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This series presents critical reviews of the present position and future trends in modern chemical research. It is addressed to all research and industrial chemists who wish to keep abreast of advances in their subject.

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Recent Aspects of Homolytic Aromatic Substitutions

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Istituto di Chimica del Politecnico, Milano, Italy

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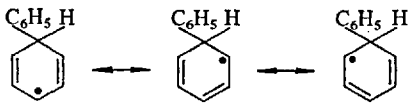
I. Introduction

Among the free radical reactions, homolytic aromatic substitution has an undoubted theoretical interest for the understanding of the reactivity of the aromatic compounds and of the free radicals. However it was considered till recent years a secondary aspect of the general problem of the aromatic substitution. It is difficult to find a modern text book of general organic chemistry in which this subject is only mentioned.

The poor interest of the organic chemists concerning the homolytic aromatic substitution mainly arose from the discouraging characteristics of the most studied reaction: the homolytic arylation [1]. A very low positional and substrate selectivity is in fact the most qualifying characteristic of this reaction. That clearly appears from the results of homolytic phenylation shown in Table 1. The fact that the partial rate factors (a measure of both positional and substrate selectivity) of the *meta* positions are all very close to unity and, in the absence of steric effects, those of *ortho* and *para* positions are slightly higher independently of the polar character of the substituent, is best explained by the stability of the intermediate cyclohexadienyl radical (*1*), which is affected by the delocalization of the odd electron into the substituent groups in *ortho* (*2*) and *para* (*3*), but not in *meta* positions



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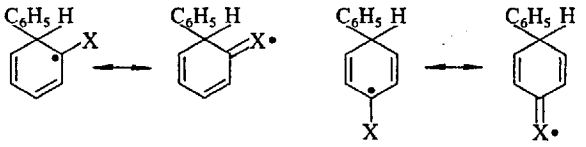

2 *3*

This point of view is supported by the unusually high values of the partial rate factors of the α- and γ-positions in the homolytic phenylation of pyridine-N-oxide [8] (α 139, β 1.5, γ 31.2) compared with those of pyridine (α 1.8, β 1.0, γ 1.2). This behavior can in fact be ascribed to the higher stability of the σ-complex which has a nitroxide type structure (*4*)

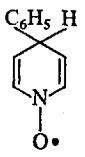

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Table 1. Partial rate factors for homolytic phenylation of benzene derivatives with benzoyl peroxide

Aromatic substrate	Partial rate factors			Refs.
	f_o	f_m	f_p	
Ph—Me	2.4	0.74	1.1	2,3)
Ph—Et	1.4	0.76	1.0	2)
Ph—Pr^i	0.60	0.81	1.0	2)
Ph—Bu^t	0.46	0.94	1.0	2)
Ph—Ph	2.1	1.0	2.5	2)
Ph—Cl	1.8	0.81	1.1	2,3)
Ph—CO_2Me	3.0	0.93	2.7	4)
Ph—CN	6.5	1.1	6.1	5)
Ph—NO_2	—5.5	0.86	4.9	2)
Ph—OMe	4.2	0.87	1.9	6)
Pyridine	1.7	1.0	0.87	7)

The results of Table 2 show that the presence of substituents in the phenyl radical modifies only slightly the whole picture. This very low selectivity affects the synthetic interest of the homolytic arylation. Generally all the free positions of an aromatic substrate are substituted, giving complex mixtures of isomers. Moreover, if the conversions are not too low, the mixtures of the reaction products become much more complex because polysubstitution occurs in all the aromatic positions.

Table 2. Partial rate factors for homolytic arylation of nitrobenzene with X-substituted phenyl radicals [1)]

X	Partial rate factors		
	f_o	f_m	f_p
m—Me	5.5	1.2	4.7
p—Me	6.1	1.2	5.8
H	5.5	0.86	4.9
m—Cl	2.2	0.58	2.2
p—Cl	2.7	0.63	2.5
m—NO_2	0.68	0.23	0.75
p—NO_2	1.64	0.43	1.6

Recently we realized that polar factors could play a much more important role in homolytic aromatic substitutions than that foreseen only few years ago and the possibility of substitutions of much greater synthetic potential became apparent [9,10].

The extensive investigation of the polar effects in homolytic aromatic substitutions has led to two important developments:

i) New free radical substitutions in homocyclic and heterocyclic aromatic series, characterized by very high positional and substrate selectivity, were found. The consequent synthetic interest is sometimes not lower than that of the main ionic substitutions, so that the homolytic substitution can now be considered a much more significant aspect of the aromatic substitution also from a synthetic point of view.

ii) Very useful models were developed for investigating the influence of the polar factors on the reactivity of free radicals, even moderately polar, such as carbon free radicals. These models are far the most general and sensitive used till now for determining the relative nucleophilicities of the carbon free radicals.

These two aspects are strictly connected because the causes determinig the synthetic interest of the new homolytic substitutions are the same as determine the interest of the ionic substitutions. The synthetic interest in fact becomes prominent when the polar effects significantly contribute in determining the global reactivity of the homolytic substitution.

At first the polarity of the radical was considered pre-eminent over all the other factors in determining the sensitivity to the polar effects, but soon it was realized that the polarity of the substrate is no less important, so that strong polar effects were observed not only with strongly polar radicals, but also with moderately polar radicals, if the aromatic substrate has a marked polar nature.

In this review the two developments concerning the synthetic aspects and the causes of the selectivity will be discussed in some homolytic substitutions with electrophilic and nucleophilic radicals.

II. Aromatic Substitution with Electrophilic Radicals. Homolytic Amination by N-Chloroamines

Very strongly electrophilic radicals are the amino radical cations, $R_2\overset{+}{\underset{\cdot}{N}}H$, which can be easily obtained from N-chloroamines; they are very versatile and react differently with alkanes [9], alkenes [11], alkynes and aromatics [11], involving potentially most of the organic compounds and showing in all cases an exceptional sensitivity to polar effects.

