoanion (**926**); quenching with methanol leads to the diene (**927**)[984] (scheme 90). (For a polarographic study of the

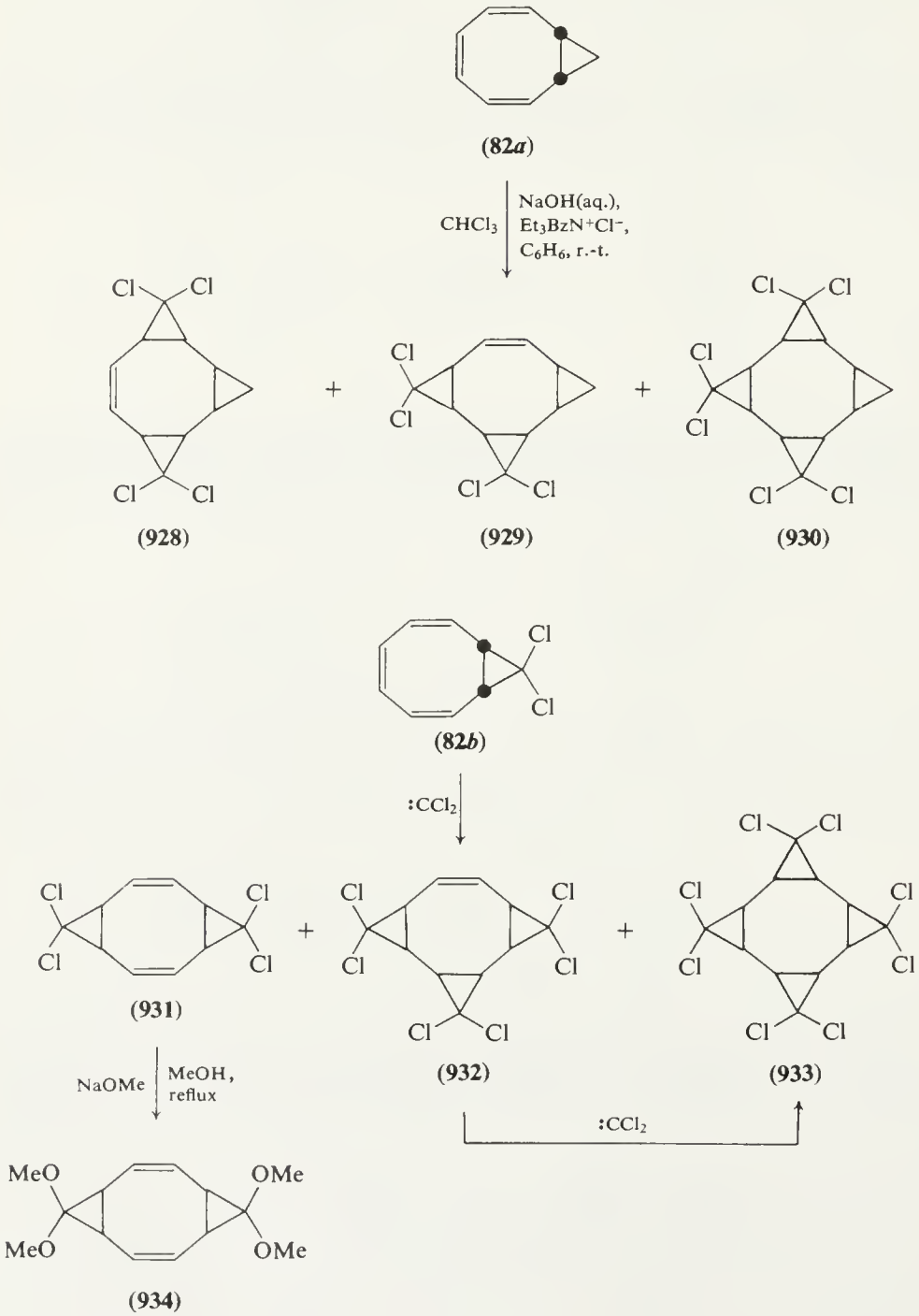
Scheme 90

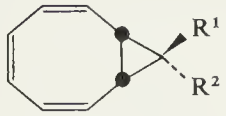


(**893**) (**925**) (**926**) (**927**)

electrochemical reduction of *trans*-bicyclo[6.1.0]nonatriene (**893**), see ref. 986.)

Cycloadditions. Reaction of bicyclo[6.1.0]nonatriene (**82*a***) with dichlorocarbene results in a mixture of the adducts (**928**) (6%), (**929**) (15%), and (**930**) (41%); the relative geometry of the ring-fusions is uncertain.[301]





Dienophile ⟶ Adducts e.g. (**935**) + (**936**)

(**82**)

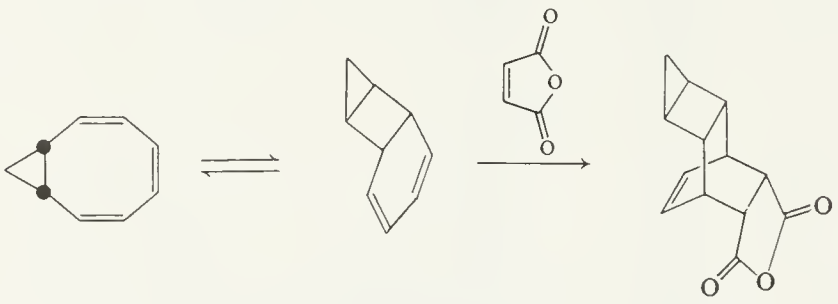
Table 114

R^1	R^2	Dienophile	Reaction conditions	Total yield (%)	Ref.
H	H	Maleic anhydride	THF or C_6H_6, reflux	90–100	996, 997, 998
D	D	Maleic anhydride	C_6H_6, reflux	—	998
H	H	*N*-Phenylmaleimide	THF, reflux	49	997, 998
H	H	Tetracyanoethylene[a]	Toluene, reflux	*ca.* 84	997, 998
CO_2Et	H	*N*-Phenylmaleimide[b]	—	—	310
CO_2Et	H	*N*-(*p*-Bromophenyl)maleimide[b]	—	—	310
Cl[c]	H	Tetracyanoethylene	THF, r.-t.	Up to 50[d]	956, (999, 1000)
Me	OAc	*N*-Phenylmaleimide[b]	THF, reflux	75	377

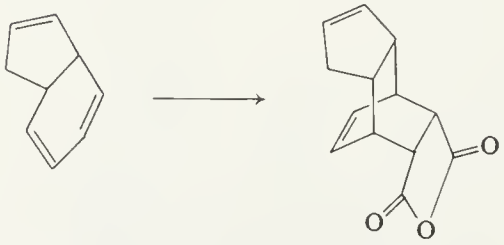
[a] Tetracyanoethylene undergoes a different type of cycloaddition in cold THF (see p. 283).
[b] Only one adduct isolated (structure uncertain).
[c] Starting material contaminated with the *syn*-isomer.
[d] Yield of major product (derived from the dihydroindene); for the minor product, see p. 284.

A similar reaction using the 9,9-dichloro-compound (**82*b***) gives the products (**931**) (7%), (**932**) (26%), and (**933**) (1.7%); the pentacyclic adduct (**933**) may be obtained in 55% yield from (**932**).[302] Treatment of the adduct (**931**) with sodium methoxide affords the diketal (**934**) (8%).[302]

The reaction of bicyclo[6.1.0]nonatriene with dienophiles is complicated by its susceptibility to thermal rearrangement (see p. 264). Thus with maleic anhydride in refluxing tetrahydrofuran or benzene two adducts (**935**) and (**936**) are formed (ratio *ca.* 3:1), these products being derived from the tricyclic valence tautomer (**937**) and the *cis*-dihydroindene (**938**) respectively. The



(**82*a***) (**937**) (**935**)



(**938**) (**936**)

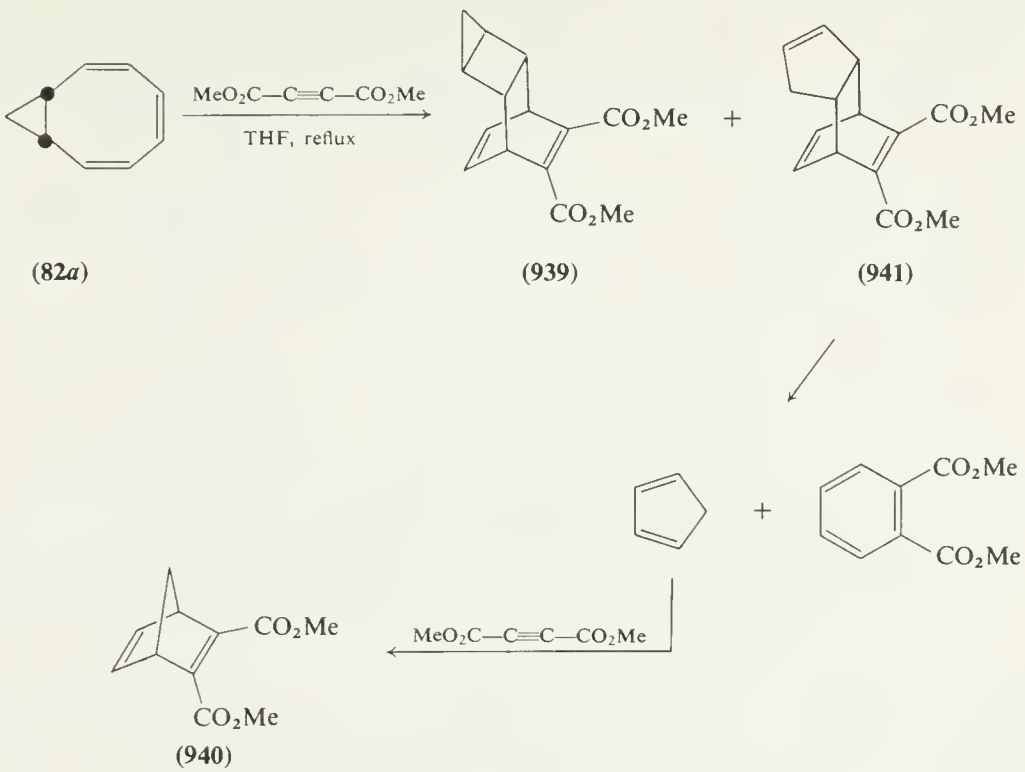
reactions of bicyclo[6.1.0]nonatrienes (**82**) with analogous dienophiles are listed in table 114.

Bicyclo[6.1.0]nonatriene reacts with dimethyl acetylenedicarboxylate to afford a single adduct (**939**). Dimethyl phthalate and the cyclopentadiene-adduct (**940**) are found as by-products, resulting from Alder–Rickert cleavage of the initially formed dihydroindene-adduct (**941**).[996, 1001] Analogues of the adduct (**939**) are formed from other acetylenic dienophiles (table 115).

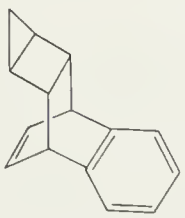
Table 115

(82) R^1	R^2	Dienophile	Reaction conditions	Yield (%)	Ref.
H	H	$MeO_2C—C\equiv C—CO_2Me$	90°	60	(996), 1001
H	H	$F_3C—C\equiv C—CF_3$	r.-t.	*ca.* 65	998
H	H	$NC—C\equiv C—CN$	THF, r.-t.	3	998
CO_2Et	H	$MeO_2C—C\equiv C—CO_2Me$	128°	—[a]	311

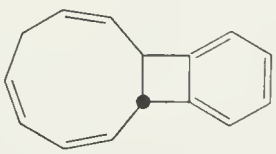
[a] Structure of adduct uncertain.



'Benzyne' forms an analogous adduct (**942**) (3%), but this is accompanied by a product of structure (**943**) (4%)[998] (*cf.* adducts of tetracyanoethylene (below) and chlorosulphonyl isocyanate (p. 285)).



(**942**)



(**943**)

The *trans*-bicyclo[7.2.0]undecatriene system (**944**) results from the addition of tetracyanoethylene to bicyclo[6.1.0]nonatriene and *anti*-9-substituted-derivatives in tetrahydrofuran (preferably at room-temperature) (table 116). This type of product is apparently formed *via* the *Z,Z,E,Z*-cyclononatetraene (**871**; R^2 = H) (see scheme 87);[1002] the reaction of this with tetracyanoethylene may possibly proceed *via* the dipolar intermediate (**945**), which may possess bis(homotropylium) stabilisation.[999, 1000] *syn*-9-Substituted derivatives of bicyclo[6.1.0]nonatriene do not react,[1003] since they cannot attain the necessary conformation for the Cope rearrangement leading to system (**871**).

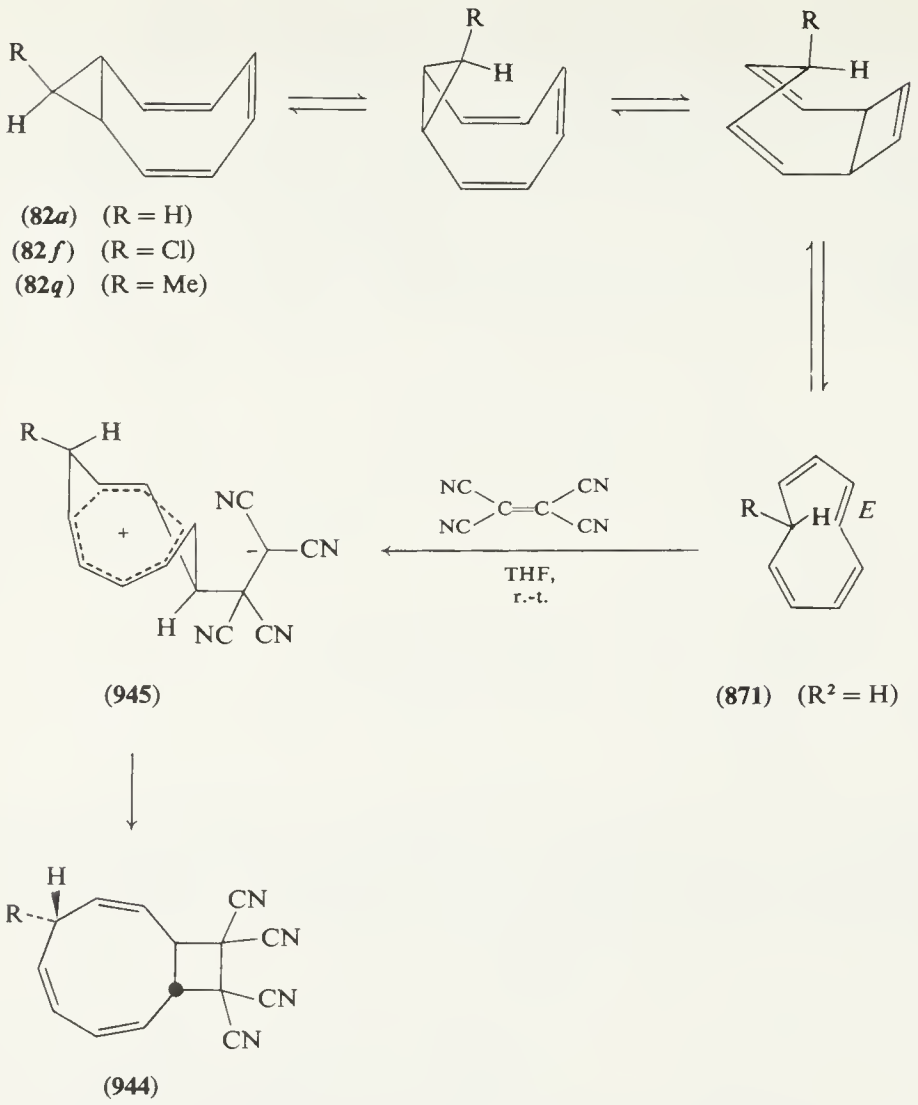
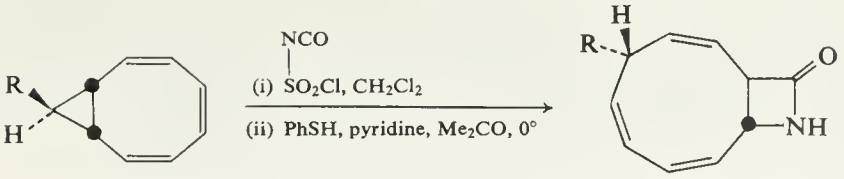


Table 116

R	Yield (%)	Ref.
H	Up to 75	743, 996–1000
Me	69	999, 1000
Cl	—[a]	999, 1000

[a] The major product is a [4 + 2] adduct of the dihydroindene (see table 114).

Similarly, *anti*-9-substituted bicyclo[6.1.0]nonatrienes on treatment with chlorosulphonyl isocyanate, followed by dechlorosulphonylation, afford the *trans*-fused β-lactams (**946**)[578,1004] (table 117). Kinetic studies appear to favour a mechanism similar to that suggested for the addition of tetracyanoethylene[1005] (see above). (For analogous reactions with the 1-, 2-, 3- and 4-



(**82***a*) (R = H)
(**82***f*) (R = Cl)
(**82***q*) (R = Me)

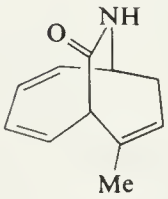
(**946**)

Table 117

R	Reaction (i), temp.	Yield (%)
H	0° → 25°	60
Me	Reflux	56
Cl[a]	r.-t.	15

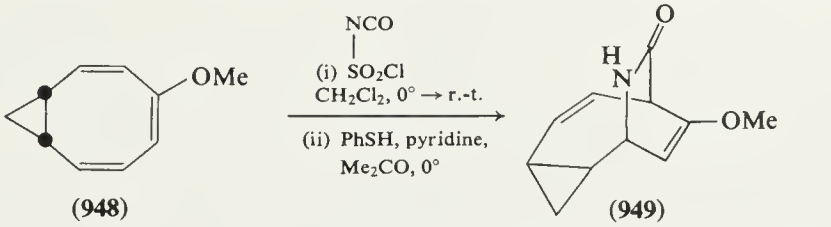
[a] Starting material contaminated with the *syn*-isomer.

methyl-derivatives (**912**)–(**915**), see refs. 578, 1003; the 2-methyl-compound gives a by-product (**947**) (5%).)



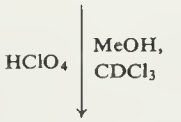
(**947**)

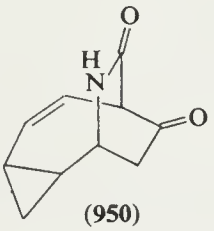
The 4-methoxy-compound (**948**) affords the product (**949**) (33.5%), which is readily converted into the ketone (**950**) (97%) in the presence of acid.[578]



(**948**)

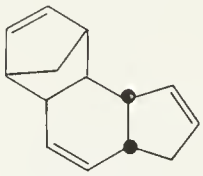
(**949**)
(Stereochemistry not certain)





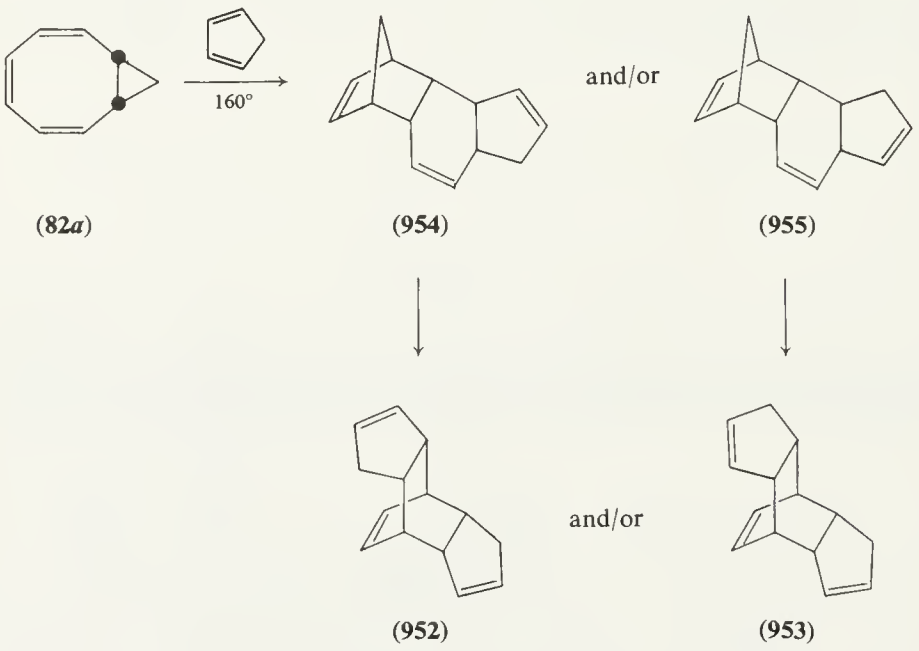
(**950**)

The reaction of cyclopentadiene with bicyclo[6.1.0]nonatriene at 160° results in a product (14%) identical with that obtained from *cis*-dihydroindene;[998] its original formulation as a norbornene derivative (**951**)[998] is not consistent with its lack of reactivity towards phenyl azide.[164]



(**951**)

It is likely that this reaction produces (**952**) and/or (**953**), partly if not entirely *via* Cope rearrangement of initially formed (**954**) and/or (**955**) (*cf.* hemicyclone below).

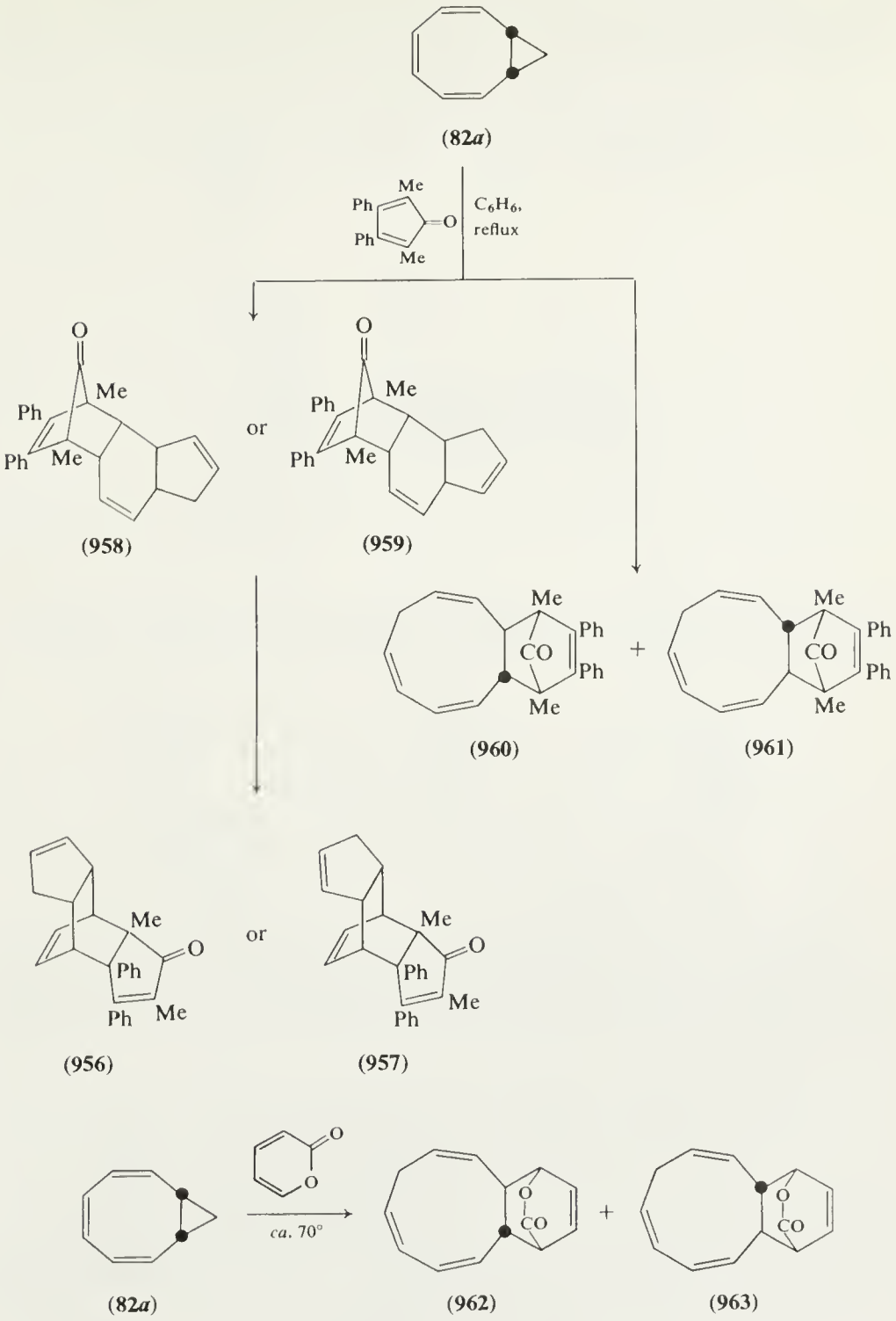


(**82***a*) (**954**) (**955**)

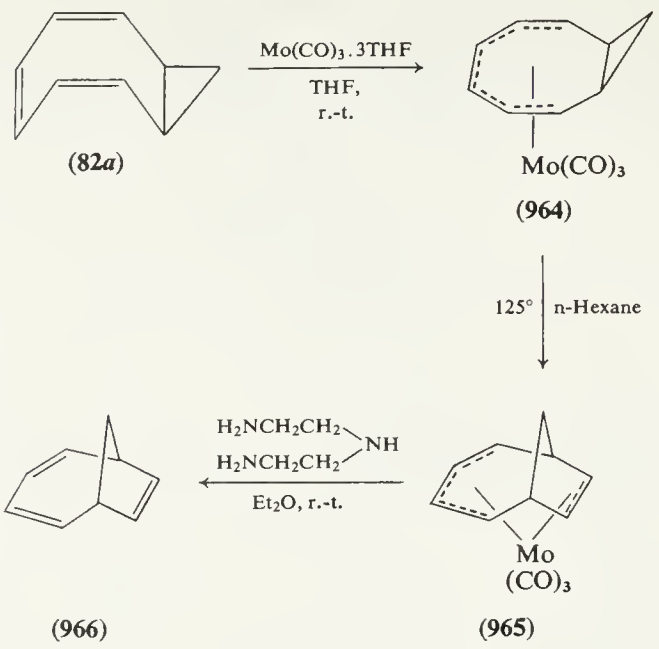
(**952**) (**953**)

With hemicyclone in refluxing benzene, bicyclo[6.1.0]nonatriene forms a product (**956**) or (**957**) (25%) resulting from Cope rearrangement of the *cis*-dihydroindene-adduct (**958**) or (**959**); in addition, adducts tentatively assigned structures (**960**) (45%) and (**961**) (30%) are produced, presumably arising from *Z,Z,E,Z*-cyclononatetraene[1006] (see scheme 87). Analogous products are apparently formed from 1,3-diphenylbenzo[*c*]furan.[1007] With α-pyrone at *ca.* 70°, a mixture of the adducts (**962**) and (**963**) is formed.[1008]

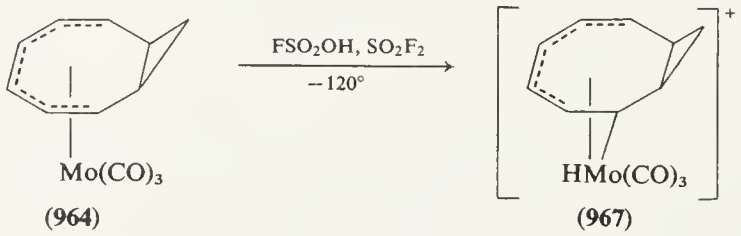
Reactions with metal derivatives. Bicyclo[6.1.0]nonatriene reacts with $Mo(CO)_3.3THF$ to give the complex (**964**) (90%); at 125° the ligand rearranges



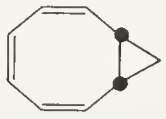
to form the bicyclo[4.2.1]nonatriene complex (**965**) (55%), which may be demetallated with diethylenetriamine to afford the hydrocarbon (**966**) (74%).[950] Protonation of the molybdenum tricarbonyl complex (**964**) in a 'super-acid'



medium occurs on the molybdenum atom, yielding a cation formulated as (**967**).[1009]



The iron tricarbonyl complexes (**968**)–(**971**) (yields in table 118) are formed by the reaction of bicyclo[6.1.0]nonatriene with $Fe(CO)_5$ under the influence of u.v. light.[1010] These complexes, together with additional products including

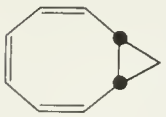


(Bicyclononatriene)$Fe(CO)_3$ (**968**)
+ (Cyclononatetraene)$Fe(CO)_3$ (**969**)
+ (Dihydroindene)$Fe(CO)_3$ (**970**)
+ (Bicyclononatriene)$Fe_2(CO)_6$ (**971**)

Table 118

Product	Yield (%)
(**968**)	15
(**969**)	35
(**970**)	6
(**971**)	1

(**972**), result from the thermal reaction of bicyclo[6.1.0]nonatriene with $Fe_2(CO)_9$ (table 119). The structures proposed[1010,1011] for these iron carbonyl



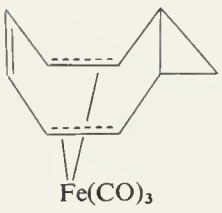
(**82***a*)

$\xrightarrow[Et_2O,\ r.\text{-}t.]{Fe_2(CO)_9}$ (**968**) + (**969**) + (**970**) + (**971**) + $(C_9H_{10})Fe(CO)_4$ (**972**)
+ two other products (not obtained pure)

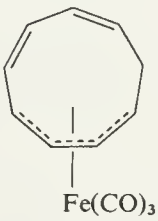
Table 119

Product	Yield (%)	Ref.
(**968**)	15	1010
(**969**)	12 (7–9)	1010, (1011)
(**970**)	46 (30–32)	1010, (1011)
(**971**)	14 (20–25)	1010, (1011)
(**972**)	8–10	1011

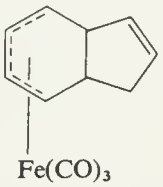
complexes are shown below (for the ^{13}C n.m.r. spectrum of (**971**), see ref. 1012).



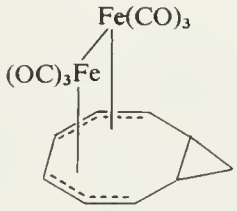
(**968**)



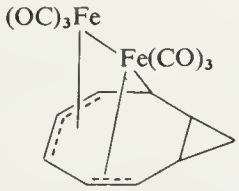
(**969**)



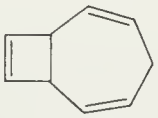
(**970**)



or



(**971**)



• $Fe(CO)_4$

(**972**)

A thermal reaction with (benzylidene-acetone)$Fe(CO)_3$ leads to a mixture of the complexes (**973**), (**970**) and (**969**) (ratio *ca.* 10:5:1, total yield *ca.* 50%).[1013]

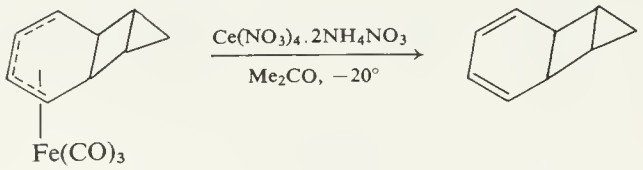
(**82***a*)

$\xrightarrow[C_6H_6,\ 55°]{(PhCH{=}CHCOCH_3)Fe(CO)_3}$ (Tricyclononadiene)$Fe(CO)_3$

(**973**)

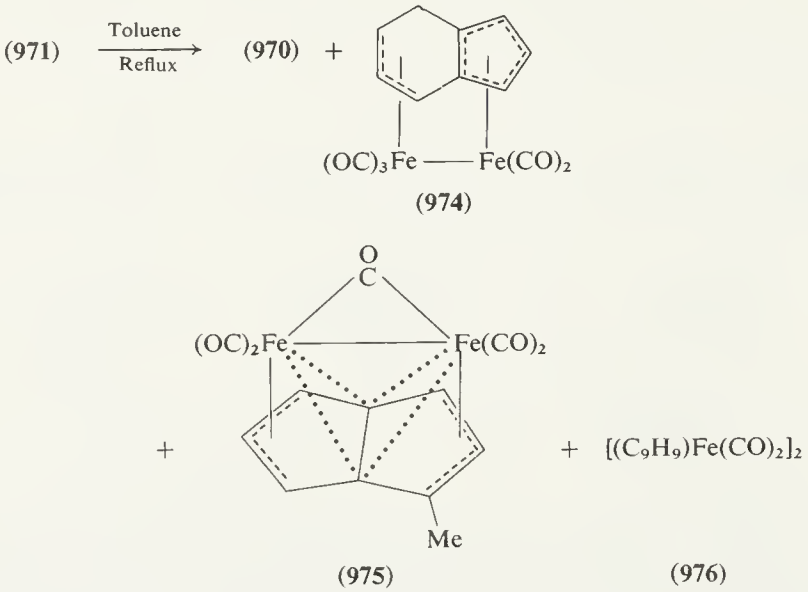
+ (**970**) + (**969**)

The principal product (**973**) is a derivative of the valence tautomer (**937**) (p. 282) of bicyclo[6.1.0]nonatriene; the free hydrocarbon may be obtained by low-temperature demetallation.[1013]

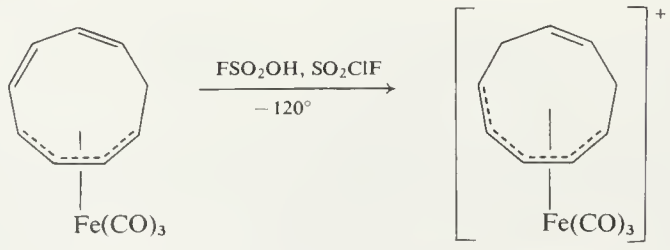


(**973**) (**937**)

Complex (**969**) rearranges at 101° to give the dihydroindene derivative (**970**).[1010] Complex (**971**) also undergoes thermal rearrangement to give (**970**) as the main product (61%); however, other products include (**974**) (1.5%), (**975**) (16%), and (**976**) (3%).[1014]



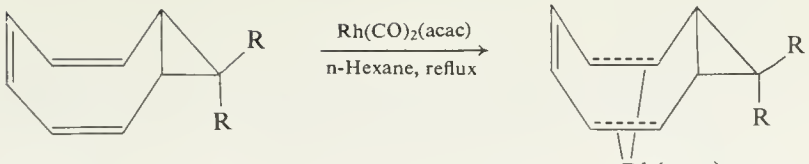
Complex (**969**) protonates to form the species (**977**).[1010]



(**969**) (**977**)

9-Methoxybicyclo[6.1.0]nonatriene forms analogues of (**970**) and (**971**).[1015]

Bicyclo[6.1.0]nonatriene and its 9,9-dimethyl-derivative react with $Rh(CO)_2(acac)$ to yield complexes of structure (**978**)[510,965] (table 120).



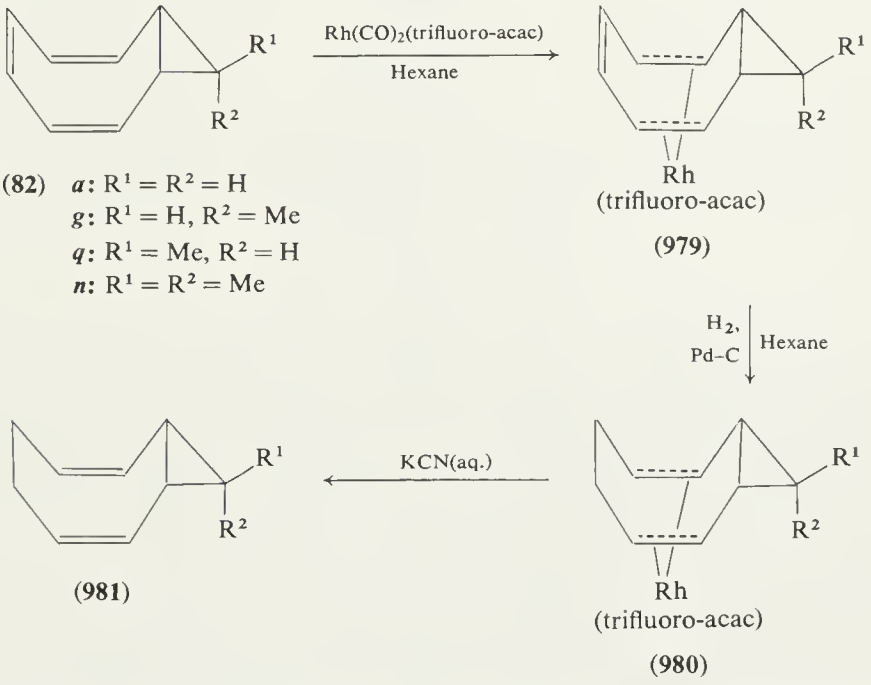
(82) (R = H, Me)

(978)

Table 120

R	Yield (%)
H	77.5
Me	59

Reaction of bicyclo[6.1.0]nonatrienes with $Rh(CO)_2$(trifluoro-acac) gives the analogous complexes (**979**) (88.5–97%); these may be converted by catalytic hydrogenation into the corresponding bicyclo[6.1.0]nona-2,6-diene complexes



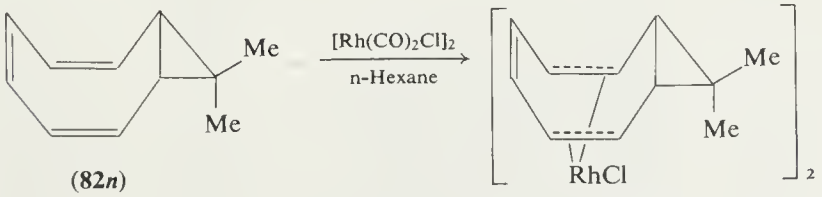
(**82**) ***a***: $R^1 = R^2 = H$
g: $R^1 = H$, $R^2 = Me$
q: $R^1 = Me$, $R^2 = H$
n: $R^1 = R^2 = Me$

(**979**)

(**981**)

(**980**)

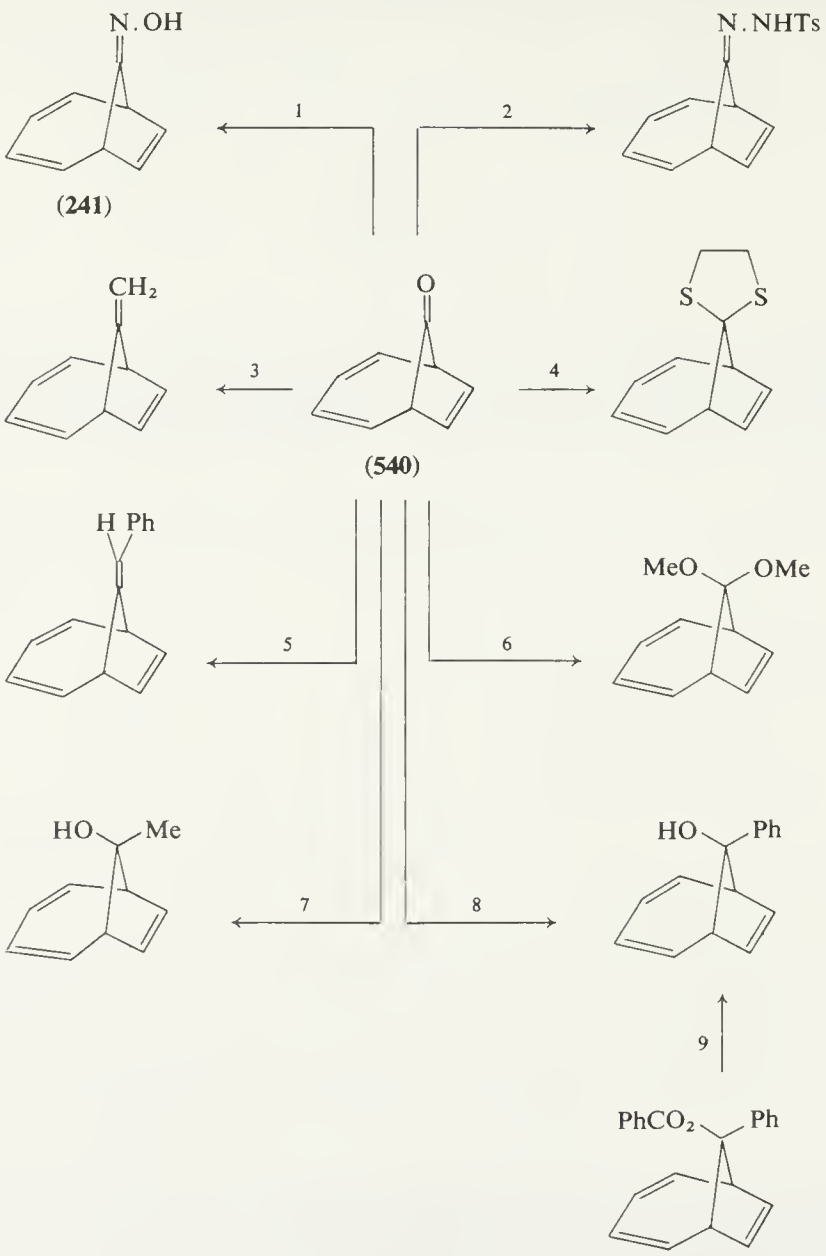
(**980**) (87–90.5%), which on treatment with aqueous potassium cyanide afford the hydrocarbons (**981**) (68–85%).[1016] The 9,9-dimethyl-compound (**82*n***), with $[Rh(CO)_2Cl]_2$, gives the dimeric complex (**982**) (82%).[965]



(**82*n***)

(**982**)

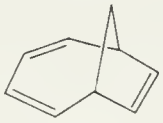
Scheme 91



Reaction	Conditions	Yield (%)	Ref.
1	NH_2OH(aq.), 0°	79	52
2	NH_2NHTs, MeOH, reflux	85	52
3	$Ph_3P{=}CH_2$, e.g. DMSO, 74°	38–77	758, 1017–1019
4	$HSCH_2CH_2SH$, $BF_3.Et_2O$, 0°	79	52
5	$Ph_3P{=}CHPh$, THF, hexane, r.-t.	62	1020
6	$(MeO)_3CH$, NH_4NO_3	—	1021
7	MeMgBr (MeMgI), Et_2O, 0°	(77), 85	(758), 1017
8	PhLi, Et_2O, 5° → r.-t.	37	52
9	'Vigorous alkaline hydrolysis'	—	1022

12. Bicyclo[4.2.1]nona-2,4,7-trienes

Bicyclo[4.2.1]nona-2,4,7-triene (**966**) is not obtainable directly from COT, but may be prepared *via* bicyclo[6.1.0]nona-2,4,6-triene (see p. 288).

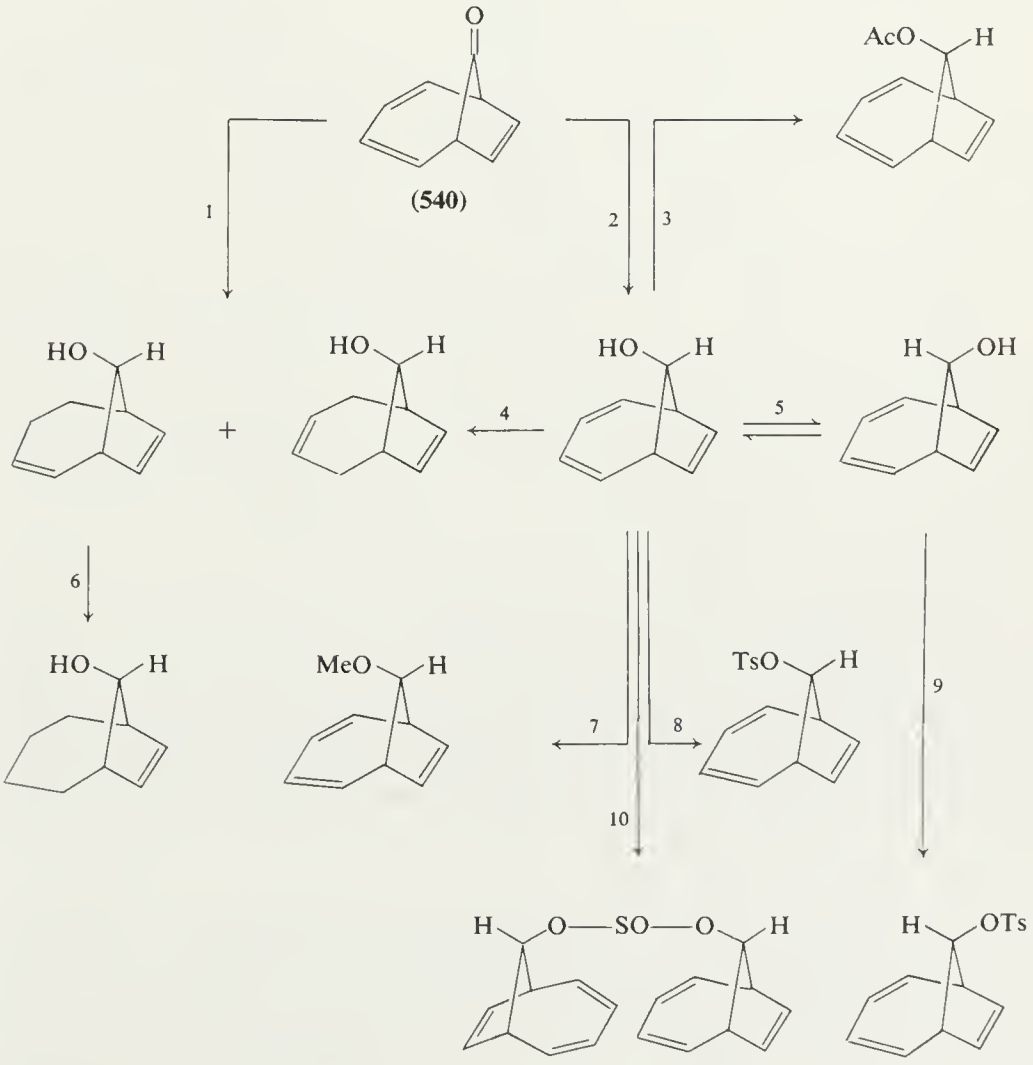


(966)

Bicyclo[4.2.1]nona-2,4,7-trien-9-one (**540**) is readily available from COT^{2-} and dimethylcarbamoyl chloride (see p. 181). For other derivatives, see pp. 176–80.

Functional group transformations. See schemes 91 and 92.

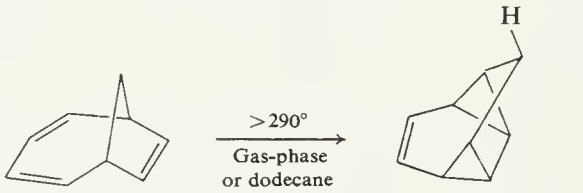
Scheme 92



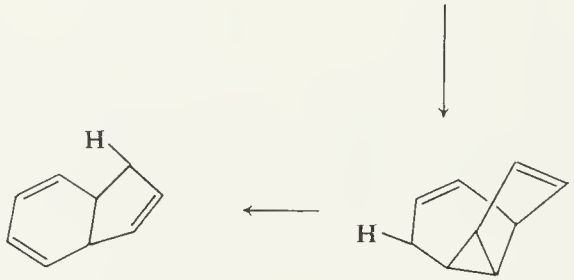
Reaction	Conditions	Yield (%)	Ref.
1	$LiAlH_4$, Et_2O, −78°	100[a]	757
2	$NaBH_4$, e.g. MeOH, 0° → r.-t.	74–95	52, 757, 758
3	Ac_2O, pyridine, reflux	70	52
4	$LiAlH_4$, Et_2O, e.g. reflux	—	757, 758, (1023)
5	$Al(OPr^i)_3$, Pr^iOH, Me_2CO, 150°	—	1024
6	$LiAlH_4$, THF, reflux	(95)	757, (1023)
7	MeI, NaH, $MeOCH_2CH_2OMe$, r.-t.	80	52
8	*p*-Me.C_6H_4.SO_2Cl, pyridine, e.g. −20°	86	52, (757, 1023)
9	—	—	1024
10	$SOCl_2$, pyridine, hexane, 0° → reflux	93	52

[a] Product ratio 4.4 : 1.

Thermal and other rearrangements. At temperatures above 290° bicyclo[4.2.1]-nonatriene (**966**) rearranges to the *cis*-dihydroindene (**938**), probably *via* an intramolecular Diels–Alder reaction and two successive [1,5] (homodienyl) hydrogen shifts.[1025]

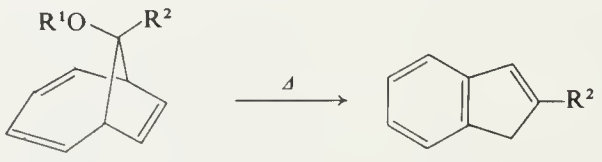


(**966**)



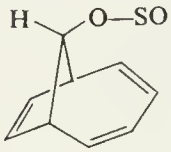
(**938**)

The esters (**983**) rearrange thermally to give indenes (**984**) (table 121). These rearrangements may involve intermediate bicyclo[4.2.1]nona-2,4,7-trien-9-yl cations (**985**),[1017] and it is convenient at this point to collect together other rearrangements which may proceed *via* this species. (For mechanistic discussions, and the possible 'homoaromaticity' and 'bicycloaromaticity' of the

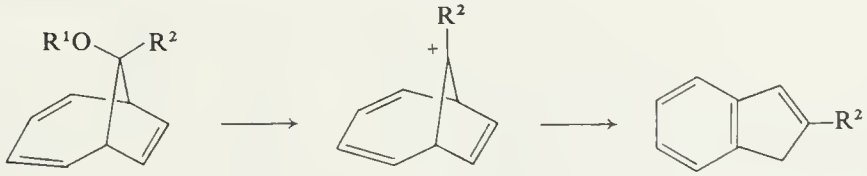


(**983**) (**984**)

Table 121

R^1	R^2	Conditions	Yield (%)	Ref.
MeCO	Me	Dimethyl sebacate, 200°	62	377
PhCO	Ph	*o*-Dichlorobenzene, reflux	68	377
p-Me.C_6H_4.SO_2	H	(G.l.c.)	—	52
p-Me.C_6H_4.SO_2	D	Dimethyl sulphoxide, 74°	>74	1017
	H	(G.l.c.)	—	52

cations (**985**), see refs. 1017, 1023, 1024, 1026.) Such rearrangements include those listed in table 122. A related process is the acid-catalysed rearrangement

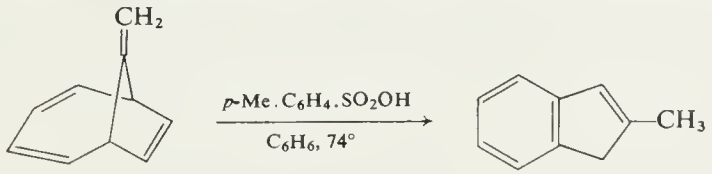


(**983**) (**985**) (**984**)

Table 122

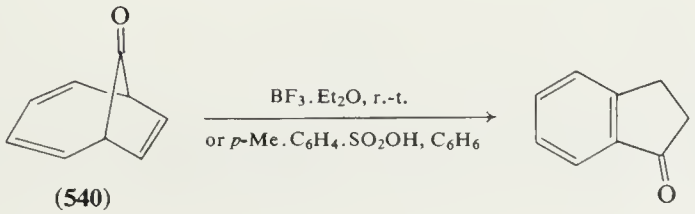
R^1	R^2	Reagents and conditions	Yield (%)	Ref.
H	Me	*p*-Me.C_6H_4.SO_2OH, C_6H_6, 74°	>80	1017, (1022)
p-Me.C_6H_4.SO_2	H	NaI, Me_2CO, reflux	59	52

of the 9-methylene-derivative (**986**) to 2-methylindene (>80%).[1017] (For the protonation of (**986**) in a 'superacid' medium at −135°, see ref. 1027.) The



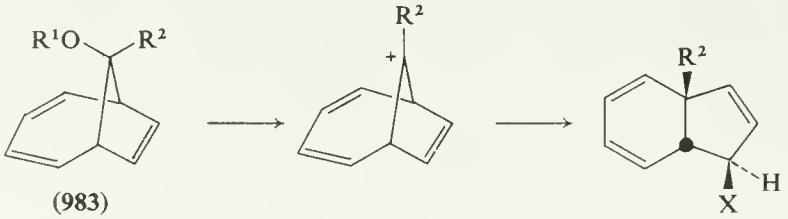
(**986**)

ketone (**540**), however, yields indan-1-one (39%), on treatment with boron trifluoride etherate[52] (or toluene-*p*-sulphonic acid[1017]).



(**540**)

An alternative rearrangement mode, involving nucleophile participation, is observed with some systems, and may lead to products of structure (**987**) (table 123).



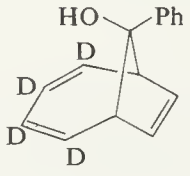
(**983**) (**987**)

Table 123

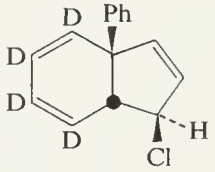
R^1	R^2	Reaction conditions	X	Yield (%)	Ref.
H[a]	Ph	$SOCl_2$, pyridine, Et_2O, r.-t.	Cl	(High)	1022
p-Me.C_6H_4.SO_2	H	$LiAlH_4$, Et_2O, 0°	H	85	52
p-Me.C_6H_4.SO_2	H	HOAc, NaOAc, 50°	OAc	99	757, 1023
p-Me.C_6H_4.SO_2	H[b]	MeOH, lutidine, reflux	OMe	77	1024

[a] The deuteriated compound (**988**) affords the product (**989**).[1028]

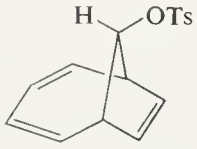
[b] The stereoisomer (**990**) gives a virtually identical result; the deuteriated derivative (**991**) affords (**992**).[1024]



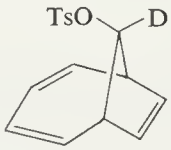
(**988**)



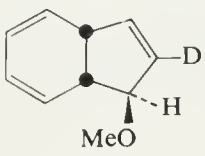
(**989**)



(**990**)

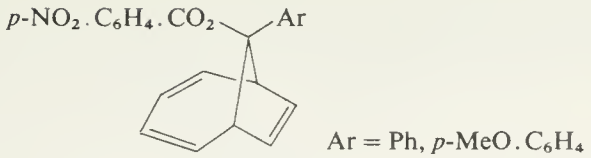


(**991**)

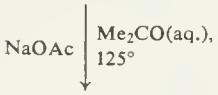


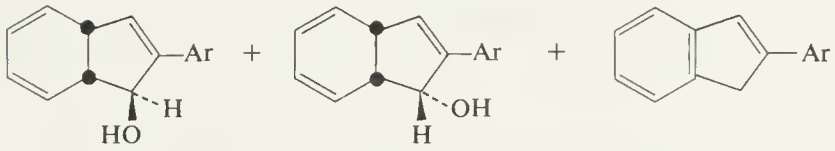
(**992**)

Solvolysis of the *p*-nitrobenzoates (**993**) yields a mixture of the products (**994**), (**995**) and (**996**) (*ca.* 80, 10 and 10% severally).[757]



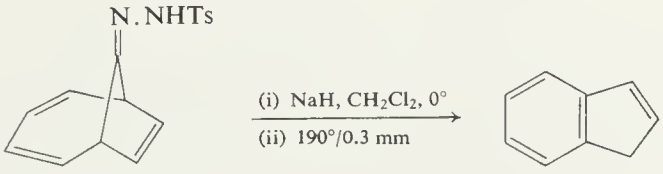
(993)





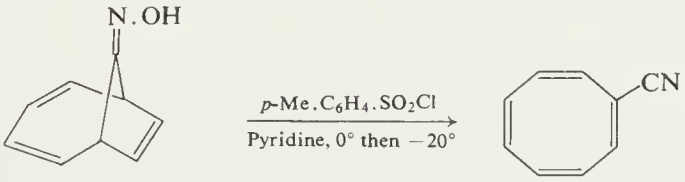
(994) (995) (996)

Thermolysis of the sodium salt of the tosylhydrazone (**997**) affords indene (40%).[52]



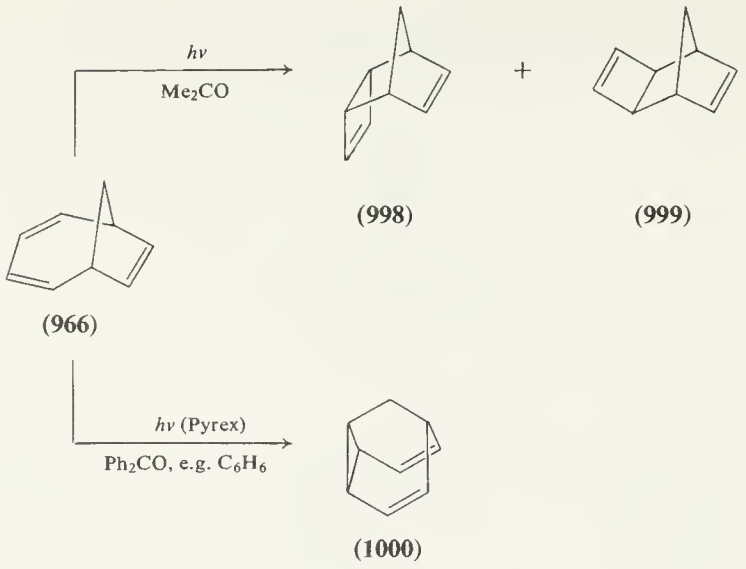
(997)

An abnormal Beckmann rearrangement of the oxime (**241**) occurs on treatment with toluene-*p*-sulphonyl chloride, with the formation of cyano-cyclo-octatetraene (57%).[52]

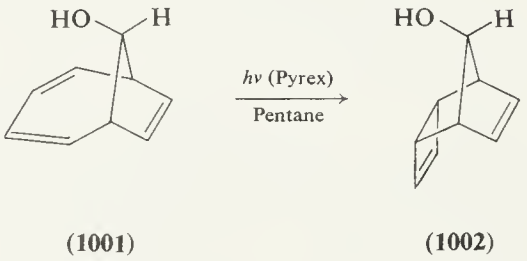


(241)

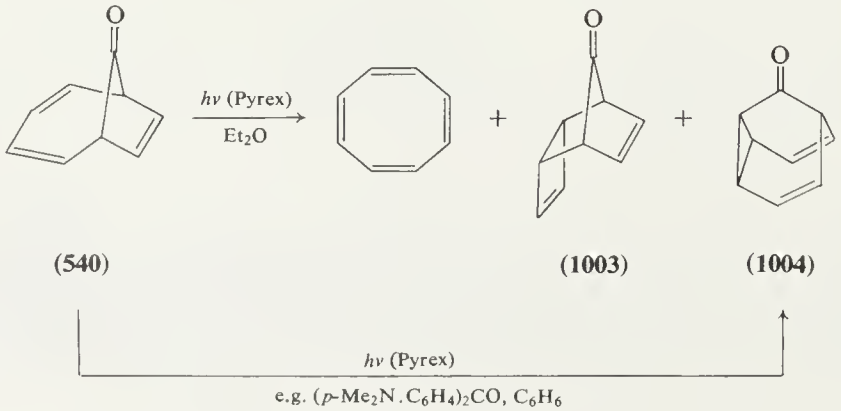
Photolysis. U.v. irradiation of bicyclo[4.2.1]nonatriene in acetone[1029] (or dioxan[1030]) affords the *endo*- and *exo*-tricyclic dienes (**998**) and (**999**) (20% and 13% respectively[1029]). In the presence of benzophenone, however, barbaralane (**1000**) is produced (up to 65%).[1031]



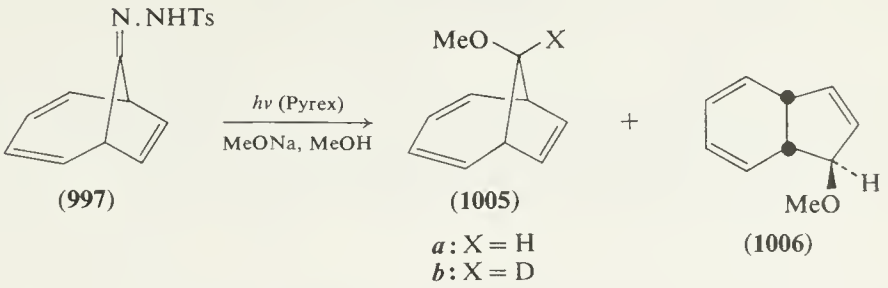
Non-sensitised irradiation of the *syn*-9-hydroxy-derivative (**1001**) gives the *endo*-tricyclic diene (**1002**) (50–60%).[1032]



In the absence of a sensitiser the 9-oxo-compound (**540**) affords COT as the main product (80–82%),[51, 52] together with minor amounts of the norbornenone (**1003**) and barbaralone (**1004**).[52] In the presence of benzophenone, fluorenone or Michler's ketone, however, barbaralone is the principal product (up to 78.5%).[51, 52, 604]



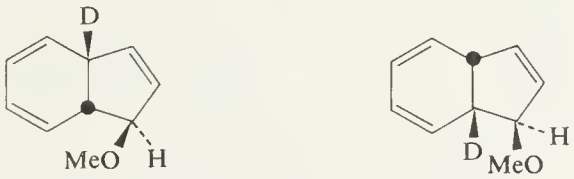
Photolysis of the sodium salt of the tosylhydrazone (**997**) leads to the *syn*-9-methoxy-compound (**1005***a*) (44%) and the dihydroindene (**1006**) (39%).[1024]



(**997**) (**1005**) (**1006**)

a: X = H
b: X = D

(In MeOD, the observed products were (**1005***b*) and a 1:1 mixture of (**1007**) and (**1008**)[1024].)

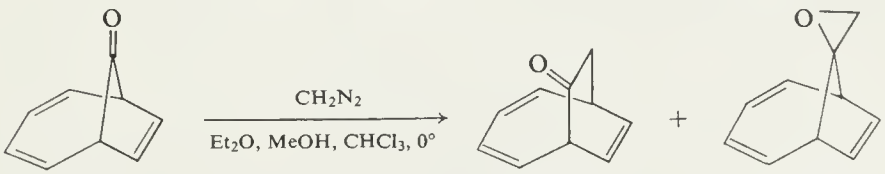


(**1007**) (**1008**)

Reduction. For examples of catalytic hydrogenation of the bicyclo[4.2.1]nonatriene system, see refs. 377, 756.

For partial reduction of the conjugated diene system in the 9-oxo-derivative (**540**) by lithium aluminium hydride, see scheme 92 (p. 293).

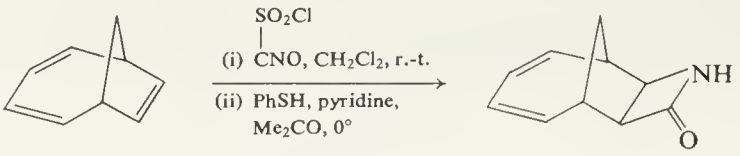
Reactions with diazoalkanes. Reaction of the ketone (**540**) with diazomethane affords the ring-expanded product (**1009**) (63%), together with the epoxide (**1010**) (27%).[52,1033] For the analogous reaction with diazoethane, see ref.



(**540**) (**1009**) (**1010**)

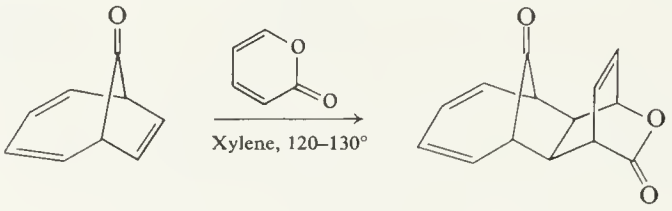
1034. The ketone (**1009**) is a useful source of bicyclo[4.2.2]decatetraene systems.[1033,1034]

Cycloadditions. Reaction of bicyclo[4.2.1]nonatriene with chlorosulphonyl isocyanate, followed by dechlorosulphonylation, gives the *exo*-β-lactam (**1011**) (80%).[1020]



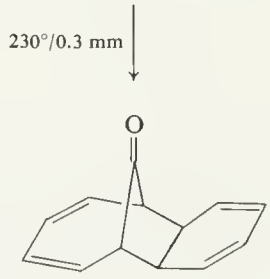
(966) **(1011)**

The ketone (**540**) adds α-pyrone to afford the product (**1012**) (34%), which on thermal decarboxylation gives the tetraene (**1013**) (70%).[1019]



(540) **(1012)**

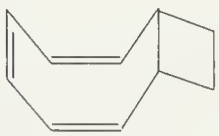
(Stereochemistry uncertain)



(1013)

13. Bicyclo[6.2.0]deca-2,4,6-trienes

The parent hydrocarbon (**515*a***) may be prepared from COT^{2-} and 1,2-dibromoethane (see p. 175).

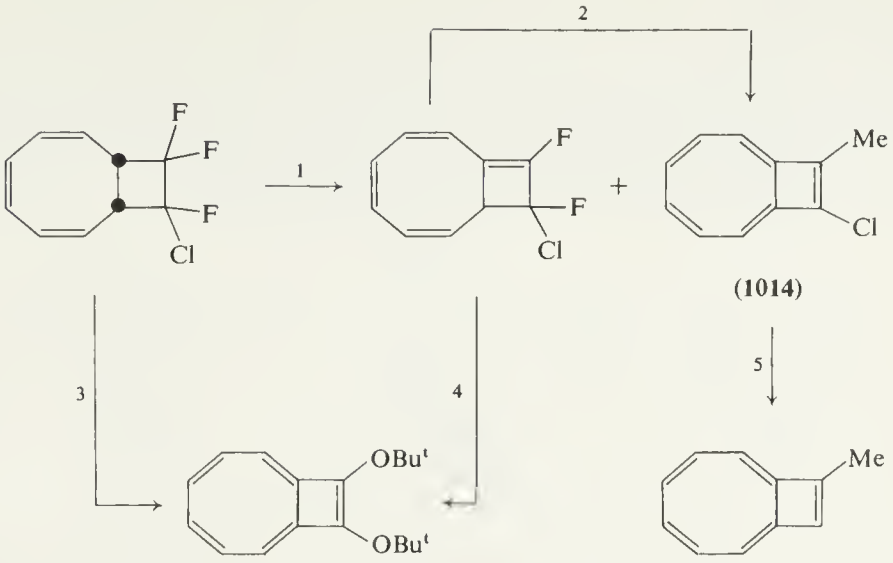


(515*a*)

9,9,10,10-Tetrahalo-derivatives of the bicyclo[6.2.0]deca-2,4,6-triene system are available from the [2 + 2] cycloaddition of 1,1-dichloro-2,2-difluoro- and chlorotrifluoroethylene to COT (see p. 39).

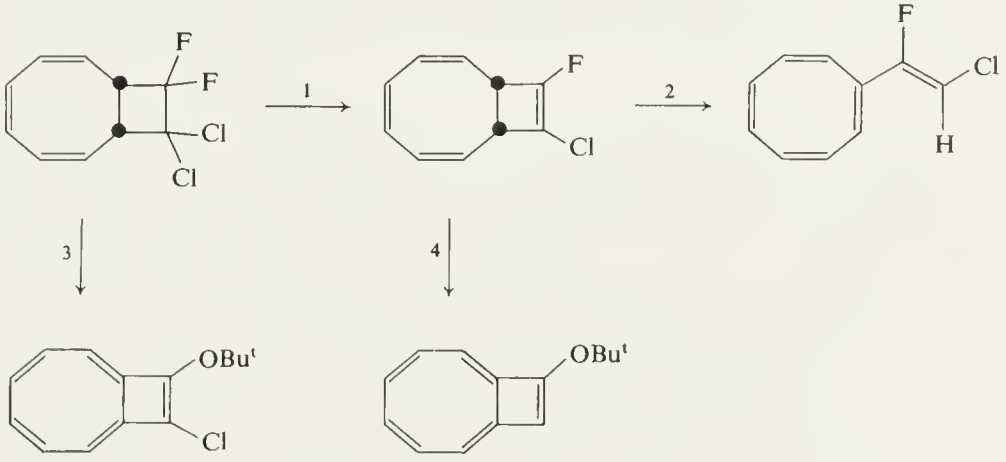
Functional group transformations. Transformations of 9,9,10,10-tetrahalo-derivatives are shown in schemes 93 and 94.

Scheme 93



Reaction	Conditions	Yield (%)	Ref.
1	MeLi, Et_2O, $-60° \rightarrow -10°$	18 + 6	325
2	MeLi, Et_2O, $-60° \rightarrow -10°$	*ca.* 3	325
3	KOBu^t, pentane, Et_2O, 30–40°	*ca.* 30	1035
4	KOBu^t, pentane, Et_2O, 20°	*ca.* 50	325
5	(i) Mg, $BrCH_2CH_2Br$, THF, 40°; (ii) EtOH	*ca.* 30	325

Scheme 94

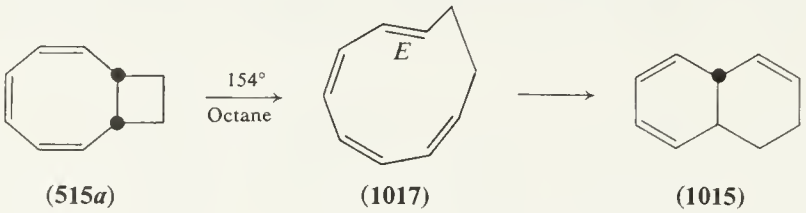


Reaction	Conditions	Yield (%)	Ref.
1[a]	MeLi, Et_2O, $-20°$ to $-10°$	*ca.* 30	(324), 325
2	NaH, $(Me_2N)_3PO$, 5–10°	*ca.* 10	325
3	KOBu^t, pentane, Et_2O, 30–40°	50	1035
4	KOBu^t, pentane, Et_2O, 30–40°	*ca.* 10	1035

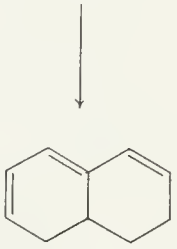
[a] Compound (**1014**) (see scheme 93) is obtained as a by-product (3%).

For further reactions of bicyclo[6.2.0]deca-1,3,5,7,9-pentaenes, see refs. 324, 325, 1035, 1036.

Thermolysis. *cis*-Bicyclo[6.2.0]deca-2,4,6-triene (**515***a*) rearranges at 154° to give the *trans*-fused product (**1015**), which on further heating isomerises to the fully conjugated system (**1016**); the suggested mechanism involves the *Z,Z,Z,E*-cyclodecatetraene (**1017**)[1037] (*cf.* scheme 86, p. 266).

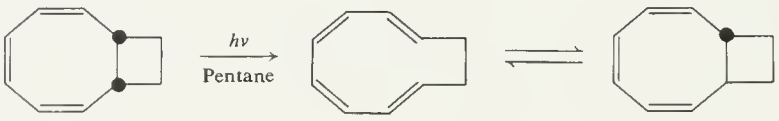


(**515***a*) (**1017**) (**1015**)

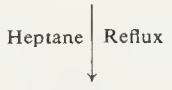


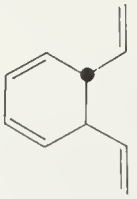
(**1016**)

Photolysis. Photochemical rearrangement of *cis*-bicyclo[6.2.0]decatriene produces the *E,Z,Z,E*-cyclodecatetraene (**1018**), which equilibrates with the *trans*-fused bicyclic isomer (**1019**); at 98° *trans*-5,6-divinylcyclohexa-1,3-diene is formed, presumably by Cope rearrangement of the monocyclic tetraene (**1018**).[751]



(**515***a*) (**1018**) (**1019**)

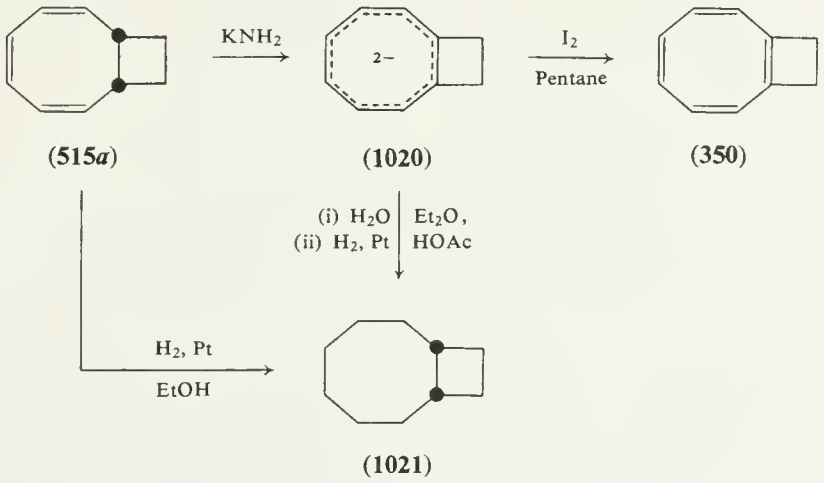




Reduction and proton-abstraction. For a polarographic study of the electrochemical reduction of the bicyclic triene (**515***a*), see ref. 986.

For catalytic hydrogenation of the bicyclo[6.2.0]decatriene system, see e.g. refs. 1038, 1039.

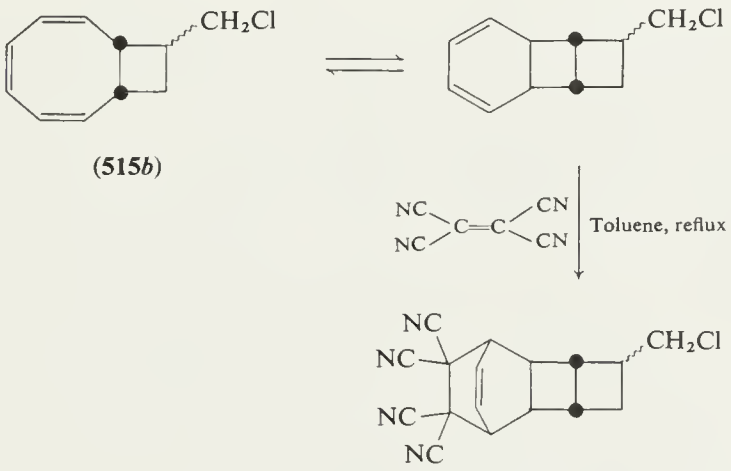
Deprotonation of *cis*-bicyclo[6.2.0]decatriene with potassium amide in liquid ammonia gives the dianion (**1020**), which with iodine affords the cyclooctatetraene (**350**); reaction of the dianion (**1020**) with wet ether, followed by catalytic hydrogenation, yields the product (**1021**) (92%), identical with that obtained by direct hydrogenation of the starting material.[1038,1040]



(**515***a*) (**1020**) (**350**)

(**1021**)

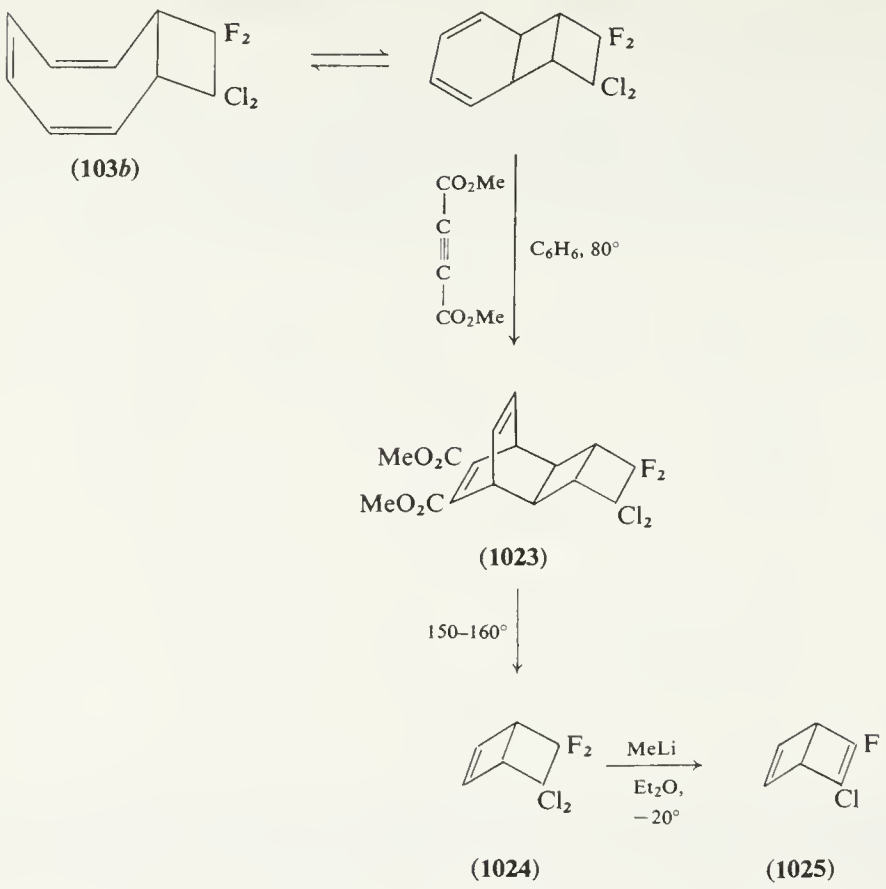
Cycloadditions. Reaction of the chloromethyl-derivative (**515***b*) with tetracyanoethylene yields an adduct (*ca.* 100%) assumed to possess structure (**1022**).[382]



(**515***b*)

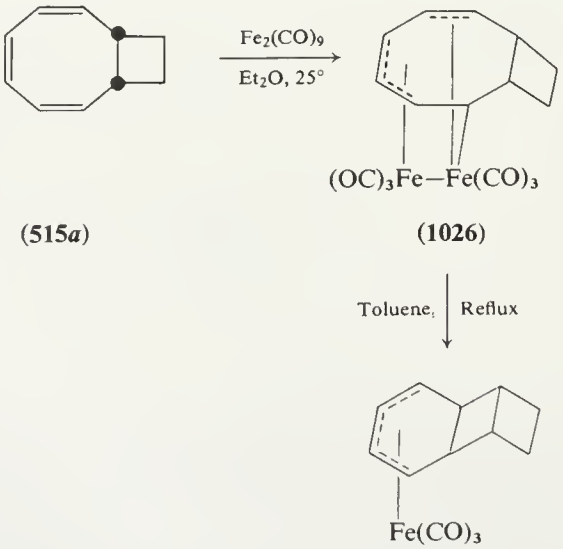
(**1022**)

The tetrasubstituted derivative (**103***b*) reacts with acetylenedicarboxylic ester to give an adduct (presumably (**1023**)) (80%), which on thermolysis yields the bicyclo[2.2.0]hexene (**1024**) (65%); treatment of this with methyllithium generates the (explosive) Dewar-benzene (**1025**) (70%).[324] (The parent hydrocarbon (**515***a*) does not react with chlorosulphonyl isocyanate[1003].)



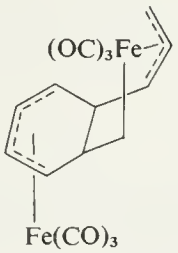
(103*b*) (1023) (1024) (1025)

Reactions with metal derivatives. *cis*-Bicyclo[6.2.0]decatriene reacts with $Fe_2(CO)_9$ to form a plethora of complexes. At room-temperature the principal product is the binuclear compound (**1026**) (23%),[1041–1043] but at higher tem-

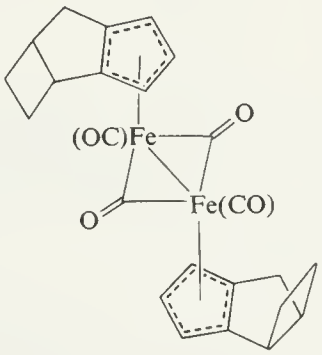


(515*a*) (1026) (1027)

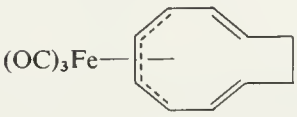
peratures this is converted (mainly) into the tricyclic mononuclear derivative (**1027**) (64–66%)[1041,1043] (this is also obtained (in very low yield) by u.v. irradiation in the presence of $Fe(CO)_5$[1013]). However, other complexes which have been isolated from this reaction (in minute yields) include (**1028**),[1041,1044] (**1029**),[1041,1043] (**1030**),[1045] (**624*a***)[1045] and (**1031**),[1045] although the last two may have resulted from contaminants in the bicyclo[6.2.0]decatriene.[1045]



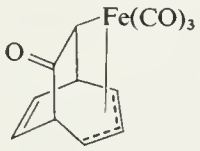
(**1028**)



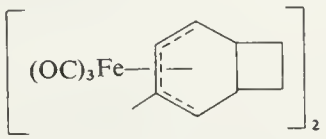
(**1029**)



(**1030**)

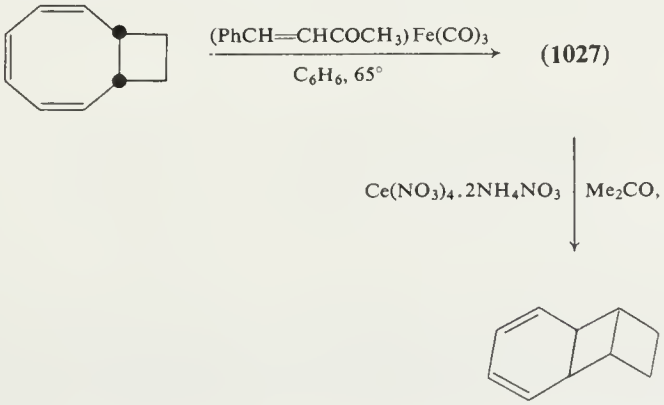


(**624*a***)



(**1031**)

With (benzylidene-acetone)$Fe(CO)_3$, the complex (**1027**) is formed in excellent yield (82%); low-temperature demetallation then affords the tricyclic diene (**1032**) (84%).[1013]



(**1032**)

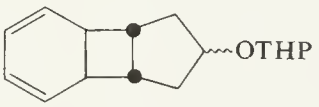
14. Bicyclo[6.3.0]undeca-2,4,6-trienes

The bicyclo[6.3.0]undeca-2,4,6-triene system (**516***a*) is formed (initially) from COT^{2-} and 1,3-dihalopropanes (see p. 176). Equilibration with the valence isomer (**517***a*) is rapid at normal temperatures, the tricyclic diene (**517***a*) predominating (*ca.* 97% at 58°).[752,753]

(**516***a*) (**517***a*)

Functional group transformations. Transformations of the tetrahydropyranyloxy-derivative (**517***b*) are given in scheme 95. (For dehydrochlorination of the chloro-derivative (**1033**), see ref. 382.)

Scheme 95



(**517***b*)

THP = 2-tetrahydropyranyl

1 ↓

$C_{11}H_{13}.OH$

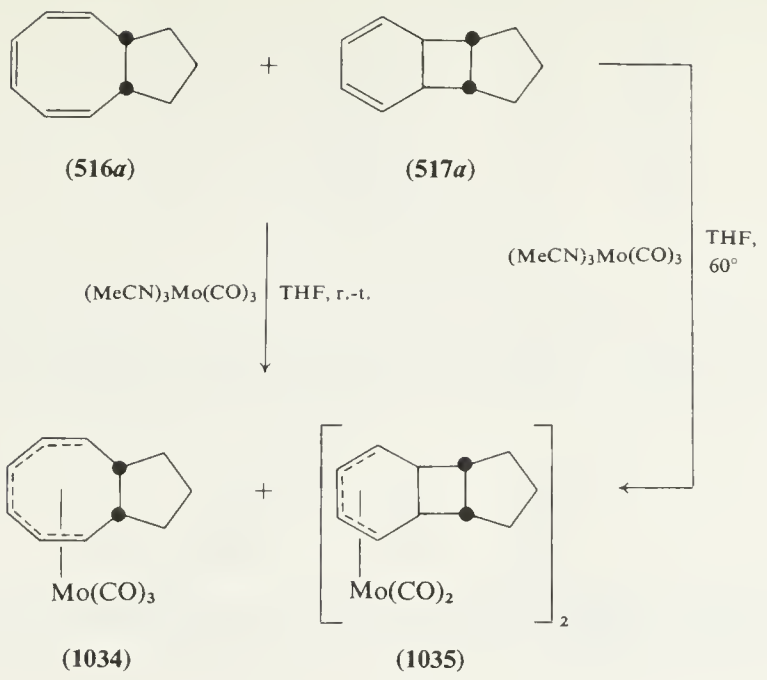
2 ↓

$C_{11}H_{13}.Cl$

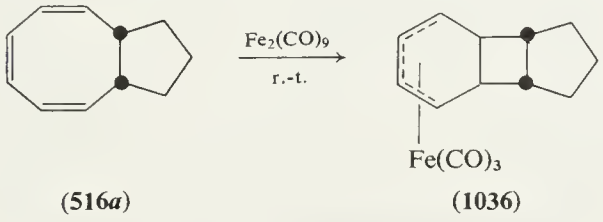
(**1033**)

Reaction	Reagents and conditions	Yield (%)	Ref.
1	Conc. HCl, MeOH, reflux	51	382
2	$POCl_3$, pyridine, 0° → 100°	*ca.* 55	382

Reactions with metal derivatives. A mixture of the valence tautomers (**516***a*) and (**517***a*) (*ca.* 1 : 3) reacts with $(MeCN)_3Mo(CO)_3$ at room-temperature to give the complexes (**1034**) (33%) and (**1035**) (6.4%); the latter may be obtained in higher yield (44%) by using the pure ligand (**517***a*) and a higher reaction temperature.[752,753]



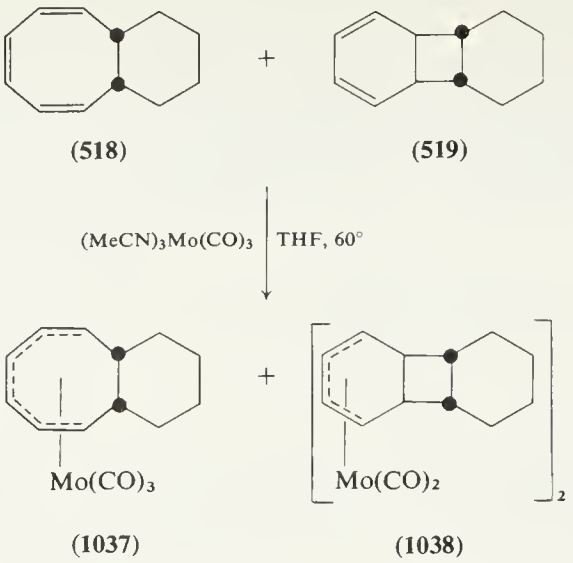
With $Fe_2(CO)_9$, the only isolated product has structure (**1036**).[752,753,1046]



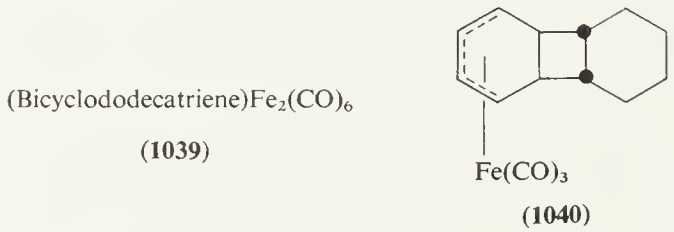
15. Bicyclo[6.4.0]dodeca-2,4,6-trienes

The parent hydrocarbon (**518**) is prepared from COT^{2-} and 1,4-dibromobutane (see p. 176). Valence tautomerism results in equilibration with the tricyclic diene (**519**) (*ca.* 50% at 114°).[752,753]

Reactions with metal derivatives. The mixture of valence tautomers (**518**) and (**519**) reacts with $(MeCN)_3Mo(CO)_3$ to afford the complexes (**1037**) (35%) and (**1038**) (9%).[752,753]



With $Fe_2(CO)_9$ (hexane, 50°) the products are (**1039**) (0.6%) (*cf.* (**1026**), p. 304) and (**1040**) (30%).[752, 753]

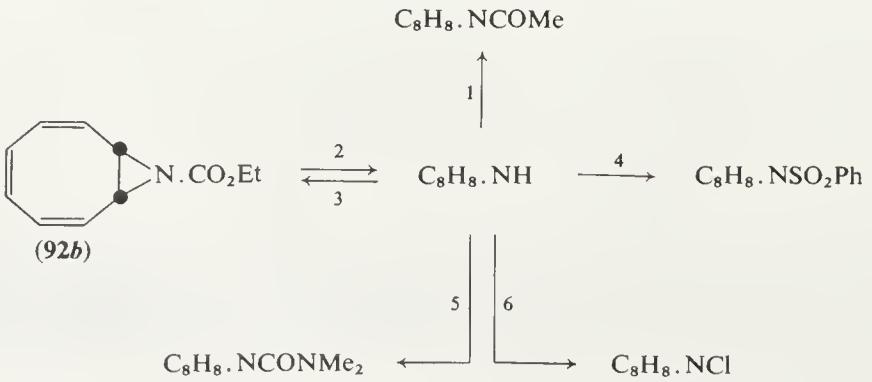


16. 9-Azabicyclo[6.1.0]nona-2,4,6-trienes

The generation of nitrenes in the presence of COT leads to the 9-azabicyclo-[6.1.0]nona-2,4,6-triene system (**92**) (see p. 37).

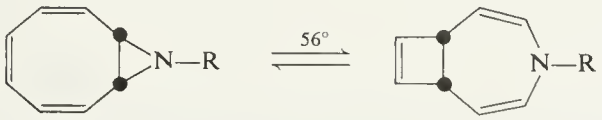
Functional group transformations. See scheme 96.

Scheme 96



Reaction	Reagents and conditions	Ref.
1	MeCOCl	1047
2	$LiAlH_4$, 0°	1047
3	$ClCO_2Et$	1047
4	$PhSO_2Cl$	1047
5	$ClCONMe_2$	1047
6	*N*-Chlorosuccinimide	1047

Thermolysis. The tendency for the *N*-substituted derivatives (**92**) to undergo thermal rearrangement to the valence isomers (**1041**) is very sensitive to the type of group attached to the nitrogen atom (table 124) (for a mechanistic discussion of this rearrangement, see ref. 317). This equilibrium may 'leak' (especially at



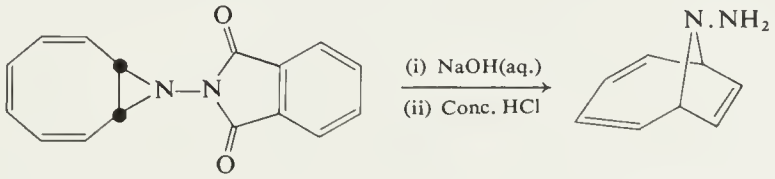
(**92**) (**1041**)

Table 124

R	Proportion of (**1041**) (%)	Ref.
COMe	*ca.* 95	1048
CO_2Me	*ca.* 95[a]	1049
CO_2Et	*ca.* 95[a]	(319), 1048
$CONMe_2$	0	1047, (1050)
CN	—[b]	317
SO_2Ph	0	1047

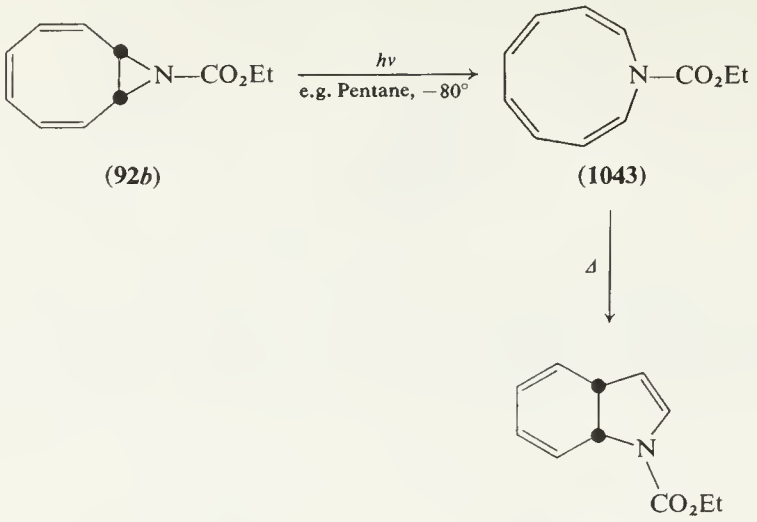
[a] Starting with (**1041**). [b] Polymerisation occurs.

higher temperatures) into other, irreversible rearrangement paths (see refs. 1048, 1049). Exceptionally, rearrangement of the compound (**92***c*) occurs on hydrolysis, which leads to the 9-azabicyclo[4.2.1]nonatriene system (**1042**) (20%).[320]



(**92***c*) (**1042**)

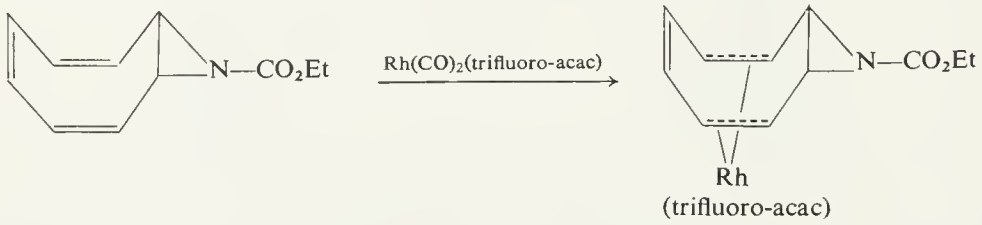
Photolysis. U.v. irradiation of the ester (**92***b*)[1051,1052] (or (**1041**; R = CO_2Et)[1051]) gives the thermally labile azonine (**1043**), which isomerises (even at room-temperature) to the *cis*-dihydroindole derivative (**1044**).[1051,1052] (For



(92*b*) (1043) (1044)

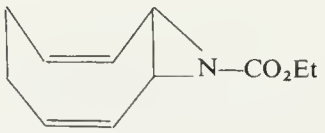
conversion of (**1043**) into the parent azonine and other *N*-substituted derivatives, see refs. 1053, 1054.)

Reactions with metal derivatives. With $Rh(CO)_2$(trifluoro-acac), the ester (**92***b*) affords the complex (**1045**) (41 %).[1055]



(92*b*) (1045)

By catalytic hydrogenation and subsequent removal of the metal, complex (**1045**) may be converted into the diene (**1046**)[1055] (see pp. 291, 317).



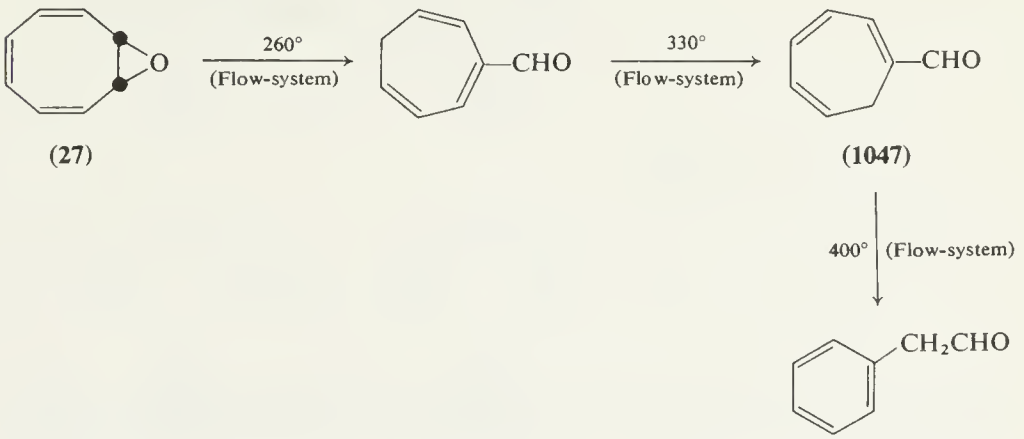
(1046)

17. 9-Oxabicyclo[6.1.0]nona-2,4,6-trienes

Treatment of COT with peracids gives the epoxide (**27**) (see p. 19).

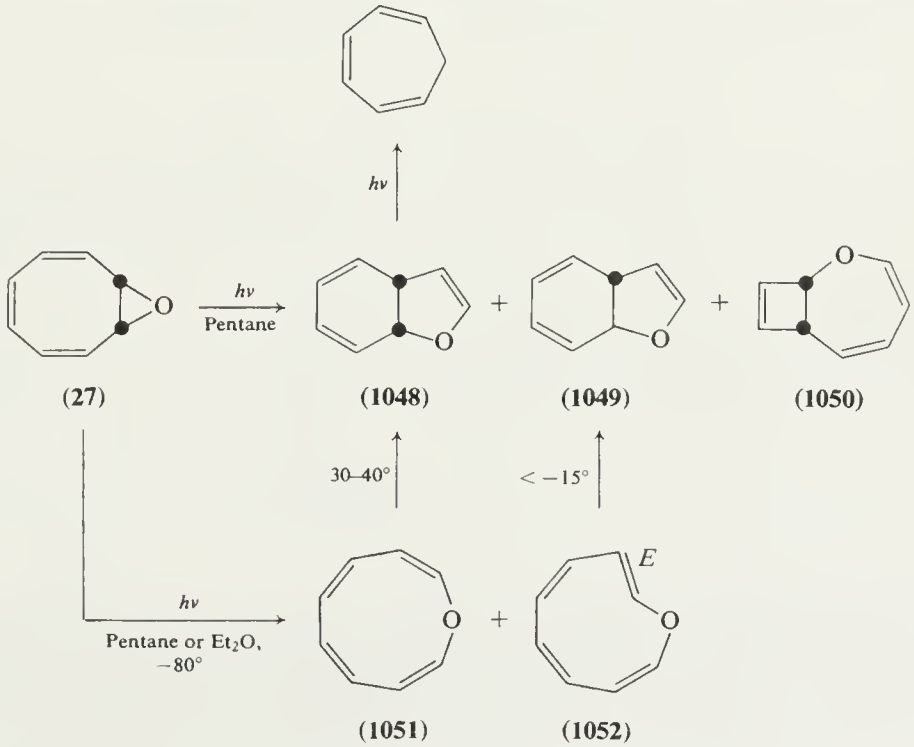
For valence tautomerism, see p. 315.

Thermolysis. Thermolysis of the epoxide (**27**) at 260° yields 3-formylcyclohepta-1,3,5-triene (45%); at 330° this rearranges to the 1-formyl-compound (**1047**) (74%), and at 400° phenylacetaldehyde is formed.[936]



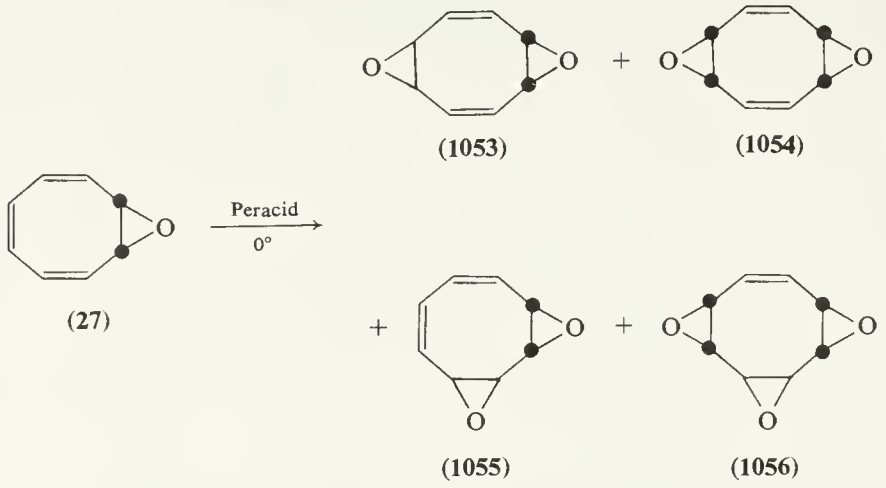
(**27**) (**1047**)

Photolysis. U.v. irradiation of the epoxide (**27**) at ordinary temperatures leads to the *cis*-bicyclic system (**1048**) (45%), its *trans*-fused stereomer (**1049**) (10%), and the cyclobutene derivative (**1050**) (6%), together with cycloheptatriene (12%).[1056–1059] At low temperatures all-*Z*-oxonin (**1051**) is formed,[1059,1060] together with a geometrical isomer (very likely the *Z,Z,Z,E*-compound (**1052**)),[1059] and these are converted thermally into the bicyclic products (**1048**) and (**1049**) respectively;[1059,1060] cycloheptatriene is known to be a photoproduct of (**1048**).[1057,1058]



(**27**) (**1048**) (**1049**) (**1050**) (**1051**) (**1052**)

Oxidation. Further epoxidation of compound (**27**) gives the di- and tri-epoxides (**1053**), (**1054**), (**1055**) and (**1056**)[1061] (table 125). At *ca.* 200°, the product

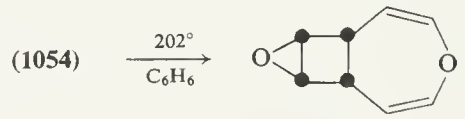


(**1053**) (**1054**) (**27**) (**1055**) (**1056**)

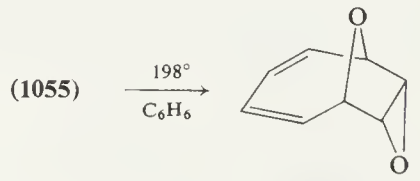
Table 125

Peracid	Yield (%) (**1053**)	(**1054**)	(**1055**)	(**1056**)
m-Cl.C_6H_4.CO_3H	*ca.* 67	24	9	—
CF_3CO_3H	30	50	5	15

(**1054**) equilibrates with the tricyclic valence isomer (**1057**) (40%), whereas compound (**1055**) is slowly transformed into the isomer (**1058**).[1061]

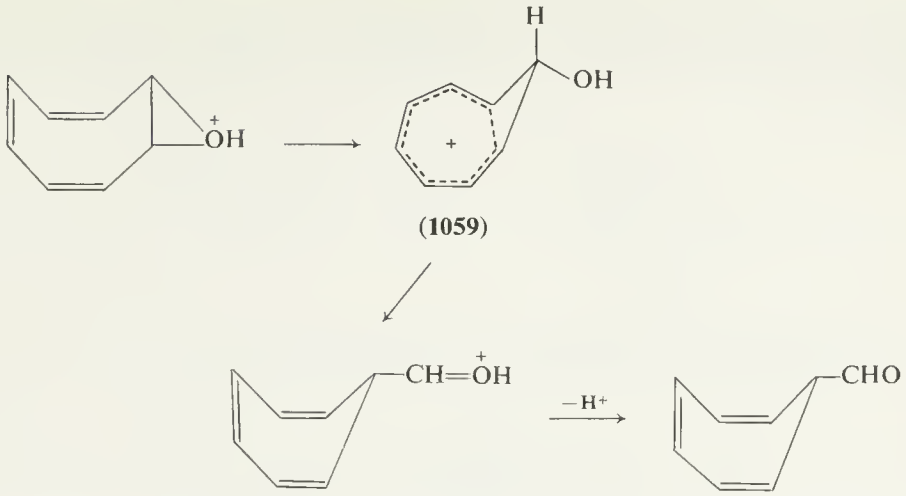


(**1057**)



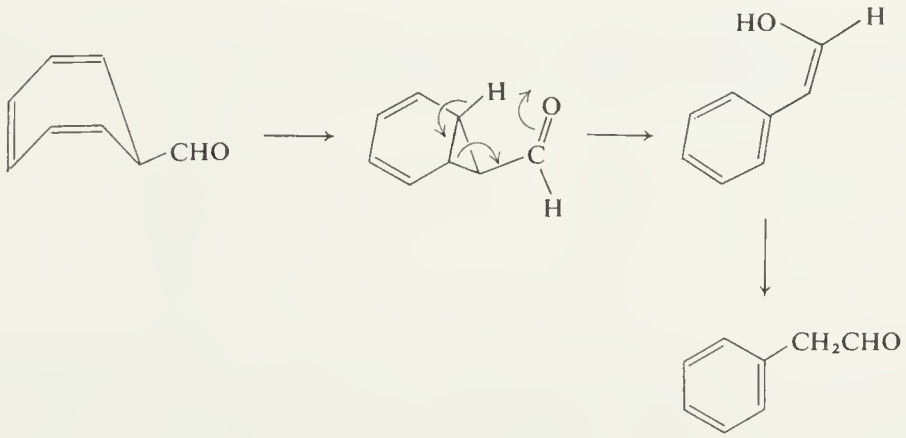
(**1058**)

Protonation. The epoxide (**27**) is very sensitive to acids, rapid rearrangement to phenylacetaldehyde occurring *via* 7-formylcyclohepta-1,3,5-triene.[1062,1063] The first, acid-catalysed stage may occur as follows,[909,1063] the hydroxyhomotropylium ion (**1059**) being detectable at −75° in fluorosulphonic acid.[909]



(1059)

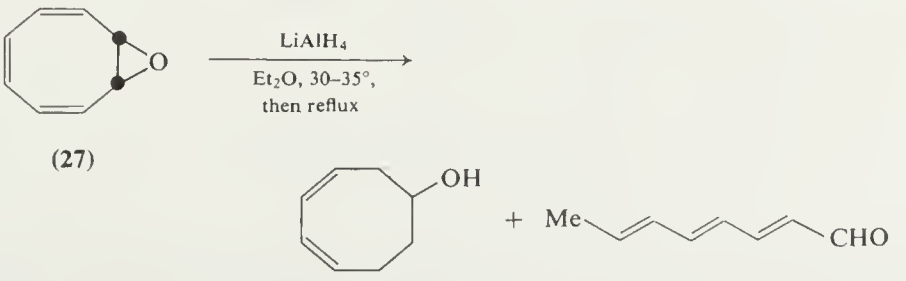
The second stage of the rearrangement does not require a catalyst and proceeds slowly even at 0°.[965]



(See also ref. 210.)

Oxidation of the epoxide (**27**) with acidic permanganate proceeds *via* the tropylium cation[1062,1063] (*cf.* COT, p. 19).

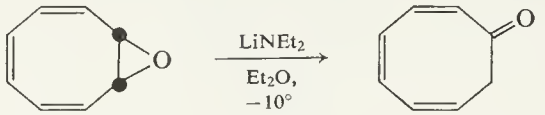
Reduction. Reaction of the epoxide (**27**) with lithium aluminium hydride gives a mixture of the dienol (**1060**) and the acyclic trienal (**755**) (total yield 58 %).[1064]



(27)

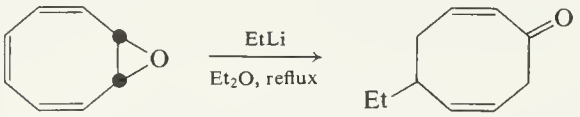
(1060) (755)

Reactions with nucleophiles. In the presence of strong bases, preferably lithium diethylamide, the epoxide (**27**) isomerises to cyclo-octa-2,4,6-trienone (80–90%).[200,941]



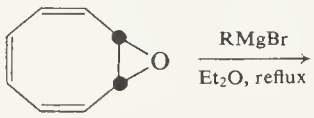
(**27**)

Reaction with ethyl-lithium gives the dienone (**1061**) (70%).[1064]

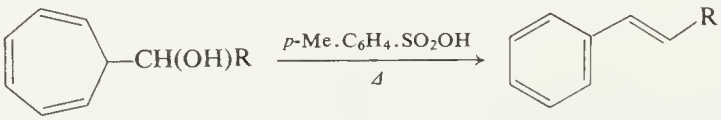


(**27**) (**1061**)

The epoxide (**27**) reacts with Grignard reagents to afford the cycloheptatrienylcarbinols (**1062**), which on acid-catalysed dehydration give β-substituted styrenes (**1063**)[202] (table 126).



(**27**)



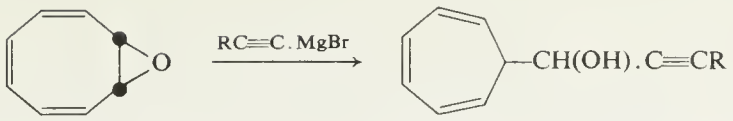
(**1062**) (**1063**)

Table 126

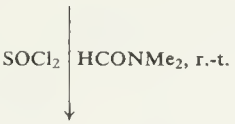
R	Yield (%) (**1062**)	(**1063**)
Et	83[a]	77
Bu[t]	23	—
Ph	73	37.5

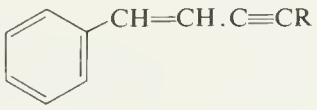
[a] The same product is obtained (71%) from triethylaluminium in n-hexane.[1064]

A similar procedure using acetylenic Grignard reagents leads to the carbinols (**1064**), and thence to the enynes (**1065**)[1065] (table 127).