A. Products of Amination

The homolytic amination by N-chloroamines is of great synthetic interest, with a selectivity and versatility comparable to those of the most selective electrophilic substitutions. The overall stoichiometry is shown by Eq. (1)

$$Ar{-}H + R_2\overset{+}{N}HCl \longrightarrow Ar{-}\overset{+}{N}HR_2 + HCl \qquad (1)$$

Several factors contribute to the synthetic success of this substitution.

i) The ready availability and the relative stability of N-chloramines, which can be obtained in high yields by chlorination of the corresponding amines, make them convenient reagents for the aromatic amination.

ii) The experimental conditions are very simple; under the best conditions, the reaction is carried out at room temperature in the presence of a catalytic amount of metal salts (Fe^{2+}, Ti^{3+}, Cu^{+}, Cr^{2+}). Concentrated sulphuric acid, aqueous solutions of sulphuric acid and mixtures of sulphuric acid and organic solvents (acetic acid, methanol, nitroalkanes) are generally used as reaction media. The solubility of the aromatic substrate is not a severe limitation; a very low solubility, such as that of benzene, alkyl benzenes or byphenyl in sulphuric acid is sufficient for the reaction to be completed in a few minutes.

iii) The yields based on N-chloroamine are often high and those based on the aromatic substrate are for the most part quantitative. The side products come from the electrophilic chlorination of the aromatic substrates activated by strongly electron-releasing groups (OH, OR, NHCOR) and from benzylic chlorination of alkylbenzenes.

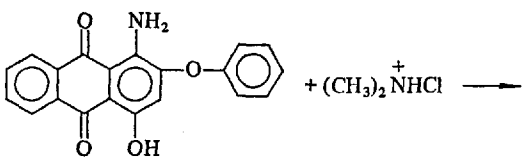
iv.) A variety of monoalkyl and dialkyl-N-chloroamines can be used. The reaction did not succeed with NH_2Cl owing to its lower stability in a strongly acidic medium. The main limitation, concerning the structure of N-chloroalkylamines, is due to steric effects. Thus yields based on N-chloramines decrease by increasing the bulk of the alkyl groups. No substitution takes place with N-chlorodiisobutylamine or N-chloro-di-*n*-butylamine; in this last case the Hofman-Löffler [12] reaction occurs. The competition of intramolecular hydrogen abstraction is not, however, the only cause of the lack of aromatic amination; in fact N-chloroalkylamines with less steric hindrance, but still capable of Hofman-Löffler rearrangement, such as N-chloro-*n*-butylamine and N-chloro-*n*-butylmethylamine also lead to aromatic amination.

v) A large variety of aromatic substrates can be readily aminated. The only limitation concerns aromatic rings with strong electron deficiency due to the presence of electron-withdrawing groups.

vi) The substrate selectivity is very high. This selectivity is exclusively due to polar effects and it is very advantageous from a synthetic point of view. Thus protonated anilines do not react under conditions in which benzene is easily aminated in a few minutes, so that the reaction does not generally lead to polysubstitution of an aromatic ring, even with total conversion of the aromatic substrate. The reaction is in fact carried out in acidic medium and the protonation of the amine formed completely deactivates the ring against subsequent attack. No other homolytic aromatic substitution in homocyclic series has this valuable synthetic characteristic.

vii) The positional selectivity is also very high, comparable with that of highly selective ionic electrophilic substitutions. The sensitivity to polar effects is mainly responsible for the positional selectivity. The great sensitivity to steric effects can contribute to further increasing the selectivity of the isomer distribution.

The amination of the anthraquinone dye 5 by N-chlorodimethylamine is a significant example of the versatility of this reaction also with complex molecules and of the exceptional substrate and positional selectivity. In fact 5 has 8 non equivalent free aromatic positions, but only the isomer 6 is formed in quantitative yield [13], with complete conversion of *5* by using only a light excess of N-chloroamine, and without formation of polysubstituted compounds [Eq. (2)].



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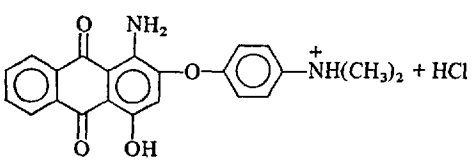

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(2)

The only exceptions, so far as orientation is concerned, are alkylbenzenes, which are attacked with poor selectivity at the meta and para positions.

The scope and the limitations of the general process will be illustrated by the behavior of the main classes of aromatic compounds.

1. Phenols, Phenol Ethers and Anilides

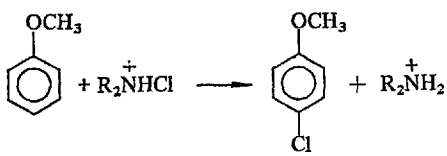
Since the reactivity of the homolytic aromatic amination is mainly determined by the electrophilic character of the amino radical cations, this class of aromatic compounds is strongly activated. Exclusive *o,p* orientation occurs without

formation of traces of the *m* isomers; the *o*:*p* ratio changes with the experimental conditions, but the *p*-isomer always prevails over the *o*-isomer. Aromatic amines cannot be aminated in the ring containing the amino group, whose protonation prevents further attack; with primary and secondary amines this limitation is easily overcome by acetylating the amine.

Table 3. Homolytic amination of phenols, phenol ethers and anilides

Aromatic substrate	N-chloro-amine	Orientation (%)	Yield (%)	Refs.
Phenol	Piperidine	*o* (9); *p* (91)	87	14)
Phenol	Dimethyl-amine	*p* *o*	59	14)
o—Cl-phenol	Piperidine	4 (80) + other isomers	92	14)
Anisole	Piperidine	*o* (8.9); *p* (91.1)	65	15)
Anisole	Dimethyl-amine	*o* (37); *p* (63)	54	15)
8-Methoxyquinoline	Dimethyl-amino	5 (100)	89	15)
Acetanilide	Dimethyl-amine	*p*, traces of *o*	93	16)
Acetanilide	Piperidine	*p*, traces of *o*	98	16)
Acetanilide	Methyl-benzyl-amine	*p* (100)	88	16)
Oxindole	Dimethyl-amine	5 (100)	86	16)

Table 3 shows some results obtained with these aromatic compounds, which require particular experimental conditions to overcome the competitive electrophilic chlorination [(Eq. (3)].



(3)

This side reaction can in fact be minimized or eliminated by working with a relatively high concentration of reducing metal salt and a low concentration of N-chloroamine. Since a too-high concentration of metal salt is not recommended, because it can increase the reduction of the N-chloroamine [Eq. (4)], the best experimental conditions are always a compromise between these opposite requirements depending on the ease of the electrophilic chlorination of each aromatic substrate

$$\overset{+}{R_2NH}Cl + 2\,Fe^{2+} \longrightarrow R_2NH + 2\,Fe^{3+} + Cl^- \qquad (4)$$

2. Polycyclic Aromatic Compounds

The results reported in Table 4 were obtained without performing optimization experiments; with the most reactive substrates, yields can probably be further increased by using the same experimental expedients employed with strongly

Table 4. Homolytic amination of polycyclic aromatic compounds

Aromatic substrate	N-chloroamine	Orientation (%)	Yield (%)	Refs.
Biphenyl	Dimethyl-amine	4 (100)	71	17)
4-Nitrobiphenyl	Dimethyl-amine	4′ (100)	86	18)
4-Nitrobiphenyl	Piperidine	4′ (100)	85	18)
4-Biphenyl-sulfonic	Dimethyl-amine	4′ (100)	86	18)
4-Dimethylacidamino-biphenyl	Dimethyl-amine	4′ (100)	90	18)
4-Chlorobiphenyl	Dimethyl-amine	4′ (100)	84	18)
Naphtalene	Dimethyl-amine	1 (97); 2 (3)	68	19)
1-Bromonaphtalene	Dimethyl-amine	5 (92) + other isomers	97	19)
Fluorene	Dimethyl-amine	2 (100)	63	17)
Fluorenone	Dimethyl-amine	2 (100)	98	18)

activated substrates. However, also in these cases, yields and selectivity are generally very high. The disubstitution observed with biphenyl and fluorene is only the result of the experimental conditions used: the hydrocarbons have a very low solubility, while the monosubstituted derivatives are completely soluble in the reaction medium. In both cases however, only one disubstituted isomer was obtained, even with total conversion of the aromatic substrates. This is another significant example of the exceptional selectivity of the reaction, because fluorene and biphenyl can give rise respectively to 16 and 9 different disubstituted isomers.

3. Aromatic Compounds with Strongly Electron-Withdrawing Groups

Substituents such as NO_2, CN, COR, $\overset{+}{N}R_3$ strongly deactivate the aromatic ring towards homolytic amination. The presence of electron-releasing groups in these compounds can counterbalance the deactivating effect of the electron-withdrawing group and allow the aromatic substrate to be easily aminated. Thus fluorenone is aminated with high yield and complete selectivity (Table 4) under conditions in which benzophenone does not react; the phenyl group in a biphenyl system strongly activates the *p*-position of the other phenyl group (the partial-rate factor of the *p*-position of biphenyl is 600). The presence of electron-withdrawing groups in polycyclic aromatic substrates (naphthalene or biphenyl derivatives of Table 4 or compound *5*) leads to amination of the unsubstituted rings.

4. Heteroaromatic Compounds

The homolytic amination is of less use with heterocyclic than with homocyclic aromatic compounds because either the heteroccylic compounds are too deactivated (protonated heteroaromatic bases) or they are unstable in the strongly acidic medium usually required by the reaction. Thus, quinoline cannot be aminated because the protonated heterocyclic nitrogen deactivates both rings. In the

8-methoxyquinoline, however, the electron-releasing effect of the methoxyl counterbalances the electron-withdrawing effect of the heterocyclic nitrogen and the homolytic amination leads in high yield to only one of the 6 possible isomers (Table 3). Heteroaromatics activated towards electrophilic species, such as furan and pyrrole, are not suitable for homolytic amination owing to their low stability under the reaction conditions. Thiophene, however, has been aminated to 2-alkylamino derivatives [13].

5. Halobenzenes and Cinnamic Esters

The halogens and the ω-substituted vinyl groups, Ar—CH=CH—X, where X is an electron-withdrawing group, deactivate the benzene ring but the orientation is prevalent in *o* and *p* positions, as for the ionic electrophilic substitutions (Table 5) Yields based on N-chloroamine are not very high with halobenzenes, owing to the deactivation of the aromatic ring and to a more marked reduction of the N-chloroamines [Eq. (4)]. Yields based on halobenzenes are always very high, the only side products being small amounts of anilines arising from the substitution of the halogen by the amino group.

Table 5. Orientation in the homolytic amination of halobenzenes [20] and methyl cinamate [21] by N-chlorodimethylamine

Aromatic substrate	*ortho*	*meta*	*para*
Chlorobenzene	18.5	5.5	76
Bromobenzene	21.6	3.4	75
Iodobenzene	6	8	86
Methyl cinnamate	—	—	100

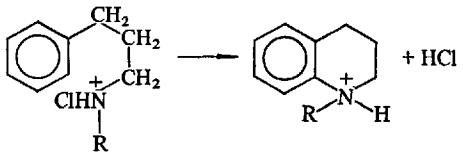
With cinnamic esters, the addition of N-chloroamines to the double bond competes with the aromatic attack [Eq. (5)]

$$C_6H_5{-}CH = CH{-}COOR + R_2\overset{+}{N}HCl \longrightarrow C_6H_5{-}CHCl{-}\underset{\underset{\overset{+}{N}HR_2}{|}}{CH}{-}COOR \qquad (5)$$

The ratio of attack at the double bond and at the aromatic ring is strongly affected by the reaction medium; the nuclear attack increases with the acidity of the medium. The sensitivity to steric effects reduces or prevents the substitution in the ortho positions.