(27) (1064)



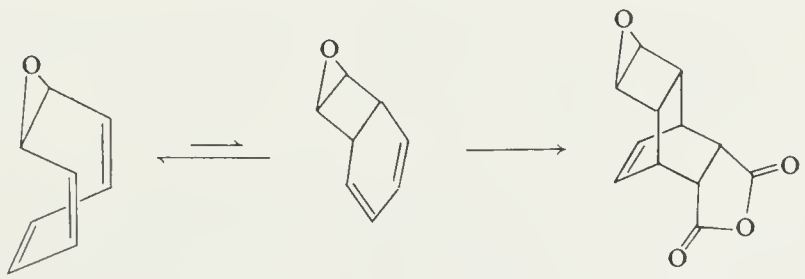


(1065)

Table 127

R	Yield (%) (1064)	(1065)
Me	75	87
Me_3C	56	82
PhCH=CH	68	83
3,4-$(MeO)_2.C_6H_3$.CH=CH	52	78
Ph[CH=CH]$_2$	41	78
Ph	65	70
2,4,6-$Me_3.C_6H_2$	57	72
4-Br.C_6H_4	64	75

Cycloadditions. The epoxide (**27**) exhibits valence tautomerism, although the equilibrium concentration of the tricyclic isomer (**1066**) is low (0.007% at 20°;[856] 0.4% at 60°[136]). [4 + 2] Cycloaddition of the valence tautomer (**1066**) and maleic anhydride yields the adduct (**1067**)[11,199] identical with the product obtained by epoxidation of the cyclo-octatetraene–maleic anhydride adduct.[199]

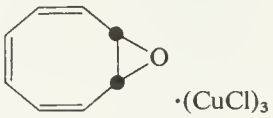


(27) (1066) (1067)

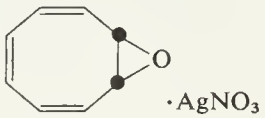
Reactions with metal derivatives. The rearrangement of the epoxide (**27**) to phenylacetaldehyde (see pp. 312–13) is promoted by e.g. lithium salts (in refluxing benzene),[1064] silver tetrafluoroborate (at 0°),[965] magnesium bromide

(in refluxing ether[202] or benzene[1064]), $[Rh(CO)_2Cl]_2$ (at −50°),[965] and $(MeCN)_2PdCl_2$ or $(MeCN)_2PtCl_2$ (at room-temperature).[1066]

Complexes (**1068**) and (**1069**) are formed almost quantitatively at room-temperature, using copper(I) chloride and silver nitrate respectively.[1066]

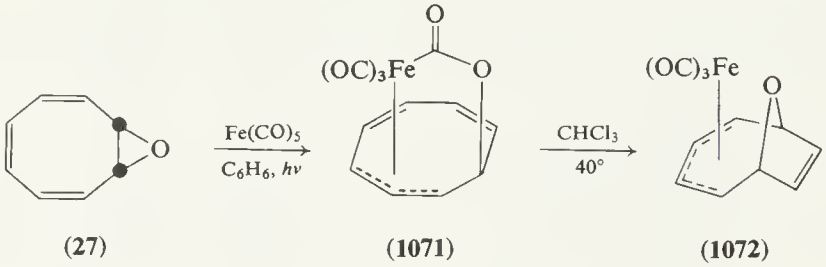


(**1068**)

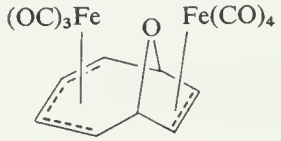


(**1069**)

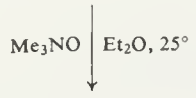
The epoxide (**27**) reacts with $Fe(CO)_5$ in u.v. light to form the binuclear complex (**1070**) (70%), *via* the intermediate (**1071**) which may be isolated (*ca.* 5%) by working at low temperature, and shown to decarbonylate to give (**1072**) at 40°; demetallation of the complex (**1070**) affords 9-oxabicyclo[4.2.1]-nona-2,4,7-triene (**1073**).[1067]

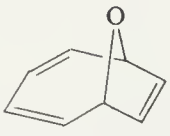


(**27**) (**1071**) (**1072**)



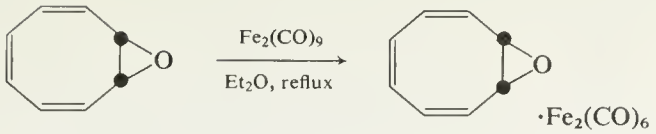
(**1070**)





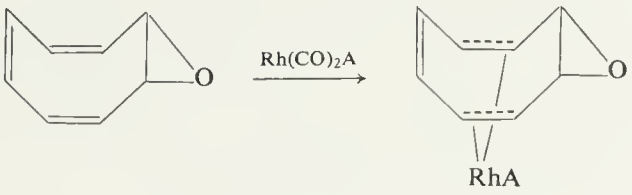
(**1073**)

Reaction of the epoxide (**27**) with $Fe_2(CO)_9$ in ether yields the binuclear complex (**1074**) (up to 6%), together with smaller quantities of complexes containing formylcycloheptatriene, cyclo-octatrienone, and COT.[1068]



(27) (1074)

The epoxide (**27**) reacts with $Rh(CO)_2(acac)$ and $Rh(CO)_2$(trifluoro-acac) to form the complexes (**1075**) (table 128). Catalytic hydrogenation and

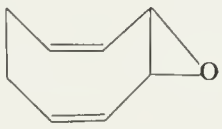


(27) (1075)

Table 128

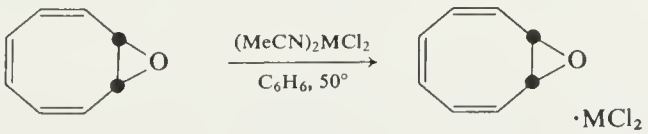
	A	Conditions	Yield (%)	Ref.
a	Acac	n-Hexane, reflux	65	510
b	Trifluoro-acac	—	85	1055

subsequent demetallation of (**1075***b*) then affords the diene (**1076**)[1055] (see pp. 291, 310).



(1076)

With $(MeCN)_2MCl_2$ (M = Pd, Pt), the epoxide (**27**) gives the complexes (**1077**; M = Pd, Pt).[1066]

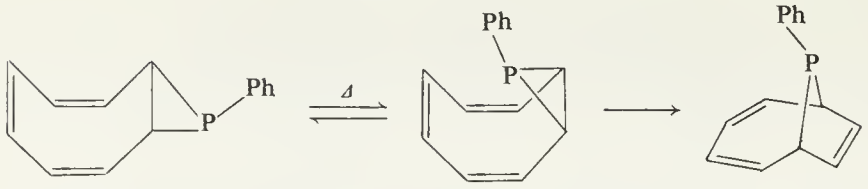


(27) (1077)

18. 9-Phosphabicyclo[6.1.0]nona-2,4,6-trienes

The *P*-phenyl derivative (**514**) results from the reaction of COT^{2-} with dichlorophenylphosphine (see p. 175).

Compound (**514**) readily rearranges (even at room-temperature, by a [1,5] sigmatropic shift) to the 9-phosphabicyclo[4.2.1]nonatriene system (**1078**) (54–69% from COT^{2-}).[380,750]

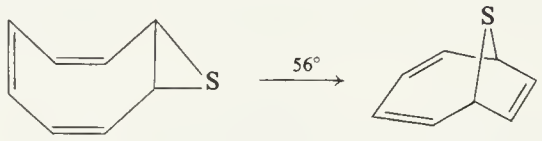


(514) (1078)

19. 9-Thiabicyclo[6.1.0]nona-2,4,6-trienes

The parent compound (**102**) is allegedly available from COT (see p. 38), or may be produced (*ca.* 80%) by u.v. irradiation of 9-thiabicyclo[4.2.1]nona-2,4,7-triene (**1079**) (see p. 325).

Rearrangement occurs at 56° (half-life *ca.* 1 h) to re-form 9-thiabicyclo-[4.2.1]nona-2,4,7-triene (**1079**)[323] (*cf.* (**514**) above).



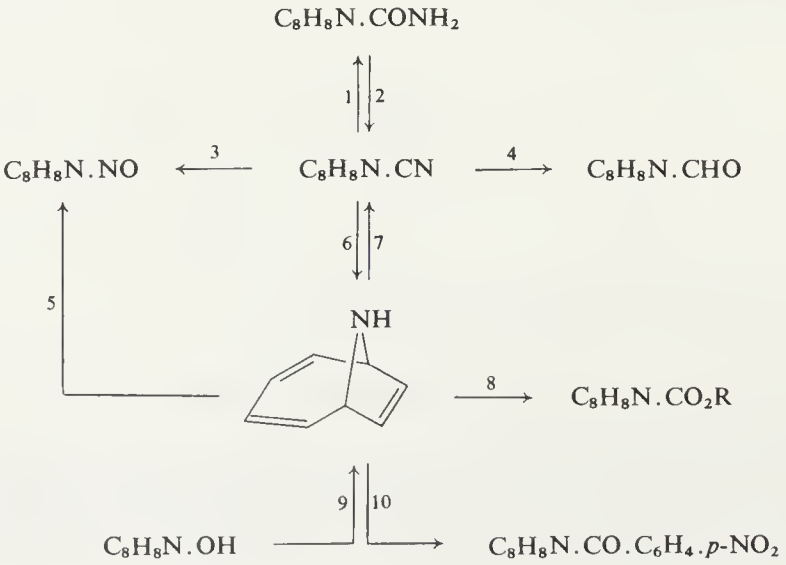
(102) (1079)

20. 9-Azabicyclo[4.2.1]nona-2,4,7-trienes

The 9-azabicyclo[4.2.1]nona-2,4,7-triene system may be generated by the reaction of triplet cyanonitrene with COT (see p. 37), or more efficiently by the reaction of isoamyl nitrite with COT^{2-} (see p. 182); in one special case the formation of this system by the rearrangement of a 9-azabicyclo[6.1.0]nona-2,4,6-triene is known (see p. 309).

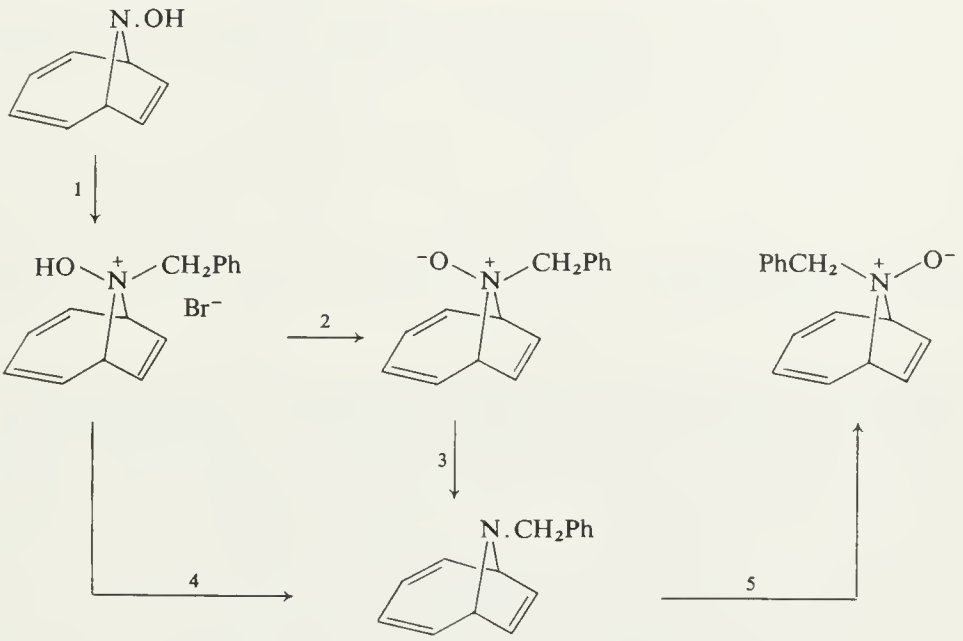
Functional group transformations. See schemes 97 and 98.

Scheme 97



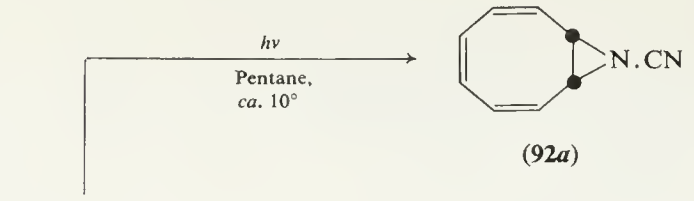
Reaction	Reagents and conditions	Yield (%)	Ref.
1	30% H_2O_2(aq.), Me_2CO, Na_2CO_3(aq.), r.-t.	52	318
	or low-temp. alkaline hydrolysis	—	318
2	*p*-Me.C_6H_4.SO_2OH, pyridine, *ca.* 100°	100	318
3	(i) KCN, MeOH, reflux; (ii) AcOH(aq.), reflux; (iii) $NaNO_2$	72	1069
4	HCO_2H, BF_3.Et_2O, reflux	64	318
5	$NaNO_2$, AcOH	72	1070
6	NaOH(aq.), Me_2CO, reflux	71	318
7	BrCN, Et_3N, CH_2Cl_2, 0° → r.-t.	98, (47)	318, (320)
8	R = Me: $ClCO_2Me$	75	320
	R = Et: $ClCO_2Et$, Et_3N, Et_2O, 0° → r.-t.	81	318
9	Zn, AcOH	61	320
10	*p*-NO_2.C_6H_4.COCl, Et_3N, C_6H_6, reflux	82	318

Scheme 98

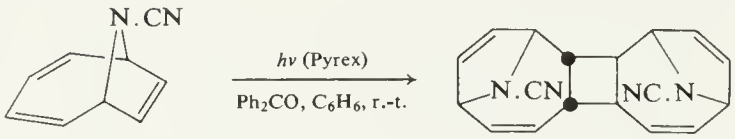


Reaction	Reagent	Yield (%)	Ref.
1	$PhCH_2Br$	89	320
2	K_2CO_3	97	320
3	Zn	—	320
4	Zn	54	320
5	H_2O_2	97	320

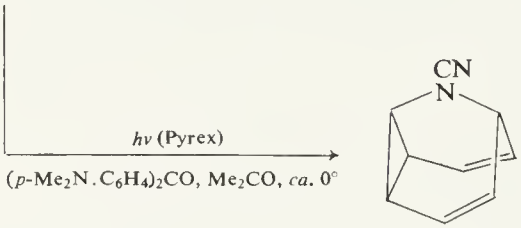
Photolysis. Light-induced rearrangement of the *N*-cyano-derivative (**93**) to the 9-azabicyclo[6.1.0]nonatriene system (**92*a***) (*ca.* 51%) occurs in the absence of a photosensitizer.[1071] In the presence of benzophenone a [2 + 2] dimer is formed (70%), the orientation of which is believed to be as shown in structure (**1080**);[1072] in the presence of Michler's ketone, however, the product is the



(92*a*)



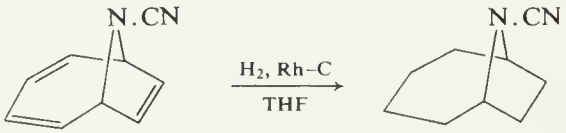
(93) (1080)



(1081)

9-azabarbaralane (**1081**) (*ca.* 70%).[1073] (Compound (**1080**) may be transformed into (**21**)[1072] (see p. 16).)

Reduction. Hydrogenation of compound (**93**), using a rhodium catalyst, yields the hexahydro-derivative (**1082**) (80%).[317]

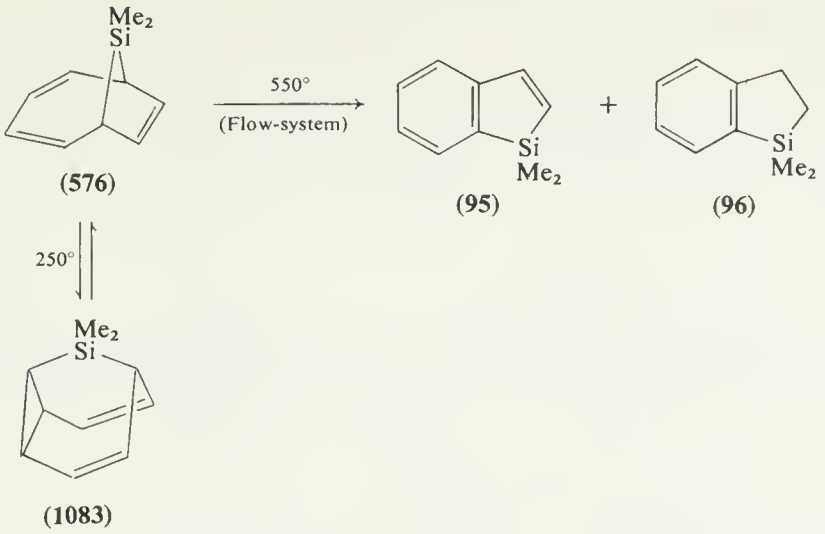


(93) (1082)

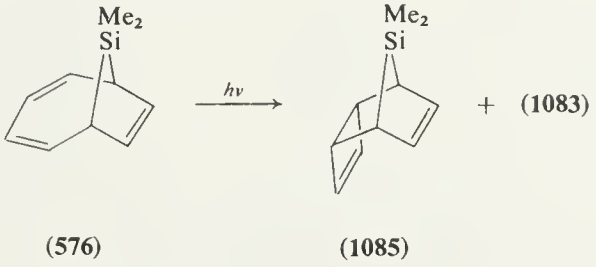
21. 9-Silabicyclo[4.2.1]nona-2,4,7-trienes

The dimethyl-derivative (**576**) may be obtained from COT and dichlorodimethylsilane in the presence of magnesium (see p. 190).

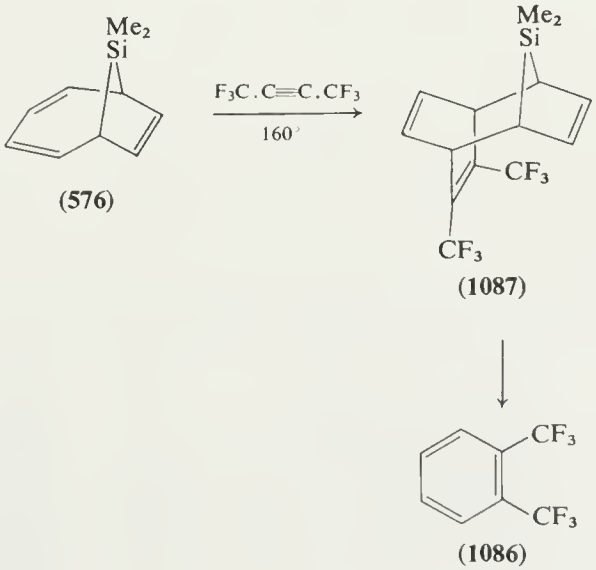
Thermolysis. At 250° the dimethyl-derivative (**576**) is partly converted (46% after 72 h) into the silabarbaralane (**1083**);[796] at 550°, the products are (**95**) (30%) and (**96**) (15%).[321]



Photolysis. U.v. irradiation of the compound (**576**) results in the tricyclic isomer (**1085**) (80%), together with the silabarbaralane (**1083**) (20%).[796]

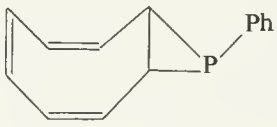


Cycloadditions. Maleic anhydride and tetracyanoethylene fail to react with the system (**576**), but hexafluorobut-2-yne yields the *o*-disubstituted benzene (**1086**), possibly *via* the adduct (**1087**).[796]

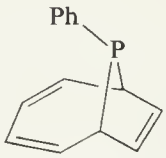


22. 9-Phosphabicyclo[4.2.1]nona-2,4,7-trienes

9-Phenyl-9-phosphabicyclo[6.1.0]nona-2,4,6-triene (**514**), which is formed by the action of dichlorophenylphosphine on COT^{2-}, isomerises (even at room-temperature) to give the 9-phosphabicyclo[4.2.1]nona-2,4,7-triene system (**1078**) (see pp. 317–18).



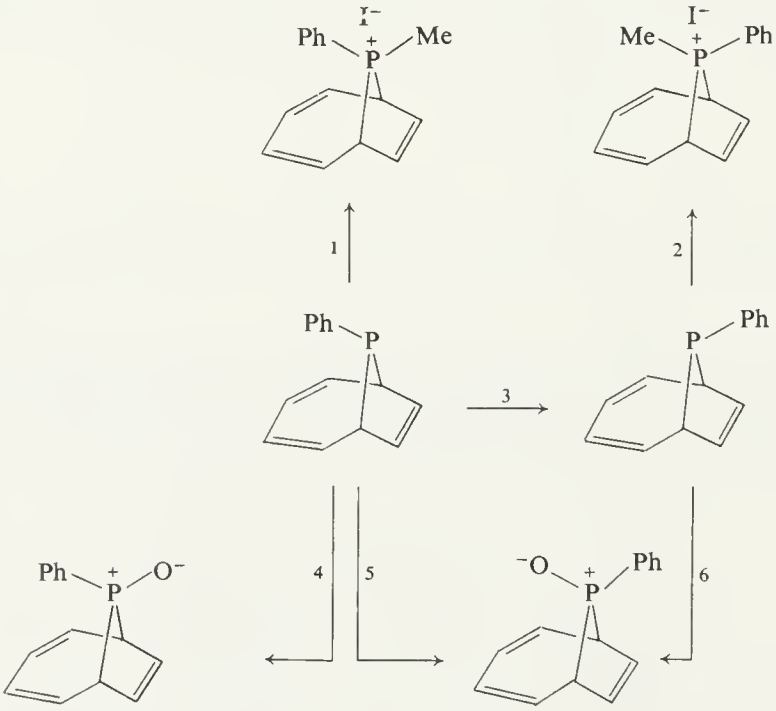
(514)



(1078)

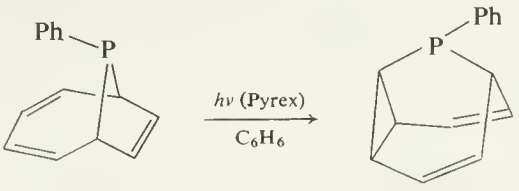
Reactions at phosphorus. See scheme 99.

Scheme 99



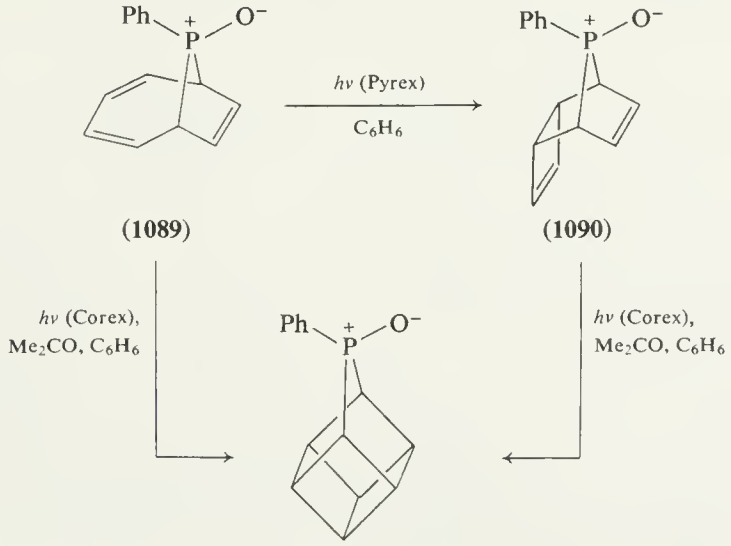
Reaction	Reagents and conditions	Yield (%)	Ref.
1	MeI, Me_2CO, cooling	81	380
2	MeI, Me_2CO, cooling	—	380
3	HCl, $CHCl_3$, 100°	—	380
4	30% H_2O_2(aq.), $CHCl_3$, 0°	(79), 90	(380), 750
5	Air, $CHCl_3$, r.-t.	42	380
6	30% H_2O_2(aq.), $CHCl_3$, 0°	84.5	380
	or air, $CHCl_3$, r.-t.	—	380

Photolysis. U.v. irradiation of compound (**1078**) affords the 9-phosphabarbaralane (**1088**) (25%).[1074]



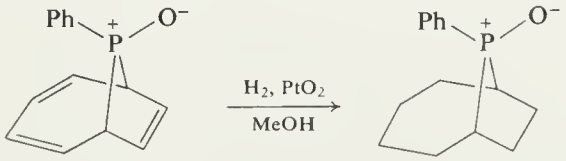
(**1078**) (**1088**)

The phosphine oxide (**1089**), however, gives the tricyclic product (**1090**) (50%), and on sensitised irradiation the phosphahomocubane (**1091**) (28–34%).[750, 1074]



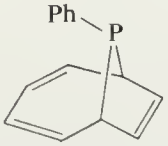
(**1089**) (**1090**) (**1091**)

Reduction. Catalytic hydrogenation (using Adam's catalyst) of the phosphine oxide (**1089**) gives the hexahydro-derivative (**1092**) (85.5%).[750]



(**1089**) (**1092**)

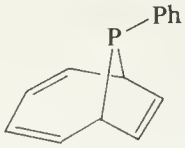
Reactions with metal derivatives. The epimeric phosphines (**1078**) and (**1093**) react with $(PhCN)_2PdCl_2$ to give complexes (**1094**) (82%) or (**1095**) (42%), and (**1096**) (33%) respectively.[380]



(**1078**)

$\xrightarrow[CHCl_3]{(PhCN)_2PdCl_2}$ $(C_{14}H_{13}P)_2PdCl_2$ (**1094**)

or $[(C_{14}H_{13}P)PdCl_2]_2$ (**1095**)

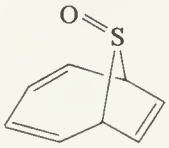


(1093)

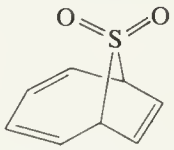
$\xrightarrow[CHCl_3]{(PhCN)_2PdCl_2}$ $(C_{14}H_{13}P)_2PdCl_2$ **(1096)**

23. 9-Thiabicyclo[4.2.1]nona-2,4,7-trienes

The sulphoxide (**107**) is formed by the addition of sulphur monoxide to COT (see pp. 39–40), and the sulphone (**108**) by the reaction of COT with sulphur dioxide in the presence of antimony(v) fluoride (see p. 40).



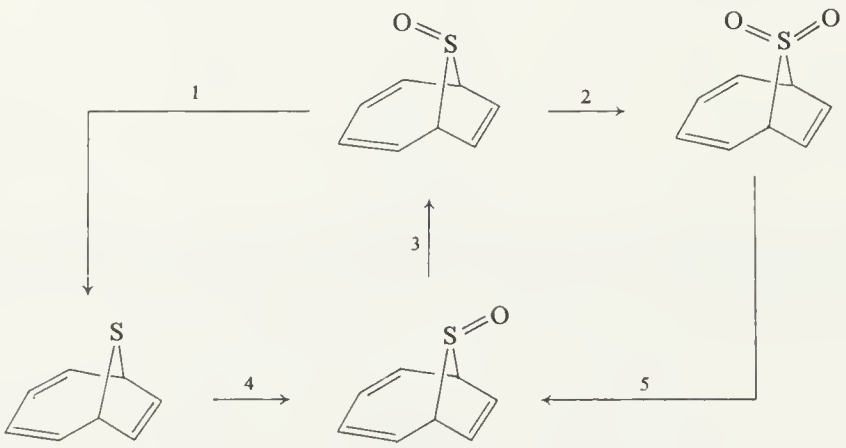
(107)



(108)

Reactions at sulphur. See scheme 100.

Scheme 100

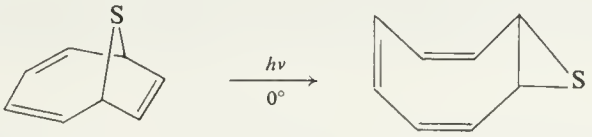


Reaction	Reagents and conditions	Yield (%)	Ref.
1	$LiAlH_4$, Et_2O, reflux	76	328
2	*m*-Cl.C_6H_4.CO_3H, CH_2Cl_2, 0° → r.-t.	75	43
3	C_6D_6, >100°	90	328
4	*m*-Cl.C_6H_4.CO_3H, CH_2Cl_2, −35° to −25°	60	328
5[a]	Bu^i_2AlH, CH_2Cl_2, reflux	36	328

[a] Reaction carried out using the 1,6-dideuterio-derivative.

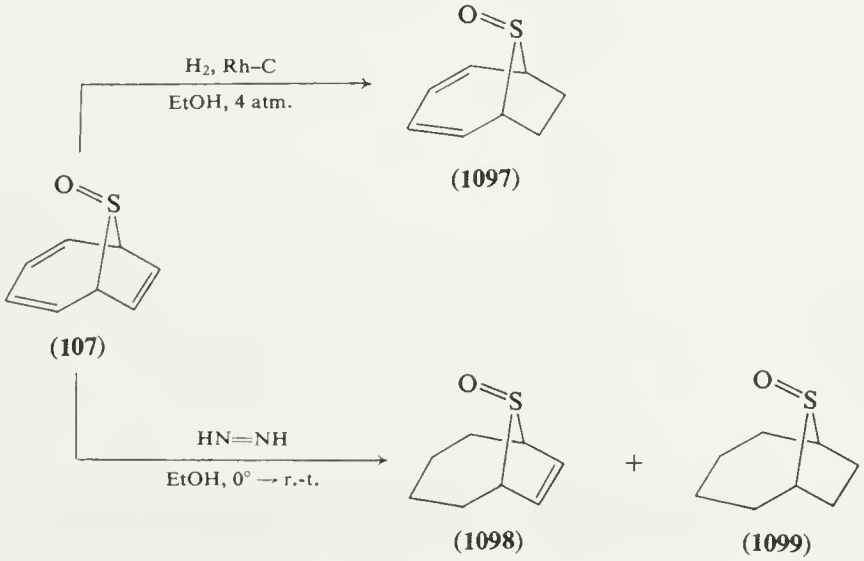
Thermolysis and photolysis. Thermolysis of the sulphone (**108**), or photolysis of either the sulphone (**108**) or the sulphoxide (**107**), gives rise to COT (see p. 5).

Photolysis of the parent compound (**1079**) gives 9-thiabicyclo[6.1.0]nona-2,4,6-triene (**102**) (*ca.* 80%).[323]



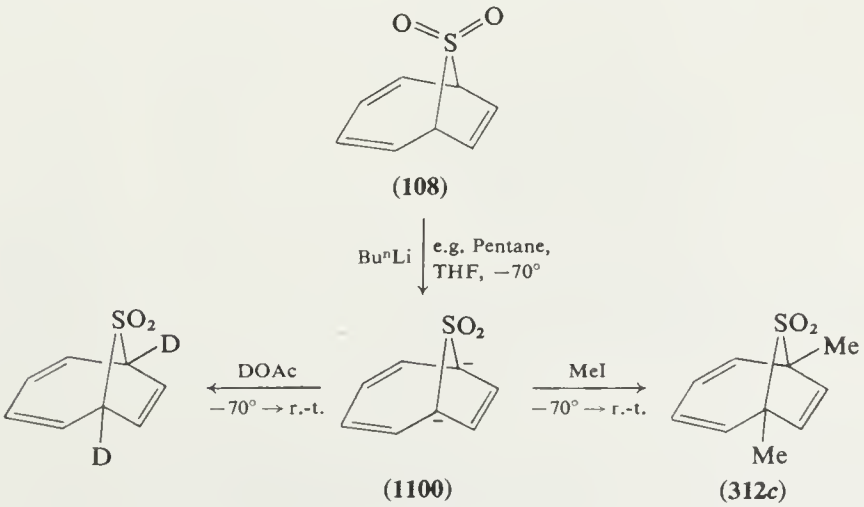
(**1079**) (**102**)

Reduction and deprotonation. Catalytic hydrogenation of the sulphoxide (**107**), using a rhodium catalyst, affords the dihydro-derivative (**1097**) (60%).[328] Reduction with di-imide gives a mixture of the products (**1098**) (*ca.* 50%) and (**1099**).[328]



(**107**) (**1097**) (**1098**) (**1099**)

With n-butyl-lithium, the sulphone (**108**) forms a dianion (**1100**),[1075] which may be deuteriated (62%)[49, 328, 1075] or methylated (100%).[43, 1075] (It is also possible to prepare a mono-anion.[1076])



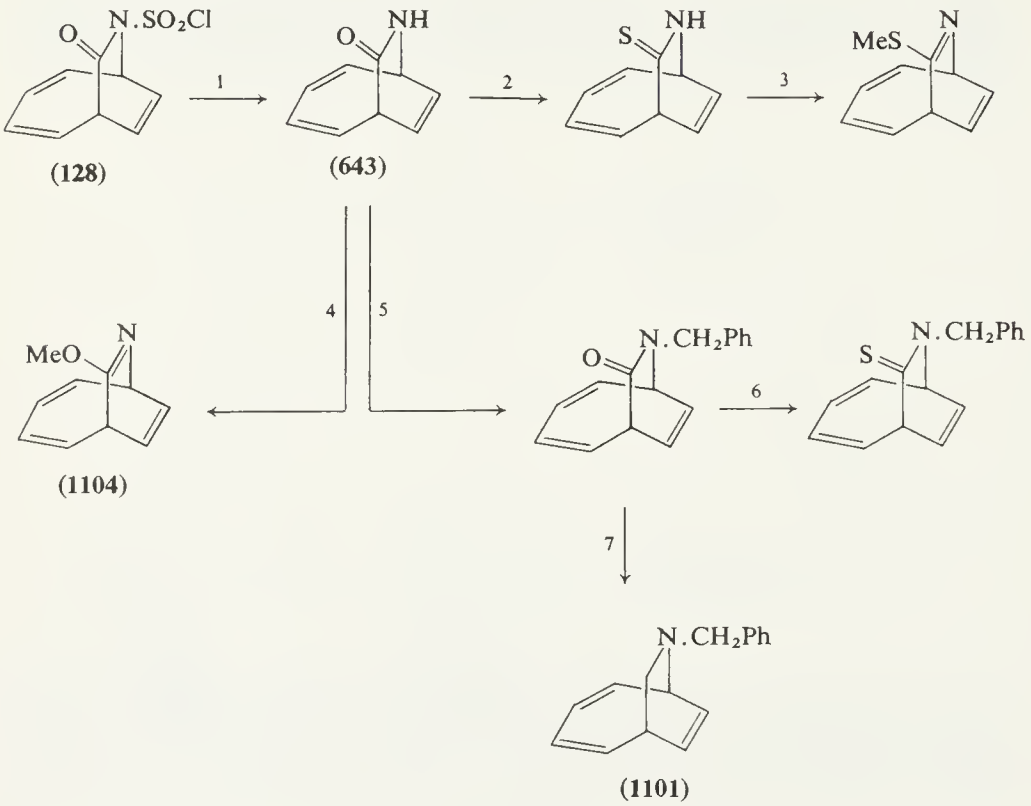
(**108**) (**1100**) (**312c**)

24. 9-Aza-10-oxobicyclo[4.2.2]deca-2,4,7-trienes

The 9-aza-10-oxobicyclo[4.2.2]deca-2,4,7-triene system (**128**) results from the addition of chlorosulphonyl isocyanate to COTs (see pp. 45–6).

Functional group transformations. See scheme 101.

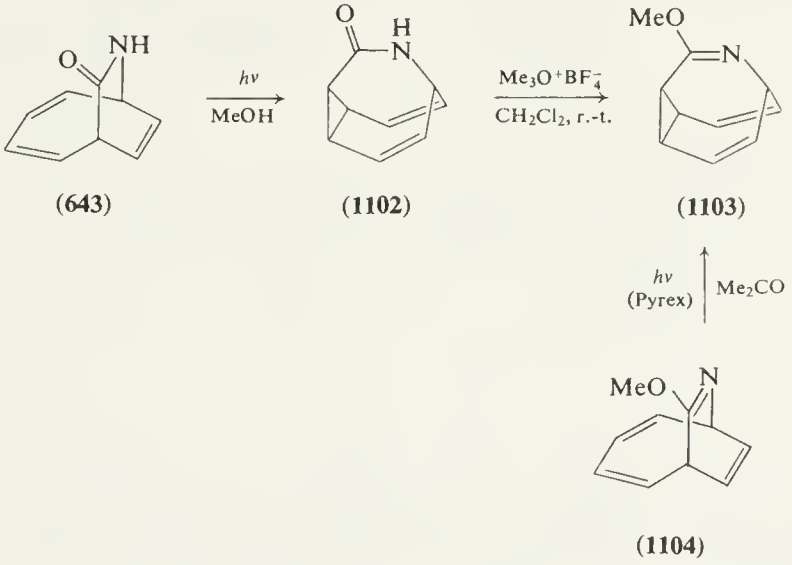
Scheme 101



Reaction	Reagents and conditions	Yield (%)	Ref.
1	PhSH, pyridine, Me_2CO, 0°	98	(366), 367
	or NaOH, Me_2CO(aq.)	65	367
2	P_2S_5, pyridine, reflux	68	1077
3	$Me_3O^+ BF_4^-$, CH_2Cl_2, r.-t.	71	1077
4	$Me_3O^+ BF_4^-$, CH_2Cl_2, r.-t.	81	(366), 367
5	(i) NaH, DMF, 65°; (ii) $PhCH_2Cl$, 45°	93	(1078), 1079
6	P_2S_5	—	1078
7	(i) $Me_3O^+ BF_4^-$, CH_2Cl_2; (ii) $NaBH_4$, MeOH, 5° → r.-t.	67	1079

For reactions 1 and 4 with derivatives of monosubstituted COTs, see ref. 367.
For rearrangements of compound (**1101**), see ref. 1079.

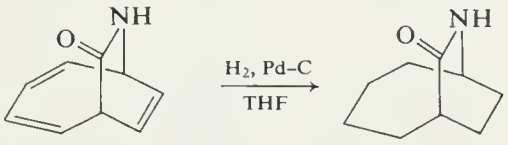
Photolysis. Light-induced rearrangement of the system (**643**) leads to the lactam-bridged homotropilidene (**1102**) (54%), convertible into the azabullvalene derivative (**1103**) (92%);[366, 1077] an improved procedure[1077] involves the acetone-sensitised photorearrangement of the imino-ether (**1104**) (see scheme 101).



(**643**) (**1102**) (**1103**) (**1104**)

For similar transformations of derivatives of monosubstituted COTs, see ref. 1077.

Reduction. Catalytic hydrogenation of the lactam (**643**) affords the hexahydro-derivative (**1105**) (69%).[367]



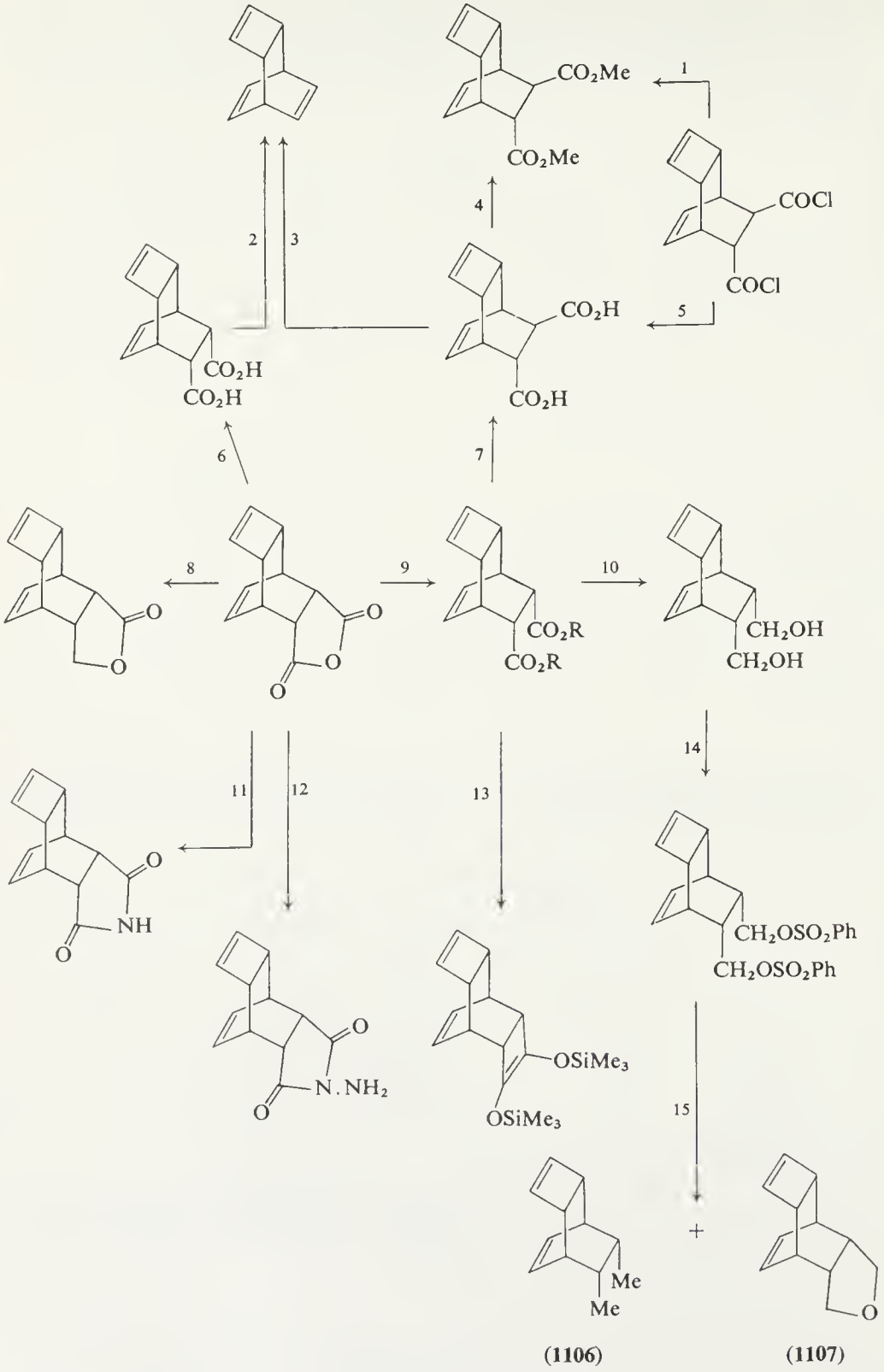
(**643**) (**1105**)

25. Tricyclo[4.2.2.0^{2,5}]deca-3,7-dienes

The tricyclo[4.2.2.0^{2,5}]deca-3,7-diene system is formed by the reaction of olefinic dienophiles with COT, which undergoes [4 + 2] cycloadditions *via* its bicyclic valence tautomer (**4**) (see pp. 42–3).

Functional group transformations. See scheme 102.

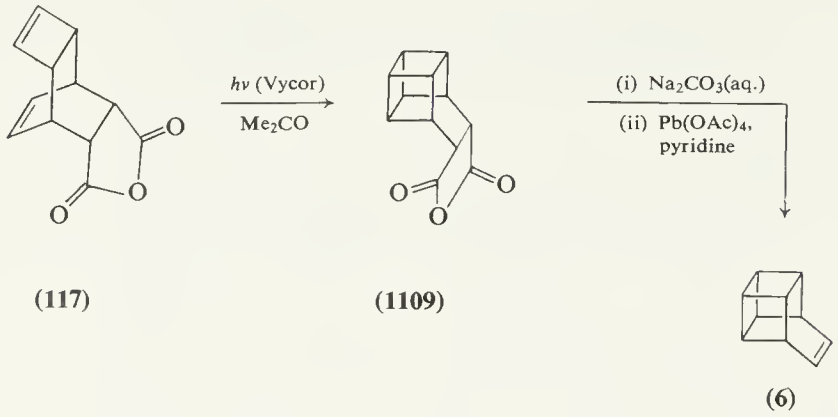
Scheme 102


CO2Me
CO2Me
1
COCl
COCl
4
2
3
CO2H
CO2H
5
CO2H
CO2H
6
7
8
9
10
CO2R
CO2R
CH2OH
CH2OH
14
11
12
13
NH
N.NH2
OSiMe3
OSiMe3
CH2OSO2Ph
CH2OSO2Ph
15
Me
Me
(1106)
(1107)

Reaction	Reagents and conditions	Yield (%)	Ref.
1	MeOH	—	340
2	$Pb(OAc)_4$, pyridine, C_6H_6, 50° → 70°;	10–15	341, 1080
	or electrolysis, Pt electrodes, pyridine(aq.), Et_3N	37	1081
3	Electrolysis, Pt electrodes, pyridine(aq.), Et_3N	53	1081
4	MeOH, H_2SO_4, reflux	80	11
5	H_2O	—	340
6	NaOH(aq.), warm	85	11
7; R = Me	(i) NaOMe, MeOH, reflux (ii) NaOH(aq.), reflux	83	11
8	$LiAlH_4$, THF, r.-t.	—	931
9; R = Me, Et, Bu^n, Bu^t, $Me_2CH[CH]_2$	ROH, H_2SO_4, reflux	86–98	11
10; R = Me	$LiAlH_4$, Et_2O, reflux	98–99	341
11	NH_3(aq.), 120°	61	11
12	NH_2NH_2, MeCN, HOAc	74	1082
13; R = Me	Me_3SiCl, Na, xylene, 40° → 80°	—	1083
14	$PhSO_2Cl$, pyridine, −5° → 0°	64[a]	341
15	$LiAlH_4$, Et_2O, reflux	47 (**1106**) *ca.* 50 (**1107**)	341

[a] The cyclic ether (**1107**) is a by-product.

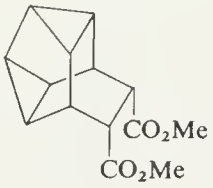
Photolysis. U.v. irradiation of the maleic anhydride adduct (**117**), or the di-ester (**1108**), in acetone yields the caged product (**1109**) (40%)[355, 1084] or (**1110**) (35%);[1085] hydrolysis and subsequent oxidative bis-decarboxylation of these 1,1′-bishomocubane derivatives leads to basketene (**6**).[1084, 1085]



(**117**) (**1109**) (**6**)

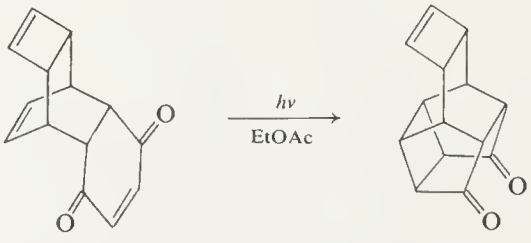
(**1108**) (**1110**)

For the silver-catalysed rearrangement of the di-ester (**1110**) to the isomer (**1112**), see ref. 1086.



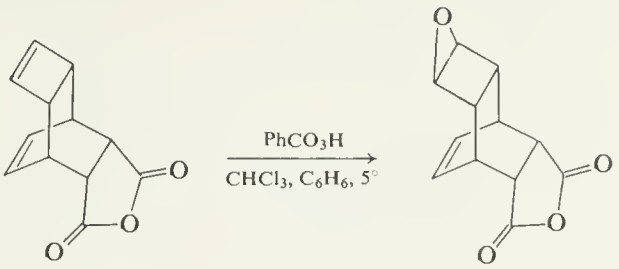
(**1112**)

A different type of cage-structure (**105**) results (90%) from irradiation of the *p*-benzoquinone adduct (**106**).[1087]

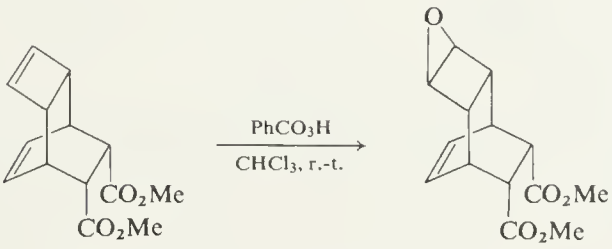


(**106**) (**105**)

Oxidation. Epoxidation of the anhydride (**117**) or the dimethyl ester (**1108**) gives the *exo*-epoxide, (**1067**) (66%)[199] or (**1113**) (61%).[11]

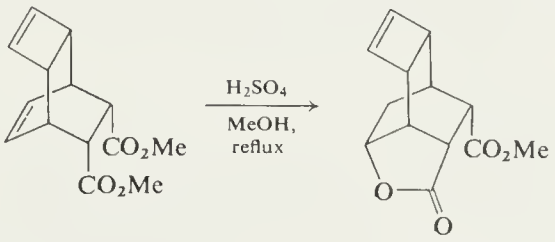


(**117**) (**1067**)



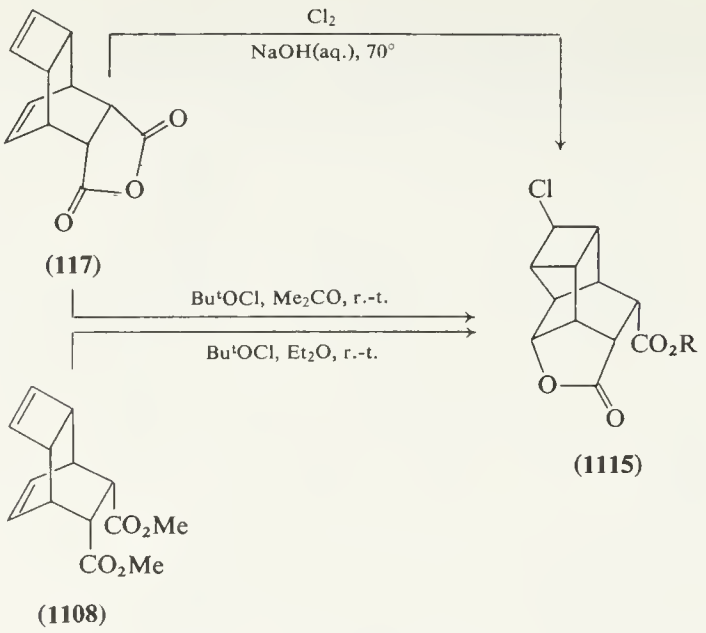
(**1108**) (**1113**)

Reactions with electrophiles. Electrophilic attack on the *endo*-9,10-disubstituted tricyclo[4.2.2.0^{2,5}]deca-3,7-diene system usually occurs on the less hindered *exo*-face of the 3,4-double bond, and is frequently followed by transannular ring-closure involving the 7,8-double bond, a functional group or the solvent also participating. Exceptionally, the dimethyl ester (**1108**) reacts with sulphuric acid in methanol to afford the lactone-ester (**1114**) (90%).[340]

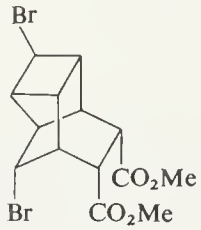


(**1108**) (**1114**)

Reaction of the anhydride (**117**) with chlorine in aqueous sodium hydroxide,[11] or t-butyl hypochlorite,[1088] gives the chloro-lactone-carboxylic acid (**1115**; R = H) (77.5% or 97% respectively); the dimethyl ester (**1108**) affords the analogous product (**1115**; R = Me) (93%).[1088]



Reactions of the anhydride (**117**) etc. with bromine are summarised in scheme 103.



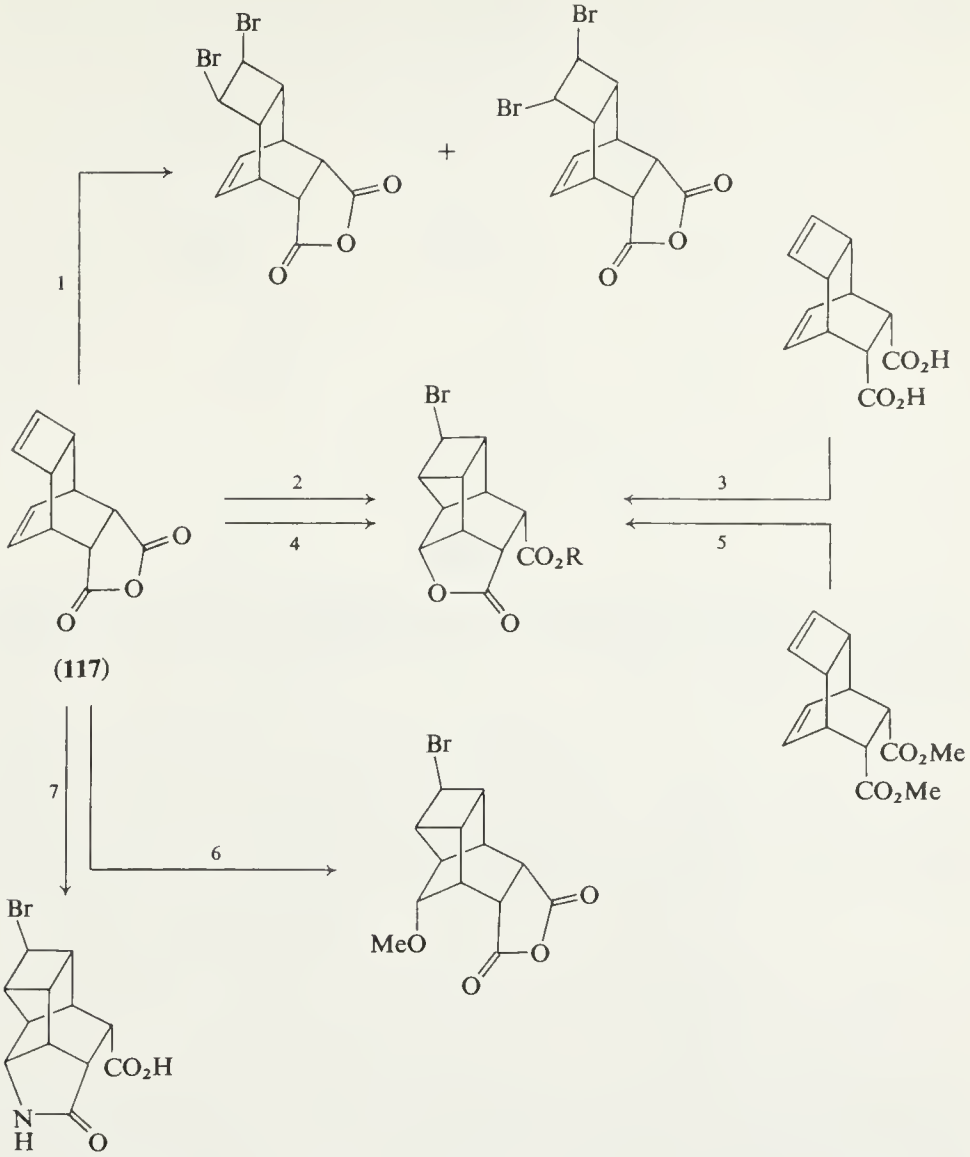
(**1116**)

The *trans*-dicarboxylic acid (**1117**), in aqueous potassium hydroxide, reacts with bromine to give the bromo-lactone-carboxylic acid (**1118**),[340] (*cf.* ref. 1088).