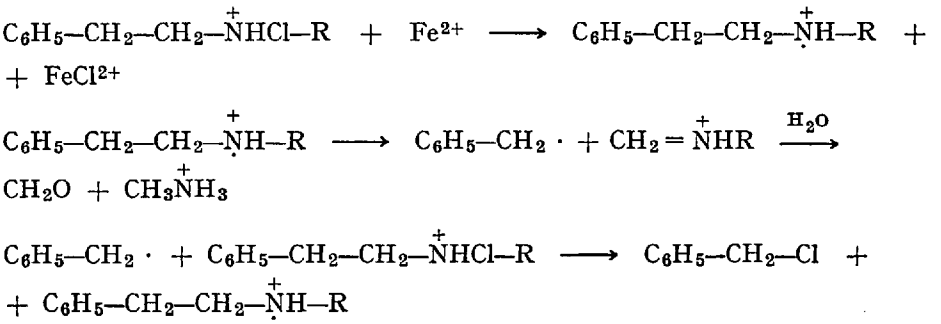
6. Intramolecular Amination

High yields of tetrahydroquinolines were obtained by intramolecular amination of N-chloro-3-phenylpropylamines [22,32] [Eq. (6)].



(6)

Lower yields of indoline were obtained from N-chloro-2-phenylethyl-amine owing to a competitive chain process leading to benzyl chloride, formaldehyde and methylamine (Scheme 1)



Scheme 1

7. Benzene and Alkylbenzenes

All the previous results show that the homolytic amination is not distinguishable from a highly selective electrophilic reaction, with regard to orientation and reactivity. In contrast, the results of Table 6 show that alkylbenzenes are the

Table 6. Homolytic amination of benzene and alkyl benzenes

Aromatic substrate	N-chloroamine	Conversion (%)	Yields[1] (%)	Refs.
Benzene	Dimethul-amine	79	100	24)
Benzene	Piperidine	70	100	24)
Benzene	Morpholine	70	100	24)
Benzene	Methyl-benzyl-amine	61	100	24)
Benzene	Methyl-n-propyl-amine	51	100	24)
Benzene	Methylamine	60	80	25)
Benzene	Ethylamine	58	75	25)
Benzene	Cyclohexyl	60	75	25)
Toluene	Dimethyl-amine	—	82[2])	26)
			o (9.6)	
			m (54.2)	
			p (36.2)	
t-Butylbenzene	Dimethyl-amine	—	72[2])	21)
			o (0)	
			m (22.8)	
			p (77.2)	

Table 6. Continued

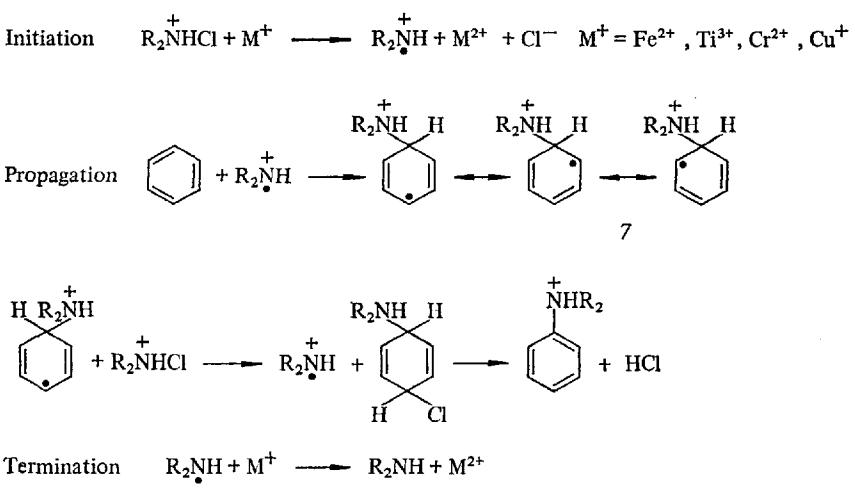
Aromatic substrate	N-chloroamine	Conversion %	Yields[1] %	Refs.
o-Xylene	Dimethyl-amine	—	96[2] 3 (4.8) 4 (95.2)	27)
m-Xylene	Dimethyl-amine	—	80[2] 2 (0.5) 4 (28) 5 (71.5)	26)

[1]) Based on converted benzene.
[2]) Based on N-chloroamine.

exception to this general behavior because a low selectivity is observed in meta and para positions. The reaction is very sensitive to steric effects so that no attack takes place in the *ortho* positions of *t*-butylbenzene. Also the positional selectivity observed with *o* and *m*-xylenes must be mainly ascribed to steric effects. Benzylic attack also occurs with alkylbenzenes; the ratio between benzylic and nuclear attack is strongly affected by the acidity of the medium and by the steric characteristics of the alkylamino radicals. The good yields based on N-chloroamines and on the aromatic substrates (Table 4) indicate however that under the best conditions the benzylic attack is rather low ($< 5\%$).

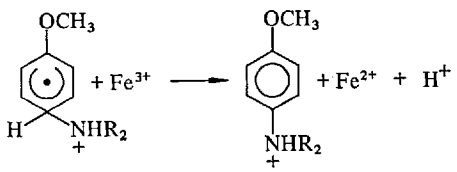
B. Mechanism of the Homolytic Amination

The free radical chain process of the Scheme 2 has been suggested on the ground of the general characteristics of the reaction [9,11].



Scheme 2

The incursion of a redox chain characterized by the Eq. (7) into the propagation steps of Scheme 2 has been suggested in the case of activated aromatic substrates [9,11] (phenol, phenol ethers, anilides)



(7)

This oxidation [Eq. (7)] is favored by the easier oxidability of the cyclohexadienyl radical and by the experimental conditions used in these cases, in which there is always a very low concentration of N-chloroamine and a relatively high concentration of metal salt.

Generally, when the electrophilic chlorination is not a serious competitive process, the reaction is in fact carried out in the presence of a very low concentration of metal salt, which has a very low solubility in the reaction medium, and high concentration of N-chloroamine.

To be acceptable, the mechanism of the homolytic amination must explain the two main macroscopic phenomena in apparent discrepancy: the very high positional and substrate selectivity with most of the aromatic substrates, and the low positional selectivity with alkylbenzenes.