(**1117**) (**1118**)

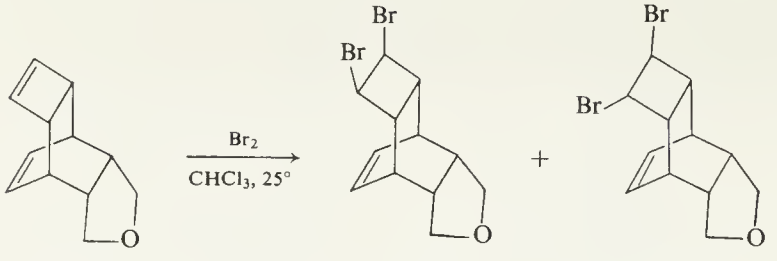
With bromine in chloroform, the cyclic ether (**1107**) affords a mixture of the dibromides (**1119**) (9%), (**1120**) (1%), and (**1121**) (15%).[931]

Scheme 103

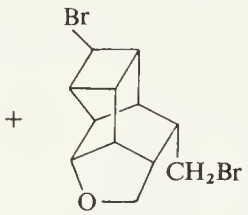


Reaction	Reagents and conditions	Yield (%)	Ref.
1	Br_2, $CHCl_3$, r.-t.	*ca.* 40 (*cis*) *ca.* 30 (*trans*)	931
2	Br_2, MeOH KOH(aq.), r.-t.	86[a]	11
3	Br_2, MeOH, r.-t.	57[b]	11
4	Br_2, HOAc, r.-t.	95[a]	1088
5	Br_2, $CHCl_3$, r.-t. Br_2, MeOH, r.-t.	86[b,c] 54[b]	(340), 1088 11
6	Br_2, MeOH, r.-t.	38	1088
7	Br_2, MeCN, r.-t. Br_2, PhCN, r.-t.	98 80	1088

[a] R = H
[b] R = Me
[c] Formation of a dibromide, possibly of structure (**1116**) (*cf.* ref. 1088) may also occur.[11,340]

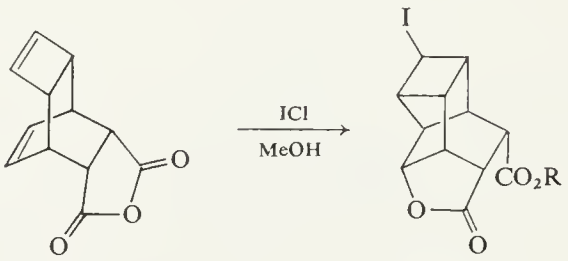


(1107) **(1119)** **(1120)**



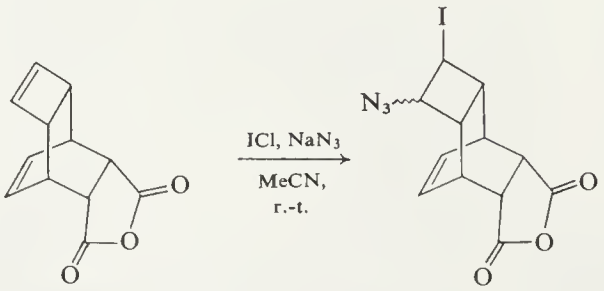
(1121)

With iodine monochloride in methanol, the anhydride (**117**) gives a mixture of the iodo-lactone-ester (**1122**; R = Me) (39%) and the carboxylic acid (**1122**; R = H) (20%).[1088]



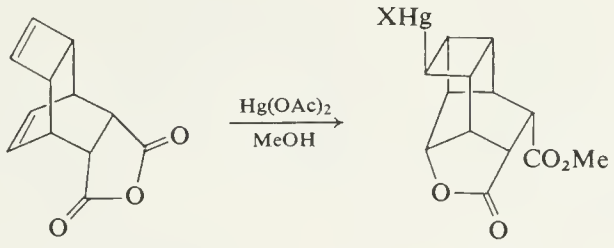
(117) **(1122)**

Iodine azide (from iodine monochloride and sodium azide) adds to the 3,4-double bond of the anhydride (**117**) to give the product (**1123**) (characterised as the acetylenedicarboxylic ester-adduct).[1088]

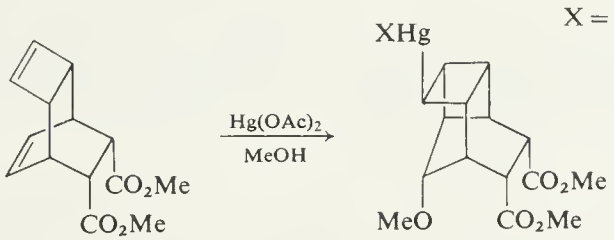


(117) **(1123)**

The anhydride (**117**) and the di-ester (**1108**) react with mercury(II) acetate in methanol to form (after work-up as the chloro-mercurials) products originally formulated as (**1124**) and (**1125**) respectively[342] (but see appendix).

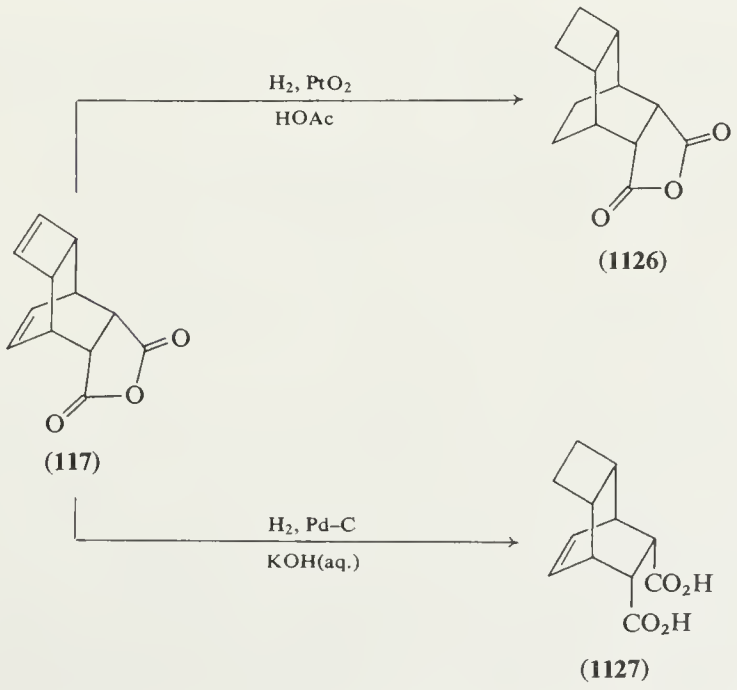


(**117**) (**1124**)



(**1108**) (**1125**)

Reduction. Hydrogenation of the anhydride (**117**) in the presence of e.g. Adam's catalyst yields the tetrahydro-derivative (**1126**).[260] Selective hydrogenation of the 3,4-double bond to give the dihydro-derivative (**1127**) is readily achieved, however, by the use of e.g. palladium-on-carbon in aqueous potassium hydroxide (yield 89%).[11]

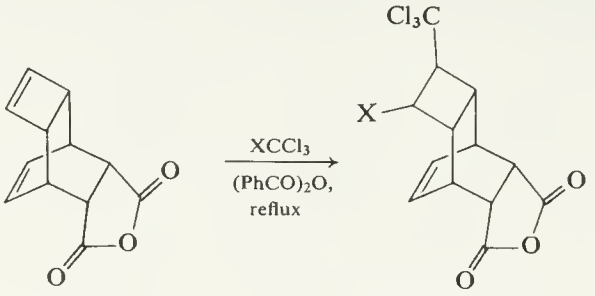


(**1126**)

(**117**)

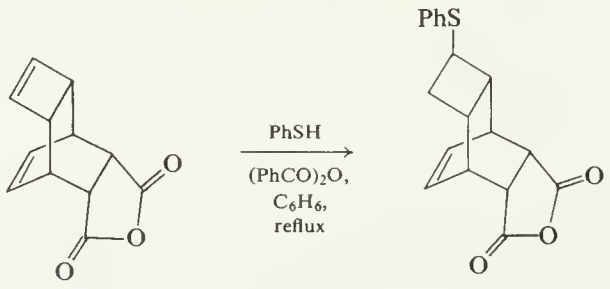
(**1127**)

Reactions with free radicals. The radical addition of carbon tetrachloride and bromotrichloromethane to the anhydride (**117**) gives products (**1128*a***) (70%)



(**117**) (**1128**) ***a***: X = Cl
b: X = Br

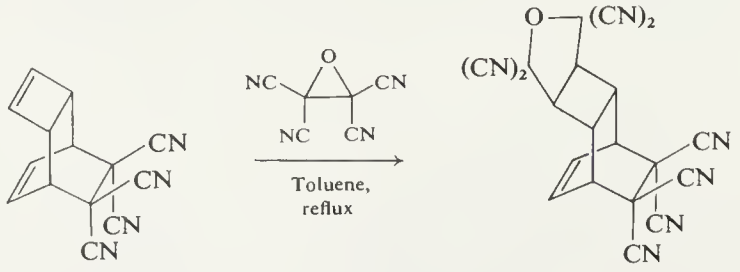
and (**1128*b***) (69%) respectively.[1089] Thiophenol apparently affords the analogous product (**1129**) (61%).[1089]



(**117**) (**1129**)

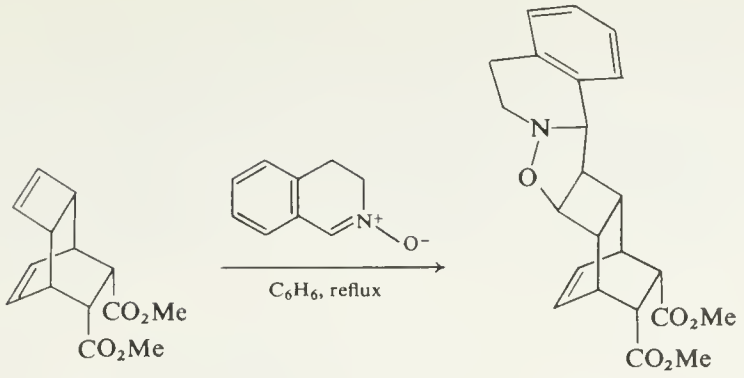
Cycloadditions. Intermolecular cycloadditions of the *endo*-9,10-disubstituted tricyclo[4.2.2.0^{2,5}]deca-3,7-diene system occur specifically on the *exo*-face of the 3,4-double bond.

The tetracyanoethylene adduct (**1130**) undergoes 1,3-dipolar addition with tetracyanoethylene oxide to give the product (**1131**) (66%).[337]



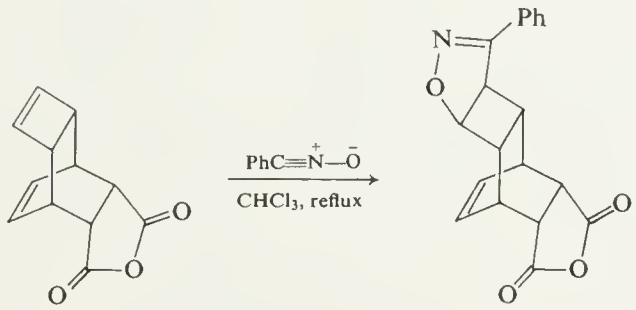
(**1130**) (**1131**)

With the nitrone 3,4-dihydroisoquinoline *N*-oxide, the di-ester (**1108**) affords the adduct (**1132**) (82%).[335] Similarly, the anhydride (**117**) and the

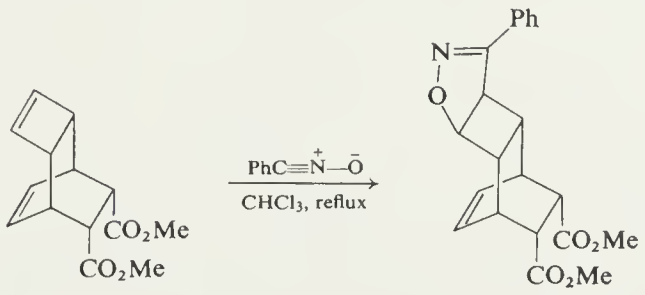


(**1108**) (**1132**)

di-ester (**1108**) add benzonitrile oxide to give the products (**1133**) (80–85%) and (**1134**) (90%) respectively.[331,334]



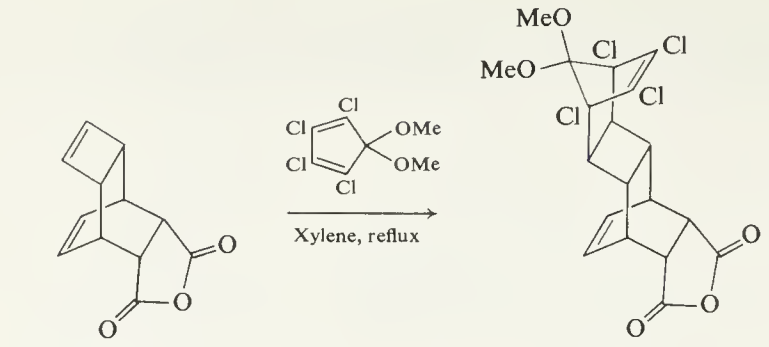
(**117**) (**1133**)



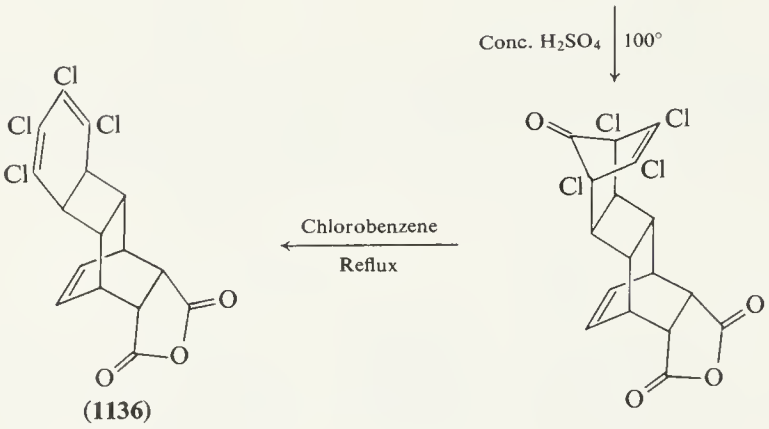
(**1108**) (**1134**)

The 3,4-double bond of the tricyclo[4.2.2.0^{2,5}]deca-3,7-diene system behaves as an excellent dienophile towards electron-deficient dienes.

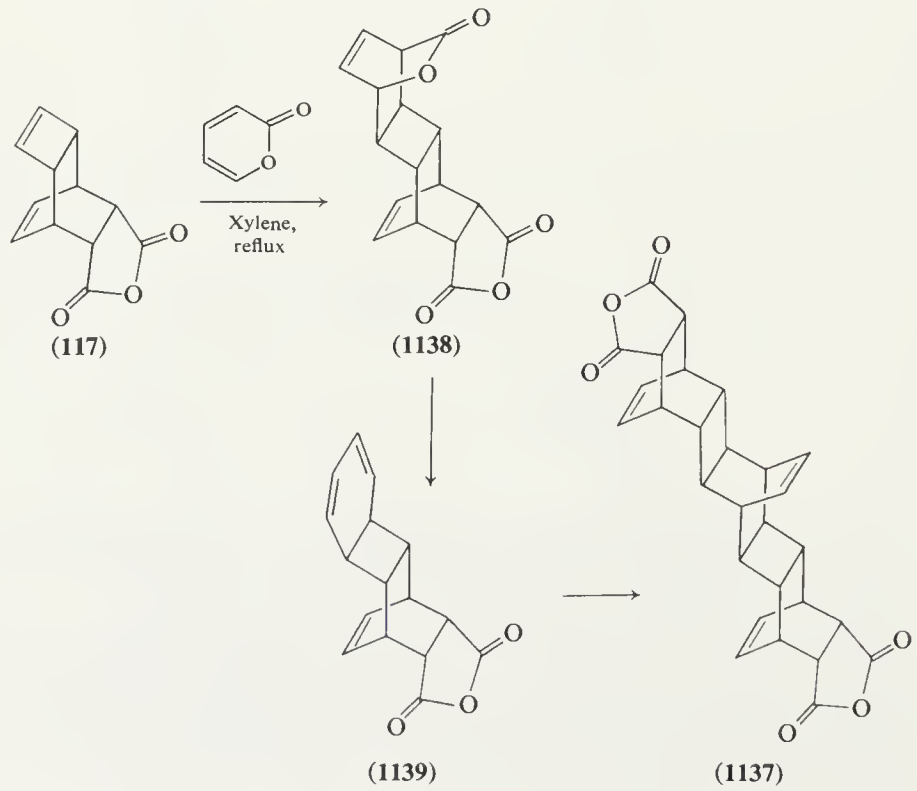
1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene adds to the anhydride (**117**) exclusively in the *endo*-mode (*exo*-addition being inhibited by the bulky methoxy-groups) to form the product (**1135**) (79%); hydrolysis of the ketal group in (**1135**), followed by thermal extrusion of carbon monoxide, results in the product (**1136**).[1090]



(117) **(1135)**



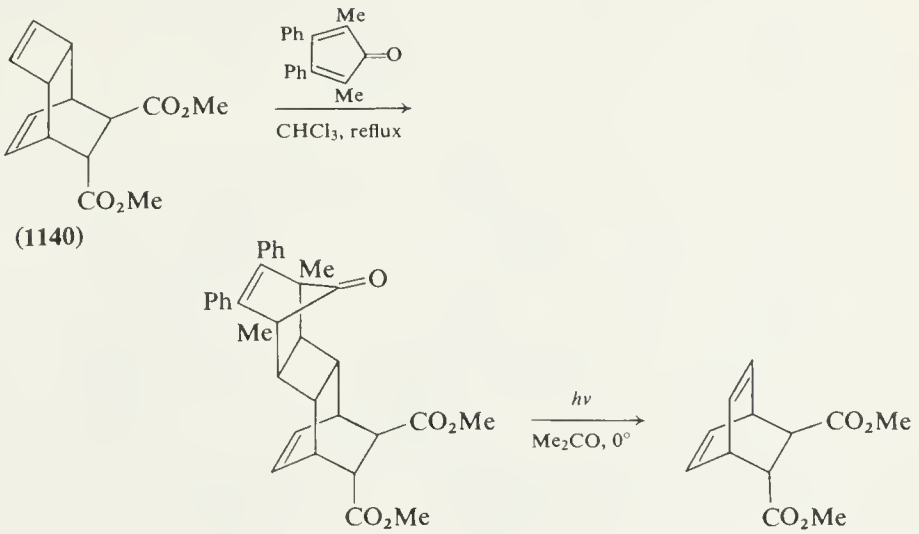
(1136)



(117) **(1138)** **(1139)** **(1137)**

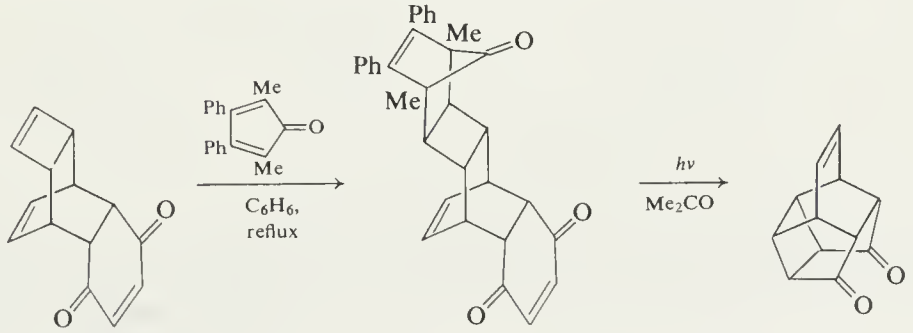
The reaction of α-pyrone with the anhydride (**117**) in refluxing xylene yields the product (**1137**) (86%), presumably *via* an initial lactone-bridged adduct (**1138**) (stereochemistry uncertain) and the decarboxylated derivative (**1139**), which then adds a second molecule of the dienophile[1091] (see pp. 340, 341).

The *trans*-dimethyl ester (**1140**) adds hemicyclone to give the adduct (**1141**) (stereochemistry uncertain) (76%); photolysis of this product leads to the bicyclic diene (**1142**) (62%).[1092]



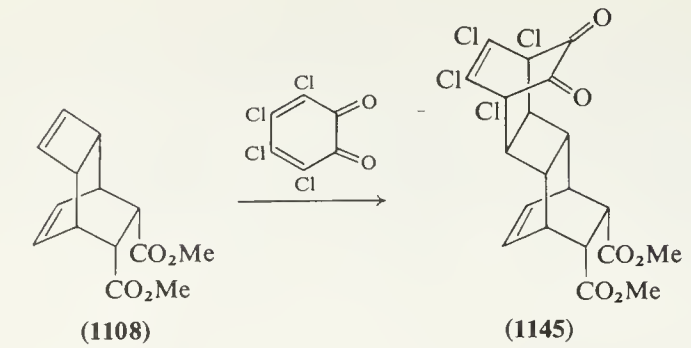
(**1140**) (**1141**) (**1142**)

Similarly, the addition of hemicyclone to the *p*-benzoquinone adduct (**106**) gives a product (**1143**) (80%) (stereochemistry uncertain); photolysis then affords the caged compound (**1144**) in excellent yield.[1093]

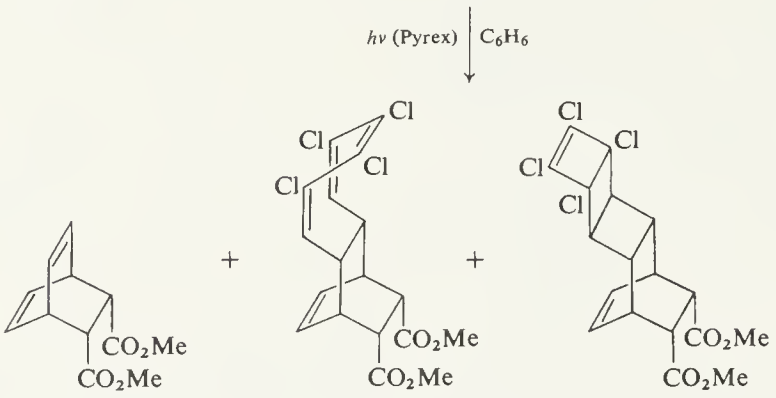


(**106**) (**1143**) (**1144**)

The di-ester (**1108**) reacts with tetrachloro-*o*-benzoquinone to form the adduct (**1145**), which on photolysis gives rise to the products (**1146**) (63%) and (**1147**) (12%); the formation of compound (**1148**) becomes significant with increase in the concentration of the starting material.[1094]

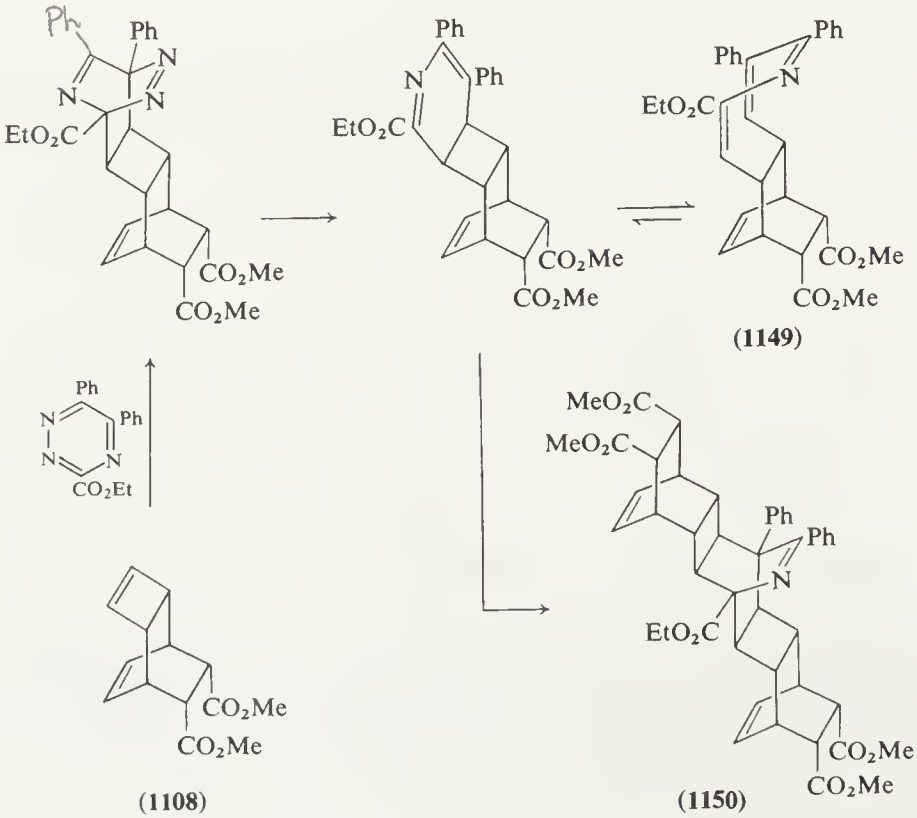


(1108) **(1145)**



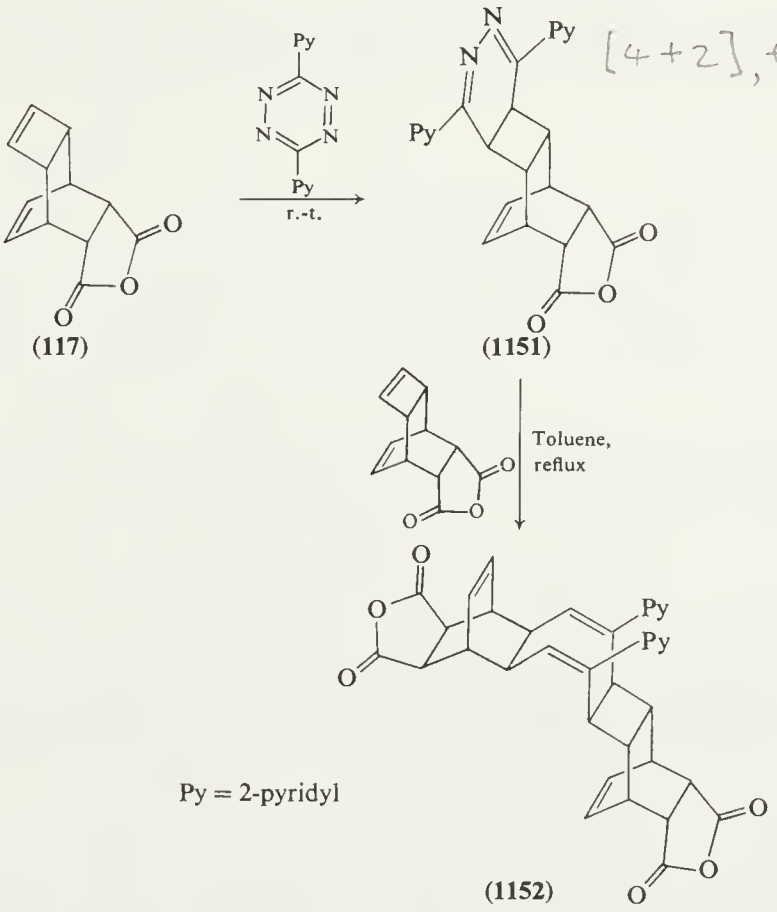
(1146) **(1147)** **(1148)**

(Stereochemistry uncertain)



With 3-ethoxycarbonyl-5,6-diphenyl-1,2,4-triazine, the di-ester (**1108**) yields a mixture of the products (**1149**) and (**1150**).[1095]

Reaction of the anhydride (**117**) with 3,6-di(2′-pyridyl)-*s*-tetrazine occurs at room-temperature to give the adduct (**1151**); an analogous product is obtained from the di-ester (**1108**).[1096] These 4,5-dihydropyridazine derivatives (which are prone to aerial oxidation) behave as dienes in [4 + 2] cycloadditions, and e.g. the adduct (**1151**) reacts with a second molecule of the anhydride (**117**) in refluxing toluene to afford a product formulated as (**1152**).[1096]

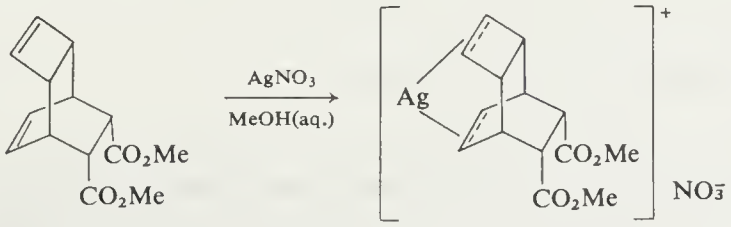


(**117**) (**1151**) (**1152**)

Py = 2-pyridyl

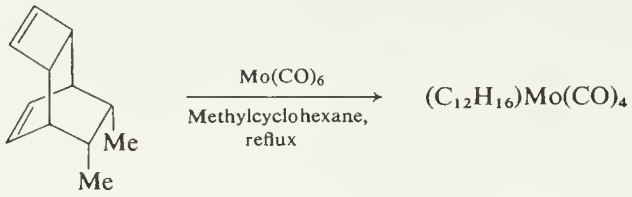
(Stereochemistry not certain)

Reactions with metal derivatives. The dimethyl ester (**1108**) forms a silver nitrate complex, presumably of structure (**1153**) (80.5%); the cyclic ether (**1107**) gives a similar product (**70**%).[341]



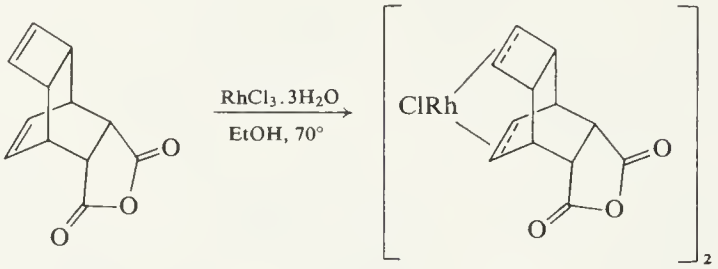
(**1108**) (**1153**)

The dimethyl-derivative (**1106**) reacts with $Mo(CO)_6$ to give the tetracarbonyl complex (**1154**) (68%).[341]



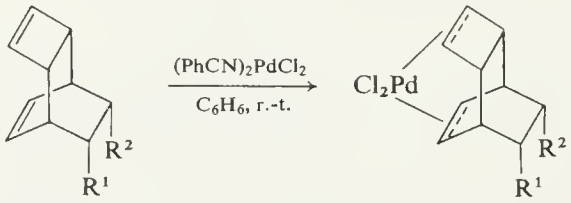
(**1106**) (**1154**)

A (probably) dimeric rhodium complex (**1155**) (28%) is formed by the anhydride (**117**).[339]



(**1155**)

Palladium complexes (**1156**) are readily formed from $(PhCN)_2PdCl_2$ and the system (**1157**)[341] (table 129).



(**1157**) (**1156**)

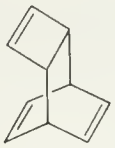
Table 129

R^1	R^2	Yield (%)
Me	Me	92
CH_2OH	CH_2OH	63
H_2C	CH_2	63
	O	
CO_2Me	CO_2Me	72

26. Tricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes

The reaction of COT with acetylenic dienophiles leads to tricyclo[4.2.2.0^{2,5}]-decatrienes (see pp. 42–3); the parent compound (**1158**) ('Nenitzescu's hydrocarbon') may be obtained from the COT–maleic anhydride adduct (**117**) (see

p. 328). The triene (**1158**) is a member of a set of $C_{10}H_{10}$ isomers which lie on interconnected energy surfaces. Most of these hydrocarbons have COT as

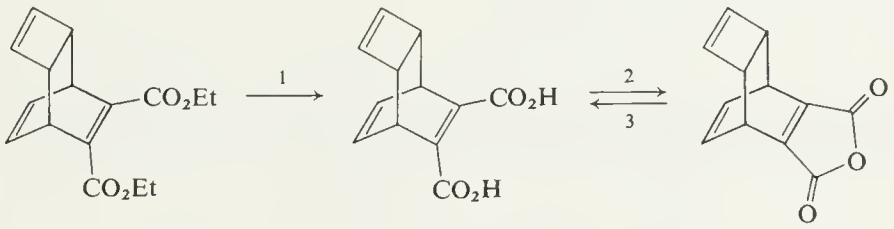


(**1158**)

their common progenitor; for a review of their numerous thermal, photochemical, and metal-catalysed interconversions, see ref. 1097.

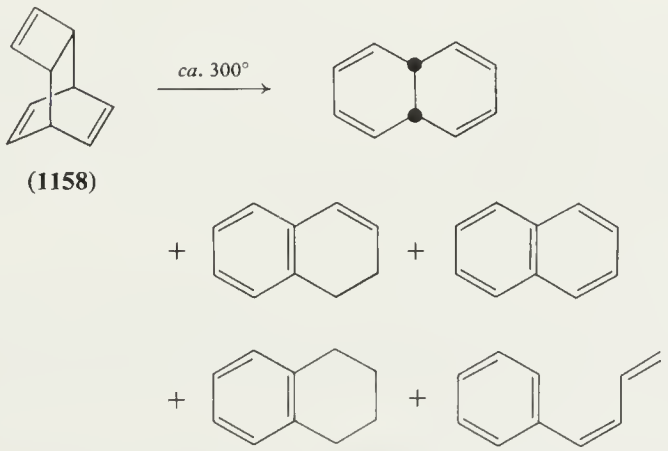
Functional group transformations. See scheme 104.

Scheme 104



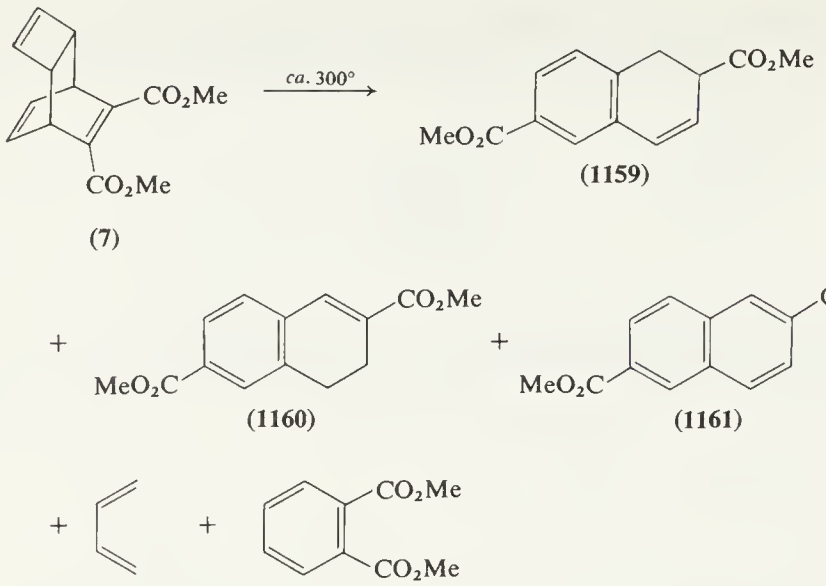
Reaction	Reagents and conditions	Yield (%)	Ref.
1	NaOH, MeOH(aq.), reflux	63	11
2	Ac_2O, C_6H_6, *ca.* 100°	—	11
3	NaOH(aq.)	—	11

Thermolysis. Thermolysis of the triene (**1158**) at *ca.* 300° affords *cis*-9,10-dihydronaphthalene, and further products resulting from hydrogen shift and transfer processes.[1080,1098,1099] Similar thermolysis of the diester (**7**) yields a



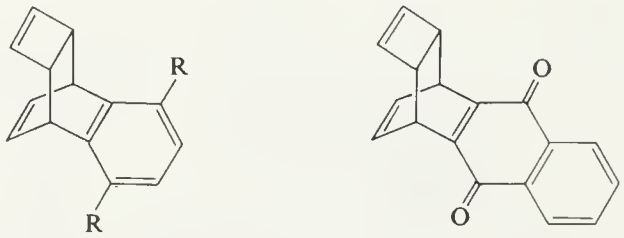
(**1158**)

mixture of the dihydronaphthalenes (**1159**) and (**1160**) (27%) and the naphthalene (**1161**) (17–25%),[342,352] together with buta-1,3-diene (15–17%) and



(7) (1159) (1160) (1161)

dimethyl phthalate (30–32%).[352] (For the thermolysis products of the benzo-derivatives (**1162**), and of the quinone (**119**), see refs. 352, 1099, 1100.)



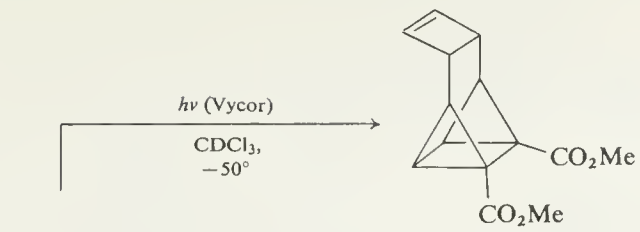
(**1162**) (**119**)

R = H, OMe, OAc

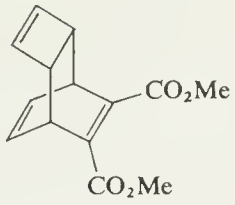
Photolysis. U.v. irradiation of the diester (**7**) at −50° produces the caged isomer (**1163**) (up to 61% conversion); this reverts to starting material at higher temperatures (half-life 16 min at *ca.* 2°).[1101] Irradiation at 10° results in the cyclobutadiene dimer (**5**) (16–18%), together with dimethyl phthalate (37–40%), COT (5–7%) and benzene; the intermediacy of cyclobutadiene in this photolysis is revealed by trapping experiments.[56]

Reduction. Selective hydrogenation of the 3,4-double bond in (**7**) may be effected to give the dihydro-derivative (**698**) (82%),[353] which on further hydrogenation affords (after hydrolysis) the *trans*-dicarboxylic acid (**1164**) (83%).[260]

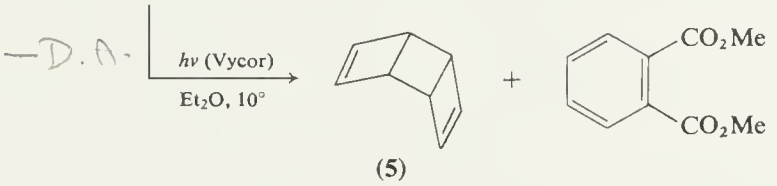
Cycloadditions. Both the 3,4- and the 7,8-double bonds of the di-ester (**7**) take part in 1,3-dipolar cycloadditions; thus 3,4-dihydroisoquinoline *N*-oxide gives the adducts (**1165**) (43%) and (**1166**) (37.5%).[335]



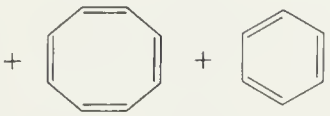
(1163)

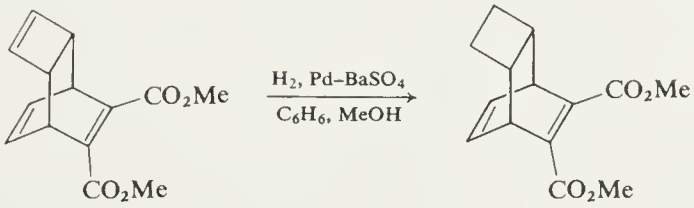


(7)

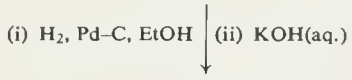


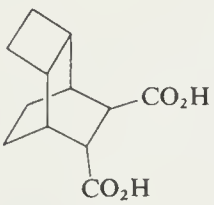
(5)



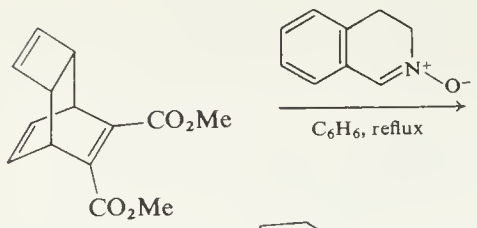


(7) **(698)**

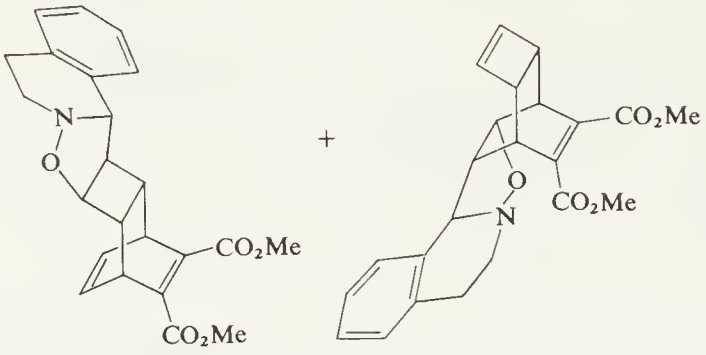




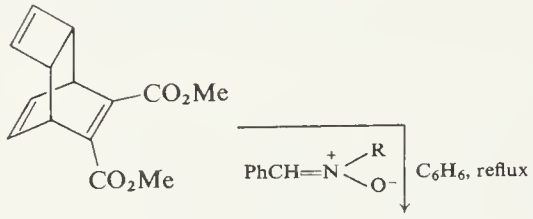
(1164)



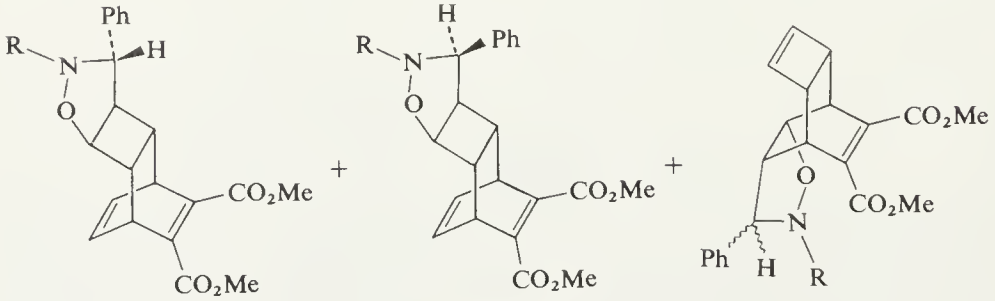
(7)



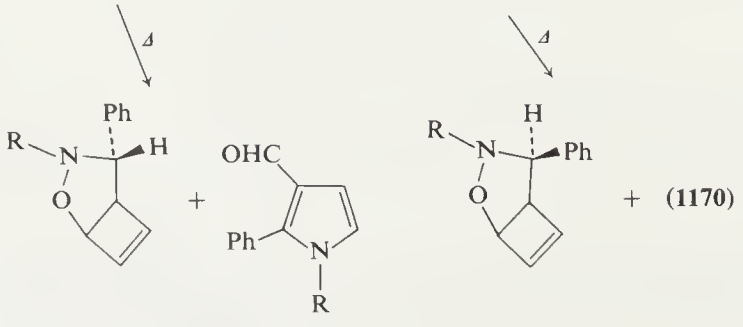
(1165) (1166)



(7)



(1167) (1168) (1169)

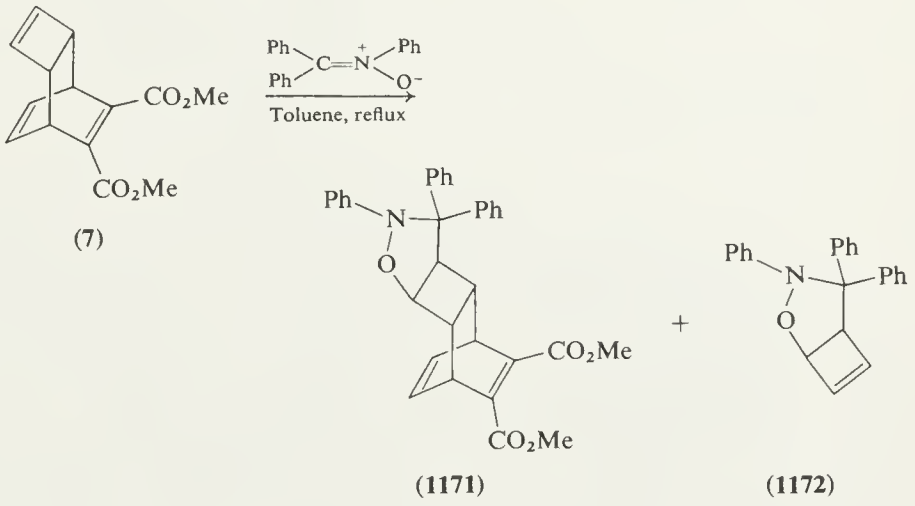


(1170) (1170)

Table 130

R	Yield (%) (1167)	(1168)	(1169)
Me	43	18	22
Ph	27	54	6
p-Cl.C_6H_4	25	57	(Very low)

Nitrones of structure PhCH=N(O)R afford a pair of stereoisomers (**1167**) and (**1168**), and a single stereoisomer of the other structural type (**1169**); when R is an aromatic group, Alder–Rickert fragmentation of the adducts (**1167**) and (**1168**) is accompanied by rearrangement to the 3-formylpyrrole (**1170**)[335] (table 130). The addition of the triphenylnitrone Ph_2C=N(O)Ph to the di-ester (**7**) is sluggish, and prolonged refluxing in toluene results in a mixture of the adduct (**1171**) (16%) and its thermolysis product (**1172**) (17%).[335]



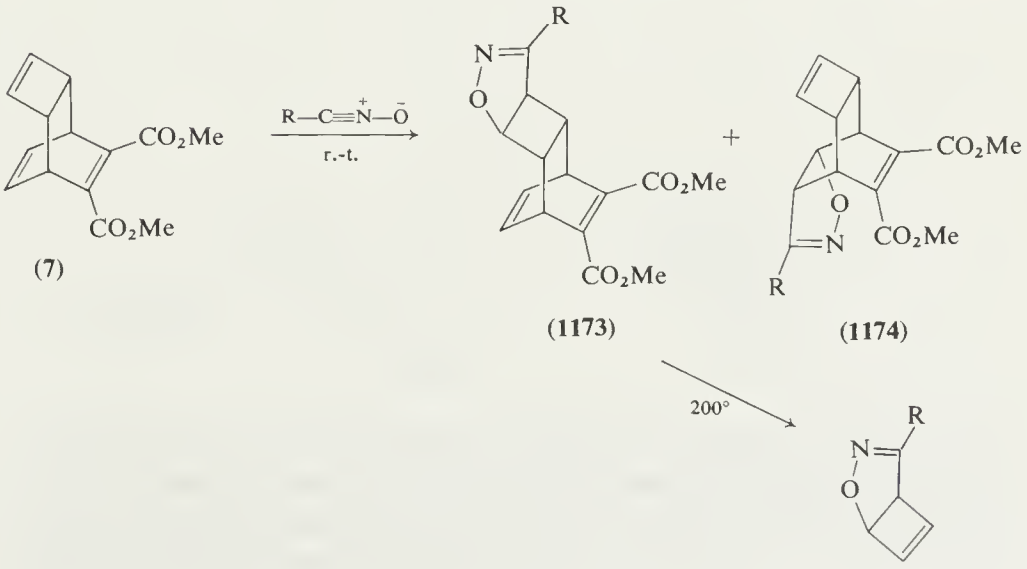
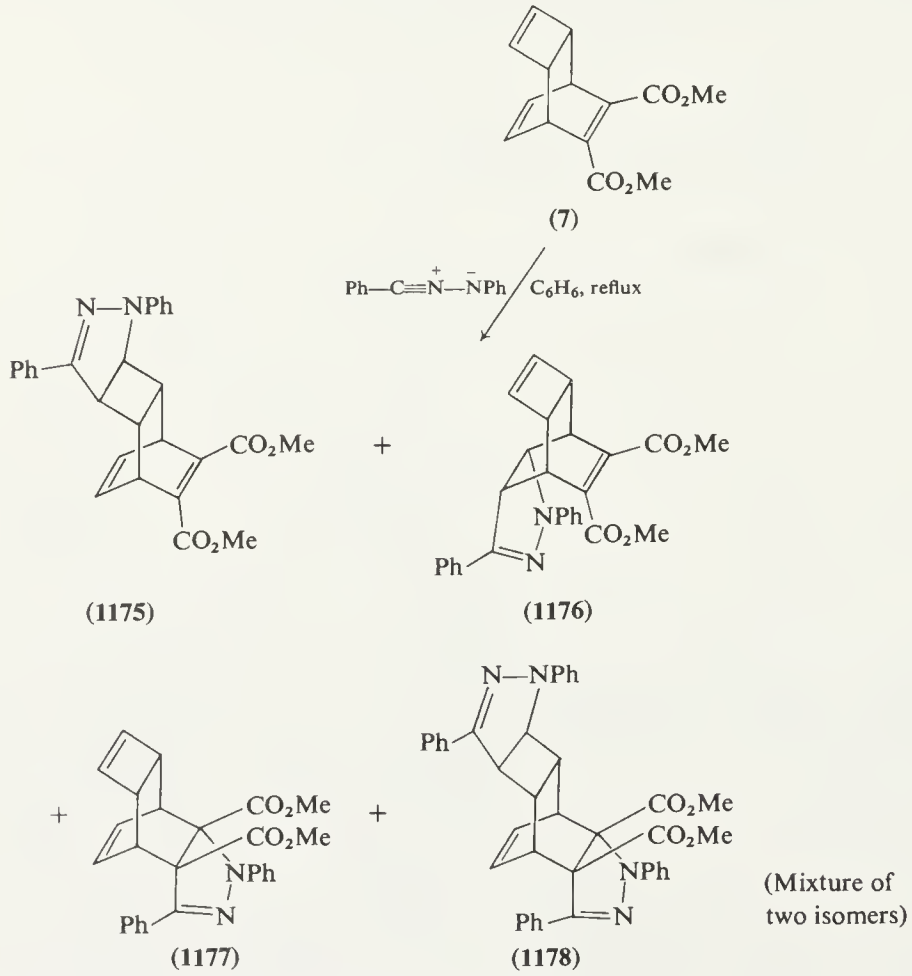


Table 131

R	Yield (%) (1173)	(1174)
Ph	17	—
p-Br.C_6H_4	18.5	—

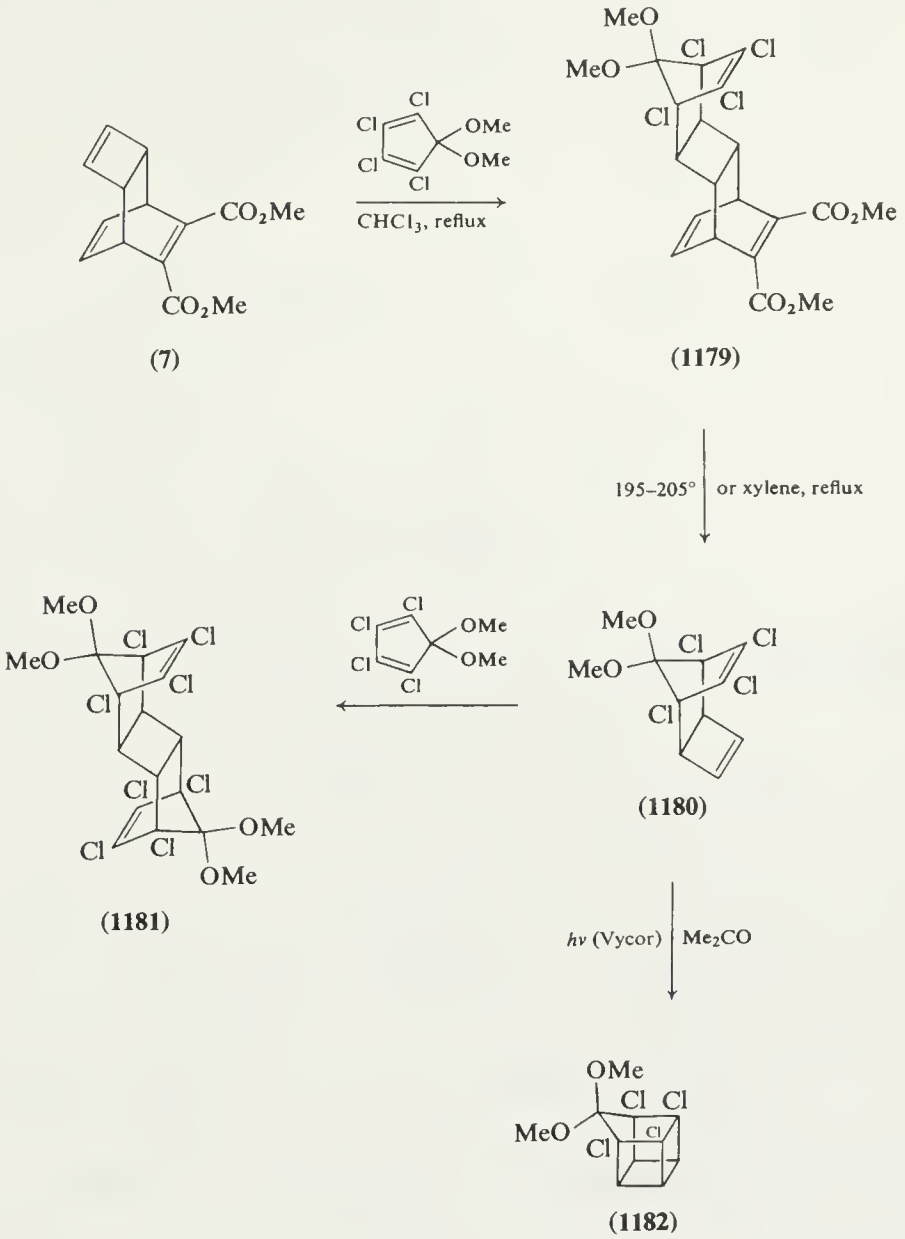
Nitrile oxides also afford two types of adduct, (**1173**) and (**1174**) (table 131); thermolysis of the former gives the expected products.[331]

The nitrile imine Ph—C≡$\overset{+}{N}$—$\overset{-}{N}$Ph cycloadds to each of the three double bonds in the di-ester (**7**); the isolated products are (**1175**) (18%), (**1176**) (51%), (**1177**) (18%) and the 2:1 adduct (**1178**) (2.3%).[336] (Further reactions of (**1175**)–(**1177**) are described in ref. 336.)