The high positional and substrate selectivity, mostly observed and exclusively due to polar effects, has been ascribed to a transition state more similar to a charge-transfer complex [9,11,28] (*8*) than to the intermediate cyclohexadienyl radical (*7* in Scheme 2).

8

All the structural factors which favor an electron-transfer by stabilizing the polar form (*8*) decrease the activation energy and determine the very high sensitivity of the polar effects of the amination reaction.

The same exceptional sensitivity to polar factors was also observed with amino radicals in the addition to olefinic systems [11,29] (no addition takes place, for example, with acrylic monomers).

The partial rate factors and the isomer distribution in the amination by dimethylamino radical cation of toluene, isopropylbenzene, *t*-butylbenzene, biphenyl and naphtalene are reported in Table 7. These partial rate factors are far the highest ever observed in homolytic substitutions so that the general character of the homolytic amination allows a more relevant analogy to be drawn with the electrophilic substitutions than with the homolytic arylation, the only homolytic substitution for which numerous and accurate quantitative data exist in homocyclic aromatic series.

It has been verified that the isomer distribution is definitely not a result of isomerization, nor is it supposed to be due to superposition of an ionic (Kovacie

Table 7. Isomer ratios and partial rate factors for the amination of alkylbenzenes, biphenyl and naphtalene by Me_2NHCl [28]

Aromatic substrate	Isomer distribution (%)			Partial rate factors		
	ortho	*meta*	*para*	*ortho*	*meta*	*para*
Toluene	5.6	22.6	71.8	2	8	51
Isopropylbenzene	1.1	23.4	75.5	0.3	6.2	42
t-Butylbenzene	—	14.6	85.4	—	2.3	27
Biphenyl	—	—	100	—	—	598
Naphtalene [13]	(α) 97	(β) 3	—	(α) 95,700	(β) 2950	—

reaction [30]) and a radical amination (no reaction takes place in the absence of reducing metal salt under the same conditions).

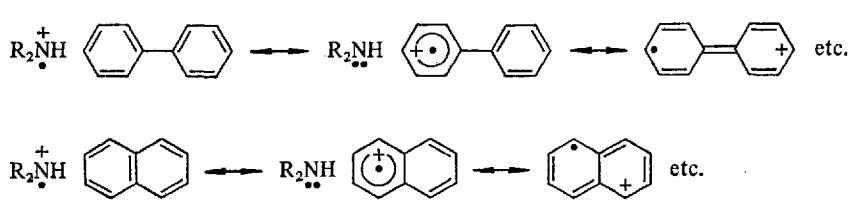
The most significant features of the results of the Table 7 are the following:

i) Very high sensitivity to steric effects. The absence of *ortho* isomers from *t*-butylbenzene and biphenyl and the low percentage from toluene and isopropylbenzene must in fact be attributed to steric effects; this phenomenon is also confirmed by the results obtained from xylenes (Table 6).

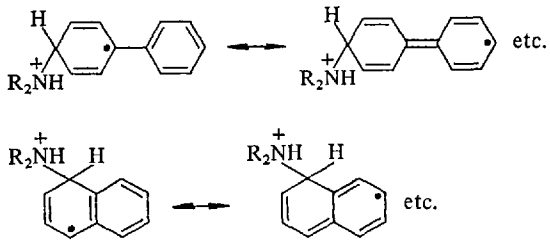
ii) Very high sensitivity to inductive effects. As the reactivity of *meta* positions can be considered as best reflecting the inductive effect due to the polar nature of the attacking radical, the partial rate factor for the *meta*-attack on toluene indicates that the sensitivity of the homolytic amination to inductive effects is very high, of the order of magnitude of the most selective electrophilic reactions.

Such high sensitivity of amino radical cations to steric and inductive effects was also observed in hydrogen abstraction processes from saturated hydrocarbons [31,32].

iii) High sensitivity to conjugative polar effects. The great positional and substrate selectivity of biphenyl and naphtalene may be in principle due to two separate causes: either to conjugative polar effects as for electrophilic reactions (Scheme 3) or to resonance stabilization of the intermediate radicals (Scheme 4). The first effect was considered much more important for two reasons: the high selectivity shown by aromatic compounds such as phenol, anisole, acetanilide and the fact that, in the absence of marked polar effects, as in homolytic phenylation of biphenyl, the partial rate factor of the para position has a rather low value (2.5), not differing greatly from those of the *ortho* (2.1) and *meta* (1.0) positions [2].



Scheme 3



Scheme 4

iv) The low positional selectivity of the alkylbenzenes, the increase from toluene to *t*-butylbenzene and the fact that the position 4 of biphenyl is considerably more activated than the corresponding position of toluene was explained by assuming that a transition state similar to a charge-transfer complex (*8*) is scarcely sensitive to hyperconjugative polar effects, while it is sensitive to inductive and conjugative polar effects. In terms of Hammett σ-constants [33], the low positional selectivity of toluene would be related to the σ_m^0 (−0.07) and σ_p^0 (−0.12) constants, but not to the σ_p^+ (−0.31), which would include hyperconjugation of the C—H bonds of the methyl and would considerably increase the positional selectivity. In contrast, the higher positional and substrate selectivity of biphenyl would be related to the σ_p^+ (−0.18) constant which includes resonance effects, σ_m^0 and σ_p^0 being respectively +0.10 and +0.04.

v) The sequences of the partial rate factors of the meta and para positions of toluene, isopropylbenzene and t-butylbenzene disagree with an inductive order of reactivity, as assumed in iv). Above all, the sequence of the partial rate factors of the *meta* positions is inexplicable on the basis of electronic effects. The apparent discrepancy was explained by the exceptional sensitivity to steric effects of dialkylamino radical cations. In a transition state similar to a charge-transfer complex, in which a defined primary valence bond is not developed, steric effects, including steric inhibition of solvation, would affect the total reactivity of the substrates and therefore also the partial rate factors of the *meta* and *para* positions [28]. The results obtained increasing the size of the alkyl group in dialkylamino radical cations (Table 8) support such an explanation. The results of Table 8 also show the influence of the structure of the amino radical on the selec-