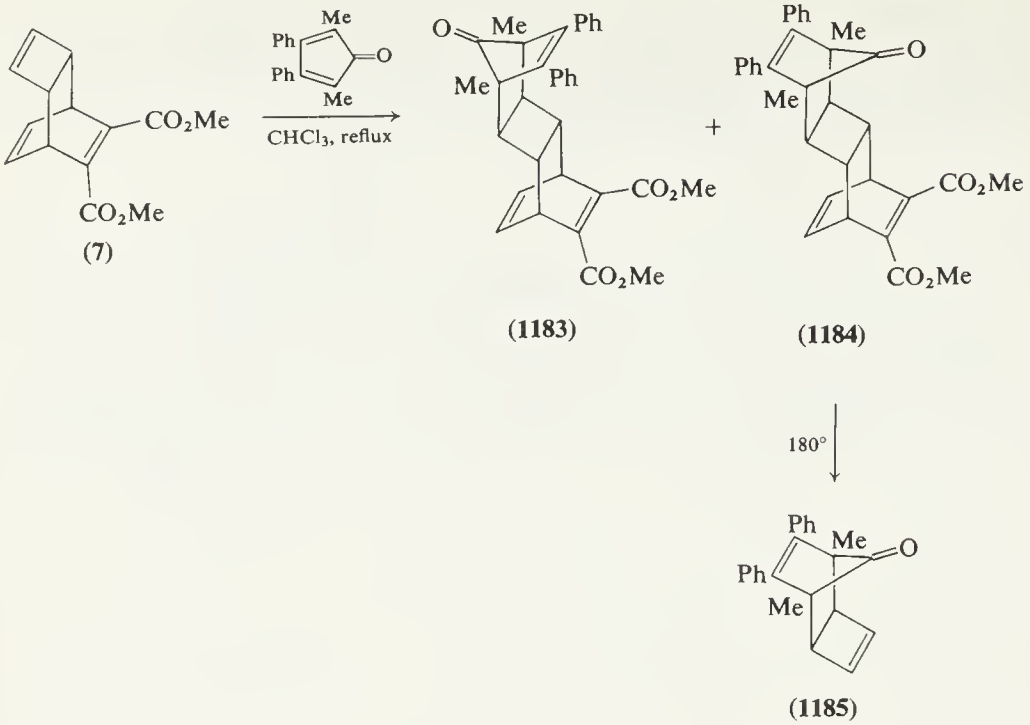


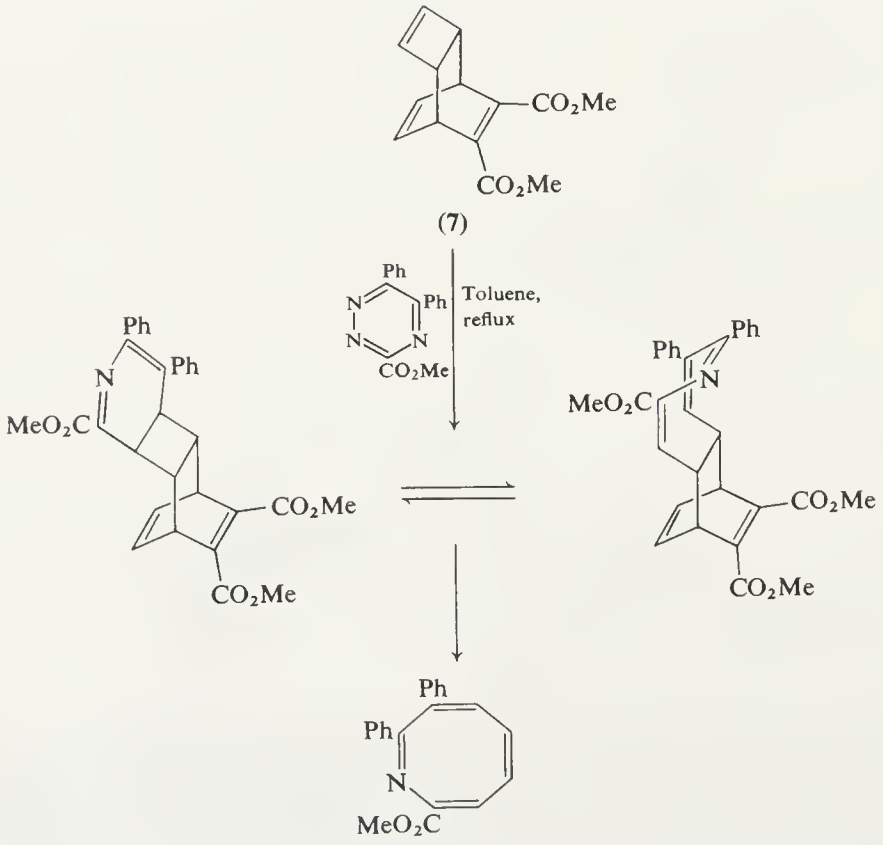
With 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene in refluxing chloroform, the di-ester (**7**) yields the *endo*-[4 + 2] adduct (**1179**) (up to 76%)[1090,1102,1103] Thermolysis of this product at *ca.* 200°,[1102,1103] or in refluxing xylene,[1090]) affords a quantitative yield of the cyclobutene (**1180**); if

the initial Diels–Alder reaction is carried out in refluxing xylene, the product (**1181**) is formed.[1090] Photo-caging of the cyclobutene (**1180**) gives the homocubane derivative (**1182**) in nearly quantitative yield.[1090,1102,1103] (For further reactions of (**1182**), see refs. 1103, 1104.)



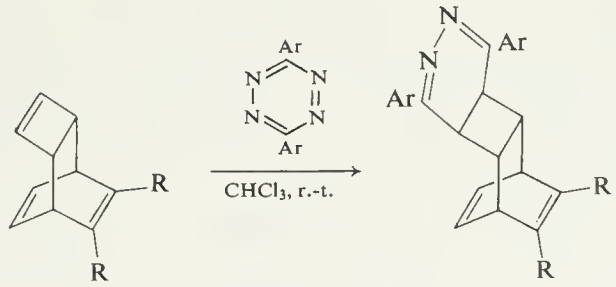
Hemicyclone reacts with the di-ester (**7**) to give a mixture of *endo*- and *exo*-adducts, (**1183**) and (**1184**) respectively, the *exo*-compound (**1184**) predominating (*ca.* 6:1).[1105] Alder–Rickert cleavage of (**1184**) affords the cyclobutene derivative (**1185**) in high yield.[1105]


Me
Ph
Ph
O
Me
CHCl3, reflux
CO2Me
CO2Me
(7)
O
Me
Ph
Me
Ph
CO2Me
CO2Me
(1183)
+
Ph
Me
Ph
Me
O
CO2Me
CO2Me
(1184)
180°
Ph
Me
Ph
Me
O
(1185)


CO2Me
CO2Me
(7)
Ph
N
N
Ph
CO2Me
Toluene,
reflux
Ph
Ph
N
MeO2C
CO2Me
CO2Me
Ph
Ph
N
MeO2C
CO2Me
CO2Me
Ph
Ph
N
MeO2C
(1186)

Prolonged reaction of the di-ester (**7**) with 3-methoxycarbonyl-5,6-diphenyl-1,2,4-triazine in refluxing toluene gives the azocine (**1186**) (60%).[1095]

With 3,6-diaryl-*s*-tetrazines, the trienes (**7**) and (**1158**) form the products (**1187**), which have high thermal stability[1106] (table 132).



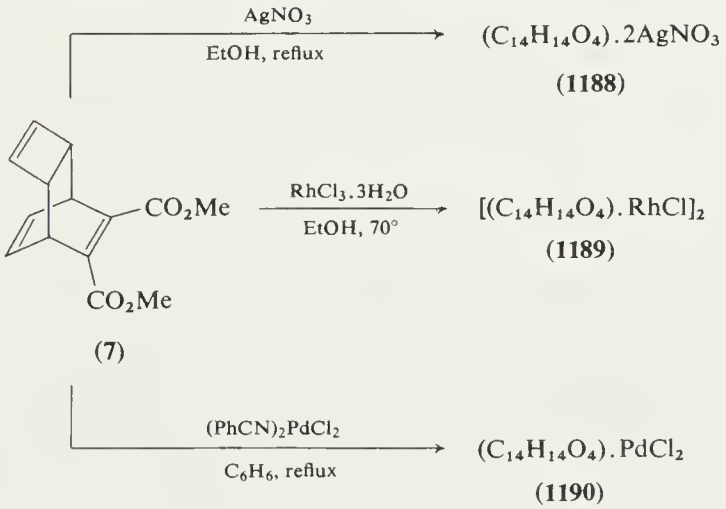
(**7**) (R = CO_2Me)
(**1158**) (R = H)

(**1187**)

Table 132

R	Ar	Yield (%)
CO_2Me	Ph	77
H	2-Pyridyl	—
CO_2Me	2-Pyridyl	80

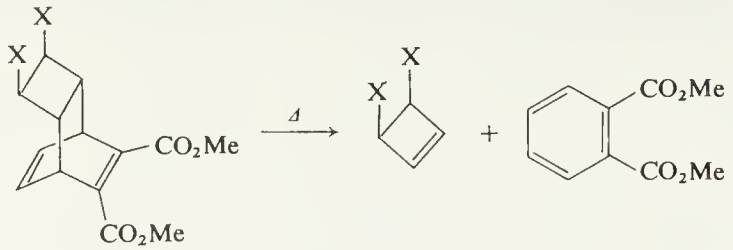
Reactions with metal derivatives. The di-ester (**7**) forms a 1:2 complex (**1188**) with silver nitrate.[341] A dimeric rhodium complex (**1189**) is known.[339] With $(PhCN)_2PdCl_2$, a complex (**1190**) (70%) is produced.[341]



27. Tricyclo[4.2.2.0^{2,5}]deca-7,9-dienes

The tricyclo[4.2.2.0^{2,5}]deca-7,9-diene system results from the cycloaddition of bicyclo[4.2.0]octa-2,4-dienes to e.g. dimethyl acetylenedicarboxylate (see pp. 220, 248–9).

Thermolysis. Alder–Rickert fragmentation of the *cis*-disubstituted compounds (**805**) affords *cis*-3,4-disubstituted cyclobutenes (**1191**) (table 133). (*cis*-3,4-



(**805**) (**1191**)

Table 133

X	Conditions	Yield (%)	Ref.
H, (D)[a]	200°/100 mm	95[b]	260, (1107)
Cl[c]	190°/5 mm	—	228

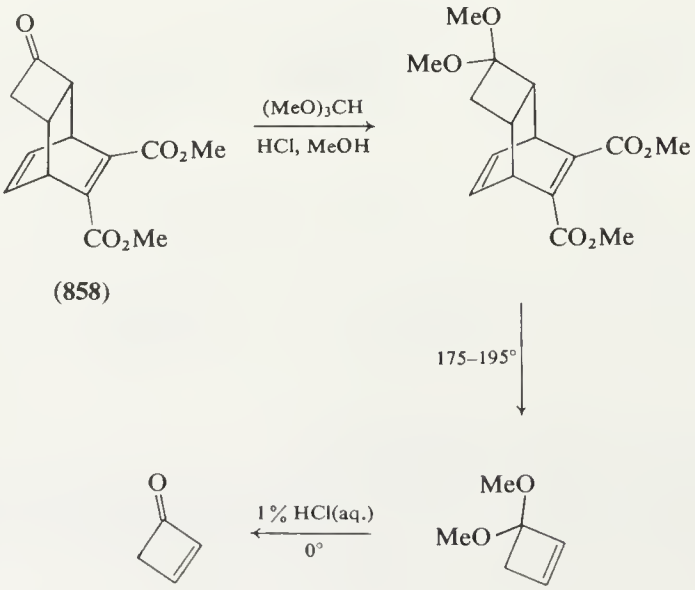
[a] Hexadeuteriocyclobutene may be obtained from the analogous adduct prepared from decadeuteriocyclo-octa-1,3,5-triene.[262]

[b] Overall yield from COT is 34–39%.[353]

[c] A mixture of the *cis*- and *trans*-dichloro-compounds (**805***a*) and (**806***a*) may be used for the preparation of *cis*-dichlorocyclobutene (40–43% from COT).[228,929]

Dichlorocyclobutene is a convenient precursor of (cyclobutadiene)-$Fe(CO)_3$,[1108] and thence of cyclobutadiene itself.[1109])

This useful cyclobutene synthesis (see also p. 220) provides a route to cyclobutenone from the adduct (**858**) of cyclo-octatrienone[1110] (see p. 261).



(**858**)

In contrast, thermolysis of the *trans*-3,4-disubstituted compounds (**806**) leads to 1,4-disubstituted *E,E*-buta-1,3-dienes (**1192**), by conrotatory ring-opening of the intermediate cyclobutenes (**1193**) (table 134). (For synthetic uses of 1,4-diacetoxybutadiene, see ref. 207.)

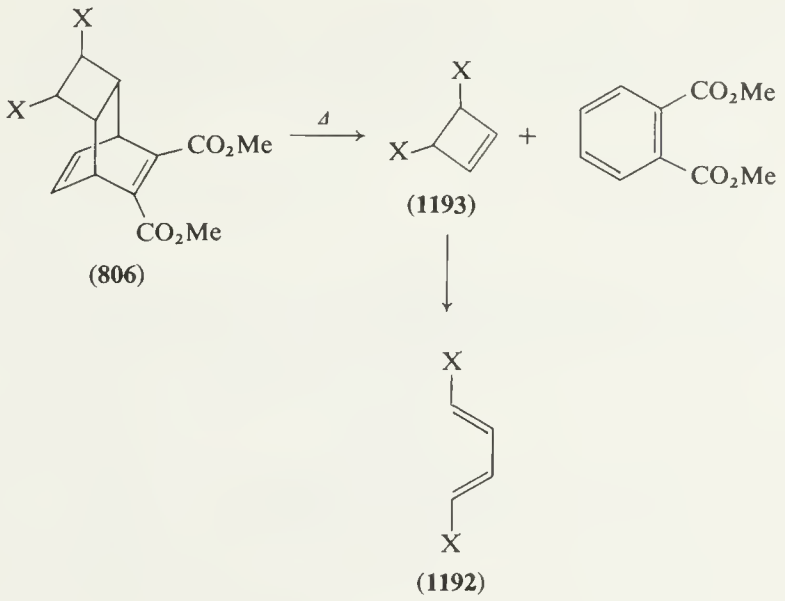


Table 134

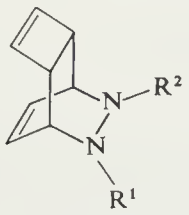
X	Conditions	Yield (%)	Ref.
OAc	180–220°/18 mm	64	(11), 1111
	170–200°/18–20 mm	41–49[a]	207
Cl[b]	140–150°/17 mm	85	(11), 1111
Br	*ca.* 200°	80	11

[a] Overall yield from the diacetoxy-diene (**28**).
[b] The starting material was apparently a mixture of the *cis*- and *trans*-dichloro-compounds (**38**/**39**).

Reduction. For catalytic hydrogenation of various tricyclo[4.2.2.0^{2,5}]deca-7,9-dienes, see ref. 11.

28. 9,10-Diazatricyclo[4.2.2.0^{2,5}]deca-3,7-dienes

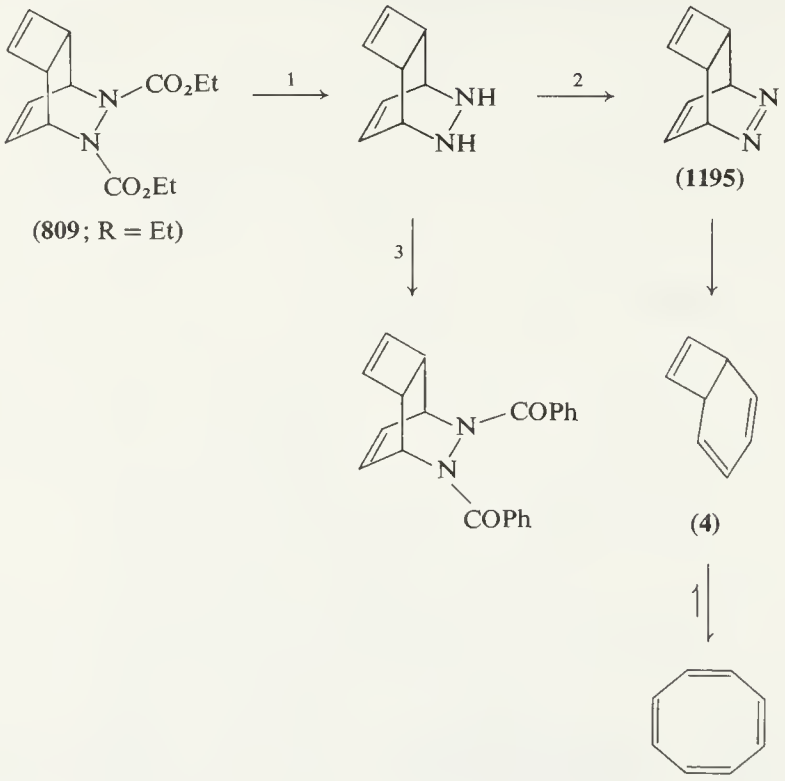
In general these diaza-compounds, of basic structure (**1194**), are best prepared *indirectly* from COTs, *viz.* by reaction with bromine, followed by [4 + 2] cycloaddition of azo-dienophiles, and finally debromination (see pp. 248–9).



(**1194**)

Functional group transformations. See schemes 105 and 106.

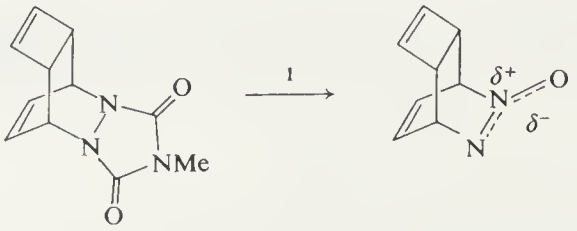
Scheme 105



Reaction	Reagents and conditions	Yield (%)	Ref.
1	KOH, EtOH, 80°	78	40
2	MnO_2, n-hexane, −10° to −15°	—[a]	40
3	PhCOCl, NaOH(aq.), 0°	51	40

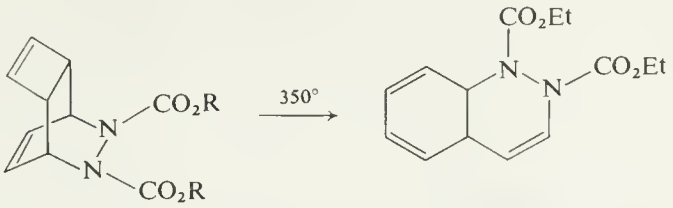
[a] The initial product (**1195**) extrudes nitrogen to give (**4**) (40–70%).

Scheme 106



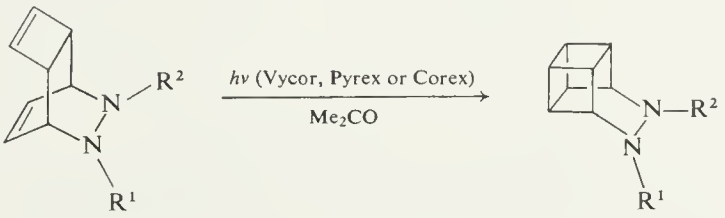
Reaction	Reagents and conditions	Yield (%)	Ref.
1	H_2O_2, KOH(aq.), 80–95°	65	1112

Thermolysis. At 350° the di-ester (**809**; R = Et) (see p. 249) rearranges to the bicyclic compound (**1196**) (73%).[1113]



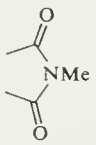
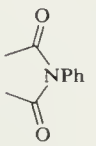
(**809**) (R = Et) (**1196**)

Photolysis. U.v. irradiation of the 9,10-diazatricyclo[4.2.2.0^{2,5}]deca-3,7-dienes (**1194**) in the presence of acetone furnishes the cage-compounds (**1197**) (table



(**1194**) (**1197**)

Table 135

R^1	R^2	Yield (%)	Ref.
CO_2Et	CO_2Et	80	40
		—	1102
		84–85	569, 1114

135). The *C*-substituted derivatives (**287**)–(**290**) (see pp. 104–5) likewise afford the products (**1198**)–(**1200**)[569] (table 136).

Silver-catalysed rearrangement of diazabasketanes, e.g. (**1197**), yields diazasnoutanes, e.g. (**1201**);[41, 569, 1114, 1115] for the transformation of diazasnoutanes into semibullvalenes, see refs. 41, 716, 1114, 1115.

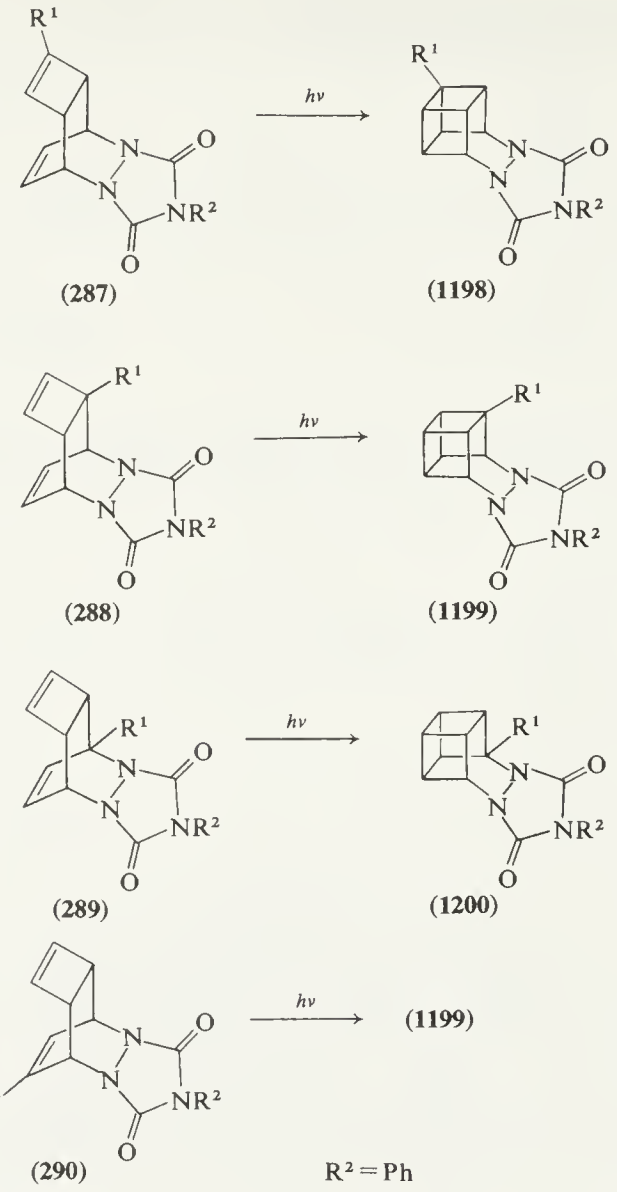
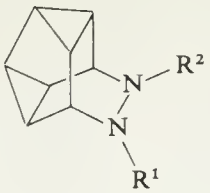


Table 136

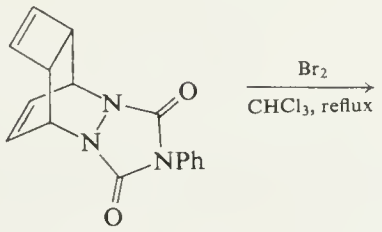
	R¹	Yield (%)		R¹	Yield (%)
(287)	Me	72	(288)	Me	93
	Ph[a]	30		Ph	42
	CH_2OAc	82		CH_2OAc[b]	72
	CH_2OMe	24		CH_2OMe	34
	CN	92		CN	80
(289)	CH_2OAc	70		F	56
	CH_2OMe	64			
	CO_2Me	35	(290)	Ph	21
	CN	50		CH_2OAc[b]	72

[a] *N*-Methyl-compound used. [b] Mixture (1 : 1) of (**288**) and (**290**)

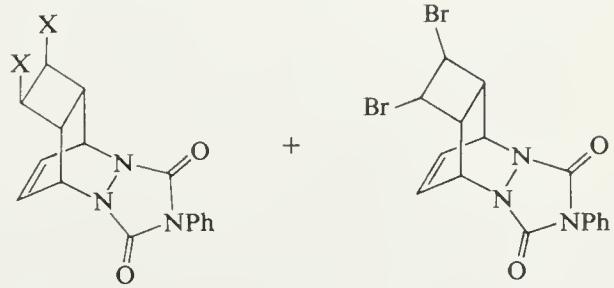


(1201)

Bromination. The addition of bromine to the derivative (**125***a*) (p. 46) apparently leads to a mixture of the *cis*- and *trans*-dibromides, (**1202***a*) (20%) and (**1203**) (40%).[931] (For the *cis*-dichloride (**1202***b*), see ref. 362.)



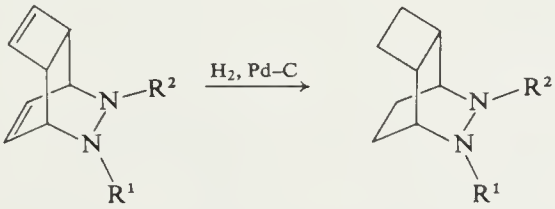
(125*a*)



(1202) **(1203)**

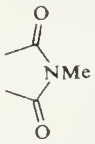
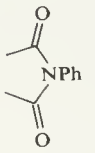
a: X = Br
b: X = Cl

Reduction. Catalytic hydrogenation of the diaza-compounds (**1194**) in the presence of palladium-on-carbon affords the tetrahydro-derivatives (**1204**) (table 137). (For further reactions of system (**1204**), see refs. 874, 1117.)



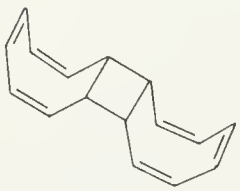
(1194) **(1204)**

Table 137

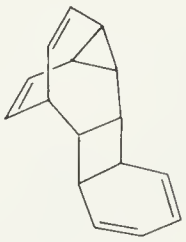
R^1	R^2	Solvent	Yield (%)	Ref.
COPh	COPh	EtOAc	82	40
CO_2Et	CO_2Et	MeOH	88	40
		EtOAc	100	930
		EtOAc	—	362

29. Oligomers of cyclo-octatetraenes

Four dimers, (**9**)–(**12**), and a tetramer (**23**) result from thermal treatment of COT (see pp. 11–17).

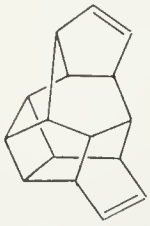


(**9**)

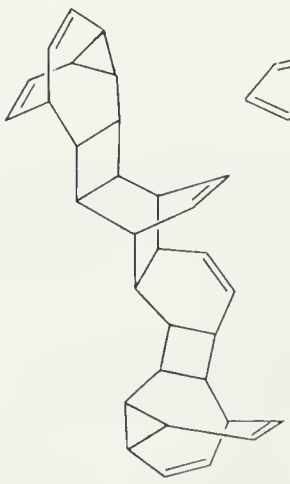


(**10**)*

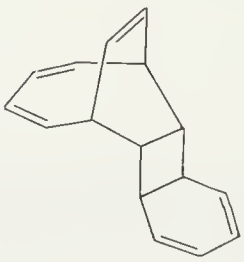
(**11**)



(**12**)



(**23**)*



(**193**)

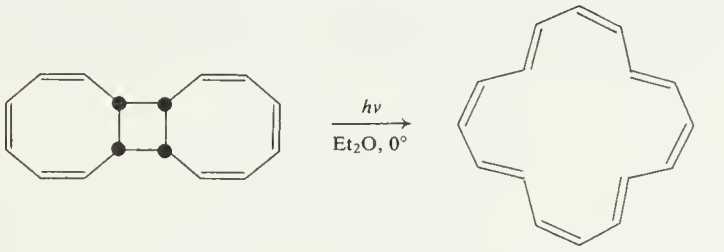
* Structures (**10**) and (**23**) are fluxional; only one of the interconverting forms is illustrated.

Additionally, a fifth dimer, (**193**), is produced by the action of $H_4Ru_4(CO)_{12}$ on COT (see pp. 67–8).

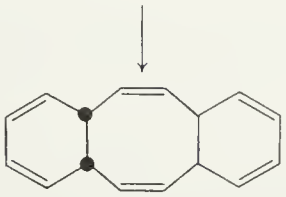
(*a*) *Dimer* (**9**)

Thermolysis. At 100°, dimer (**9**) slowly produces COT and dimer (**10**).[159,169]

Photolysis. U.v. irradiation of dimer (**9**) provides a convenient route to [16]-annulene (**1205**) (60%);[1118,1119] this polyene has a half-life of *ca.* 44 h at 20°, gradually transforming into the tricyclic isomer (**1206**) (90%).[1119]

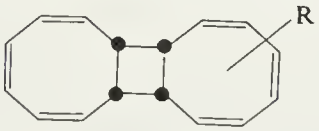


(**9**) (**1205**)



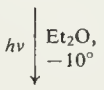
(**1206**)

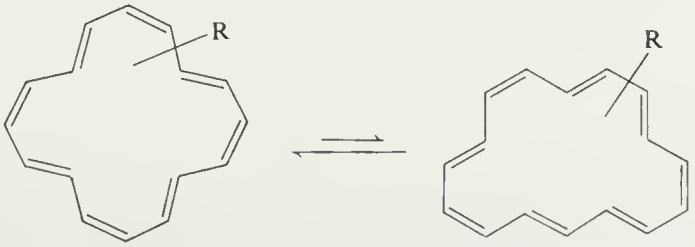
Photolysis of the substituted dimers (**278**) (see p. 102) similarly generates the monosubstituted [16]annulenes (**1207**) in low yields.[160,580]



R = Ph, CO_2Me, F, Cl

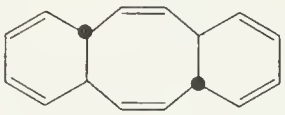
(**278**)



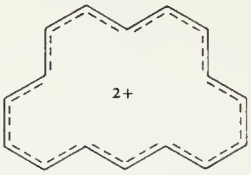


(**1207***a*) (**1207***b*)

Photolysis of [16]annulene affords the stereoisomer (**1208**).[1119] For the dication (**1209**), see ref. 1120.

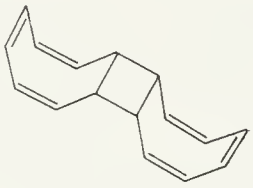


(**1208**)

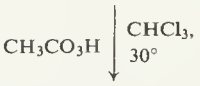


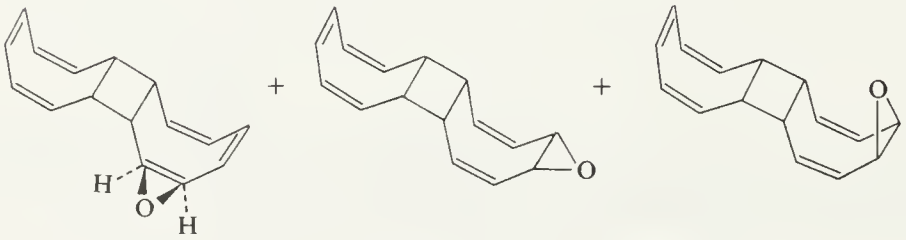
(**1209**)

Oxidation. Treatment of dimer (**9**) with peracetic acid gives the epoxide (**1210**) as the main product (*ca.* 45%),[1121,1122] together with small amounts of the isomers (**1211**) and (**1212**).[1122] Photolysis of these epoxides leads to oxa[17]-



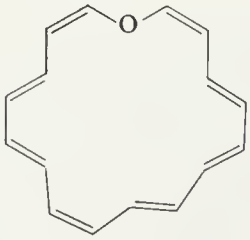
(**9**)





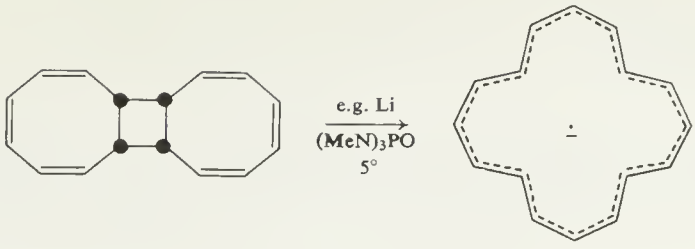
(**1210**) (**1211**) (**1212**)

annulenes (differing in the sequence and individual numbers of *Z* and *E* double bonds), one of which may be assigned the provisional structure (**1213**).[1122]

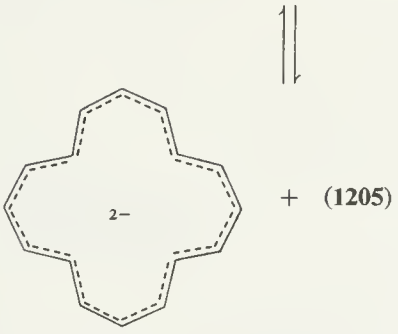


(**1213**)

Reduction and deprotonation. Dimer (**9**) reacts with alkali metals to give the radical anion of [16]annulene (**1214**), which equilibrates with the dianion (**1215**) and the neutral hydrocarbon (**1205**)[1123] (*cf.* $COT^{\cdot-}$, p. 28).



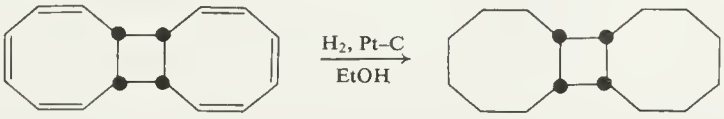
(9) (1214)



+ (1205)

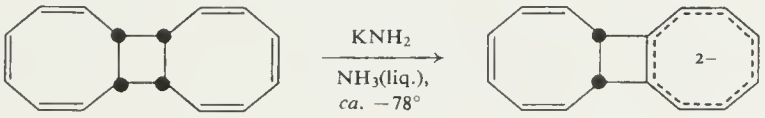
(1215)

Catalytic hydrogenation of dimer (**9**) gives a hexahydro-derivative,[156,159] which may now be formulated as (**1216**).

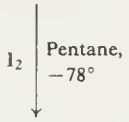


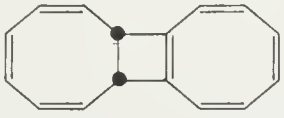
(9) (1216)

Deprotonation of (**9**) with potassium amide in liquid ammonia affords the dianion (**1217**) (see p. 217), which with iodine gives the extremely labile product (**1218**).[1038]



(9) (1217)

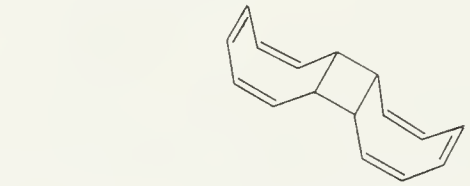




(1218)

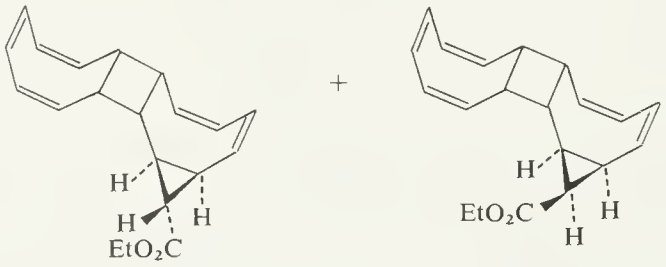
Dimer (**9**) catalyses H–D exchange in COT in the presence of $KOCPr^n_3$–Pr^n_3COD (see p. 31).

Cycloadditions. The reaction of dimer (**9**) with diazoacetic ester in the presence of copper powder results in the products (**1219**) (*ca.* 11%) and (**1220**) (*ca.* 3%), together with an inseparable mixture (*ca.* 6%) of (**1221**) and (**1222**).[1124] For

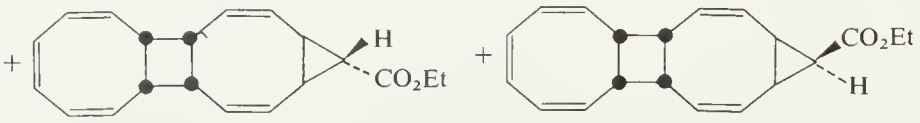


(**9**)

N_2CHCO_2Et, Cu, 100°

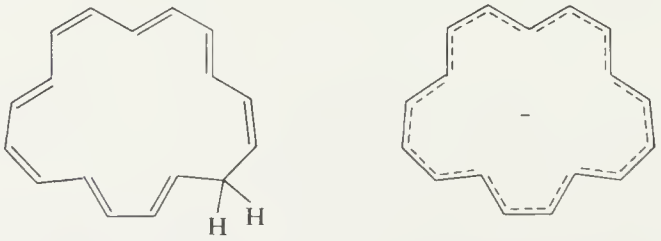


(**1219**) (**1220**)



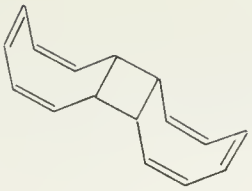
(**1221**) (**1222**)

the conversion of these products into cycloheptadecaoctaenes, one of which may be formulated as (**1223**), and the generation of the [17]annulenyl anion (**1224**), see ref. 1124.



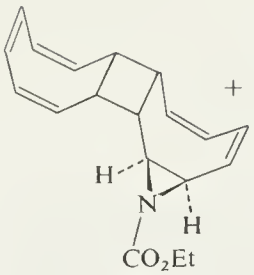
(**1223**) (**1224**)

Addition of *N*-(ethoxycarbonyl)nitrene produces the adducts (**1225**) (*ca.* 20%), (**1226**) (*ca.* 9%), and (**1227**) (*ca.* 9%), the latter probably resulting

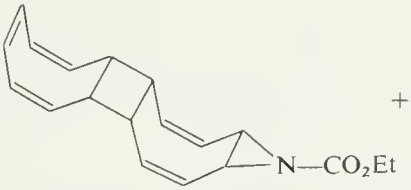


(9)

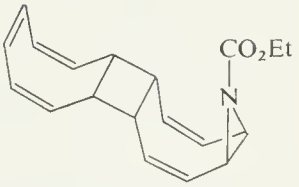
CH_2Cl_2, 20° | *p*-$NO_2.C_6H_4.SO_2ONHCO_2Et$, Et_3N

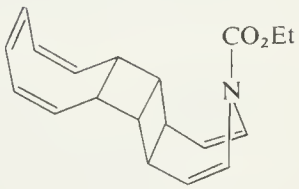


(1225)



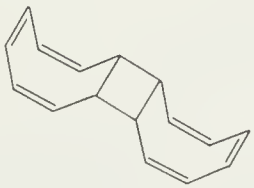
(1226)



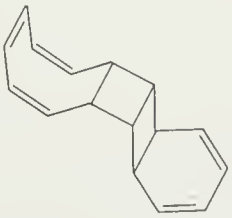


(1227)

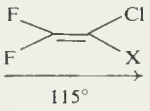
from a Cope rearrangement.[1125] Photolysis of the aziridines (**1225**) and (**1226**) affords a mixture of three aza[17]annulenes (configurations uncertain).[1125]

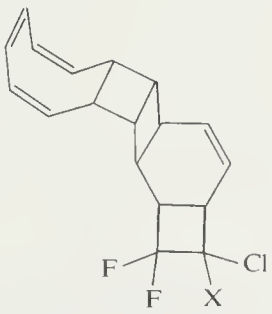


(9)



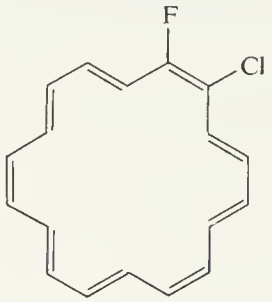
(1228)





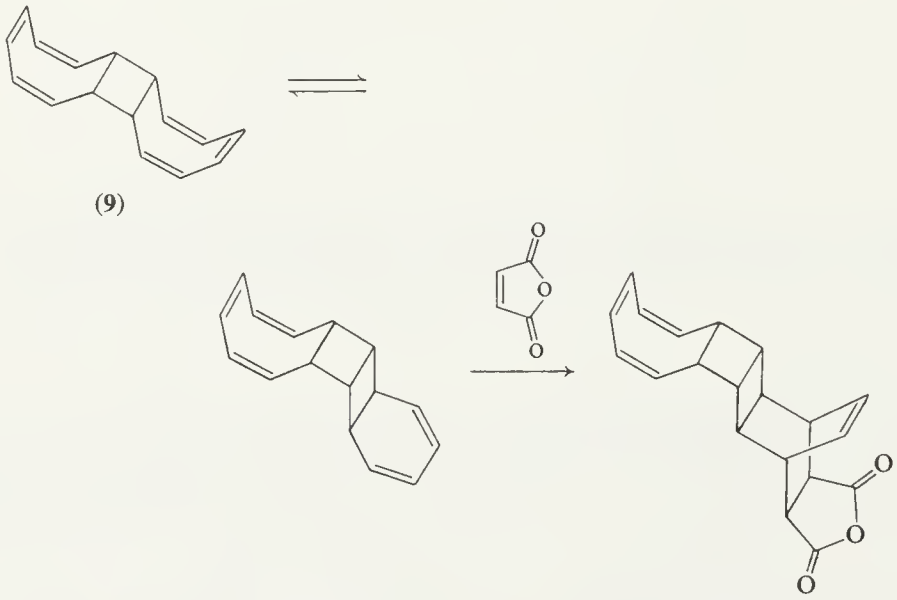
(1229) *a*: X = Cl
b: X = F

With 1,1-dichloro-2,2-difluoroethylene, a [2 + 2] cycloaddion occurs *via* the valence tautomer (**1228**), forming the adduct (**1229*a***) (21%); chlorotrifluoroethylene reacts similarly to give (**1229*b***) (*ca.* 0.8%).[1126] The conversion of (**1229*a***) into the 1,2-dihalo[18]annulene (**1230**) may be achieved.[1126]



(1230)

Dimer (**9**) reacts with dienophiles *via* the valence tautomer (**1228**); thus with maleic anhydride, the initial product is the 1 : 1 adduct (**1231**) (stereochemistry presumed) (table 138). Further reaction with maleic anhydride produces the

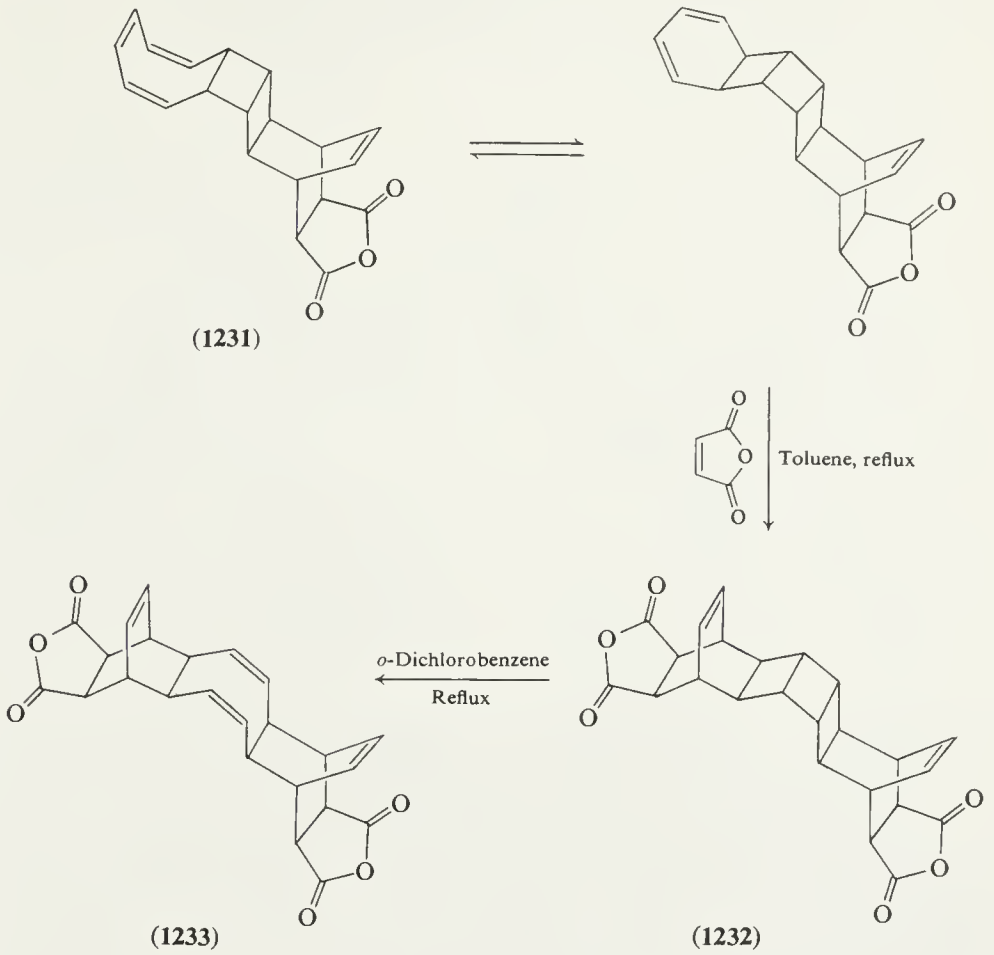


(9) **(1228)** **(1231)**

Table 138

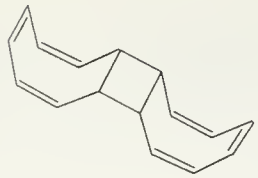
Dienophile	Reaction conditions	Yield (%)	Ref.
Maleic anhydride	—	—	156
	THF, 100°	51	159
	C_6H_6, reflux	33	1127
p-Benzoquinone	—	—	156

2:1 adduct (**1232**) (84% from (**9**)), which at *ca.* 180° undergoes a symmetry-forbidden ring-opening to give the product (**1233**) (81%);[1127] an analogous product is formed by the reaction of dimer (**9**) with citraconic anhydride at 180°.[1127,1128]

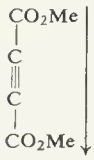


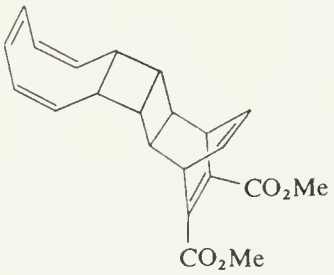
The reaction of dimer (**9**) with dimethyl acetylenedicarboxylate at 80° also gives 1:1 (**1234**) and 2:1 (**1235**) adducts, but with an excess of the dienophile at 100–120° compound (**1236**) is produced;[34] presumably, Alder–Rickert cleavage of the 2:1 adduct (**1235**) is followed by a 'forbidden' cyclobutene ring-opening and then further addition of the dienophile. At 150°, the 1:1 adduct (**1234**) fragments to give the hydrocarbon (**1237**); this adds acetylenedicarboxylic ester to form the product (**1238**).[34] As a consequence of these transformations, the compounds (**9**), (**1234**), (**1235**), (**1237**) and (**1238**) all yield the product (**1236**) when treated with an excess of dimethyl acetylenedicarboxylate at 100–120°.[34]

The thermal conversion of the hydrocarbon (**1237**) into the bridged isomer (**1239**) is described in refs. 34 and 933; photochemical rearrangement at −100° leads to the [12]annulene (**1240**).[1129]

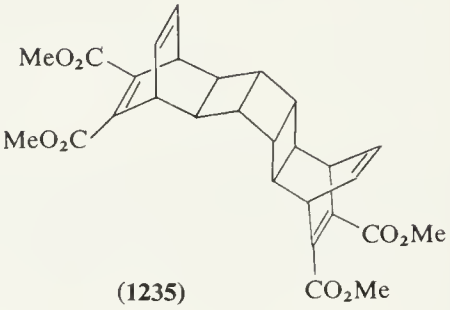


(9)



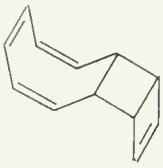


(1234)



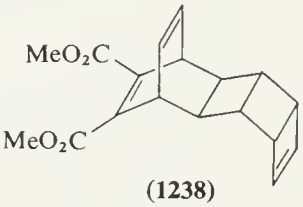
(1235)

150°

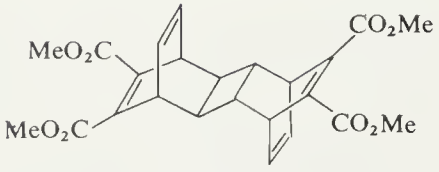


(1237)

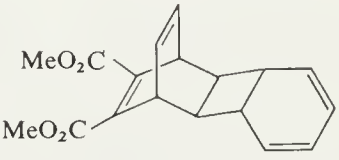
100–120°

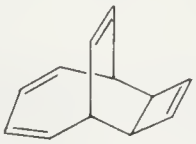


(1238)

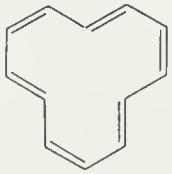


(1236)



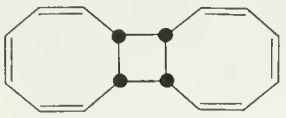


(1239)



(1240)

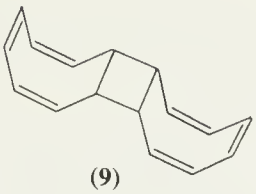
Reactions with metal derivatives. Dimer (**9**) forms a silver nitrate complex (**1241**).[156]



(**9**)

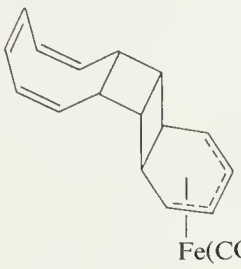
$\xrightarrow{AgNO_3}$ $(C_{16}H_{16}).2AgNO_3$

(**1241**)



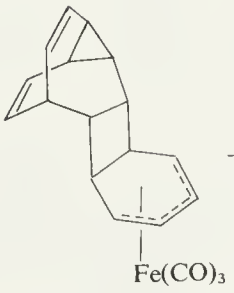
(**9**)

$Fe(CO)_5$, Δ, $h\nu$



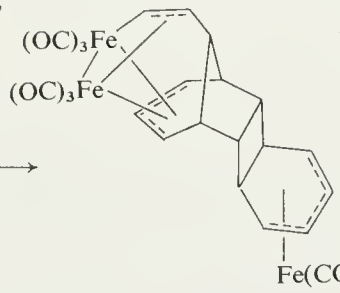
(**180**)

+



(**179**)

$Fe(CO)_5$, C_6H_6, Δ, $h\nu$

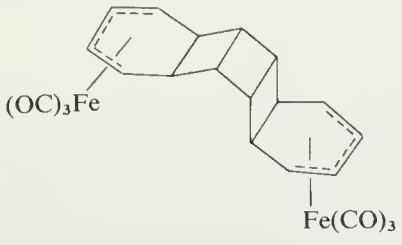


(**1242**)

$Fe(CO)_5$, C_6H_6, Δ, $h\nu$

$Fe(CO)_5$, Toluene, 185°

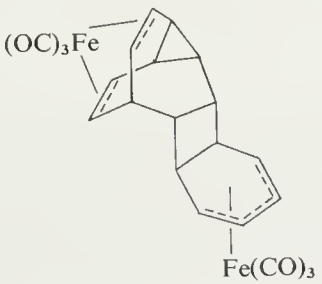
Toluene, 185°



(**1243**)

(Stereochemistry assumed)

+



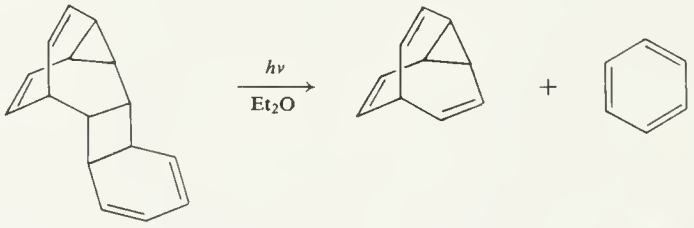
(**1244**)

Iron carbonyl complexes of dimer (**9**) can be produced from COT and $(COT)Fe(CO)_3$ (see p. 64). Dimer (**9**) reacts with $Fe(CO)_5$ when heated and irradiated with u.v. light, giving the complexes (**180**) and (**179**)[470] (see p. 63); both (**180**) and (**179**) react further with $Fe(CO)_5$ to form the product (**1242**),[470,1130] which on thermolysis gives (**1243**) and (**1244**).[470]

(*b*) *Dimer* (**10**)

Thermolysis. Thermal treatment of dimer (**10**) produces dimer (**11**), which rearranges to dimer (**12**) (see pp. 11–13); in addition, dimer (**10**) undergoes Diels–Alder dimerisation to afford the tetramer (**23**) (see p. 17).

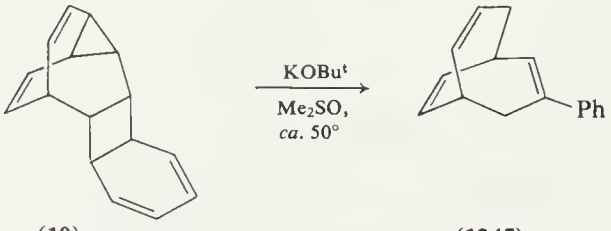
Photolysis. The photolysis of dimer (**10**) provides an efficient synthesis of bullvalene (**892**) (75%).[1131]



(**10**) (**892**)

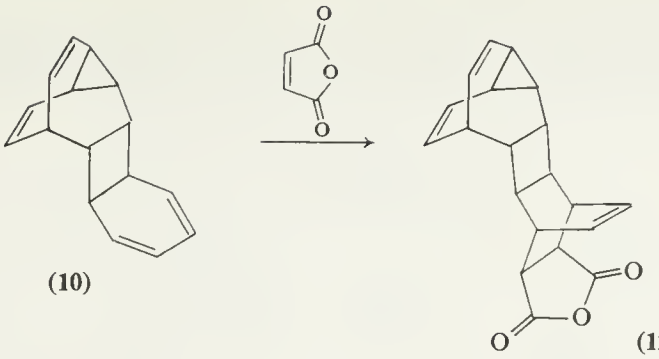
Reduction. Catalytic hydrogenation of dimer (**10**) affords octahydro- and decahydro-derivatives of uncertain structure.[156,159]

Reaction with base. With potassium t-butoxide, dimer (**10**) isomerises to give the product (**1245**) (70–80%) (which is convertible into phenylbullvalene).[1132]



(**10**) (**1245**)

Cycloadditions. Dimer (**10**) is highly reactive as the diene component in Diels–Alder additions, e.g. it reacts with maleic anhydride to form the adduct (**1246**) (stereochemistry presumed). Similar adducts are obtained from other olefinic dienophiles (table 139). For conversion of the vinylene carbonate-adduct (**1247**) into the C_{18}-hydrocarbon (**1248**), and further reactions, see refs. 1134, 1135.

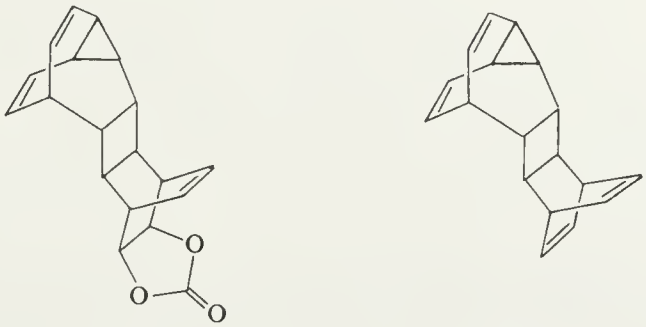


(10) (1246)

Table 139

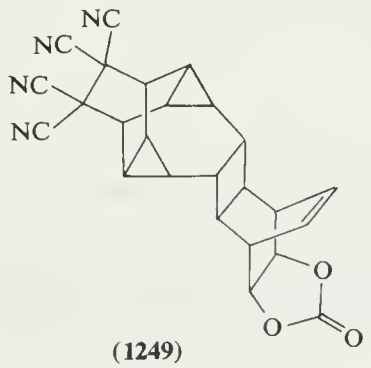
Dienophile	Reaction conditions	Yield (%)	Ref.
Maleic anhydride	Et_2O, 20°	85	159
Diethyl fumarate	Et_2O, 20°	73	159
Citraconic anhydride	*o*-Dichlorobenzene	25	1128
Tetracyanoethylene	C_6H_6, r.-t.	66	164
Cyclopent-2-enone	COT, reflux[a]	5	164
p-Benzoquinone	—	—	156
Vinylene carbonate	COT, 180°[a]	—	1133

[a] The dienophile reacted with the dimer (**10**) formed *in situ*.



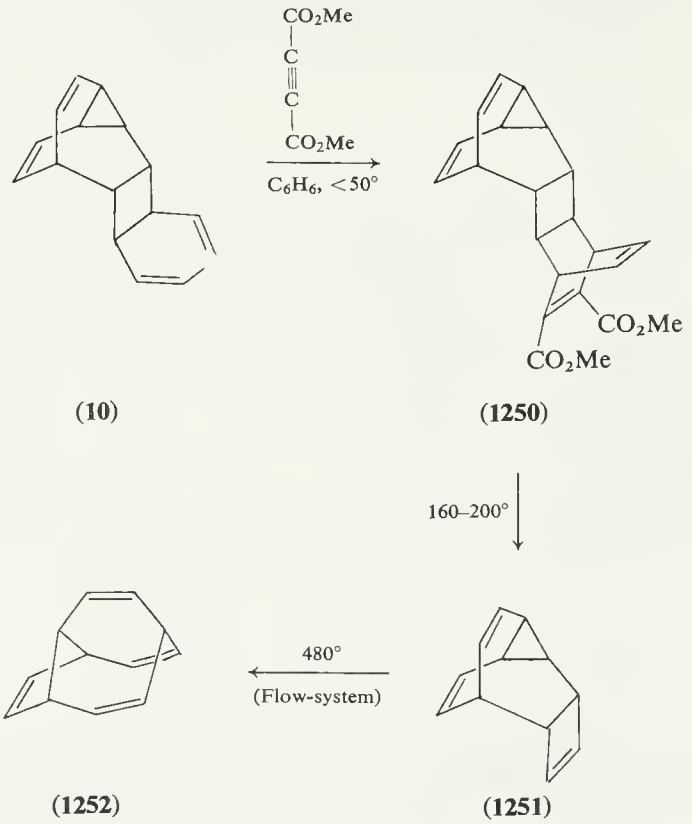
(1247) (1248)

The homotropilidene system of these Diels–Alder adducts is capable of undergoing a formal [2 + 2 + 2] cycloaddition with tetracyanoethylene; thus in refluxing toluene the vinylene carbonate-adduct (**1247**) reacts to give the product (**1249**) (53%).[164]



(1249)

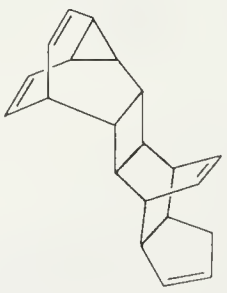
With dimethyl acetylenedicarboxylate, dimer (**10**) affords the adduct (**1250**) (89%), which at 160–200° yields the hydrocarbon (**1251**) (67%);[159] at 480° this product rearranges to the isomer (**1252**) (31%).[1136]



(**10**) (**1250**)

(**1252**) (**1251**)

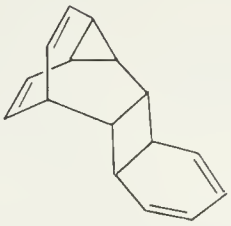
An adduct of dimer (**10**) is formed in low yield (15%) from COT and cyclopentadiene at 190°.[998] An independent synthesis of the product indicates structure (**1253**), probably formed by Cope rearrangement following an initial Diels–Alder reaction in which dimer (**10**) adopts a dienophilic role.[164]



(**1253**)

The Diels–Alder dimerisation of dimer (**10**) has already been mentioned (see p. 14).

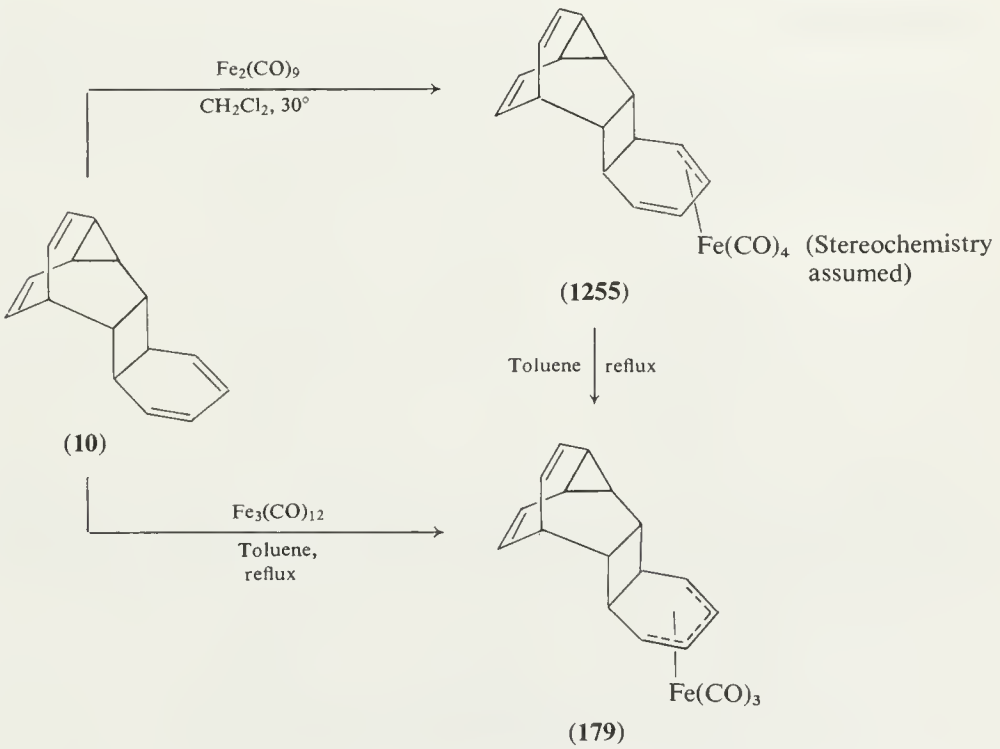
Reactions with metal derivatives. Dimer (**10**) reacts with silver nitrate to form a complex (**1254**).[156]



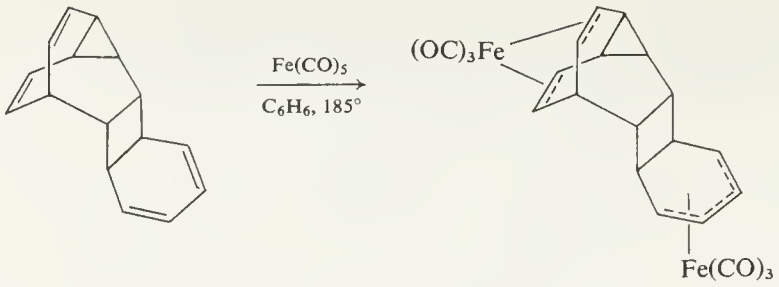
$\xrightarrow{AgNO_3}$ $(C_{16}H_{16}).2AgNO_3$

(**10**) (**1254**)

Iron carbonyl complexes of dimer (**10**) are produced from (COT)$Fe(CO)_3$ and COT (see p. 64), and these may also be prepared directly from dimer (**10**). Thus under mild reaction conditions $Fe_2(CO)_9$ affords the product (**1255**) (15%), which readily loses carbon monoxide with the formation of the tricarbonyl complex (**179**); this is also produced from dimer (**10**) and $Fe_3(CO)_{12}$ in refluxing toluene.[470] Reaction of dimer (**10**) with $Fe(CO)_5$ under vigorous

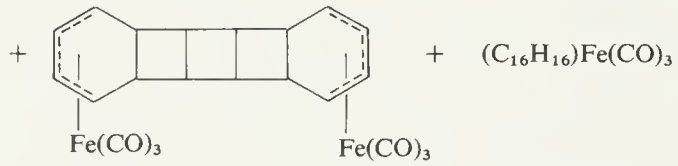


conditions produces the binuclear complex (**1244**) (3%), together with an apparent derivative (**1243**) of dimer (**9**) (4%), and a small amount of a complex (**1256**) (structure unknown).[470] Complexes (**1244**) and (**1243**) may also be obtained from (**1242**), which may be prepared from (**179**) and $Fe(CO)_5$[470] (see p. 367).



(10) **(1244)**

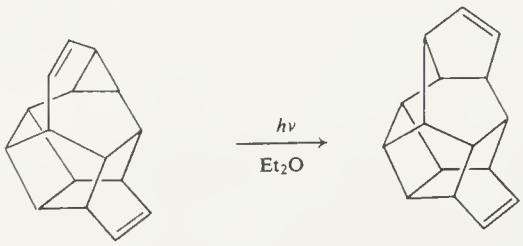
(Stereochemistry assumed)



(1243) **(1256)**

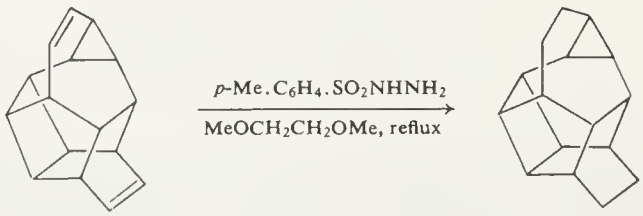
(*c*) *Dimer* (**11**)

Thermolysis and photolysis. Dimer (**11**) undergoes a thermal vinylcyclopropane → cyclopentene rearrangement to give dimer (**12**) (see p. 13); the same rearrangement may be effected photochemically (65–70%).[172]



(11) **(12)**

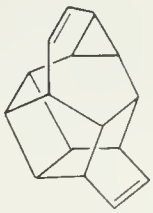
Reduction. Reduction of dimer (**11**), using di-imide (generated from *p*-toluenesulphonylhydrazine), affords the tetrahydro-derivative (**1257**) (93%).[164]



(11) **(1257)**

Catalytic hydrogenation of dimer (**11**) gives tetrahydro- and hexahydro-derivatives of uncertain structure.[11,155]

Reactions with metal derivatives. Dimer (**11**) forms 1:1 (**1258**) and 1:2 (**1259**) complexes with silver nitrate.[155]



(**11**)

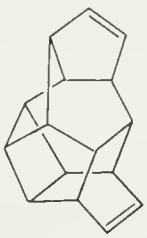
$\xrightarrow[\text{EtOH, } HOCH_2CH_2OH]{AgNO_3}$ $(C_{16}H_{16}).AgNO_3$ (**1258**)

$\xrightarrow{AgNO_3(aq.)}$ $(C_{16}H_{16}).2AgNO_3$ (**1259**)

(*d*) *Dimer* (**12**)

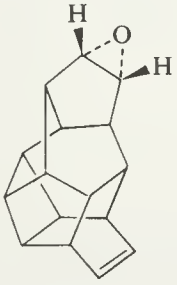
The two double bonds of structure (**12**) show a marked difference in reactivity, the cyclopentene double bond resembling that in a norbornene system.

Oxidation. Stereoselective epoxidation of the cyclopentene double bond may be effected to give the epoxide (**1260**) (84%).[164]



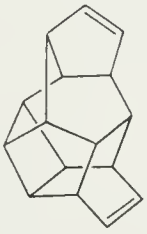
(**12**)

$\xrightarrow[CH_2Cl_2, \text{ r.-t.}]{m\text{-}Cl.C_6H_4.CO_3H}$



(**1260**)

Reduction. Catalytic hydrogenation of dimer (**12**) affords a tetrahydro-derivative,[155] presumably of structure (**1261**).

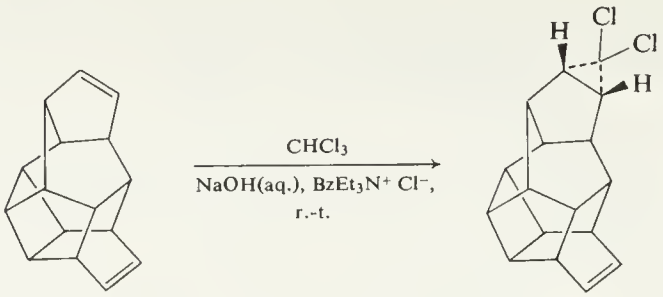


(**12**)

$\xrightarrow[\substack{EtOH,\\ 50°}]{H_2, PtO_2}$

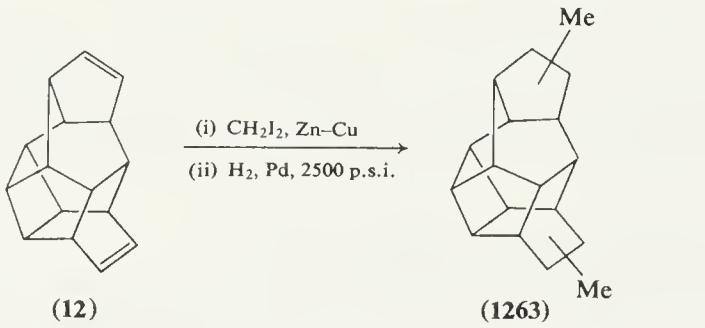
(**1261**)

Cycloadditions. Reaction of the dimer (**12**) with dichlorocarbene results in the product (**1262**) (52%).[164] Cyclopropanation of both double bonds of the

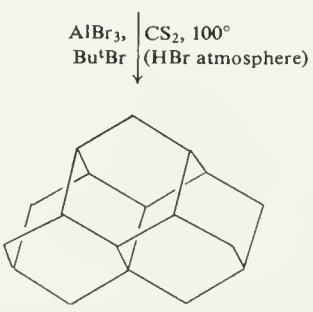


(12) (1262)

dimer (**12**), followed by hydrogenolysis of the cyclopropane rings, affords a dimethyl-compound (**1263**), which on treatment with aluminium bromide–t-butyl bromide rearranges to triamantane (**1264**) (2–5%).[1137]

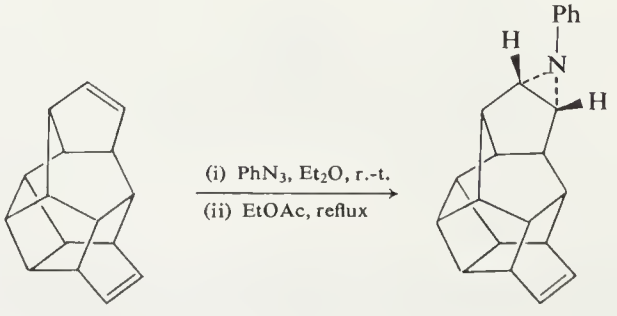


(12) (1263)



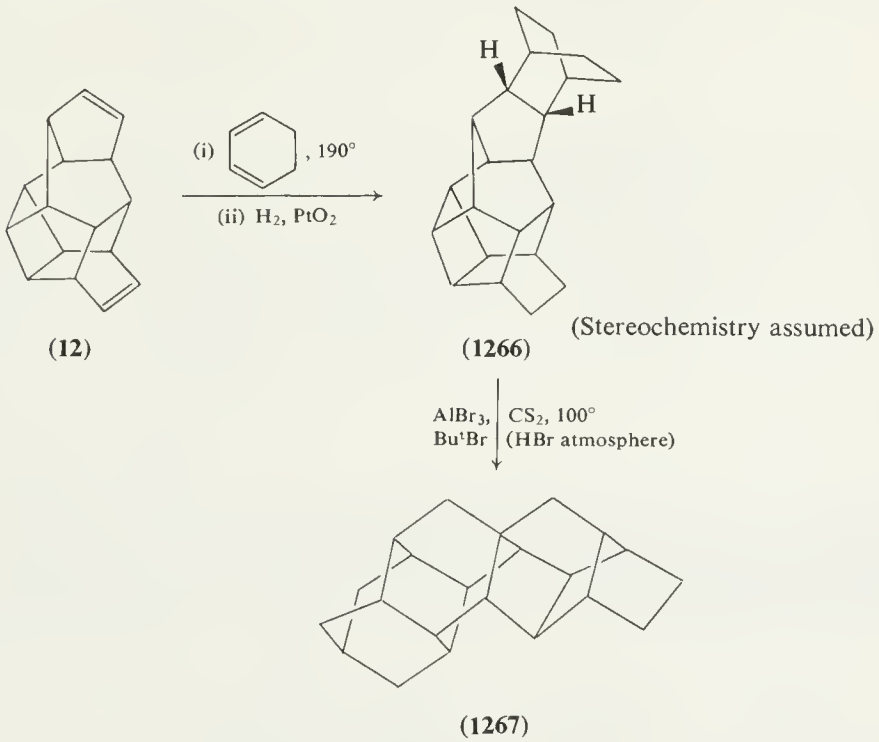
(1264)

1,3-Dipolar addition of phenyl azide to dimer (**12**), followed by thermal extrusion of nitrogen, leads to the *N*-phenylaziridine (**1265**) (69%).[164]



(12) (1265)

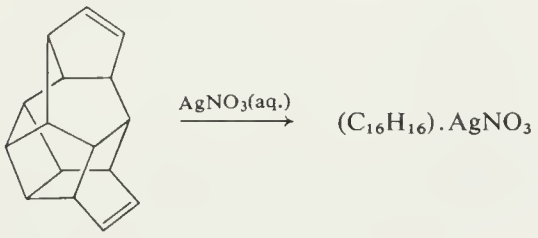
[4 + 2] Cycloaddition of cyclohexa-1,3-diene to dimer (**12**) affords a 1:1 adduct, the catalytic hydrogenation of which results in the tetrahydro-derivative (**1266**); rearrangement in the presence of aluminium bromide–t-butyl bromide then gives, not the hoped-for tetramantane system, but the isomer (**1267**) ('bastardane') (5–8 %).[1138]



(**12**) (**1266**) (Stereochemistry assumed)

(**1267**)

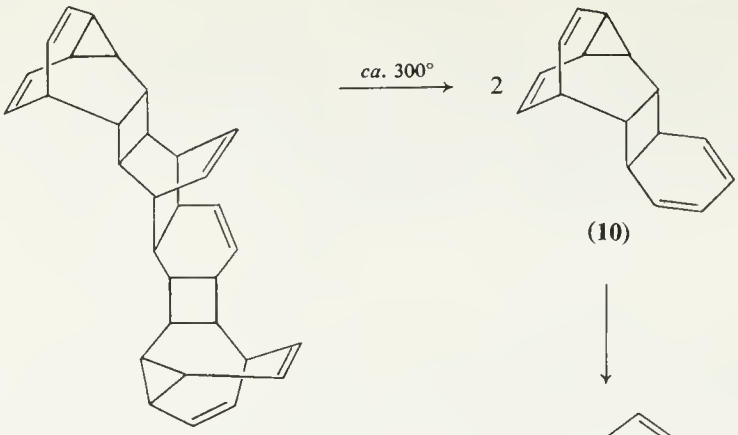
Reaction with metal derivatives. Dimer (**12**) forms a complex (**1268**) with silver nitrate[155] (for the X-ray crystal structure of (**1268**), see refs. 161, 162).



(**12**) (**1268**)

(*e*) *Tetramer* (**23**)

Thermolysis. The tetramer (**23**) fragments at *ca.* 300° to give dimer (**12**) in good yield (78 %), presumably *via* a *retro*-Diels–Alder reaction and subsequent reorganisation (see p. 13) of dimer (**10**).[164]

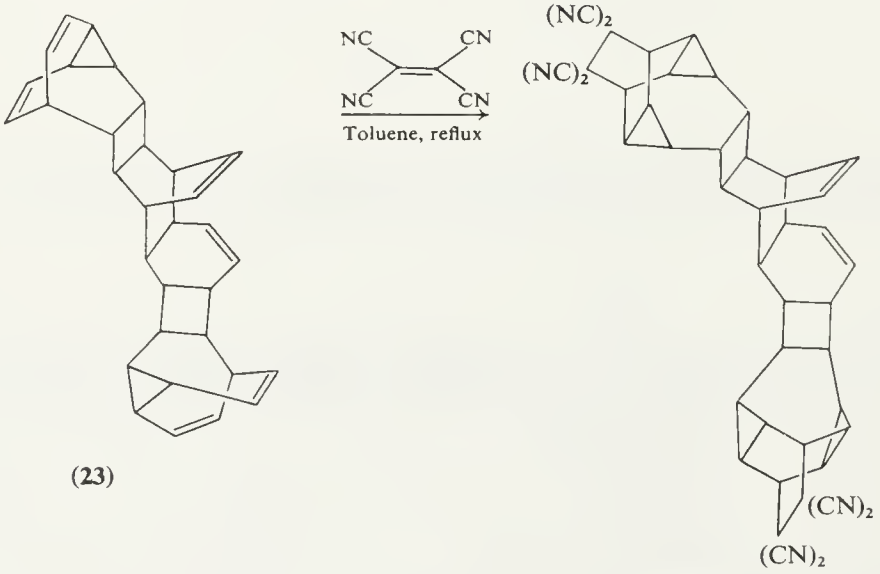


(23)

(10)

(12)

Cycloadditions. With tetracyanoethylene, both of the homotropilidene systems of the tetramer (**23**) undergo formal [2 + 2 + 2] cycloaddition, resulting in the 2:1 adduct (**1269**) (54%).[164]



(23)

(1269)

Appendix

In order to make the work as complete and up-to-date as possible, the following additional material was collected after the completion of the main typescript; *Chemical Abstracts* was consulted to the end of vol. **86** and the literature has been covered, with a few inevitable omissions, up to the end of 1976 (only the *keyword* indexes for *Chem. Abs.* **85** and **86** were available).

The pages to which the new material relates are given in the margin.

page

1. Cyclo-octatetraene

2 The acetylene tetramerisation catalysis is now thought to involve a di-metal centre.[1116]

6 For electrochemical potentials (oxidation and reduction) of COT, using various electrodes and solvents, see ref. 1139.

11 Additions to table 5:

	Ref.
Molecular geometry	1140
Bond hybridisation	1141
Resonance	1142
Heat of formation	1140, 1143
Ionisation potential	1140, 1144
Magnetic properties	1145

13 The temperature-dependent 100 MHz p.m.r. spectrum of dimer (**10**) is shown in ref. 172.

22 For a theoretical calculation on the homotropylium ion (**35**), see ref. 1146.

28 For the effect of potassium iodide on the rate of electron-transfer between COT^{2-} (**60**) and $COT^{\dot{-}}$ (**61**) in hexamethylphosphoramide, see ref. 1147.

E.s.r. spectroscopic studies of $COT^{\dot{-}}$ produced by the action of X-rays on $2M^{+}\ COT^{2-}.2$ diglyme (M = K, Rb) are described in ref. 1148.

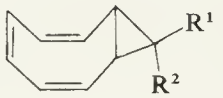
Further evidence for the planarity of $COT^{\dot{-}}$ is provided by photo-ionisation experiments on alkali metal cyclo-octatetraenides.[1149]

For additional theoretical studies on $COT^{\dot{-}}$ and COT^{2-}, see refs. 1150 and 1151 respectively.

29 A comparison of various platinum catalysts for the hydrogenation of COT is made in ref. 1152.

32 For a theoretical study of the reaction of COT with methyl and ethyl radicals, see ref. 1153.

35 The reaction of COT with CD_2N_2 (in the presence of copper(I) chloride) provides 9,9-dideuteriobicyclo[6.1.0]nonatriene (**82**; $R^1 = R^2 = D$).[950]



(82)

Products of structure (**82**; R^1 = 1-naphthyl, 2-naphthyl, 9-anthryl; R^2 = H) and (**82**; $R^1 = R^2$ = Ph) are formed by u.v. irradiation of the appropriate diazo-compounds in the presence of COT.[1154] In one case the *syn*-isomer (**82**; R^1 = H, R^2 = 2-naphthyl) may also be isolated.[1154]

37 For the ^{13}C n.m.r. spectrum of compound (**93**), see ref. 1155.

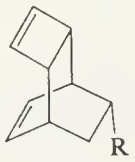
38 Doubt has been cast on the authenticity of the photo-reaction claimed to result in the thi-iran (**102**).[1156]

40 For the reaction of COT with sulphur dioxide in the presence of antimony(V) fluoride, see also ref. 1157.

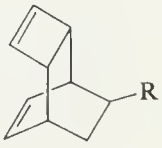
42 Additions to table 11:

Dienophile	Solvent	Temp. (°C)	Yield (%)	Ref.
Acrylonitrile	—	180	88[e]	1158
Acryloyl chloride	—	130–140	80[e]	1159
Maleic anhydride	—	170–180	95	1160
Hexafluorobut-2-yne	—	150	75	1161

[e] Mixture of *endo*- and *exo*-adducts, (**1270**) and (**1271**) respectively.



(1270)

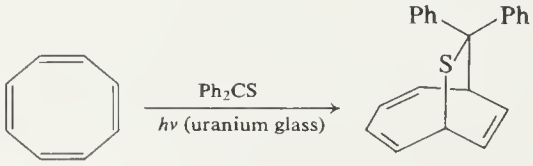


(1271)

a: R = CN *b*: R = COCl

46 For triazolinedione adducts (**126**; R = CH_2Ph, $C_6H_4.p$-OMe), see ref. 1162.

Thiobenzophenone photo-adds to COT, giving the bridged product (**1272**) (58%).[1163]



(1272)

49 For the heats of formation of sodium and potassium cyclo-octatetraenides, see refs. 1164, 1165.

E.s.r. spectroscopic studies of ion-pairing in potassium cyclo-octatetraenide (in hexamethylphosphoramide) are described in ref. 1166.

For photo-ionisation of alkali metal cyclo-octatetraenides in a solvent 'glass' at 77 K, see ref. 1149.

50 COT reacts with copper(I) acetate to give complex (**145c**) (60%).[1167]

$$\text{COT} \xrightarrow[\text{Et}_2\text{O, r.-t.}]{\text{CuOAc}} (\text{COT})(\text{CuX})_2 \quad (\mathbf{145})$$

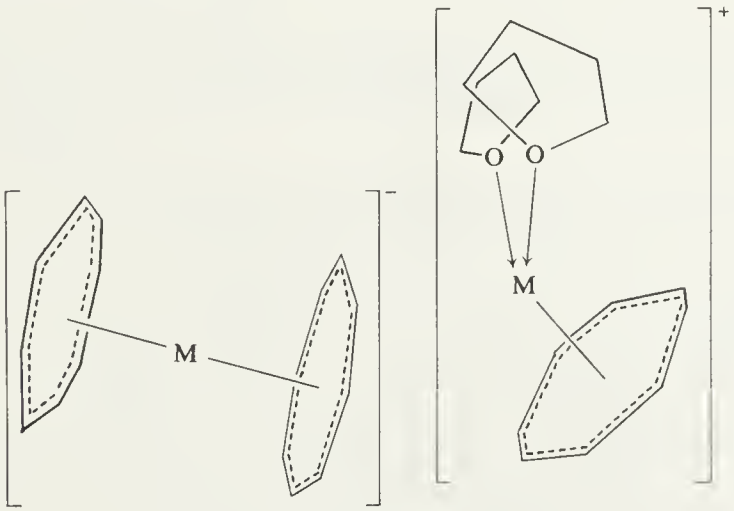
a: X = OAc

53 Lanthanide metal atoms (produced by high-temperature evaporation) react with frozen COT to form the complexes (**1273**).[1168]

$$\text{COT} \xrightarrow[-196°]{\text{M(vapour)}} (\text{COT})_3\text{M}_2 \quad (\mathbf{1273})$$

M = La, Nd, Er[1169]

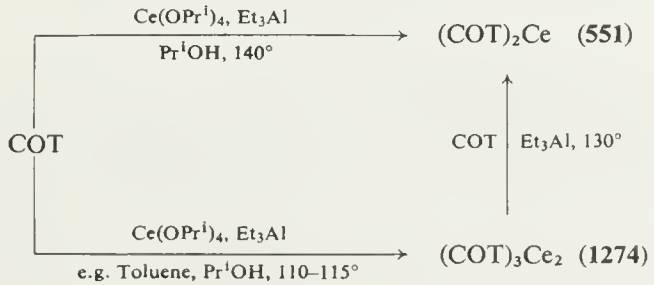
The neodymium complex (as the tetrahydrofuranate) possesses the ionic structure illustrated below.[1168]



(**1273**; M = Nd) (THF-Solvated)

Reduction of cerium(IV) isopropoxide with triethylaluminium in the presence of an excess of COT gives the complex (**551**) (p. 184) (66%); the use of a limited amount of COT leads to a different product (**1274**) (67%), which may be converted into (**551**) by treatment with COT.[1170]

The complex (**551**) is isomorphous with $(\text{COT})_2\text{M}$ (**155**; M = Th, U) (see pp. 185–6).

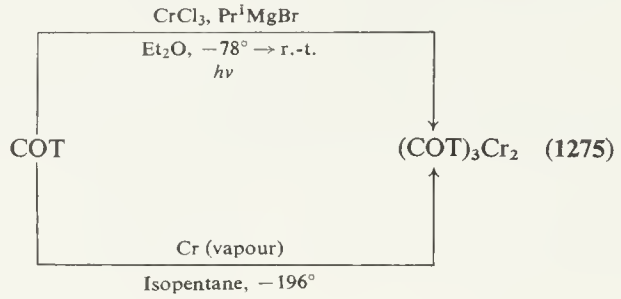


page

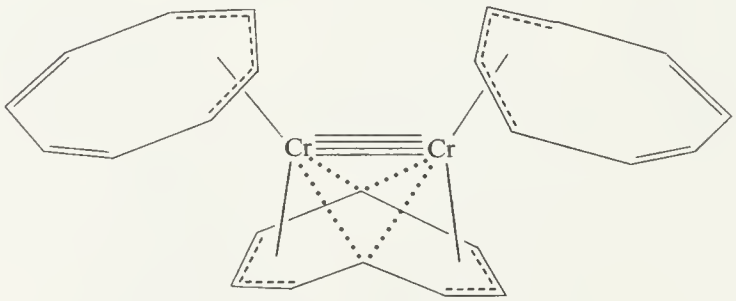
54 For the electronic absorption spectrum of $(COT)_2Ti$ (**159**), see ref. 1171.

55 For an X-ray structure determination of $(COT)ZrCl_2.THF$ (**161**), see ref. 1172.

57 Treatment of COT with chromium(III) chloride and isopropylmagnesium bromide gives the complex (**1275**) (72%);[1173] the same product results from the condensation of COT with chromium vapour at −196° (43%)[1174] (see p. 379).



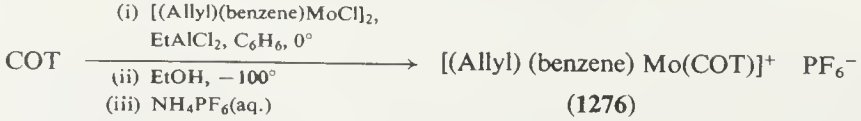
The structure of the product may be represented as follows.[1175]



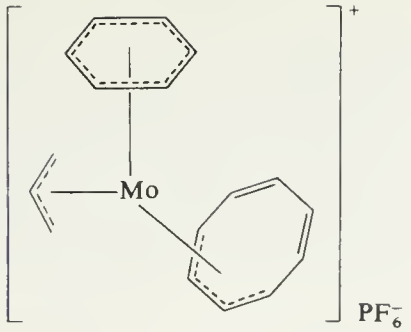
(1275)

59 For further ^{13}C n.m.r. studies of $(COT)M(CO)_3$ (**168**; M = Cr, Mo), see ref. 1176.

COT may be converted into the product (**1276**) (50%) by means of the following reaction sequence.[1177]



The suggested structure of this salt is as shown.

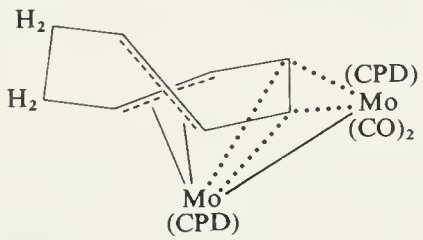


(1276)

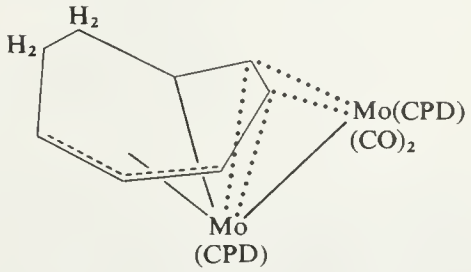
COT reacts with $[(CPD)Mo(CO)_3]_2$ to give a purple complex (**1277**).[1178]

$$\text{COT} \xrightarrow[\text{Octane, reflux}]{[(CPD)Mo(CO)_3]_2} (C_8H_8)Mo_2(CPD)_2(CO)_2 \quad \textbf{(1277)}$$

The structure of this product is as shown. It rearranges in polar solvents (seemingly by an intramolecular hydrogen-shift) to an orange isomer of structure (**1278**).[1178]



(1277)

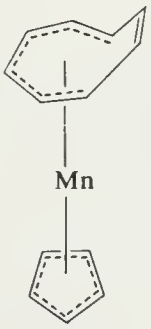


(1278)

60 A light-induced reaction of $(CPD)Mn(CO)_3$ with COT leads to the thermally unstable product (**1279**).[1179]

$$\text{COT} \xrightarrow[\text{n-Heptane, } h\nu]{(CPD)Mn(CO)_3} (COT)Mn(CPD) \quad \textbf{(1279)}$$

The product may be formulated as shown.



(1279)

page

62 The operation of 1,2-shifts of the iron atom in $(COT)Fe(CO)_3$ (**177**) is revealed by ^{13}C n.m.r. spectroscopy.[1180]

The motion of the COT moiety in solid $(COT)Fe(CO)_3$ has been investigated using pulsed n.m.r. spectroscopy.[1181]

For the He(I) photo-electron spectrum of $(COT)Fe(CO)_3$, see ref. 1182.

63 For the preparation of $(COT)Fe(CO)_3$ (86%) using $Fe_2(CO)_9$, see ref. 1183.

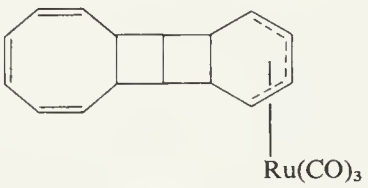
The same reagent has been employed for the preparation of $(C_8D_8)Fe(CO)_3$.[1184]

65 The proposed fluxional process in $(COT)Ru(CO)_3$ (**184**) is confirmed by ^{13}C n.m.r. studies.[1180]

66 For an X-ray structure determination of $(C_8H_9)_2Ru_3(CO)_6$ (**189**), see ref. 1185.

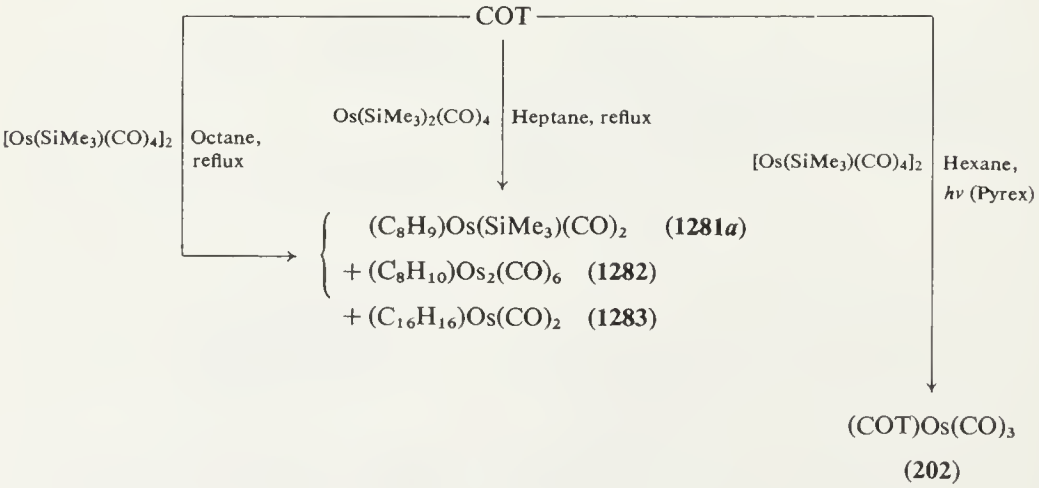
67 For pulsed n.m.r. studies of solid $(COT)_2Ru_3(CO)_4$ (**192**), see ref. 1181.

68 Details of the displacement of COD from $(COD)Ru(CO)_3$ to give $(COT)Ru(CO)_3$ (**184**) (*ca.* 100%) have been published.[1186] The use of prolonged reaction times leads to a product $(C_{16}H_{16})Ru(CO)_3$, for which structure (**1280**) is suggested [1186] (*cf.* (**180**), p. 63).



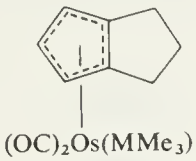
(**1280**)

70 Treatment of COT with $Os(SiMe_3)_2(CO)_4$ in refluxing heptane leads to the complexes (**1281*a***) (46%), (**1282**) (5%), and (**1283**) (probably containing dimeric COT); (**1281*a***) (62%) and (**1282**) (4%) are also obtained by a thermal reaction with $[Os(SiMe_3)(CO)_4]_2$, but a light-induced reaction gives compound (**202**) (23%).[1187]

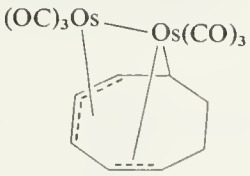


Similarly, with $Os(GeMe_3)_2(CO)_4$ in refluxing octane the main product is (**1281***b*) (54%); another product is a tricarbonyl compound of formula $(C_{16}H_{16})Os(CO)_3$.[1187]

Complexes (**1281***a*) and (**1281***b*) are apparently analogues of the ruthenium derivatives (**737**) (see p. 230), and (**1282**) of the iron and ruthenium compounds (**734**) and (**736**) (see p. 229).



(**1281**)
a: M = Si
b: M = Ge

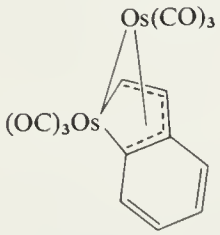


(**1282**)

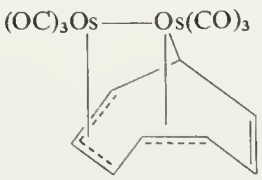
Reaction of COT with $OsMe_2(CO)_4$ gives a mixture of products, the main component being (**1284**) (21%).[1187]

$$\text{COT} \xrightarrow[\text{Octane, reflux}]{OsMe_2(CO)_4} \begin{array}{ll} (\text{COT})Os_2(CO)_6 & (\mathbf{1285}) \\ +\,(C_8H_6)Os_2(CO)_6 & (\mathbf{1284}) \\ +\,(C_8H_7Me)Os(CO)_3 & (\mathbf{1287}) \\ +\,(C_{16}H_{16})Os(CO)_3 & (\mathbf{1286}) \end{array}$$

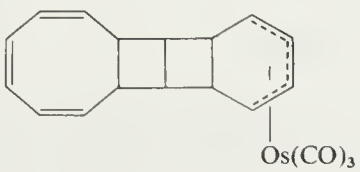
Compound (**1284**) contains an osma-indenyl system; (**1285**) is similar to the ruthenium complex (**186**) (p. 65); the complex of dimeric COT, (**1286**), is probably an analogue of (**180**) (see p. 63); the formulation of (**1287**) is tentative.



(**1284**)



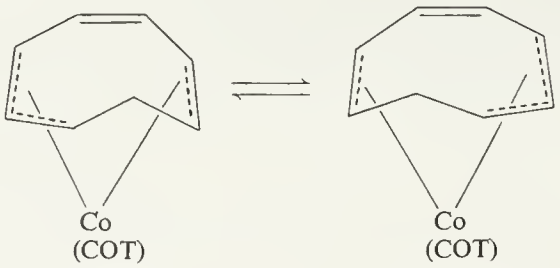
(**1285**)



(**1286**)

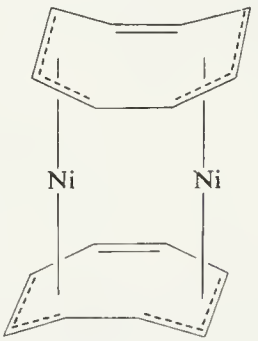
page

71 The complex (cyclo-octatrienyl)Co(COT), originally formulated as (**203**), is now assigned structure (**1288**); interconversion of the enantiomeric forms (**1288*a***) and (**1288*b***) occurs in solution.[1188]



(**1288*a***) (**1288*b***)

76 An X-ray structure determination of the complex (**218**) shows that it is dimeric, with the two nickel atoms sandwiched between COT ligands; the exact nature of the bonding is uncertain, but one possibility is shown below.[1189]



(**218**)

77 COT inhibits deuterium-exchange in the system cyclo-octene/Pd–Al_2O_3/Mg/D_2O/NaCl.[1190]

2. Substituted cyclo-octatetraenes

Monosubstituted derivatives

80 Addition to table 17:

R	Yield (%)	Ref.
CO_2Me	37	1191, 1192

Addition to table 18:

R	Yield (%)	Ref.
$PhCH_2$	13 (based on unrecovered COT)	1193

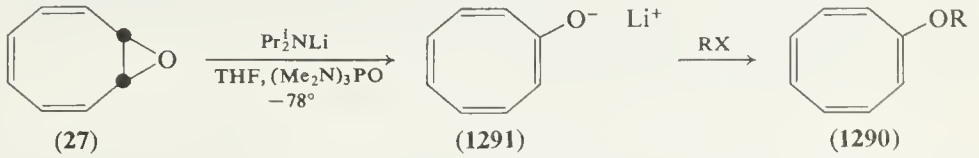
81 Addition to table 20:

Reagent	R	Yield (%)	Ref.
$Bu^tBr(CuI)$	Bu^t	13	1194

Bicyclo-octatetraenyl may be prepared (84%) from bromocyclo-octatetraene *via* the lithio-derivative[1195] (*cf.* table 20).

82 Tritylation of $(COT)Fe(CO)_3$ (**177**), followed by demetallation of the product $Ph_3C.C_8H_7.Fe(CO)_3$ (**1289**) (see p. 406), gives tritylcyclo-octatetraene.[1196]

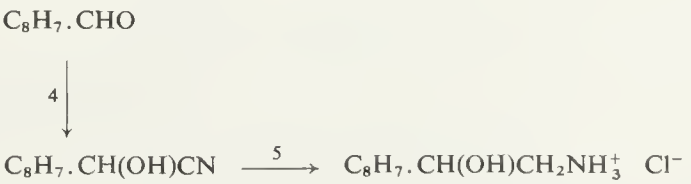
A few oxygenated COTs (**1290**) have been obtained by alkylation or acylation of the enolate anion (**1291**), generated by deprotonation of the epoxide (**27**) with lithium di-isopropylamide (see table 143, p. 420).[1197]



(**27**) (**1291**) (**1290**)

R = Et, CO_2Et, Ac

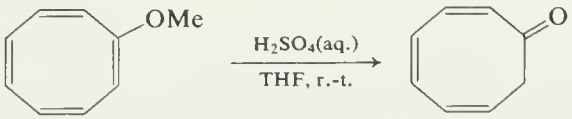
90 Additions to scheme 29:



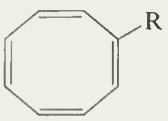
Reaction	Reagents and conditions	Yield (%)	Ref.
1	MnO_2, CCl_4, 25°	84	1191
4	NaCN, conc. HCl, Et_2O(aq.), 5°	96	1191
5	$LiAlH_4$, glyme, reflux	17	1191

Scheme 30, reaction 5: see also ref. 1191.

96 The hydrolysis of methoxycyclo-octatetraene provides a high-yield (94%) preparation of cyclo-octatrienone.[1198]



100 For the electrochemical and alkali metal reduction of the monosubstituted COTs (**227**; R = Bu^t, $SiMe_3$, $GeMe_3$, $SnMe_3$), see ref. 1194.



(**227**)

106 For e.s.r. spectral studies of ion-pairing in the potassium salts of monosubstituted COTs (**227**; R = cyclo-octatetraenyl, OBu^t) (in hexamethylphosphoramide), see ref. 1166.

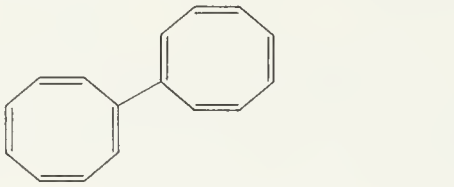
In the radical anion and the dianion derived from bicyclo-octatetraenyl, delocalisation extends over both rings.[1166]

107 Addition to table 39:

R	Reagents and conditions	Yield (%)	Ref.
OMe	$Fe_3(CO)_{12}$, octane, reflux	79	1198

A binuclear complex (**299**; R = OMe) is also formed (10%).

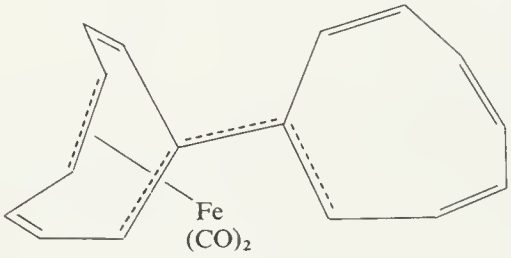
Reaction of bicyclo-octatetraenyl with iron carbonyls (*cf.* table 39) leads to the complexes (**1292**) (up to 16%) and (**1293**), together with (COT)$Fe(CO)_3$ (**177**) and (COT)$Fe_2(CO)_6$ (**178**).[1195]



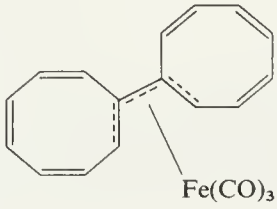
(Bicyclo-octatetraenyl)$Fe(CO)_2$ (**1292**)

+ (Bicyclo-octatetraenyl)$Fe(CO)_3$ (**1293**)

The structures of these products are as follows.



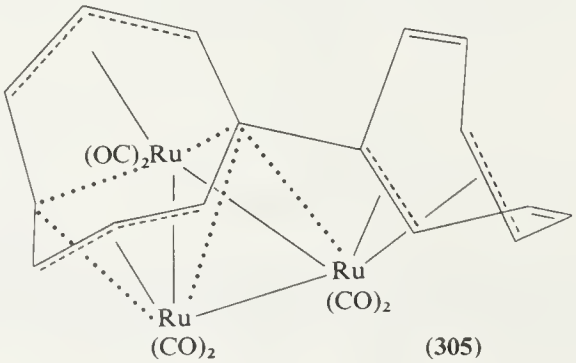
(1292)



(1293)

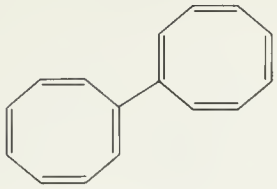
(Bonding of metal to 1,3-diene system omitted.)

108 For full details of the preparation of (bicyclo-octatetraenyl)$Ru_3(CO)_6$ (**305**) (80%), see ref. 1195; the unique structure of this product is shown below.



(305)

Bicyclo-octatetraenyl reacts with $[Ru(SiMe_3)(CO)_4]_2$ to give the complex (**1294**) (9%).[1195]



$[Ru(SiMe_3)(CO)_4]_2$ | Heptane, reflux

(Bicyclo-octatetraenyl)$Ru_2(SiMe_3)_2(CO)_4$ (**1294**)

This product appears to be an analogue of (**198***b*) (p. 69). With $Os_3(CO)_{12}$ in refluxing xylene, bicyclo-octatetraenyl gives a minute yield of the complex (**1295**)[1195] (*cf.* (**1292**), p. 386).

(Bicyclo-octatetraenyl)$Os(CO)_2$ (**1295**)

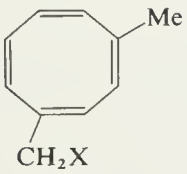
Disubstituted derivatives

110 Addition to table 42:

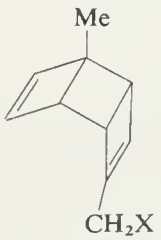
R^1	R^2	Yield (%)	Ref.
CO_2Me	CO_2Me	16–18	1199

111 Details of the conversion of monobromo- into 1,4-dibromocyclo-octatetraene (77%) are given in ref. 1187; see, however, ref. 43.

The 1,4-disubstituted COTs (**1296**) have been mentioned as products resulting from thermolysis of the tricyclic dienes (**1297**).[1200]



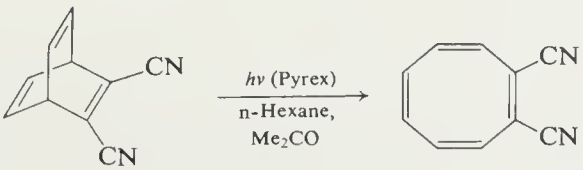
(**1296**)



(**1297**)

X = CN, CO_2Me

112 1,2-Dicyanocyclo-octatetraene is formed (quantitatively) by u.v. irradiation of the dicyanobarrelene (**1298**)[1201]



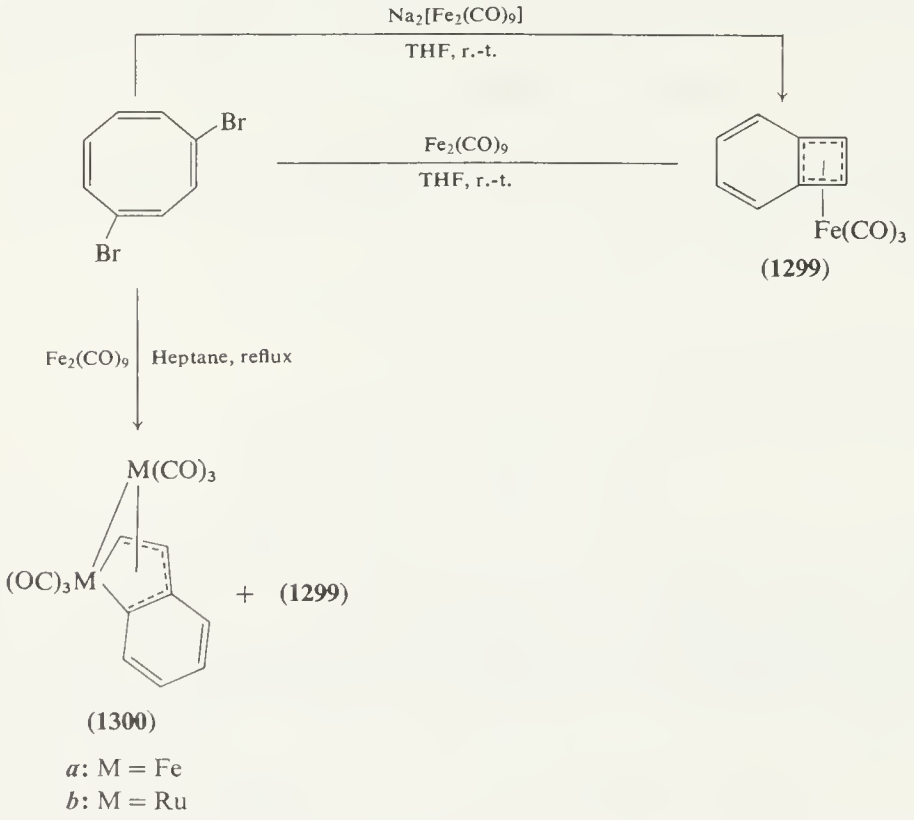
(**1298**)

page

115 For the p.m.r. spectrum of 1,2-dimethylcyclo-octatetraene, see ref. 43.

120 For the radical anions of 1,4- and 1,5-dimethylcyclo-octatetraene, generated by low-temperature electrolysis, see ref. 1202.

122 Reaction of 1,4-dibromocyclo-octatetraene with $Na_2[Fe_2(CO)_9]$ or $Fe_2(CO)_9$ at room-temperature gives the benzocyclobutadiene complex (**1299**) (64% or 22% respectively); with $Fe_2(CO)_9$ in refluxing heptane, however, the main product is the ferra-indenyl system (**1300*a***)[1187] (*cf.*(**1284**), p. 383).



(**1300**)

a: M = Fe
b: M = Ru

Similarly, $Ru_3(CO)_{12}$ in refluxing hexane yields the ruthenium analogue (**1300*b***) (18%).[1187]

Annulated and bridged derivatives

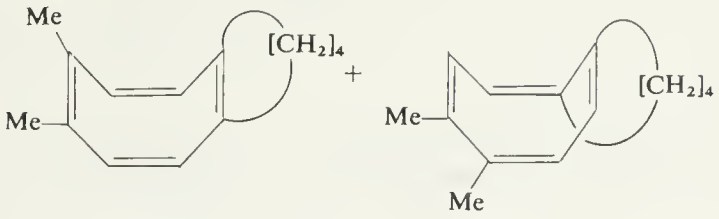
128 Thermolysis of the propellatriene (**1301**) leads to a mixture (*ca.* 1:1) of the bond-shift isomers (**1302*a***) and (**1302*b***) (74%).[1203]

130 Treatment of the diyne (**1303**) with $Ni(CO)_4$ affords the bisannulated COT (**1304**) (80%).[1204]

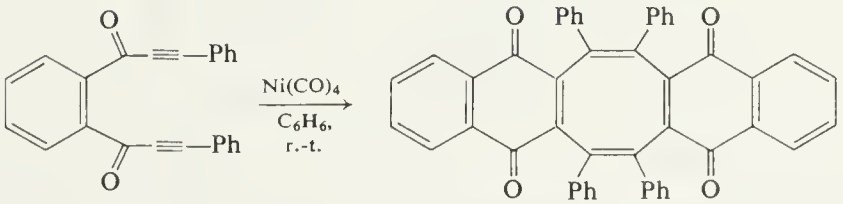
A similar product is obtained (38%) from the naphthalene analogue.[1204]

Treatment of the di-ester (**7**) with acecyclone etc. in refluxing xylene leads to 1,2-annulated 3,8-disubstituted COTs (**1305**), presumably *via* initial adducts of structure (**1306**) which undergo decarbonylation and Alder–Rickert cleavage to give (**1307**), valence tautomers of the observed products.[1205]

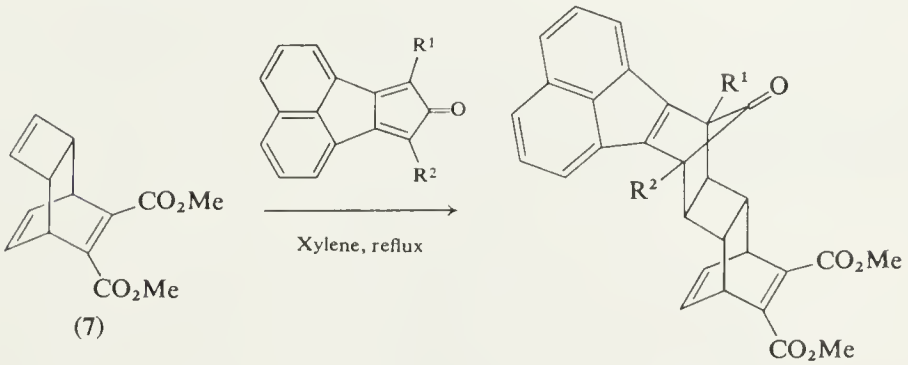
(1301)



(1302*a*) (1302*b*)



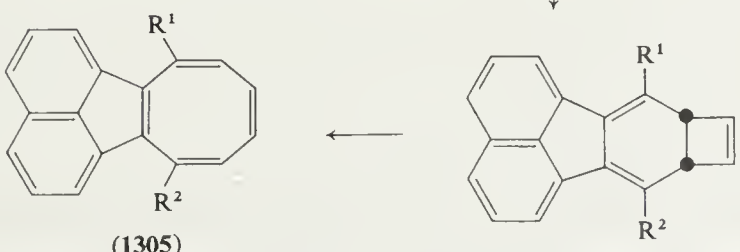
(1303) (1304)



(7)

(1306)

(Stereochemistry uncertain.)