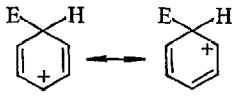
Table 8. Partial rate factors for amination of toluene, *t*-butylbenzene and *o*-xylene by amino radical cations [28]

Amine	Toluene			*t*-Butylbenzene		*o*-Xylene	
	o	*m*	*p*	*m*	*p*	3	4
Dimethylamine	2	8	51	2.3	27	6.4	230
Diethylamine	1	6.2	66	2.1	23.5	5.4	205
Piperidine	—	—	—	—	—	1.4	185
Morpholine	—	—	—	—	—	2.4	630

tivity. The highest selectivity was obtained with morpholine, the least basic amine (pK 5.6), while the lowest selectivity was observed with piperidine, the most basic (pK 2.8), their steric requirements being substantially identical, in agreement with the expected polar character.

On the basis of the mechanistic conclusion reached for the homolytic amination of alkylbenzenes, a new explanation was suggested for the much-discussed Baker-Nathan and inductive order in electrophilic substitutions of alkylbenzenes.

Most of the electrophilic substitutions follow the Baker-Nathan order (toluene more reactive than *t*-butylbenzene); for few substitutions (*i.e.* nitration) the opposite inductive order holds. According to the new explanation [28] the Baker-Nathan order would be associated with a transition state of the Wheland classical type (*9*),



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whereas the inductive order would hold when a charge-transfer character significantly contributes to the transition state, as for the homolytic amination. In nitration this charge-transfer character would be related to the particular stability of the NO_2 molecule (*10*).

10

III. Substitutions of Heteroaromatic Bases by Nucleophilic Carbon Free Radicals

The substitutions with nucleophilic radicals become particularly interesting only with electron-deficient aromatic substrates, as the ionic nucleophilic substitutions. Carbon free radicals are the most common nucleophilic radicals and they are obviously among the most important organic free radicals. Heteroaromatic bases on the other hand are electron-deficient aromatic substrates which readily react with nucleophilic species. The protonation of heteroaromatic bases strongly increases their electron-deficient nature and therefore the reactivity towards nucleophilic reagents, while the reactivity towards electrophilic species is strongly reduced. Thus the change from =CH−, to=$\overset{+}{\text{N}}$H−, in going from benzene to protonated pyridine, reduces the rate of tritiation about 10^{18} times [34]. Moreover, treating the heterocyclic nitrogen atom of the pyridine as a substituent in a benzene ring, the exceptionally high value of 4 was estimated for the σ-Hammett constant of the *p*-position in the protonated pyridine [35], the corresponding value of the unprotonated pyridine [36] being 0.93. The increased nucleophilic reactivity of protonated heteroaromatic bases cannot be mostly exploited with ionic nucleophilic species, which cause as primary effects deprotonation of the bases. This incompatibility does not occur with nucleophilic radicals; that made it possible to take advantage of the increased nucleophilic reactivity following protonation in order to find new types of homolytic substitutions characterized by very high positional and substrate selectivity and consequently by great synthetic interest. Moreover, protonated heteroaromatic bases have provided the most general and sensitive models till now used for determining the structure: nucleophilicity relationship of the main carbon free radicals. The factors which determine the nucleophilic behavior of the carbon free radicals have in fact an intrinsic theoretical interest and also greatly contribute to clarifying the causes of the observed selectivity in the aromatic substitutions.

A. Homolytic Alkylation

The synthetic success of the homolytic alkylation of heteroaromatic bases, as well as that of other free-radical substitutions, is mainly determined by the following factors:

i) Availability of the radical sources.

ii) Positional and substrate selectivity.

iii) Rearomatization of the intermediate σ-complex.

i) A large variety of thermal, redox and photochemical sources of alkyl radicals used in the alkylation of heteroatomic bases has been recently reviewed [10]. Alkylation in acidic aqueous medium has proved to be particularly convenient by using the oxidative decarboxylation of carboxylic acids by peroxydisulphate. This source is cheap, readily available and very versatile. A very large number of primary, secondary and tertiary alkyl radicals can be obtained from the corre-

sponding carboxylic acids under very simple experimental conditions. The alkyl radicals are formed according to the Schemes 5 und 6

$$S_2O_8^{2-} + Ag^+ \longrightarrow SO_4^{-\cdot} + SO_4^{2-} + Ag^{2+}$$
$$SO_4^{-\cdot} + Ag^+ \longrightarrow SO_4^{2-} + Ag^{2+}$$
$$R{-}COOH + Ag^{2+} \longrightarrow R\cdot + CO_2 + H^+ + Ag^+$$

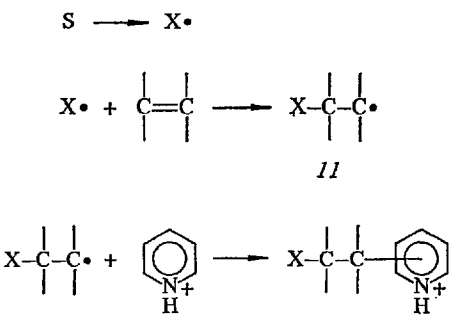
Scheme 5

$$S_2O_8^{2-} \longrightarrow 2\,SO_4^{-\cdot}$$
$$R{-}COO^- + SO_4^{-\cdot} \longrightarrow R\cdot + CO_2 + SO_4^{2-}$$

Scheme 6

The method of Scheme 5 permits carrying out the reaction in strongly acidic-medium and necessarily requires the presence of the silver salt catalyst [37]. The method of Scheme 6 uses solutions of carboxylic acids and sodium carboxylate; it is useful with heteroaromatic bases, such as thiazoles or diazines, which complex the silver salt and reduce its catalytic activity [38].