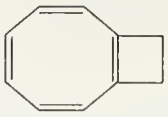
(1305) (1307)

$R^1 = R^2 =$ Me, Pr^i, Ph, CO_2Et $R^1 =$ Me, $R^2 =$ Ph

$R^1 =$ Me, $R^2 =$ Pr^i $R^1 =$ Et, $R^2 = CO_2Et$

page

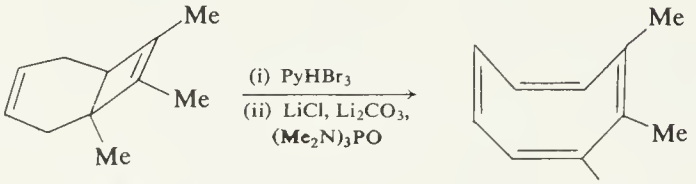
132 For e.s.r. spectral data on the radical anion of compound (**350**), see ref. 1206.



(**350**)

Trisubstituted derivatives

134 Bromination–dehydrobromination of the bicyclic diene (**1308**) leads to 1,2,3-trimethylcyclo-octatetraene (69 %)[1207] (*cf.* p. 140)

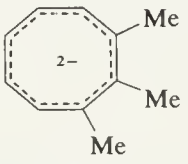


(**1308**)

(+)-1,2,3-Trimethylcyclo-octatetraene may be obtained by using (+)-(**1308**).[1207]

The ability of this substituted COT to support optical activity results from the inhibition of bond-shift and ring-inversion. Racemisation occurs at 160° in diglyme ($\Delta G^{\ddagger} = 31.7$ kcal mol^{-1}).[1207]

The dianion (**1309**) may be obtained from 1,2,3-trimethylcyclo-octatetraene by the action of potassium in ND_3.[1207]



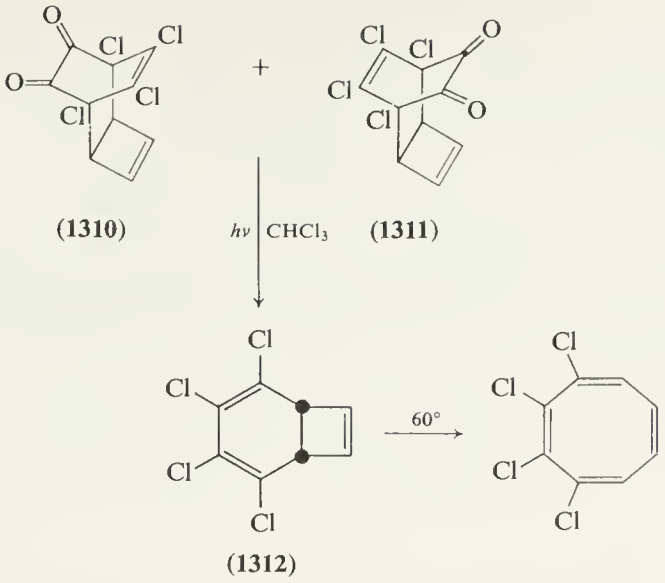
(**1309**)

Tetrasubstituted derivatives

137 Photolysis of a mixture of the *endo*- and *exo*-dicarbonyl-bridged compounds (**1310**) and (**1311**) (see p. 426) affords the bicyclo[4.2.0]octa-2,4,7-triene (**1312**), which isomerises to 1,2,3,8-tetrachlorocyclo-octatetraene at 60° (half-life 15 min.).[1208]

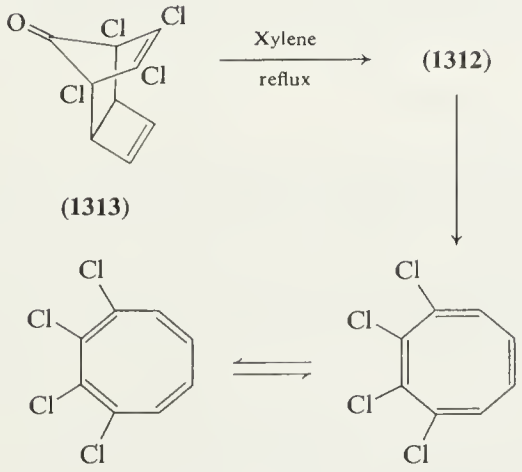
In contrast, thermolysis of the carbonyl-bridged compound (**1313**) leads to a mixture of 1,2,3,8- and 1,2,3,4-tetrachlorocyclo-octatetraene[1209] (see p. 392).

139 For details of the preparation of 1,2,4,7- and 1,3,5,7-tetraphenylcyclo-octatetraene from the quaternary ammonium salt (**403**), see ref. 1210.

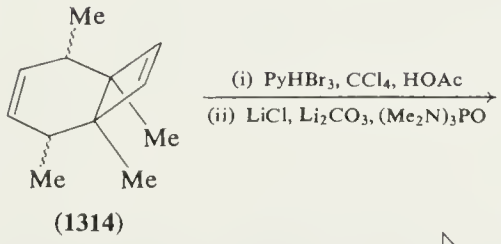


(1310) (1311)

(1312)



(1313)



(1314)

(1315*a*) (1315*b*)

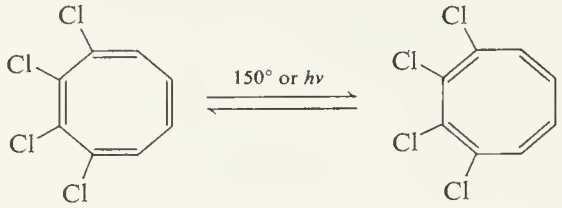
page

For full details of the preparation of 1,2,3,4- and 1,2,3,8-tetramethylcyclo-octatetraenes from compounds (**409**) and (**408**) respectively, see ref. 1203.

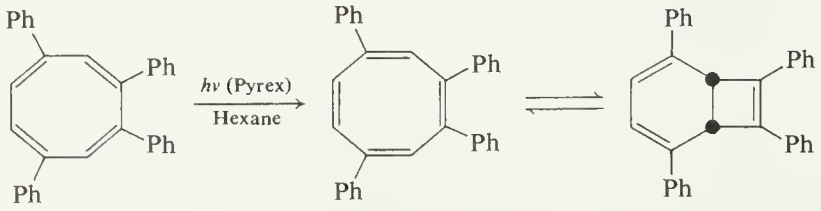
Bromination–dehydrobromination of the bicyclic diene (**1314**) leads to a mixture of the bond-shift isomers (**1315*a***) and (**1315*b***) (ratio *ca.* 1 : 10; 92 %)[1203] (*cf.* (**416*a***) $\rightleftharpoons$ (**416*b***), p. 142).

142 For full details concerning the isolable bond-shift isomers (**415*a***) and (**415*b***), see ref. 1203.

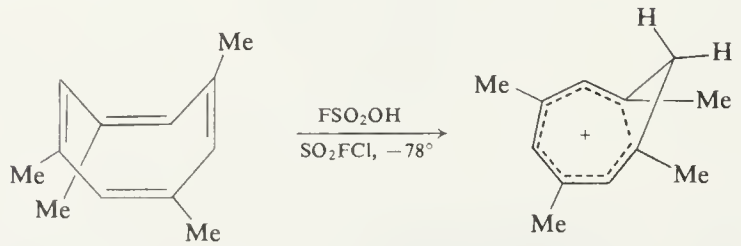
Like the tetramethyl-analogue (**415*a***), 1,2,3,8-tetrachlorocyclo-octatetraene is stable, although equilibration with its bond-shift isomer may be induced by heating or irradiation.[1208]



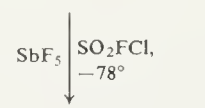
15 The photo-product of 1,3,6,8-tetraphenylcyclo-octatetraene, originally formulated as (**423**), is now known to be an equimolar mixture of 1,2,4,7-tetraphenylcyclo-octatetraene and its valence tautomer (**1316**) (yields up to 58 %).[1210]

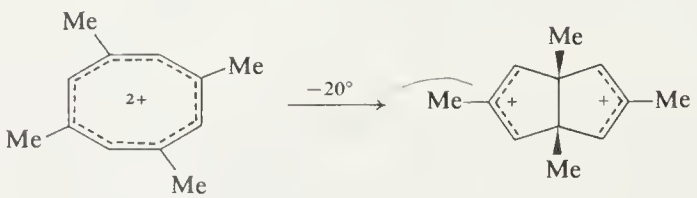


(**1316**)



(**1317**)





(**1318**) (**1319**)

For epoxidation of 1,2,3,4-tetramethylcyclo-octatetraene, see ref. 1203.

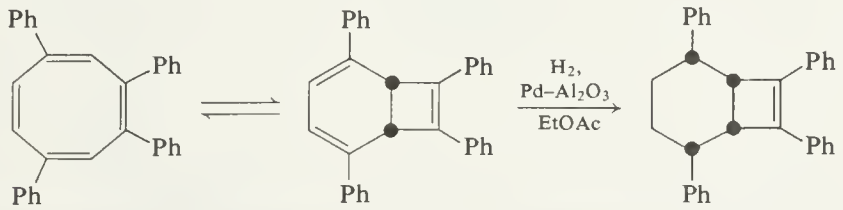
Protonation of 1,3,5,7-tetramethylcyclo-octatetraene occurs in FSO_2OH–SO_2FCl at −78° to give the homotropylium ion (**1317**). In SbF_5–SO_2FCl, however, the dication (**1318**) is produced; at −20° this rearranges to (**1319**)[1211] (*cf.* (**486**), p. 162).

(For a theoretical study of COT^{2+}, see ref. 1151.)

For e.s.r. spectral studies on the radical anion of 1,3,5,7-tetramethylcyclo-octatetraene, produced by the action of X-rays on $2K^+$ $TMCOT^{2-}$.2 diglyme, see ref. 1148.

For details of the preparation of the dianion (**424**), see ref. 1203.

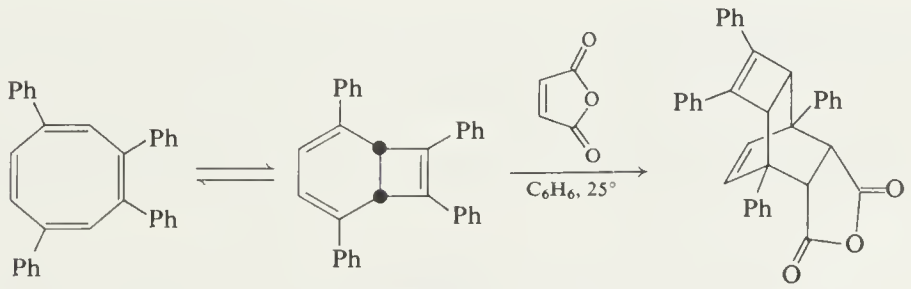
146 The catalytic hydrogenation of an equimolar mixture of 1,2,4,7-tetraphenylcyclo-octatetraene and its valence tautomer (see p. 392) yields the product (**1320**) quantitatively.[1210]



(**1316**) (**1320**)

147 For details of the *N*-phenyltriazolinedione adducts (**433**) and (**434**), and their use in the separation of 1,2,3,4- and 1,2,3,8-tetramethylcyclo-octatetraene, see ref. 1203.

The mixture of 1,2,4,7-tetraphenylcyclo-octatetraene and its valence tautomer (see p. 392) reacts with maleic anhydride to give the adduct (**1321**) (90%).[1210]

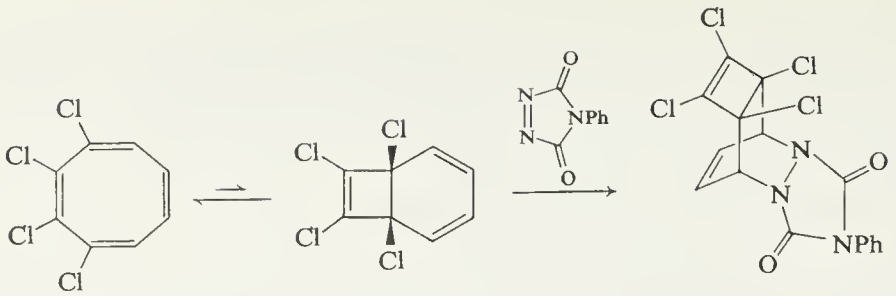


(**1316**) (**1321**)

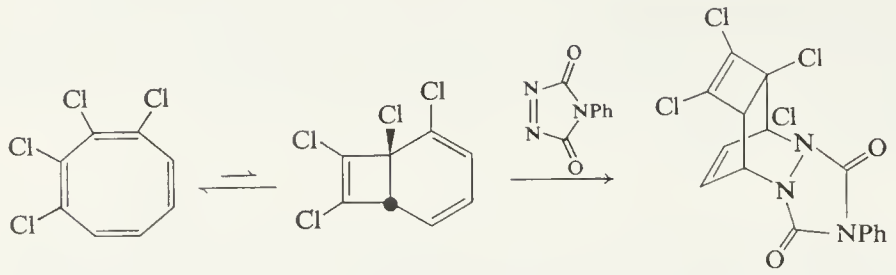
A similar adduct is obtained (78%, based on unrecovered tetraphenylcyclo-octatetraene) with dimethyl acetylenedicarboxylate.[1210]

1,2,3,8-Tetrachlorocyclo-octatetraene gives the *N*-phenyltriazolinedione adduct (**1322**).[1208]

A similar reaction with 1,2,3,4-tetrachlorocyclo-octatetraene (in admixture with its bond-shift isomer) affords the adduct (**1323**).[1208]



(1322)



(1323)

148 For full details of the preparation of the iron tricarbonyl complexes (**437**) and (**438**), see ref. 1203.

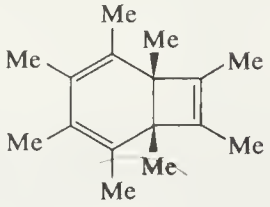
Pentasubstituted derivatives

151 For full details of the preparation of 1,2,3,4,6- and 1,2,3,5,8-pentamethyl-cyclo-octatetraene, see ref. 1203.

Octasubstituted derivatives

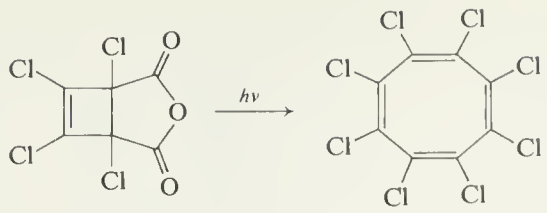
155 For further details of the preparation of octakis(trifluoromethyl)cyclo-octatetraene, see ref. 1212.

Octamethylcyclo-octatetraene results (85%) from the bicyclic triene (**1324**) at room-temperature.[1213]



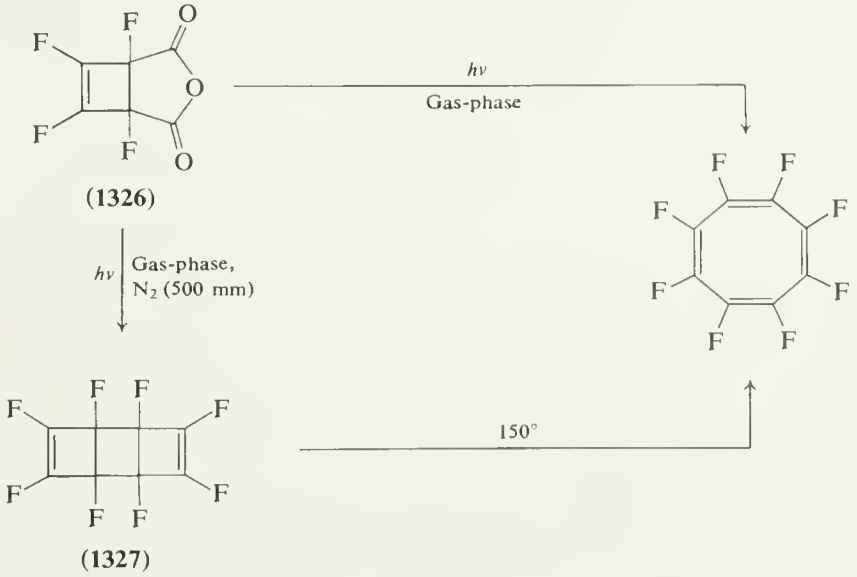
(1324)

159 U.v. irradiation of the tetrachloro-anhydride (**1325**) leads to octachloro-cyclo-octatetraene[1214] (*cf.* (**477**)).



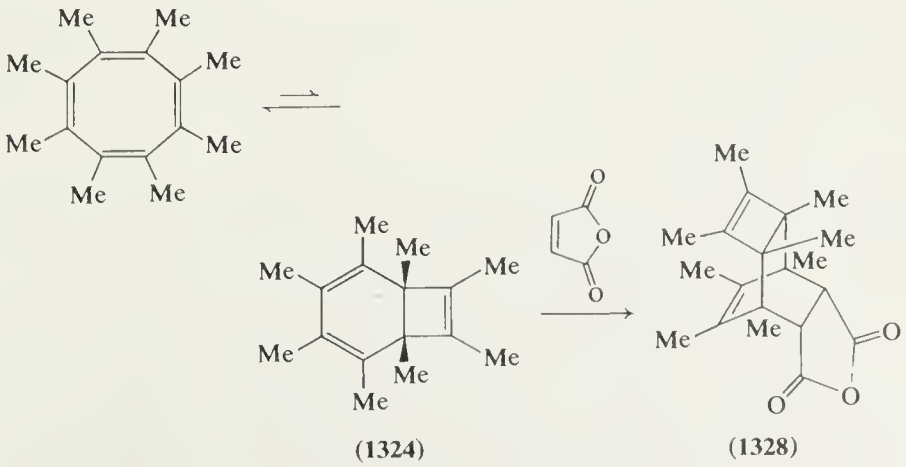
(1325)

Similarly, photolysis of the tetrafluoro-anhydride (**1326**) in the gas-phase gives octafluorocyclo-octatetraene; in the presence of nitrogen, the cyclo-butadiene dimer (**1327**) may be isolated (41 %), and subsequently subjected to thermal rearrangement.[1215]



(1326) (1327)

163 Octamethylcyclo-octatetraene reacts with maleic anhydride to give the adduct (**1328**); analogous products are formed from other dienophiles (table 140) (for reactions with the isolated valence tautomer (**1324**), see ref. 1213).

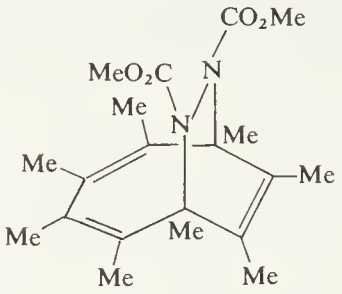


(1324) (1328)

Table 140

Dienophile	Conditions	Yield (%)	Ref.
Maleic anhydride	Toluene, reflux	96	1213
Tetracyanoethylene	Benzene, reflux	74	1213
Dimethyl acetylenedicarboxylate	Toluene, reflux	50	1213
Dicyanoacetylene	Benzene, r.-t.	68	1213
Dimethyl azodicarboxylate	Toluene, reflux	88[a]	1213
N-phenyltriazolinedione	Benzene, reflux	83	1213

[a] A by-product of structure (**1329**) is isolable.

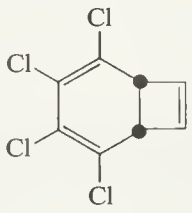


(**1329**)

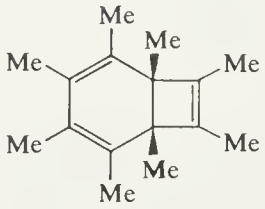
3. Further reactions of compounds derived from cyclo-octatetraenes

Bicyclo[4.2.0]octa-2,4,7-trienes

165 For the preparation of the tetrachloro-derivative (**1312**), which is stable at room-temperature, see p. 391.



(**1312**)

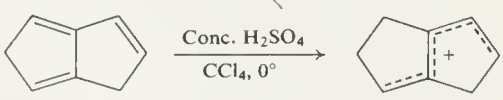


(**1324**)

For the (low-temperature) preparation of the octamethyl-derivative (**1324**), see ref. 1213.

Bicyclo[3.3.0]octa-1,4,6-triene

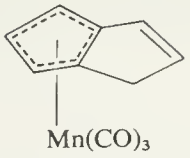
168 Protonation of the dihydropentalene (**24**) leads to the cation (**667**).[852]



(**24**) (**667**)

For reaction of compound (**24**) with maleic anhydride, see also ref. 1216.

For the manganese complex (**1330**), see ref. 1216.

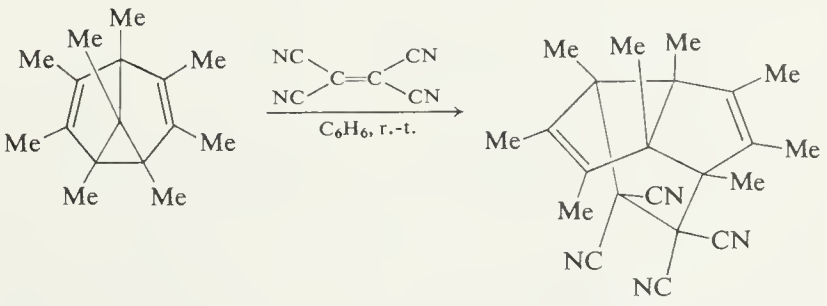


(1330)

Semibullvalenes

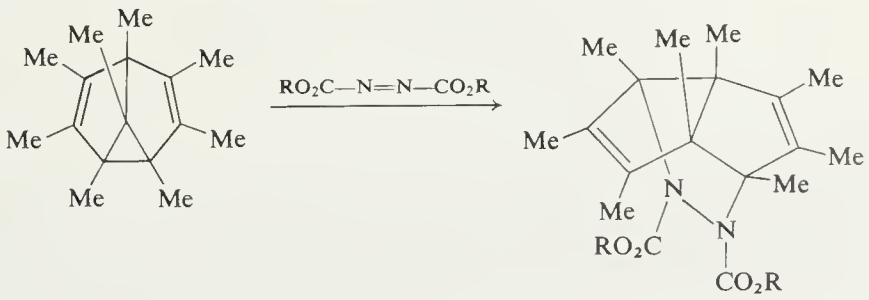
169 For the ^{13}C n.m.r. spectrum of semibullvalene, see ref. 1217.
For estimation of the fluxional barrier, see ref. 1218.

170 The reaction of octamethylsemibullvalene with tetracyanoethylene is now known to result in structure (**1331**) (88 %).[705, 1213]



(1331)

Similar products (**1332**) are formed from azodicarboxylic esters (table 141).



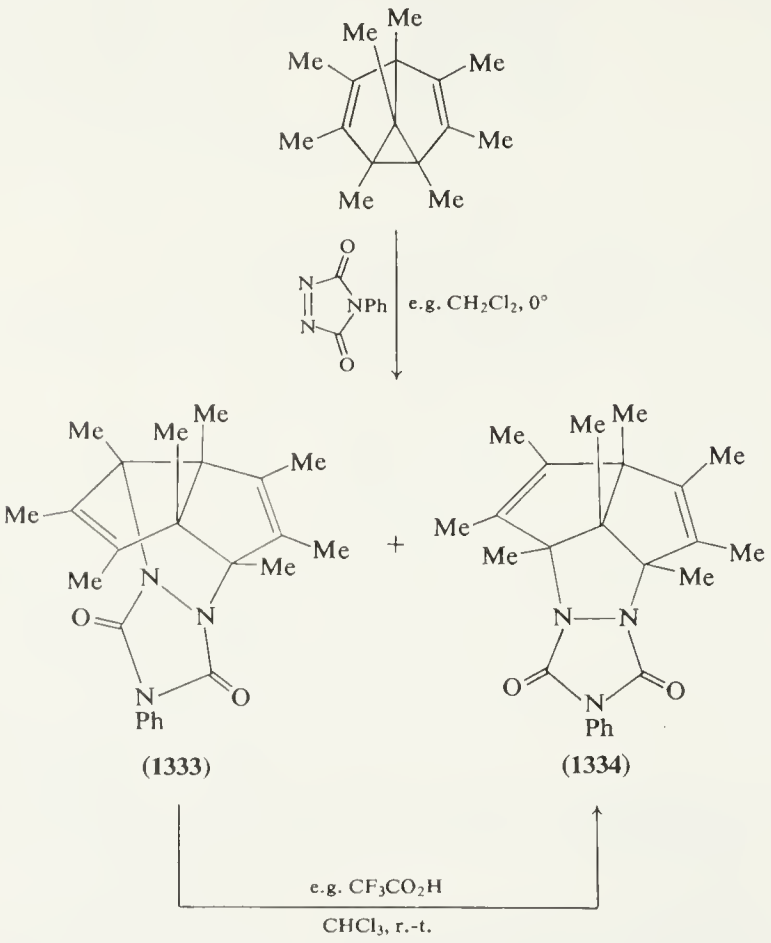
(1332)

Table 141

R	Conditions	Yield (%)	Ref.
Me	C_6H_6, 80°	81	1213
Et	80°	62	705, 1213
	Cyclohexane, *hν*(Pyrex)	—	1213
CH_2CCl_3	—	—	1219
CH_2Ph	C_6H_6, 30° → r.–t.	74	1213

page

With *N*-phenyltriazolinedione, however, a mixture of the adducts (**1333**) and (**1334**) is obtained; the former rearranges quantitatively to the latter in methanol at 60°, or when its solution in chloroform is treated with trifluoroacetic acid or silica. [1219]



Lithium, sodium and potassium derivatives

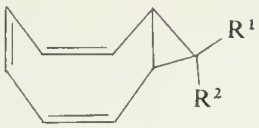
172 Anion radicals are produced by the action of COT^{2-} on *o*- or *p*-nitrophenyl thiocyanates and methyl *o*-nitrobenzenesulphenate.[1220]

For electron-transfer from COT^{2-} to azobenzene and azoxybenzene, see ref. 1221.

For the formation of benzylcyclo-octatetraene from the dianion by treatment with iodine, see ref. 1193.

174 For the reactions of $2Li^+$ COT^{2-} with benzal chlorides, leading to products of structure (**82**; $R^2 = H$) (*cf.* table 63), see the superscribed references.

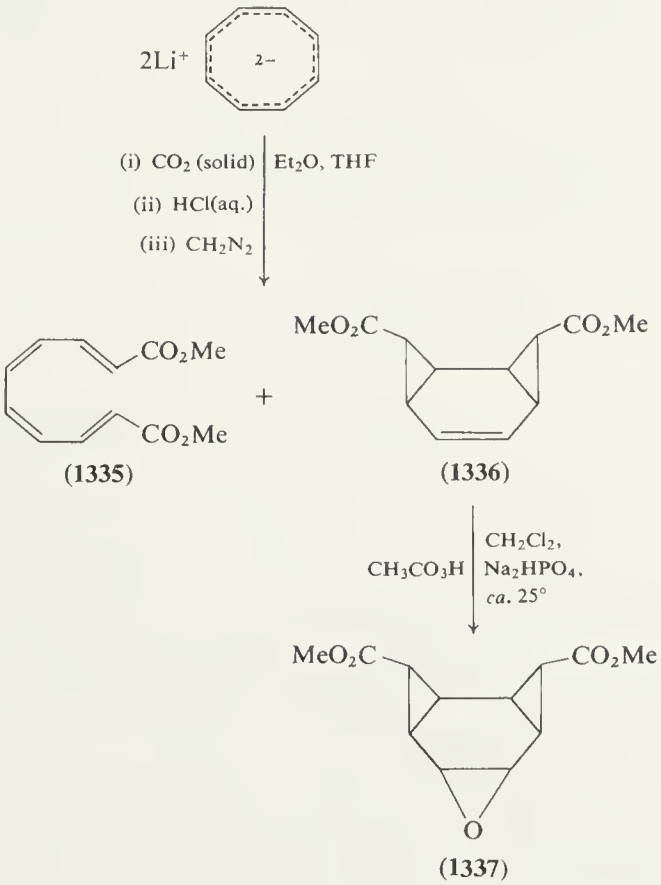
178 Re-examination of the reaction of COT^{2-} with carbon dioxide has shown that the initial products are, after esterification, (**1335**) (6%) and (**1336**) (29%); these equilibrate in solution at room-temperature (ratio *ca.* 1:4).[1222]



(82)

R^1 = Ph,[1154, 1193] *p*-Me.C_6H_4,[1154] *p*-CF_3.C_6H_4,[1154] *p*-MeO.C_6H_4,[1154] *p*-Cl.C_6H_4,[1154] *p*-Br.C_6H_4[1154]

R^2 = H



The tricyclic di-ester (**1336**) may be converted into the epoxide (**1337**) (84%).[1222]

183 Reaction of 2,5-dithiocyanatothiophene with COT^{2-} in the presence of 18-crown-6 results in a linear polymer.[1223]

The complex (**1338**) results (almost quantitatively) from $2K^+$ COT^{2-} and $ScCl_3$.3THF; the product reacts with more $2K^+$ COT^{2-} to give the ionic complex (**1339**)[1224] (*cf.* (**550**), p. 184).

$$2K^+\ COT^{2-} \xrightarrow{ScCl_3.3THF} (COT)ScCl.THF \quad (1338)$$

$$(1338) \xrightarrow{2K^+\ COT^{2-}} K^+\ [(COT)_2Sc]^- \quad (1339)$$

page

184 For MO calculations on $[(COT)_2Ce]^-$, see ref. 1225.

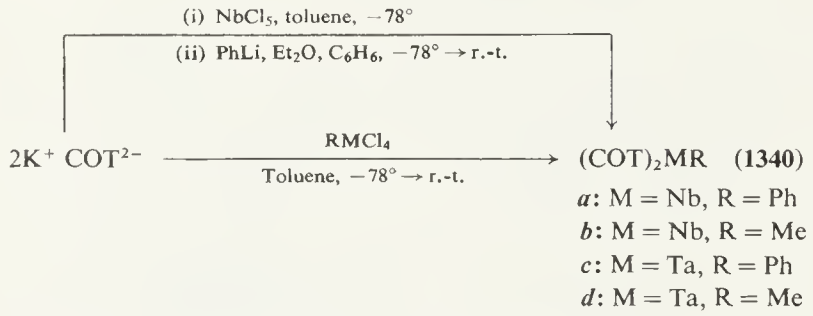
186 Magnetic susceptibility data are available on the following uranium complexes: $(COT)_2U$ (**155**; M = U),[1226] (phenylcyclo-octatetraene)$_2$U (**554**; R = Ph, M = U),[1227] $(TMCOT)_2U$ (**555*a***),[1227] and (1,3,5,7-tetraphenylcyclo-octatetraene)$_2$U (**555*c***).[1227]

The crystal structure of the uranium complex (**555*c***) is described in ref. 1228.

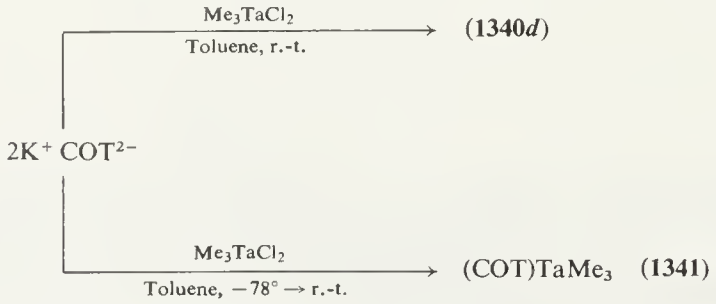
187 Full details of the preparation of $[(COT)TiCl.THF]_2$ (**560**) and $[(COT)TiCl]_4$ (**561**) are given in ref. 1229.

For magnetic susceptibility and electronic and e.p.r. spectra of $(COT)_2V$, see ref. 1171.

188 Reaction of $2K^+$ COT^{2-} with niobium(v) chloride followed by phenyllithium affords the complex (**1340*a***) (*ca.* 40%), together with the salt (**563*a***) (*ca.* 20%); analogous products (**1340*b*–*d***) are (best) obtained from $RMCl_4$ (M = Nb, Ta).[1230]



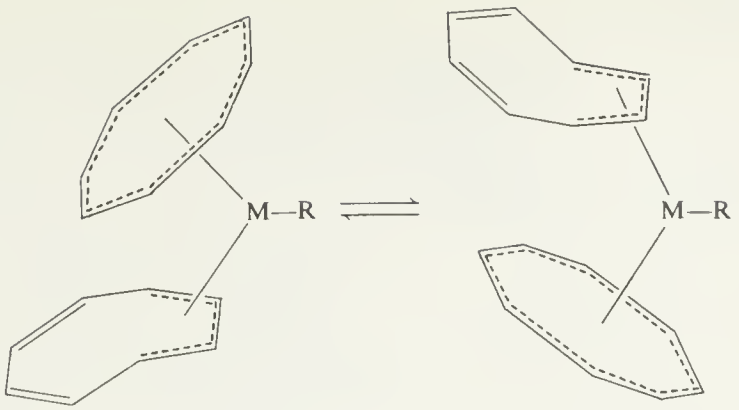
Complex (**1340*d***) is also available by reaction with Me_3TaCl_2 at room-temperature; at −78° this reagent gives rise to the trimethyl-derivative (**1341**).[1230]



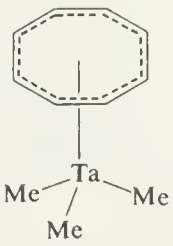
It is suggested that the general structure of $(COT)_2MR$ (**1340**) is likely to be similar to that of $(COT)_2Zr.THF$ (**160*a***) (see p. 55), and that the observed fluxional behaviour involves the illustrated process.[1230]
The trimethyl-derivative (**1341**) is formulated as shown.

For an examination of the fluxional behaviour of (COT)Ru(NBD) (**566**), using ^1H and ^{13}C n.m.r. spectroscopy, see ref. 1231.

Reaction of COT^{2-} with $[(arene)RuCl_2]_2$ or $(arene)RuCl_2.Py$ affords complexes of structure (**1342**) (30–50%).[1232]



(1340)



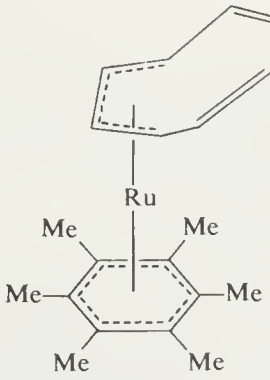
(1341)

$$2M^+\ COT^{2-} \xrightarrow[\text{or (arene)}RuCl_2.Py]{[(\text{Arene})RuCl_2]_2} (\text{Arene})Ru(COT) \quad \textbf{(1342)}$$

M = Li, Na, K

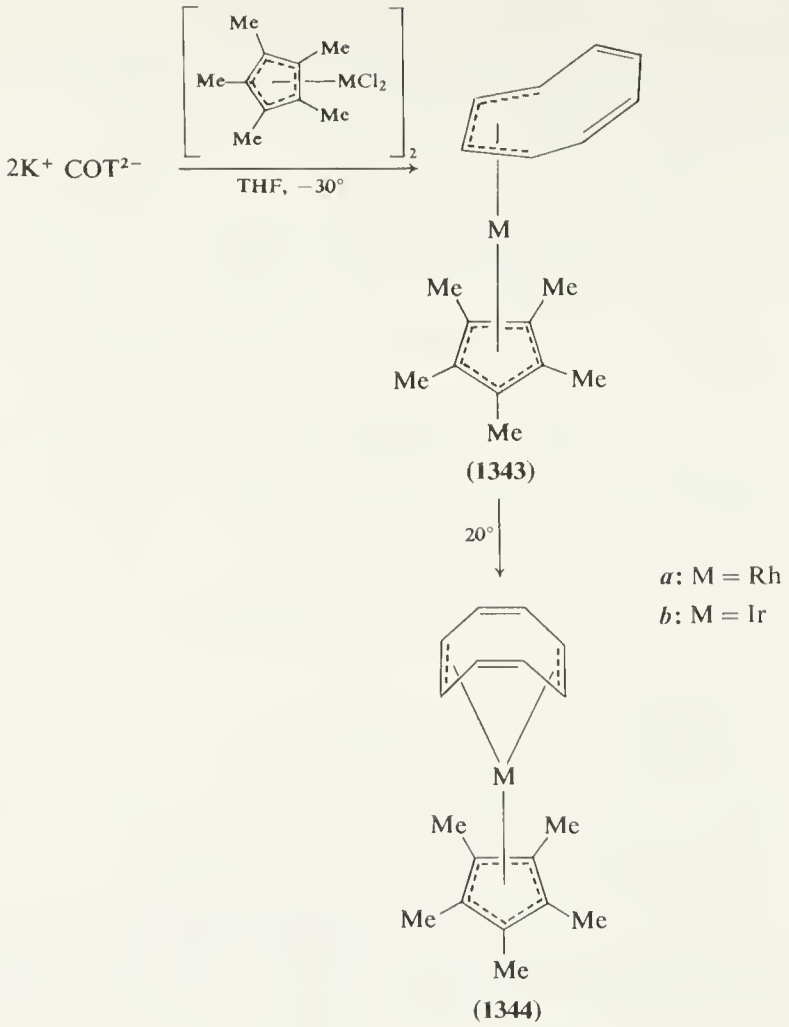
arene = benzene, mesitylene, hexamethylbenzene

The structure of the (fluxional) hexamethylbenzene complex is as shown.[1232]

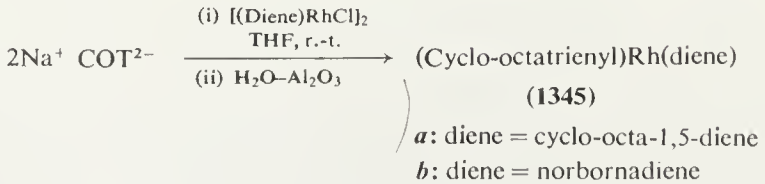


(**1342**; arene = hexamethylbenzene)

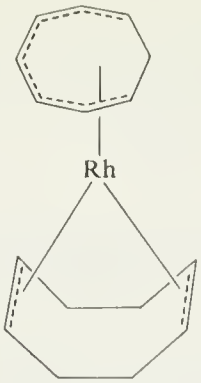
189 The rhodium and iridium complexes $[(\text{pentamethylcyclopentadienyl})MCl_2]_2$ react with COT^{2-} at low temperatures to give low yields of the fluxional products (**1343**); these isomerise at 20° in solution to afford complexes of structure (**1344**).[1233]



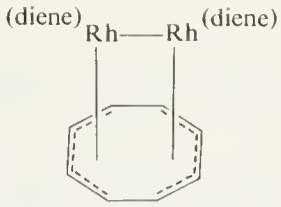
Reaction of COT^{2-} with the rhodium complexes $[(COD)RhCl]_2$ and $[(NBD)RhCl]_2$, followed by treatment with moist alumina, gives the cyclo-octatrienyl complexes (**1345**) (96% and 49% respectively).[1234]



Using a modified work-up procedure, the product $(COT)Rh_2(COD)_2$ (**1346***a*) may be obtained (12%), and in pentane solution the complex (**1345***a*) is slowly converted into $(cyclo\text{-}octatrienyl)_2Rh_2(COD)$ (**1347**) (76%); complex (**1345***b*) in pentane containing COT slowly gives (**1346***b*) (43%).[1234]

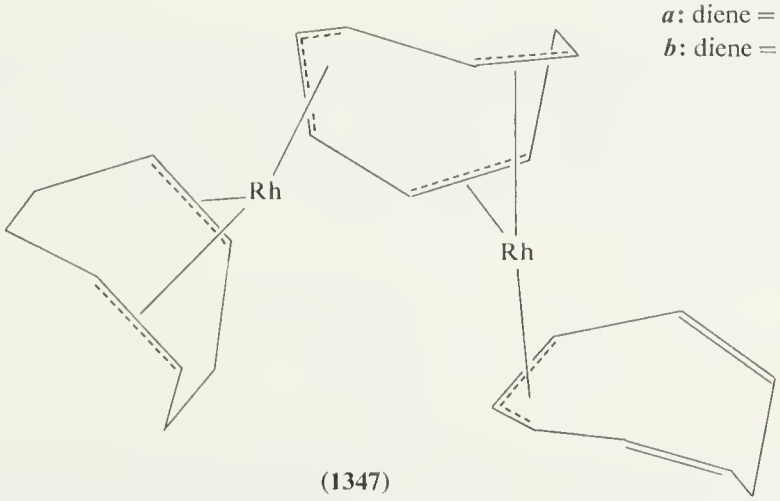


(**1345***a*)



(**1346**)

a: diene = COD
b: diene = NBD



(**1347**)

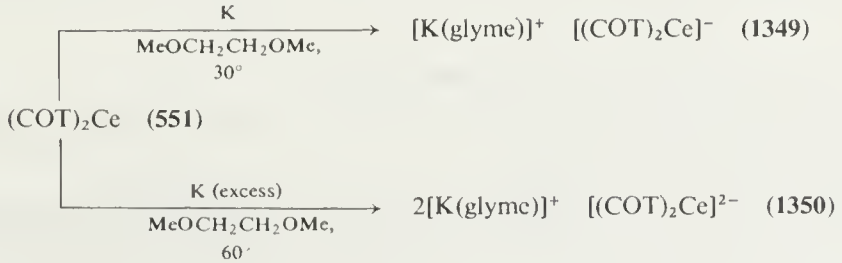
For the use of $2Li^+$ COT^{2-} as a dechlorinating agent in the preparation of e.g. $(COD)_2Pd$ from (COD) $PdCl_2$, see ref. 1235.

Scandium and lanthanide derivatives

190 The scandium complex (**1338**) (p. 399) reacts with sodium cyclopentadienide, yielding a product (**1348**) (up to 55%)[1224] (*cf.* (**552**)).

(COT)Sc(CPD) (**1348**)

The complex $(COT)_2Ce$ (**551**) reacts with potassium to form the salt (**1349**) (84%) (*cf.* (**550**), p. 184); with an excess of the alkali metal, further electron transfer results in the product (**1350**) (50%).[1170]



Actinide derivatives

191 The action of microwave-discharged argon on $(COT)_2U$ vapour provides a (relatively) low-temperature generation of uranium vapour.[1236]

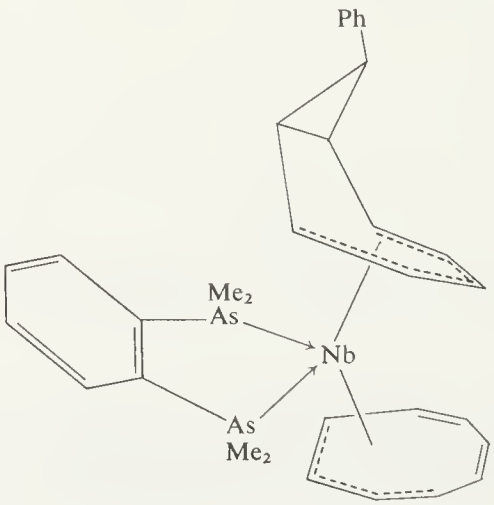
Titanium, zirconium and hafnium derivatives

193 Reaction of (COT)Ti(CPD) (**165**) with n-butyl-lithium leads to metallation, predominantly in the cyclopentadienyl ring.[1237]

For discussion of the i.r. and p.m.r. spectra of the complexes $(COT)M(allyl)_2$, $(COT)M(methylallyl)_2$ and $(COT)M(crotyl)_2$ (M = Zr, Hf), see ref. 1238.

Niobium and tantalum derivatives

194 Complexes $(COT)_2MR$ (**1340**) (M = Nb, Ta) and $(COT)TaMe_3$ (**1341**) (p. 400) form adducts with donor ligands such as $Me_2P[CH_2]_2PMe_2$ and *o*-$(Me_2As)_2.C_6H_4$; when R = Ph, reaction in refluxing toluene results in the transfer of the phenyl group from the metal to the coordinated COT, giving products such as (**1351**).[1230]



(**1351**)

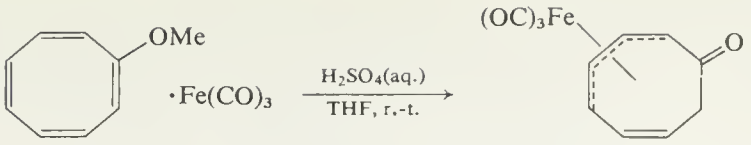
Molybdenum derivatives

194 For u.v. and i.r. spectroscopic data on $(COT)Mo(PBu_3)_2(CO)_2$, see ref. 1239.

Iron, ruthenium and osmium derivatives

196 For a review of the iron, ruthenium and osmium carbonyl complexes of COT and its derivatives, see ref. 1240.

198 Hydrolysis of the iron tricarbonyl complex of methoxycyclo-octatetraene, (**298**; R = OMe), affords the cyclo-octatrienone complex (**300**) (90%).[1198]



(**298**; R = OMe) (**300**)

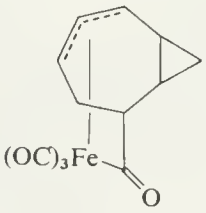
Full details of the thermal isomerisation of the iron tricarbonyl complexes of substituted COTs are given in ref. 1241.

199 For pulsed n.m.r. studies of solid $(COT)Fe_2(CO)_5$ (**612**), see ref. 1181.

200 For reactions of protonated $(COT)Fe(CO)_3$, (**614**), with nucleophiles, see ref. 1242.

201 A high-yield (90%) preparation of the salt (**621**) is described in ref. 1183.

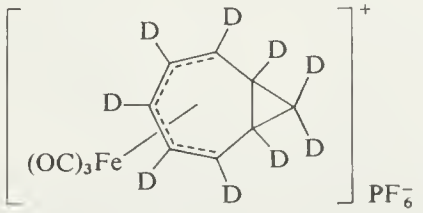
Treatment of the salt (**621**) with sodium borohydride has been shown to result in a mixture of the complexes (**622**) (72%) and (**1352**) (18%).[1183, 1243]



(**1352**)

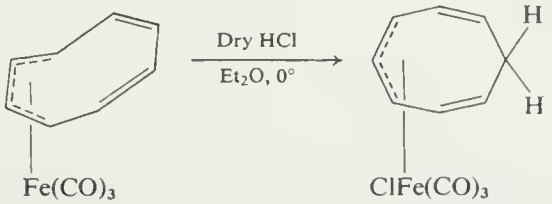
(For further reactions of (**622**), see ref. 1183.)

The preparation of the salt (**1353**) (*cf.* (**621**)) and its reaction with sodium borohydride are described in ref. 1184.



(**1353**)

The complex (**177**) reacts with dry hydrogen chloride in ether to give the product (**1354**) (57%).[1244]

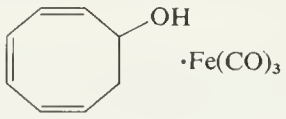


(**177**) (**1354**)

page

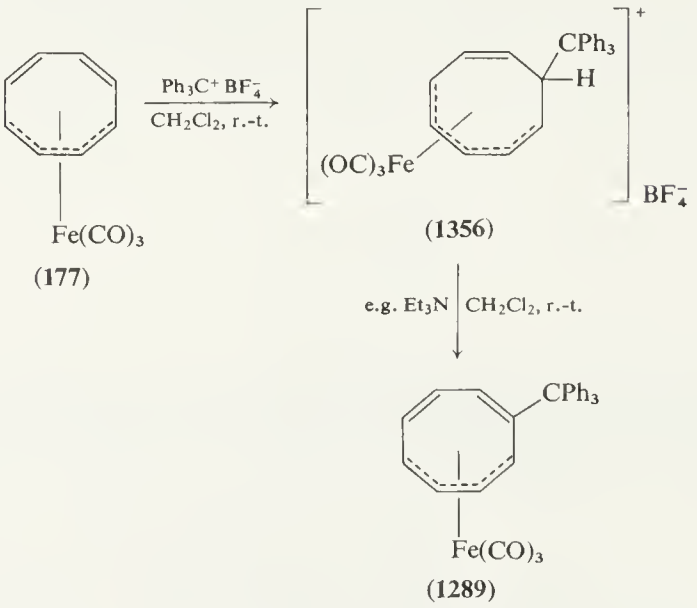
202 Full details of the formation of complexes (**624**) have been published.[1245]

Treatment of $(COT)Fe(CO)_3$ (**177**) with boron trifluoride etherate in chloroform–acetic acid gives an unstable product of probable structure (**1355**).[1245]



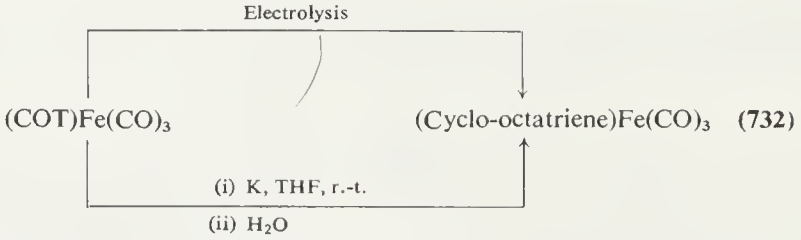
(**1355**)

204 The iron tricarbonyl complex (**177**) reacts with trityl tetrafluoroborate to afford the salt (**1356**) (81%); treatment with triethylamine or sodium methoxide then leads to the complex (**1289**) of tritylcyclo-octatetraene (74 or 59% respectively).[1196]



(For further reactions of (**1289**), see ref. 1196.)

The electrochemical reduction of $(COT)Fe(CO)_3$ (**177**) affords the cyclo-octatriene complex (**732**) (100%); alkali metal reduction proceeds in much lower yield (30%).[1246]



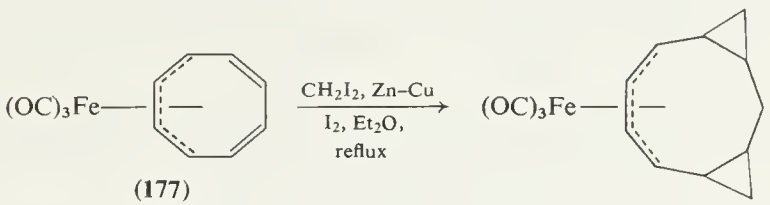
For the displacement of COT from $(COT)Fe(CO)_3$ (**177**) by $Ph_2P[CH_2]_3PPh_2$ and $Me_2P.CF_2.CH_2.PMe_2$, see ref. 1247.

Sodium bis(trimethylsilyl)amide effects the replacement of a CO ligand by CN^-, forming the product (**1357**) (70%).[1248]

$$(COT)Fe(CO)_3 \xrightarrow[C_6H_6,\ 120°]{NaN(SiMe_3)_2} Na^+\ [(COT)Fe(CO)_2CN]^-$$

(**177**) (**1357**)

Reaction of $(COT)Fe(CO)_3$ (**177**) with the Simmons–Smith reagent affords the product (**1358**) (25%).[1249]



(**177**) (**1358**)

(Stereochemistry uncertain.)

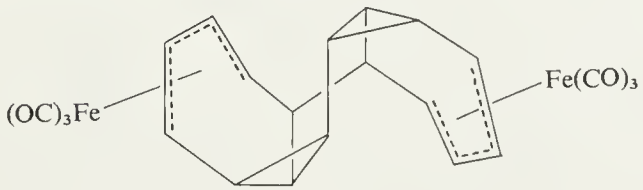
207 Attempted application of the olefin metathesis reaction to $(COT)Fe(CO)_3$ (**177**) results in several products, one of which contains dimeric COT.[1250]

$$(COT)Fe(CO)_3 \xrightarrow[Toluene,\ r.\text{-}t.]{WCl_6,\ EtOH,\ EtAlCl_2} (C_{16}H_{16})Fe_2(CO)_6$$

(**177**) (**1359**)

+ other products

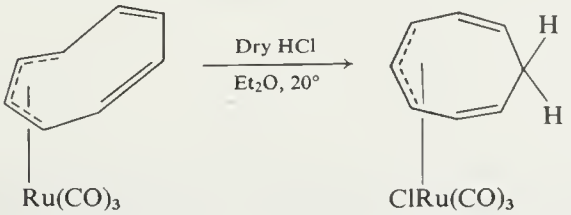
The structure of (**1359**) is as shown.



(**1359**)

208 For full details of the thermal isomerisation of ruthenium tricarbonyl complexes derived from substituted COTs, see ref. 1241.

Reaction of the complex (**184**) with dry hydrogen chloride in ether gives the product (**1360**)[1244] (*cf.* (**1354**), p. 405).



(**184**) (**1360**)

Cobalt, rhodium and iridium derivatives

211 Protonation of the rhodium complexes (**1343***a*) and (**1344***a*) (p. 402) with trifluoroacetic acid gives products similar to (**655***b*) and (**656***b*).[1233]

212 The iridium complexes (**1343***b*) and (**1344***b*) (p. 402) protonate in a fashion similar to that of (**654***c*).[1233]

Reaction of the rhodium complex (**208**) with piperidine gives the product (**1361**)[1251] (*cf.* scheme 72).

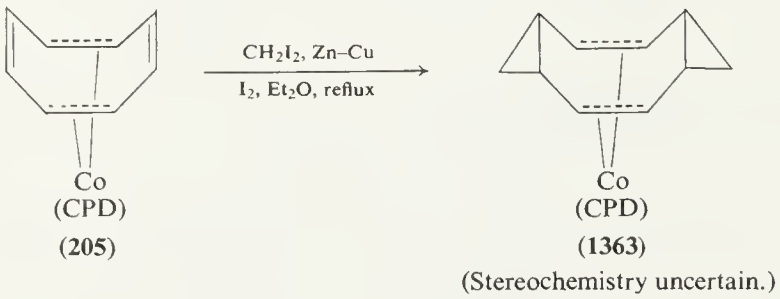
$$\underset{\textbf{(208)}}{[(COT)RhCl]_2} \xrightarrow[CH_2Cl_2,\ r.\text{-}t.]{\text{Piperidine}} \underset{\textbf{(1361)}}{(COT)RhCl(piperidine)}$$

An analogous product (COT)IrCl(piperidine) is obtained from $[(COT)IrCl]_n$ (**215**) (*cf.* the reaction with pyridine to give (**216**) (p. 75)).