The high trapping effectiveness of protonated heteroaromatic bases permits the use of the homolytic alkylation as diagnostic criteria for revealing the presence of nucleophilic alkyl radicals in a reaction. Moreover, very unusual and sophisticated sources of alkyl radicals can be used also from synthetic point of view. A general procedure recently developed is shown by the Scheme 7



Scheme 7

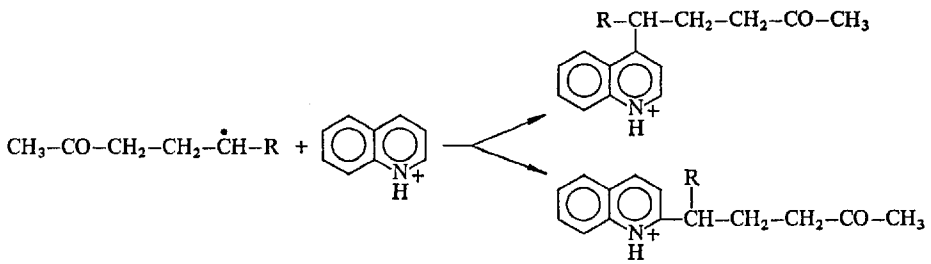
The radical source S gives rise to an electrophilic radical X·, which adds to the olefin, but does not attack the protonated base. The newly-formed alkyl radical (*11*) has enough nucleophilic character to be used for the selective alkylation of

protonated heteroaromatic bases. Typical examples [13] are shown by the Schemes 8 and 9

$$CH_3{-}CO{-}CH_3 + Mn^{3+} \longrightarrow CH_3CO{-}CH_2\bullet + Mn^{2+} + H^+$$

$$CH_3{-}CO{-}CH_2\bullet + CH_2{=}CH{-}R \longrightarrow CH_3{-}CO{-}CH_2{-}CH_2{-}\dot{C}H{-}R$$

12



Scheme 8

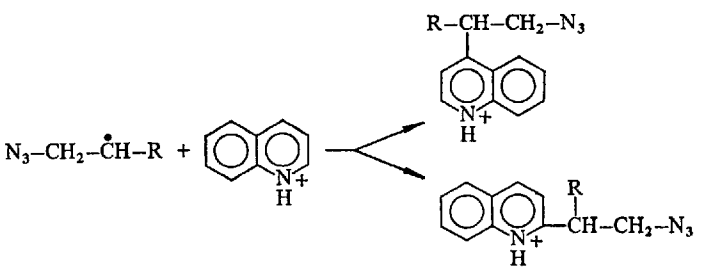
In the absence of protonated base, the radical *12* is oxidized to carbonium ion. The attack to the heteroaromatic base successfully competes with the electron-transfer oxidation.

$$H_2O_2 + Fe^{2+} \longrightarrow HO\bullet + FeOH^{2+}$$

$$HO\bullet + Fe(N_3)^{2+} \longrightarrow FeOH^{2+} + \bullet N_3$$

$$N_3\bullet + CH_2{=}CH{-}R \longrightarrow N_3{-}CH_2{-}\dot{C}H{-}R$$

13

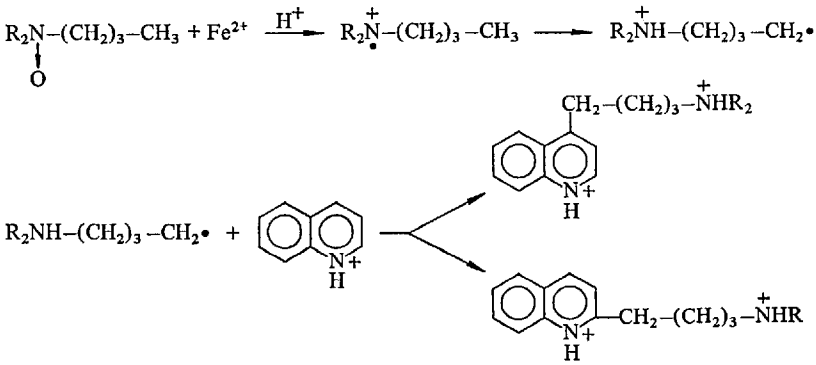


Scheme 9

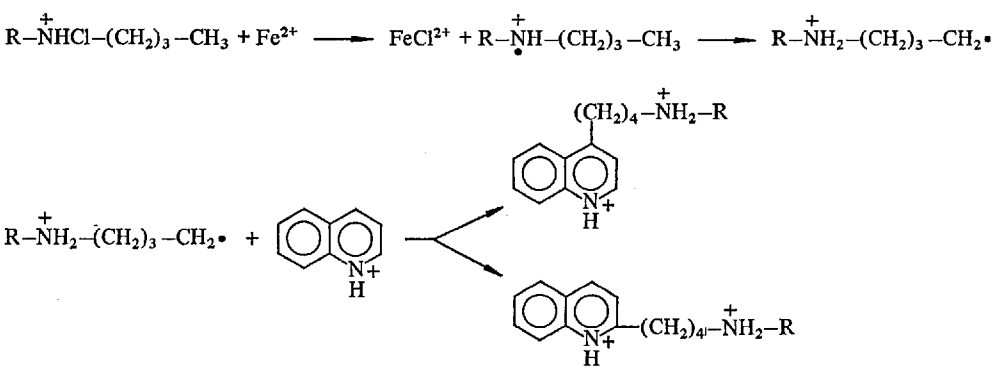
In the process of Scheme 9 the attack to the protonated base successfully competes with a ligand-transfer oxidation of the alkyl radical *13* [Eq. (8)]

$$N_3{-}CH_2{-}\dot{C}H{-}R + Fe(N_3)^{2+} \longrightarrow N_3{-}CH_2{-}\underset{\displaystyle N_3}{\underset{|}{CH}}{-}R + Fe^{2+} \qquad (8)$$

Alkyl radicals arising from rearrangements of amino radical cations have also been successfully used for the homolytic alkylation of protonated heteroaromatic bases [13,39] (Schemes 10 and 11)