213 On successive treatment with COT, bipyridyl and ammonium hexafluorophosphate, the iridium complex (**215**) forms the salt (**1362**).[1251]

$$\underset{\textbf{(215)}}{[(COT)IrCl]_n} \xrightarrow[\text{(ii) Bipyridyl}\\ \text{(iii) } NH_4PF_6\text{(aq.)}]{\text{(i) COT, } CH_2Cl_2} \underset{\textbf{(1361)}}{[(COT)Ir(bipyridyl)]^+\ PF_6^-}$$

Cyclopropanation of (COT)Co(CPD) (**205**) may be effected by the Simmons–Smith reagent to give the product (**1363**) (19%).[1249]

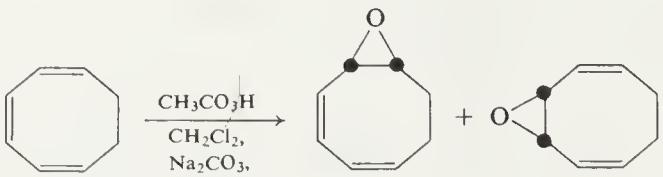


(205) **(1363)**

(Stereochemistry uncertain.)

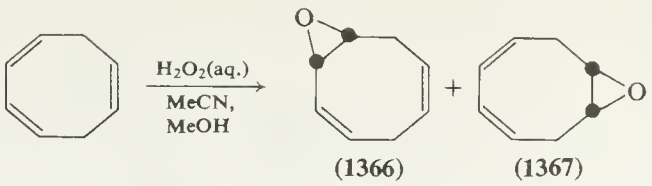
Cyclo-octatrienes

217 Epoxidation of cyclo-octa-1,3,5-triene with peracetic acid yields the isomers (**1364**) and (**1365**) (ratio 95:5; 24%).[1252]



(1364) **(1365)**

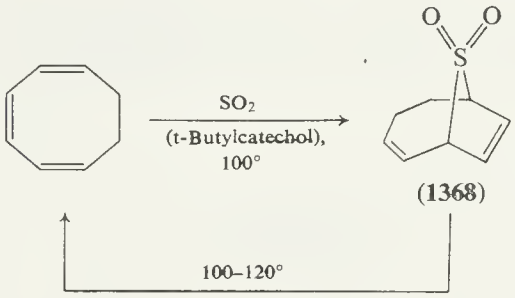
With hydrogen peroxide in acetonitrile–methanol, cyclo-octa-1,3,6-triene gives the products (**1366**) and (**1367**) (*ca.* 1:1); with perbenzoic acid, only 20% of (**1366**) is obtained.[1253]



(1366) (1367)

218 For the cyclopropanation of cyclo-octatrienes with di-iodomethane-diethylzinc, see ref. 1193.

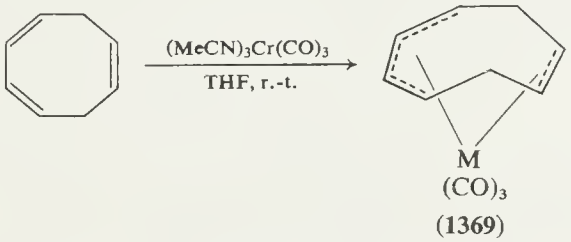
219 Cyclo-octa-1,3,5-triene reacts with sulphur dioxide at 100° to give the adduct (**1368**); at slightly higher temperatures the triene is regenerated.[1254, 1255]



(1368)

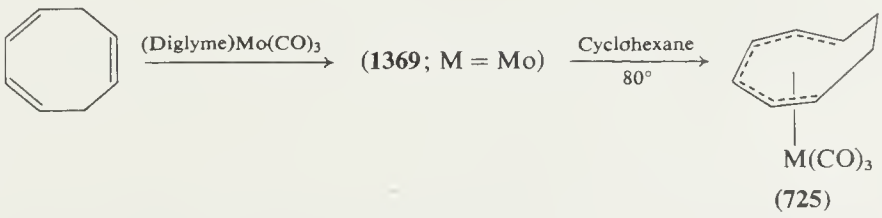
227 For ^{13}C spectral studies on (cyclo-octatriene)$M(CO)_3$ (**725**; M = Cr, Mo), see ref. 1176.

Cyclo-octa-1,3,6-triene reacts with $(MeCN)_3Cr(CO)_3$ to form the complex (**1369**; M = Cr).[1256]



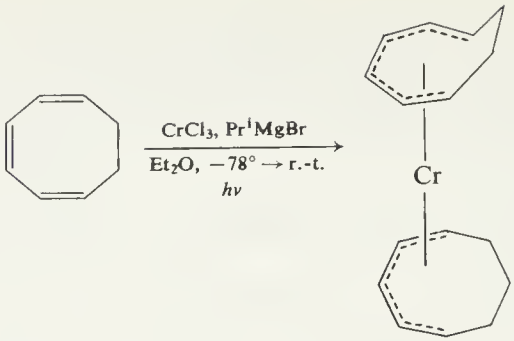
(1369)

Similarly, reaction with (diglyme)$Mo(CO)_3$ gives the complex (**1369**; M = Mo) (45%); in this case the product rearranges quantitatively at 80° to afford the complex of cyclo-octa-1,3,5-triene, (**725**; M = Mo).[1256]



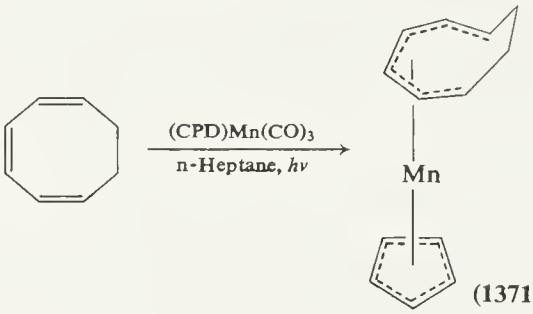
(725)

Reaction of cyclo-octa-1,3,5-triene with chromium(III) chloride and isopropylmagnesium bromide, in the presence of cyclo-octa-1,3-diene, leads to the complex (**1370**) (up to 48%).[1173]



(1370)

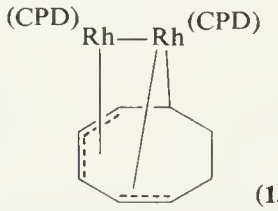
228 Cyclo-octa-1,3,5-triene reacts with (CPD)$Mn(CO)_3$ under the influence of u.v. light to give the thermally unstable complex (**1371**).[1179]



(1371)

230 For details of the reaction of cyclo-octa-1,3,5-triene with (COD)$Ru(CO)_3$ to yield the complex (bicyclo-octadiene)$Ru(CO)_3$ (**735**) (42%), see ref. 1186.

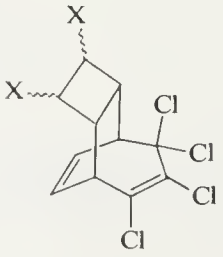
232 For the photochemical transformation of (cyclo-octatriene)Rh(CPD) (**745**) into the binuclear complex (**1372**), see ref. 1257.



(1372)

Substituted bicyclo[4.2.0]octa-2,4-dienes

248 The dichloride (**799**/**800**; X = Cl) reacts with tetrachlorocyclopropene at 75° to yield the product (**1373**) (mixture of stereoisomers; 83%).[1258]



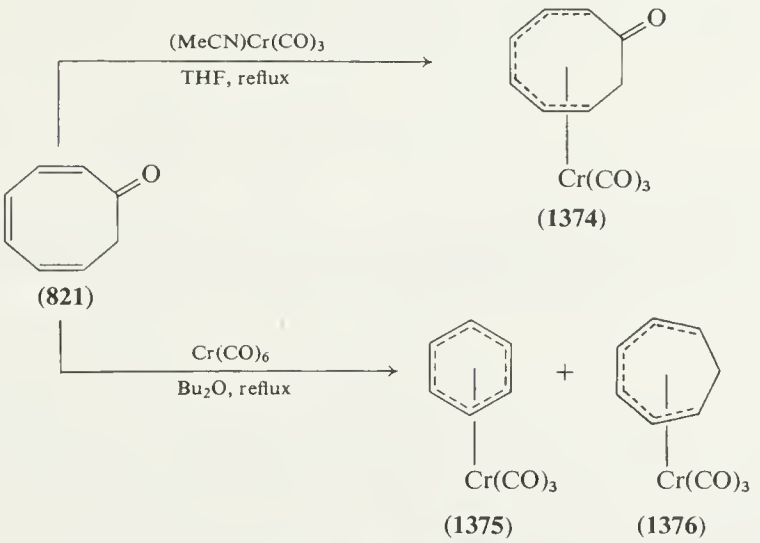
(1373)

Cyclo-octa-2,4,6-trienones

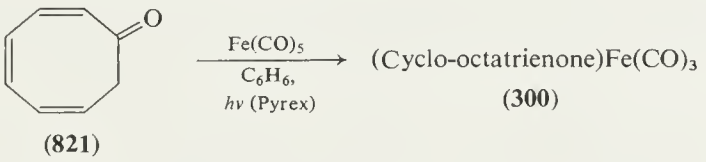
254 The trienone (**821**) may be prepared from methoxycyclo-octatetraene (see p. 385); for 8-substituted derivatives, see p. 419.

For the (low-temperature) preparation of the bicyclic dienone (**822**), see ref. 1259.

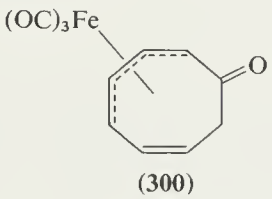
262 Reaction of cyclo-octatrienone (**821**) with $(MeCN)Cr(CO)_3$ leads to the complex (**1374**) (26%); with $Cr(CO)_6$, the products are (**1375**) (4%) and (**1376**) (11%).[1198]



Reaction of cyclo-octatrienone (**821**) with $Fe(CO)_5$, induced by u.v. radiation, gives the complex (**300**) (36%).[1259]

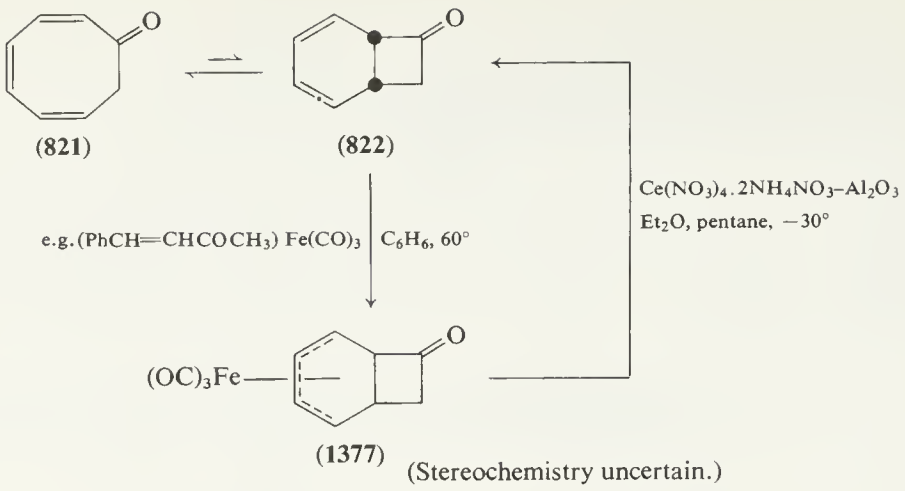


The structure of this product is apparently as shown.[1198, 1259]



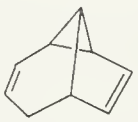
With (benzylidene-acetone)$Fe(CO)_3$[1198, 1259] or (pent-3-en-2-one)$Fe(CO)_3$,[1259] the complex (**1377**) derived from the valence tautomer (**822**) is obtained (up to 60%); demetallation of this product (at low temperature) gives the bicyclic dienone (**822**) (29%).[1259]

page



Bicyclo[6.1.0]nona-2,4,6-trienes

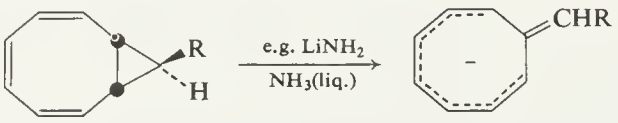
272 The formation of the homosemibullvalene (**1378**) (30%) by photolysis of bicyclo[6.1.0]nonatriene (**82*a***) has been reported.[1260]



(**1378**)

277 For details of the action of potassium in liquid ammonia on the *syn*- and *anti*-9-methylbicyclo[6.1.0]nonatrienes, (**82*g***) and (**82*q***), and on the 9,9-dimethyl-derivative (**82*n***), see ref. 1261.

For the deprotonation of compounds (**82**; $R^2 = H$) to form anions of structure (**1379**), see the superscribed refs.



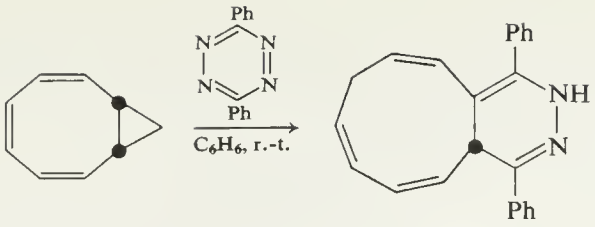
(**82**; $R^2 = H$) (**1379**)

R = Ph[1193] R = 1-naphthyl, 2-naphthyl, 9-anthryl[1154]

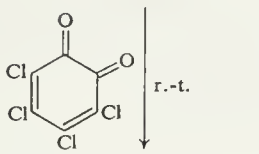
278 For an n.m.r. spectral study of topomerisation in the anion (**922**), see ref. 1262.

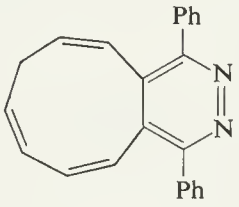
286 Reaction of bicyclo[6.1.0]nonatriene with 3,6-diphenyl-*s*-tetrazine gives the product (**1380**) (*ca.* 40%), which is readily dehydrogenated to (**1381**) (67%)[1263] (*cf.* pp. 419, 420).

The chromium complex (**1382**) is formed by the action of $(MeCN)_3Cr(CO)_3$ on bicyclo[6.1.0]nonatriene; an analogue is produced from the *anti*-9-ethoxycarbonyl-derivative (**82*h***) (yields 50–70%).[1256] Thermal rearrangement of the ligand in (**1382**) leads to the product (**1383**) (89%)[1256] (*cf.* the molybdenum complex (**964**), p. 288).

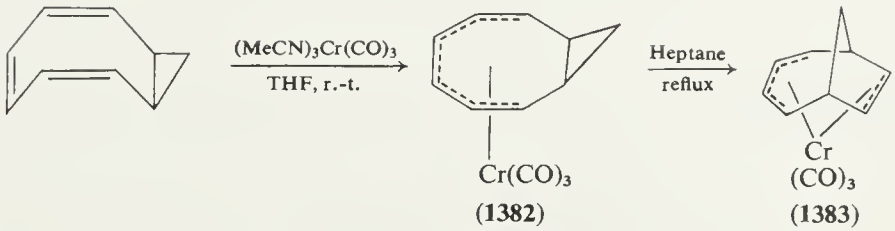


(1380)



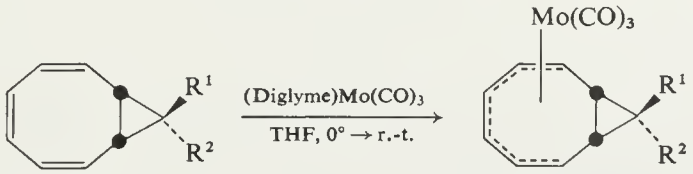


(1381)



(1382) (1383)

Molybdenum tricarbonyl complexes (**1384**) are formed from 9-substituted bicyclo[6.1.0]nonatrienes (**82*f–h***) and (diglyme)$Mo(CO)_3$[1264] (table 142).



(82) (1384)

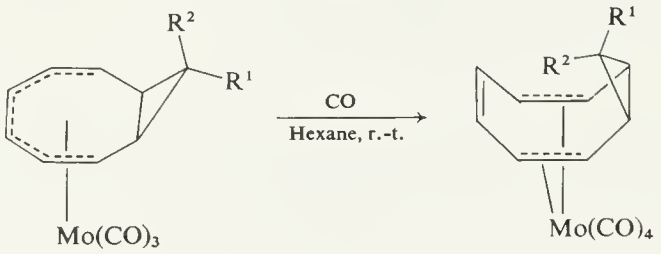
Table 142

	R^1	R^2	Yield (%)
f	Cl	H	85–95
g	H	Me	45
h	CO_2Et	H	85–95

The tungsten complex (**1385**) results (25–30%) from bicyclo[6.1.0]nonatriene and $(DMF)W(CO)_3$.[1264]

(1385)

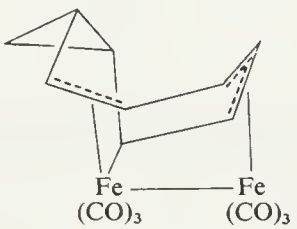
The complex (**964**) readily absorbs carbon monoxide[1264] (*cf.* (cyclo-octatriene)$Mo(CO)_3$ (**725**; M = Mo), p. 227); this behaviour is also shown by (**1384*f***) and (**1384*h***), but not by (**1384*g***), which is consistent with the illustrated stereochemistry of (**1384**) and (**1386**).[1264]



(1384) **(1386)**

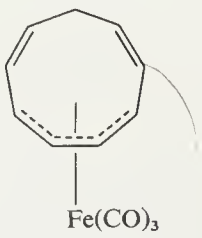
R^1 = H, Cl, CO_2Et
R^2 = H

289 The structure of (bicyclo[6.1.0]nonatriene)$Fe_2(CO)_6$ (**971**) is now known to be as illustrated.[1265]



(971)

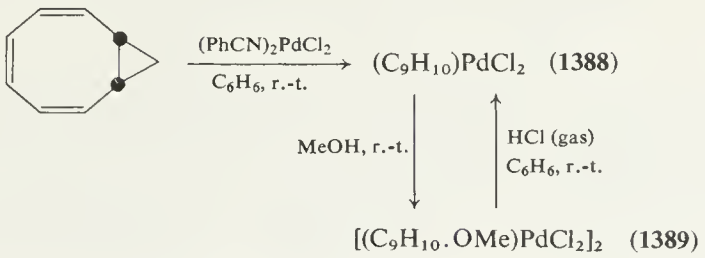
Another of the products obtained by the action of $Fe_2(CO)_9$ on bicyclo[6.1.0]-nonatriene has been identified as a bond-shift isomer of (**969**), having the structure (**1387**) shown below.[1266]



(1387)

290 At *ca.* 100°, the complex (**1387**) rearranges to (**970**)[1266] (*cf.* (**969**) and (**971**)).

291 Bicyclo[6.1.0]nonatriene reacts with $(PhCN)_2PdCl_2$ to give the complex (**1388**) (85%); treatment with methanol yields the dimeric product (**1389**), which with hydrogen chloride reverts to (**1388**).[1267]

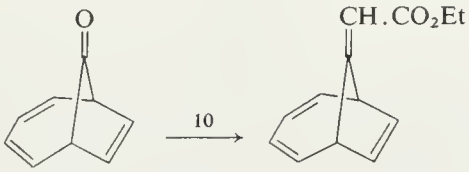


The probable structures of (**1388**) and (**1389**) are shown.

(**1388**) (**1389**)

Bicyclo[4.2.1]nona-2,4,7-trienes

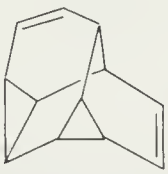
292 Addition to scheme 91:



(**540**)

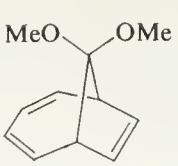
Reaction	Conditions	Yield (%)	Ref.
10	$(EtO)_2PO.CH_2CO_2Et$, NaH	—	1268

(For conversion of (**540**) into the $(CH)_{12}$ hydrocarbon (**1390**), see ref. 1268.)

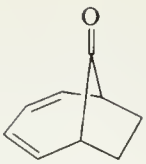


(**1390**)

For details of reaction 6, see ref. 1269. Conversion of the ketal (**1391**) into the dienone (**1392**) is also described in ref. 1269.



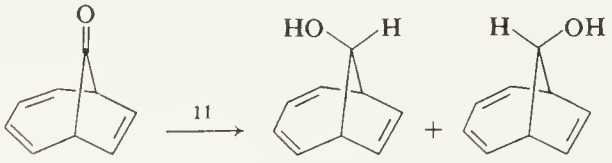
(1391)



(1392)

293 For the photo-electron spectra of the triene (**966**) and the trienone (**540**) see refs. 1270 and 1271 respectively.

Addition to scheme 92:

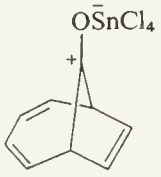


(540)

Reaction	Conditions	Yield (%)	Ref.
11	$Al(OPr^i)_3$, Me_2CO, xylene, reflux	77[b]	1272

[b] Product ratio 4:1.

For the generation of the complex (**1393**) from (**540**) and tin(IV) chloride in liquid sulphur dioxide, see ref. 1272.

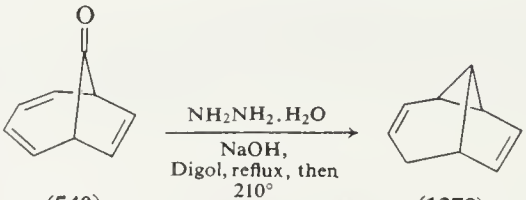


(1393)

295 For theoretical calculations on the cation (**985**; $R^2 = H$), see ref. 1272.

296 For further mechanistic discussion of the solvolysis of the epimeric tosylates (**990**) and (**991**; H instead of D), see ref. 1273.

297 Attempted reduction of the ketone (**540**) *via* the hydrazone leads to the rearranged hydrocarbon (**1378**) (95%).[1274]



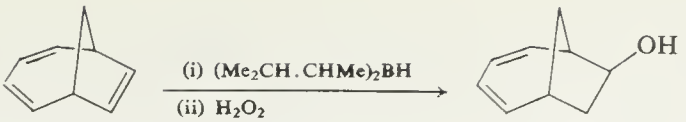
(540) (1378)

For thermolysis of the sodium salt of the tosylhydrazone (**997**), see also ref. 1275.

299 Hydroboration of bicyclo[4.2.1]nonatriene, and subsequent treatment with hydrogen peroxide, affords the dienol (**1394**) (75–80%).[1276]

(For further transformations of (**1394**), see ref. 1276.)

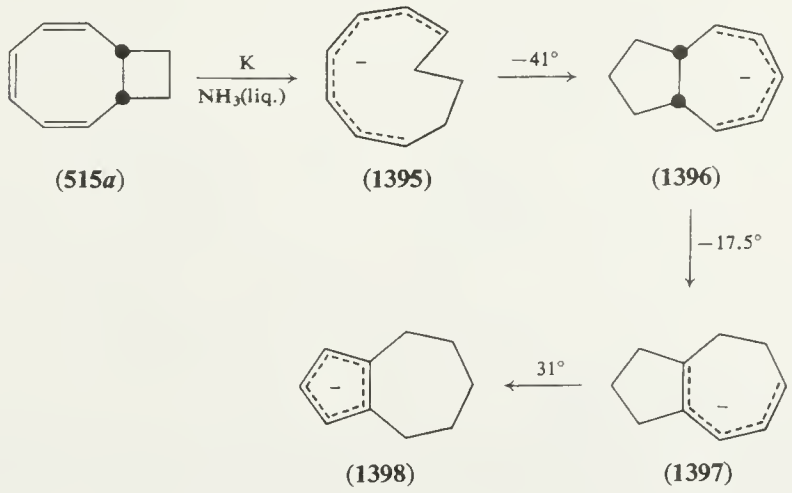
For full details of the preparation of the products (**1009**) and (**1010**), see ref. 1277.



(1394)

Bicylo[6.2.0]deca-2,4,6-trienes

303 Treatment of bicyclo[6.2.0]decatriene (**515***a*) with potassium in liquid ammonia gives the cyclodecatrienyl anion (**1395**); when the temperature is raised, rearrangement occurs *via* (**1396**) and (**1397**) to give (**1398**) as the final product.[1278]

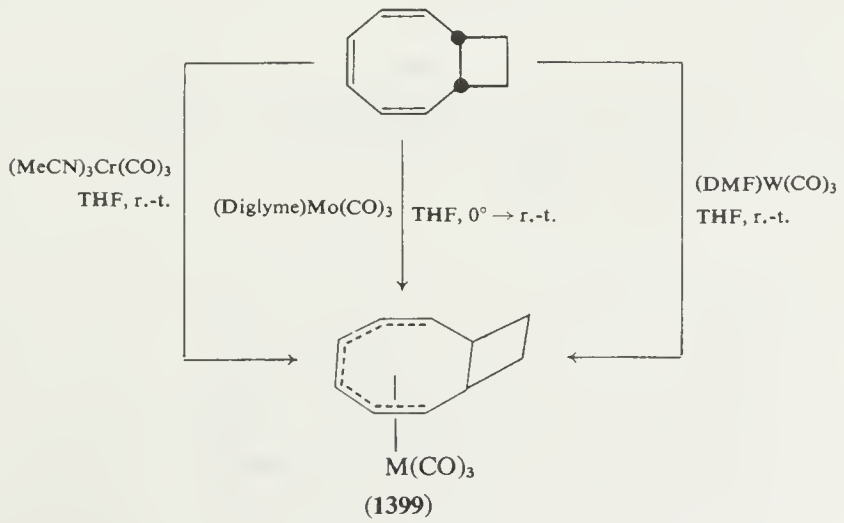


(**515***a*) (**1395**) (**1396**)

(**1398**) (**1397**)

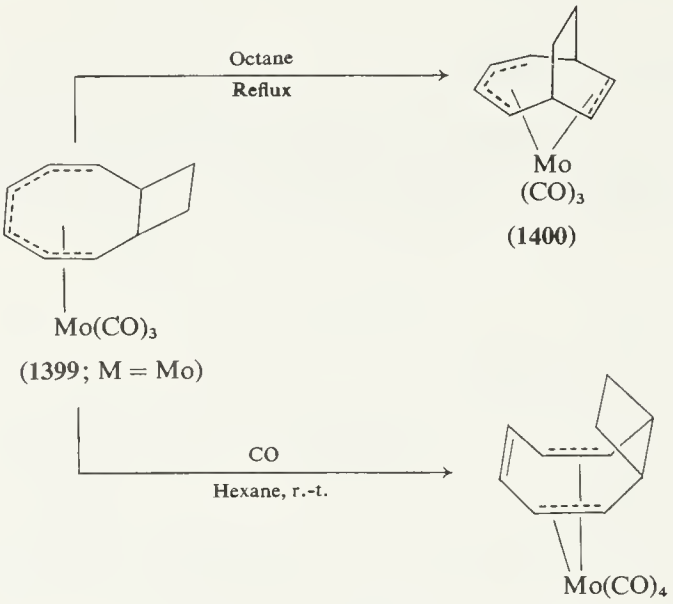
(The products obtained by 'quenching' these anions are as expected.)

304 Bicyclo[6.2.0]decatriene reacts with $(MeCN)_3Cr(CO)_3$ to give the complex (**1399**; M = Cr),[1256] with (diglyme)$Mo(CO)_3$ to give (**1399**; M = Mo) (85–95%),[1264] and with (DMF)$W(CO)_3$ to give (**1399**; M = W) (25–30%).[1264]



(**1399**)

Thermal rearrangement of the molybdenum complex (**1399**; M = Mo) leads to a derivative of bicyclo[4.2.2]decatriene, (**1400**) (55%) (*cf.* (**964**), p. 288); carbon monoxide is readily absorbed with the formation of the product (**1401**) (90–95%) (*cf.* (**725**; M = Mo), p. 227).[1264]



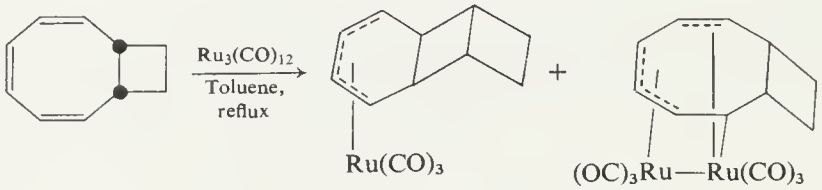
(**1400**)

(**1399**; M = Mo)

(**1401**)

For a study of the fluxional process in the complex (**1026**), using ^{13}C n.m.r. spectroscopy, see ref. 1279.

305 Bicyclo[6.2.0]decatriene (**515***a*) reacts with $Ru_3(CO)_{12}$ to afford the complexes (**1402**) (47%) and (**1403**) (20%), together with some minor products [1280] (*cf.* the analogous iron complexes (**1026**) and (**1027**), p. 304).



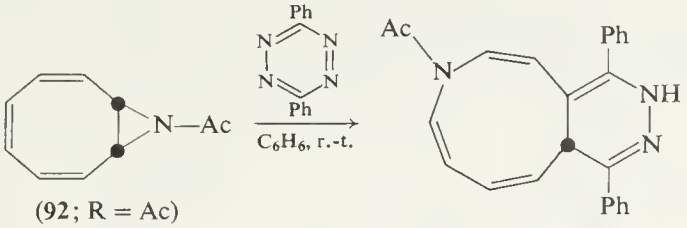
(**515***a*) (**1402**) (**1403**)

Reaction with $(PhCN)_2PdCl_2$ yields the complex (**1404**) (83%), which with methanol gives the product (**1405**)[1267] (*cf.* the analogous reaction of bicyclo[6.1.0]nonatriene, p. 415).

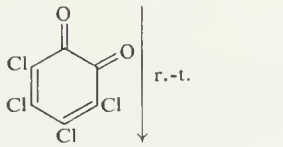
(**1404**) (**1405**)

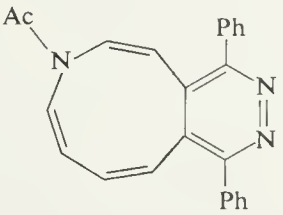
9-Azabicyclo[6.1.0]nona-2,4,6-trienes

310 Reaction of the *N*-acetyl-compound (**92**; R = Ac) with 3,6-diphenyl-*s*-tetrazine gives the product (**1406**) (75%), which is readily dehydrogenated to yield (**1407**) (85%)[1263] (*cf.* pp. 413, 420).



(92; R = Ac) (1406)

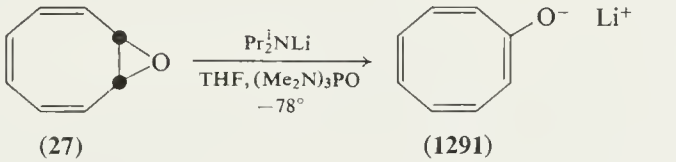




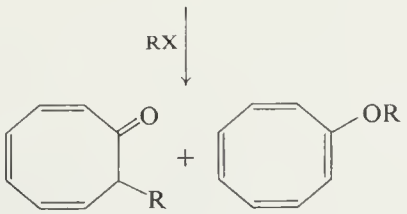
(1407)

9-Oxabicyclo[6.1.0]nona-2,4,6-trienes

314 Deprotonation of the epoxide (**27**) with lithium di-isopropylamide generates the enolate anion (**1291**) (p. 385), which may be subjected to alkylation, acylation, etc. with the formation of the substituted trienones (**1408**) and/or the oxygenated COT (**1290**)[1197] (table 143). Reaction of the enolate anion (**1291**) with diphenyl disulphide or benzeneselenenyl chloride affords the acetophenone derivatives (**1409**) and (**1410**).[1197] Cyclo-octatrienone is a



(27) (1291)

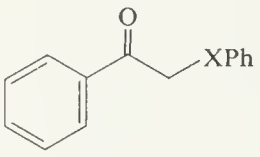


(1408) (1290)

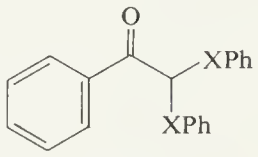
Table 143

R	X	Yield (%) (1408)	(1290)
Me	I	78	—
Et	Br	16	11
Et	I	81	—
CH_2=$CHCH_2$	Br	74	—
$PhCH_2$	Br	15	—
$PhCH_2$	I	37	—
MeCO	Cl	—	Up to 26
EtO_2C	Cl	—	Up to 63
PhS	Cl	26	—
PhSe	Br	40	—
Br	Br	51	—

major product in some of these reactions; with CH_3CO_2D at 0°, the enolate anion (**1291**) gives the deuteriated compound (**1408**; R = D) (76%).[1197]



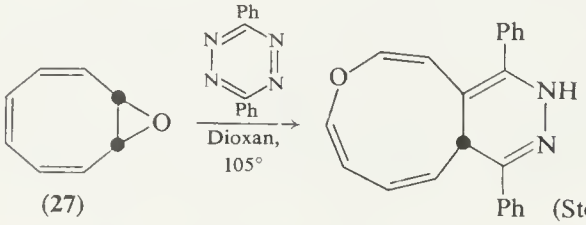
(**1409**)



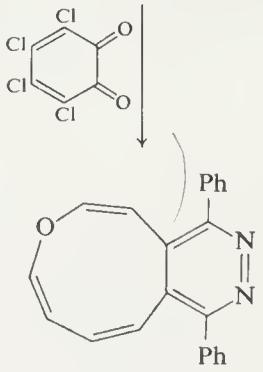
(**1410**)

X = S, Se

315 The epoxide (**27**) reacts with 3,6-diphenyl-*s*-tetrazine to yield the adduct (**1411**) (27% based on recovered tetrazine), which may be dehydrogenated to give the product (**1412**) (60%)[1281] (*cf.* pp. 413, 419).



(**27**) (**1411**) (Stereochemistry not certain.)



(**1412**)

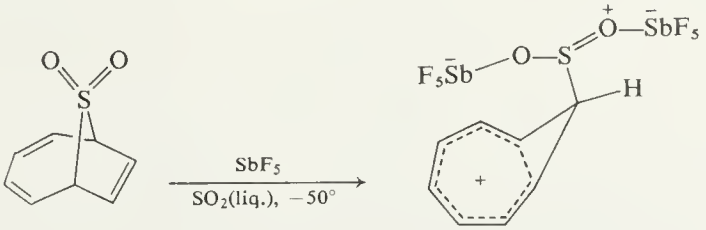
page

9-Thiabicyclo[4.2.1]nona-2,4,7-trienes

324 For the crystal structure of the sulphone (**108**), see ref. 1282.

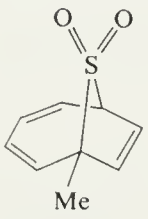
325 For further details of the deuteriation and methylation of the sulphone (**108**), see ref. 1157.

In liquid sulphur dioxide, the sulphone (**108**) reacts with antimony(v) fluoride (>2 equivalents) to form the *endo*-homotropylium-8-sulphinate complex (**1413**) (see also scheme 16, p. 40); stereochemical inversion occurs when the temperature is allowed to rise.[1157]



(108) **(1413)**

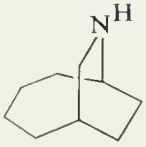
Similar products are formed from the mono-and di-methyl derivatives, (**1414**) and (**312***c*) (p. 112) respectively.[1157]



(1414)

9-Aza-10-oxobicyclo[4.2.2]deca-2,4,7-trienes

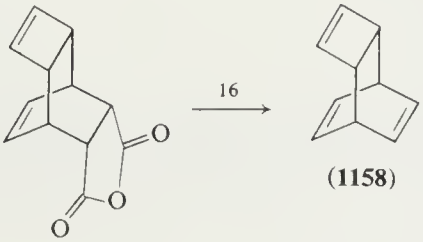
327 For the further reduction of the saturated lactam (**1105**) with lithium aluminium hydride, leading to the amine (**1415**), see ref. 1283.



(1415)

Tricyclo[4.2.2.0^{2,5}]deca-3,7-dienes

328 Addition to scheme 102:

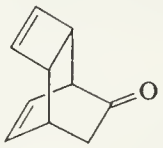


(1158)

Reaction	Reagents and conditions	Yield (%)	Ref.
16	$(Ph_3P)_2Ni(CO)_2$, diglyme, reflux	73	1160

Another preparation of 'Nenitzescu's hydrocarbon' (**1158**) (p. 421) (five steps, overall yield 44%) starts from the acryloyl chloride adducts (**1270*b***) and (**1271*b***) (p. 378).[1159]

For the conversion of the acrylonitrile adducts (**1270*a***) and (**1271*a***) into the ketone (**1416**) (50%), see ref. 1158.

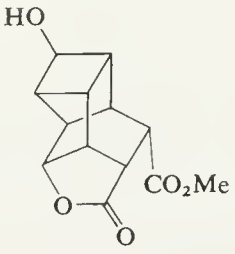


(**1416**)

For a modified preparation of (**1106**) and (**1107**) (scheme 102), see ref. 1284.

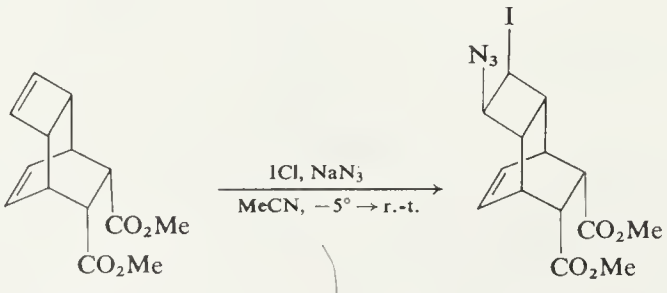
331 The epoxides (**1067**) and (**1113**) have been prepared using *m*-chloroperbenzoic acid; a minor product of the reaction with the di-ester (**1108**) is apparently a dimer of (**1113**).[1285]

Treatment of the epoxide (**1113**) with dry hydrogen chloride in methanol gives the hydroxy-lactone-ester (**1417**).[1285]



(**1417**)

334 The dimethyl ester (**1108**) reacts with iodine azide to give the product (**1418**) (80–90%), together with some iodo-lactone-ester (**1122**; R = Me).[1284, 1286, 1287]



(**1108**) (**1418**)

\+ (**1122**; R = Me)

Other derivatives (**1157**; $R^1 = R^2 = Me$ or $R^1R^2 = CH_2OCH_2$), however, afford (**1419**) in dichloromethane, and in acetonitrile participation of the solvent results in (**1420**) as the major product[1284] (table 144).

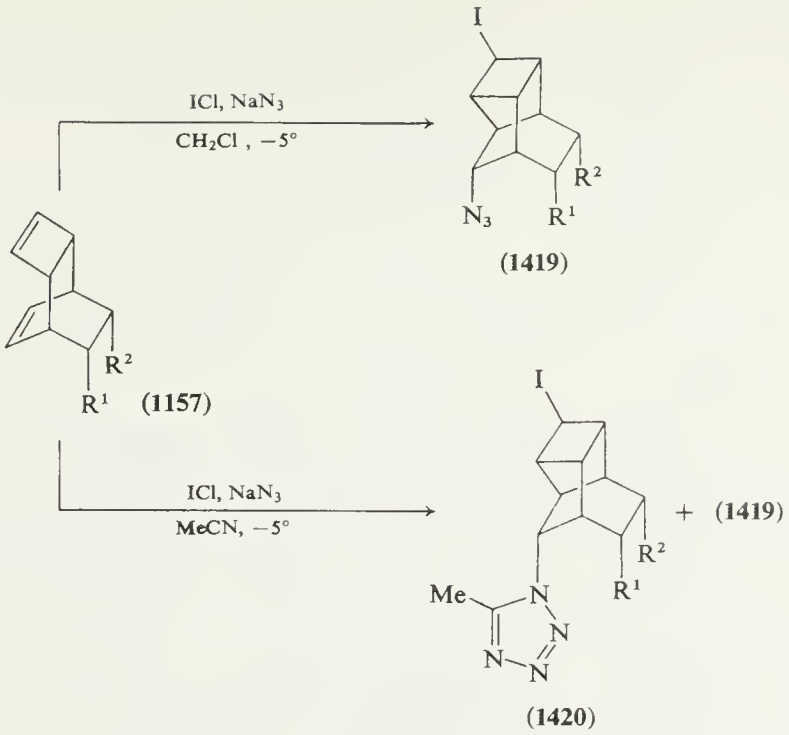
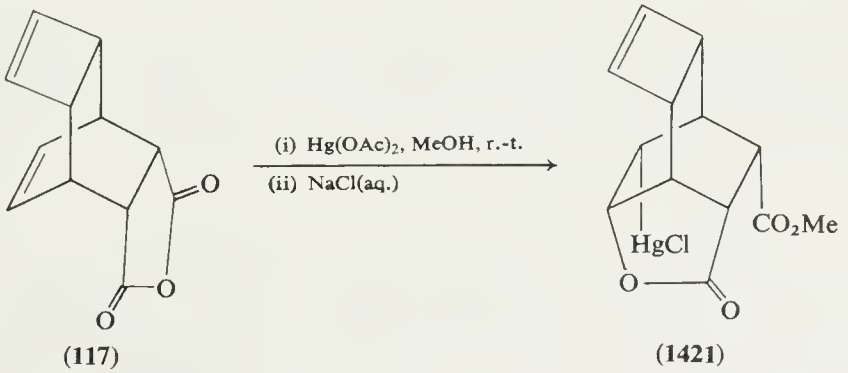


Table 144

R^1	R^2	Solvent	Yield (%) (1419)	Yield (%) (1420)
Me	Me	CH_2Cl_2	88	—
		MeCN	(Not given)	46
H_2C	CH_2	CH_2Cl_2	94	—
	O	MeCN	18	56

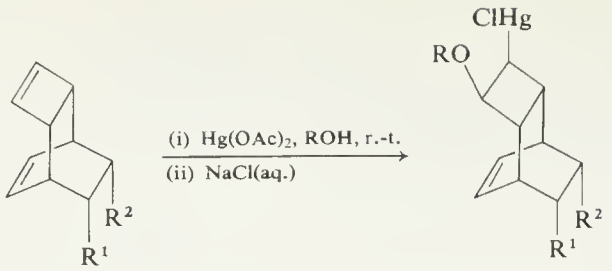
335 Treatment of the anhydride (**117**) with mercury(II) acetate in methanol followed by aqueous sodium chloride, apparently yields the lactone-ester (**1421**) (40%).[1288]



(**117**) (**1421**)

With other derivatives (**1157**), however, products of structure (**1422**) are formed (table 145). In the presence of sodium azide (in methanol), the isolated product (from the di-ester) has structure (**1423**).[1284, 1287]

page



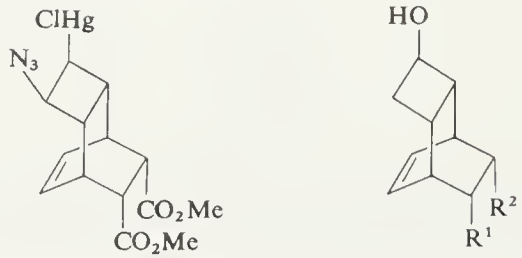
(1157) **(1422)**

Table 145

R^1	R^2	R	Yield (%)	Ref.
Me	Me	H	85[a]	1284
H_2C	CH_2	H	81[a]	1284
	O			
CO_2Me	CO_2Me	H	100[a], (12[b])	1284, (1288)
Me	Me	Me	82	1284
H_2C	CH_2	Me	82	1284
	O			
CO_2Me	CO_2Me	Me	(96), 99	(1284), 1288
CO_2Me	CO_2Me	Ac	76	1288

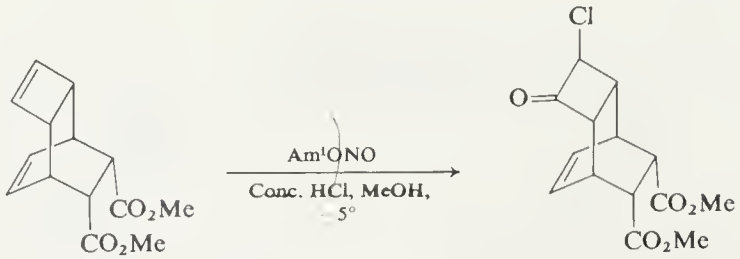
[a] Reaction in aqueous THF.
[b] Reaction in aqueous acetone.

For the demercuration of the compounds (**1422**; R = H) with sodium borohydride, resulting in products (**1424**), see ref. 1284.



(1423) **(1424)**

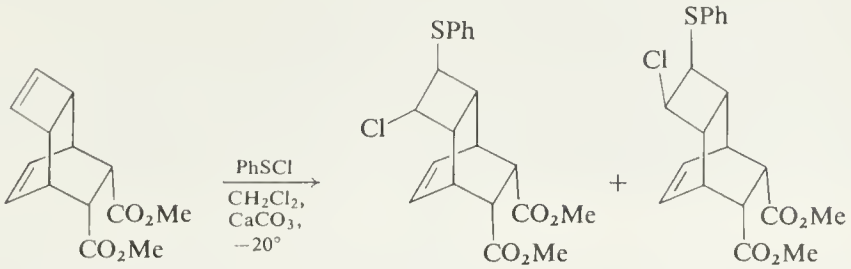
The addition of nitrosyl chloride (from isoamyl nitrite and concentrated hydrochloric acid) to the di-ester (**1108**) leads to the chloro-ketone (**1425**) (90%).[1284]



(1108) **(1425)**

Hydroboration of the di-ester (**1108**) may be used to prepare the compound (**1424**; $R^1 = R^2 = CO_2Me$) (96%).[1284]

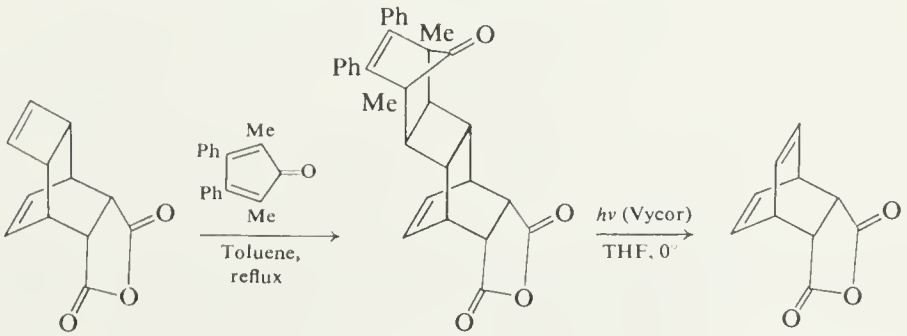
With benzenesulphenyl chloride, the di-ester (**1108**) forms a mixture of the products (**1426**) and (**1427**) in quantitative yield (ratio 3:1).[1289]



(**1108**) (**1426**) (**1427**)

A similar result is obtained with the cyclic ether (**1107**).[1289]

339 Addition of hemicyclone to the anhydride (**117**) affords the product (**1428**) (formulated as the *exo*-adduct) (98%), which on photolysis gives the diene-anhydride (**1429**) (49%).[1160]



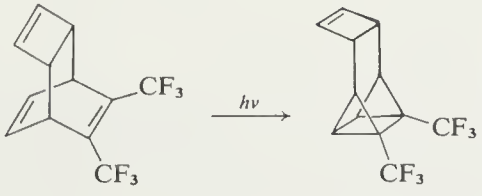
(**117**) (**1428**) (**1429**)

Similar adducts are formed from the anhydride (**117**) and other cyclones, including tetracyclone, phencyclone and 2,5-diphenyl-3,4-di(2′-pyridyl)cyclopentadienone.[1290]

For reaction of the di-ester (**1108**) with the COT dimer (**10**), see p. 427.

Tricyclo[4.2.2.0^{2,5}]deca-3,7,9-trienes

344 The bis(trifluoromethyl)-derivative (**1430**) affords the caged isomer (**1431**) (*ca.* 80% conversion) on u.v. irradiation; the cycloaddition is reversed by heat.[1291]

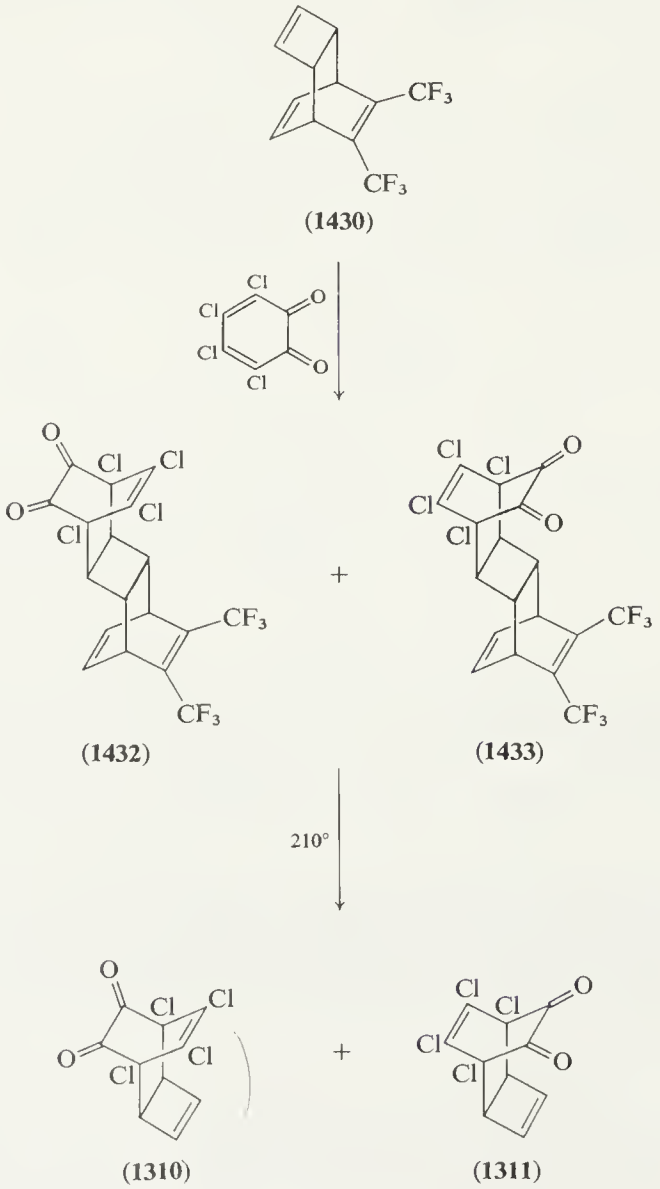


(**1430**) (**1431**)

349 For the reaction of 'Nenitzescu's hydrocarbon' (**1158**) (p. 343) with hemicyclone, and photolytic conversion of the product into barrelene (24% overall yield from COT), see ref. 1160.

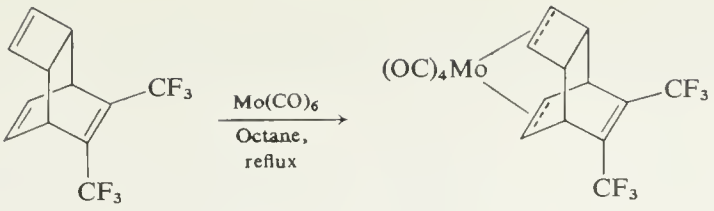
For reactions of the di-ester (**7**) with acecyclone etc., see p. 389.

The bis(trifluoromethyl)-compound (**1430**) reacts with tetrachloro-*o*-benzoquinone to give a 4:3 mixture of the *endo*- and *exo*-adducts (**1432**) and (**1433**); at 210° the cyclobutenes (**1310**) and (**1311**) are obtained. [1208]



For reaction of the di-ester (**7**) with the COT dimer (**10**), see p. 427.

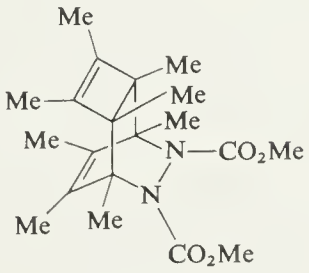
351 The bis(trifluoromethyl)-compound (**1430**) reacts with $Mo(CO)_6$ to give (in low yield) the complex (**1434**).[1161]



(1430) **(1434)**

9,10-Diazatricyclo[4.2.2.0^{2,5}]deca-3,7-dienes

354 For transformations of the octamethyl-diester (**1435**) analogous with those of (**809**; R = Et) (scheme 105), see ref. 1213.

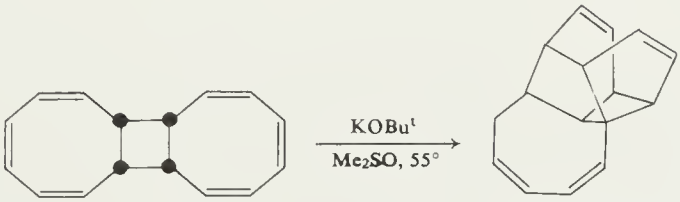


(1435)

355 For photo-caging of the octamethyl-derivative (**1435**), and the corresponding *N*-phenyltriazolinedione adduct, see ref. 1213.

Oligomers of cyclo-octatetraene

361 Treatment of dimer (**9**) with potassium t-butoxide leads to the isomer (**1436**) (77%).[1292]



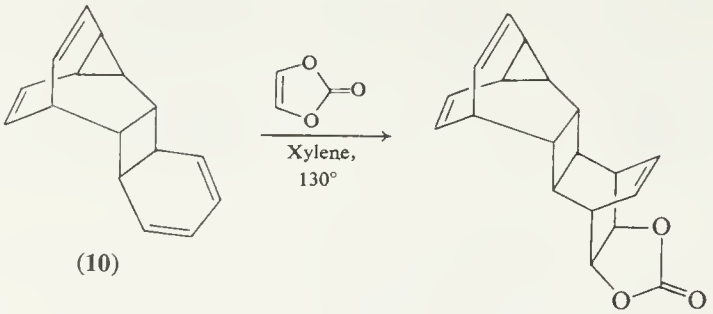
(9) **(1436)**

369 Additions to table 139 (*cf.* ref. 1293):

Dienophile	Reaction conditions	Yield (%)	Ref.
COT–dimethyl maleate adduct (**1108**)	100[a]	31	164
COT–dimethyl acetylenedicarboxylate adduct (**7**)	100[a]	10	164

[a] (See footnote to table 139.)

For details of the reaction of dimer (**10**) with vinylene carbonate, and subsequent transformations of the adduct (**1247**), see ref. 1293.



(**10**) (**1247**)

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