Scheme 10



Scheme 11

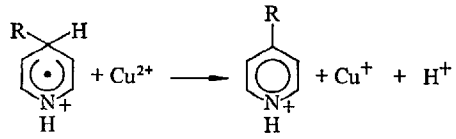
According to Scheme 11, the heteroaromatic attack overcomes the very fast competitive chlorine-transfer from the N-chloroamine [(Eq. (9)] which is a step of the free-radical chain in the Hoffman-Loeffler [12] reaction

$$\begin{aligned} &R\text{—}\overset{+}{N}H_2\text{—}(CH_2)_3\text{—}CH_2\cdot + R\text{—}\overset{+}{N}HCl\text{—}(CH_2)_3\text{—}CH_3 \longrightarrow \\ &\longrightarrow R\text{—}\overset{+}{N}H_2\text{—}(CH_2)_3\text{—}CH_2\text{—}Cl + R\text{—}\overset{+}{N}H\text{—}(CH_2)_3\text{—}CH_3 \end{aligned} \qquad (9)$$

These examples emphasize the very high versatility of the homolytic alkylation as far as the free-radical sources are concerned, and the possibility of obtaining complex substitutions in a simple way.

ii) The very high positional and substrate selectivity will be discussed in Section III.E; it greatly contributes to the synthetic success of the reaction.

iii) The rearomatization of the intermediate radical adduct (*14*) also affects the yields of the substitution. It is mainly connected with the oxidizing character of the free-radical sources. If the reactiohn medium is not sufficiently oxidizing, side reactions of the radical adduct (*14*) can become important (reduction, dimerization, disproportionation etc.). Often the presence of metal salts, such as Cu^{2+} or Fe^{3+}, is sufficient to eliminate or minimize these side reactions. These salts make the rearomatization of the radical adduct more effective (*14*) by an electron-transfer oxidation [Eq. (10)].



(10)

14

Thus the use of oxidative decarboxylation of carboxylic acids by peroxydisulphate as source of alkyl radicals is often effective enough in determining good yields of rearomatization of the radical adduct (*14*); the presence of small amounts of Fe^{3+} or Cu^{2+}, however, determines in all cases a very clean substitution reaction.

The fact that the electrophilic alkylation, which is very important in the homocyclic aromatic series is not applicable with the heteroaromatic bases and in any case would cause a completely different orientation also contributes to the synthetic interest of the homolytic alkylation. Moreover, the homolytic substitution occurs without rearrangement even in the case of the neopentyl radical [40], and without isomerization of the reaction products, which take place frequently in electrophilic alkylation.

Some results, obtained from decarboxylation of carboxylic acids are reported in Table 9. The good yields, the simple experimental conditions, the cheap and readily available sources of alkyl radicals, the large variety of alkyl radicals and heterocyclic compounds used, and the very high positional and substrate selectivity indicate that the homolytic alkylation of protonated heteroaromatic bases can be considered one of the main reactions of this class of compounds.

B. Homolytic Acylation

The homolytic acylation is practically unknown in the homocyclic aromatic series. The only intermolecular attack so far reported concerns the reaction of benzoyl radical and anthracene [49], in which the position 9 is highly reactive towards free radicals.

In contrast, the reaction is of great interest in heteroaromatic series, comparable to the corresponding electrophilic reaction in homocyclic series, as the results of Table 10 show. Several factors contribute to the synthetic interest of this substitution. Certainly, the most important factor is once again the complete selec-

Table 9. — Homolytic alkylation of protonated heteroaromatic bases by decarboxylation of carboxylic acids

Heterocyclic compound	Alkyl radical	Position of substitution (%)	Conversion (%)	Yields[1] (%)	Refs.
Pyridine	cyclohexyl	2(37); 4(63)	14	100	37)
Pyridine	*t*-Bu	2(32); 4(68)	18	100	37)
4-Cyanopyridine	Me	2(85); 2.6(15)	42	82	37)
4-Cyanopyridine	Et	2(78); 2.6(22)	77	81	37)
4-Cyanopyridine	*i*-Pr	2(67); 2.6(33)	86	88	37)
4-Cyanopyridine	*t*-Bu	2(87); 6(13)	95	98	37)
4-Cyanopyridine	$Ph—CH_2$	2; 2.6	85	94	41)
Quinoline	Me	2(23); 4(25); 2.4(52)	97	100	37)
Quinoline	*n*-Pr	2(28); 4(36); 2.4(36)	87	100	37)
Quinoline	*i*-Pr	2(13); 4(26); 2.4(61)	99	100	37)
Quinoline	cyclohexyl	2(24); 4(35); 2.4(41)	100	100	37)
Quinoline	*t*-Bu	2(100)	98	95	37)
Isoquinoline	Et	1(100)	33	100	37)
Isoquinoline	cyclohexyl	1(100)	99	84	37)
Acridine	*n*-Bu	9(100)	37	100	37)
Acridine	*i*-Pr	9(100)	66	100	37)
Quinoxoline	*i*-Pr	2(81); 2.3(19)	63	100	38)
Quinoxoline	*t*-Bu	2(100)	90	78	38)
Benzothiazole	*n*-Pr	2(100)	80	65	38)
Benzothiazole	*i*-Pr	2(100)	80	67	38)
Benzothiazole	*t*-Bu	2(100)	70	74	38)
Imidazole	*i*-Pr	2(100)	—	88[2]	42)
Imidazole	*t*-Bu	2(100)	—	80[2]	42)
Benzimidazole	cyclohexyl	2(100)	—	70[2]	42)
Benzimidazole	*t*-Bu	2(100)	—	68[2]	42)
5-Chloro-benzimidazole	*i*-Pr	2(100)	—	78[2]	42)
Pyrazole	*t*-Bu	5	64	72	43)
Pyridine-N-oxide	*t*-Bu	2(43); 4(57)	—	62[2]	44)

[1]) Yield based on the converted heterocyclic compound.
[2]) Yield based on the used heterocyclic compound; conversions are not generally quantitative

tivity of attack which takes place only at positions α and γ to the protonated heterocyclic nitrogen and does not normally lead to secondary products; therefore yields based on converted aromatic substrates are usually very high. A large variety of heteroaromatic bases and acyl radicals can be used under very simple experimental conditions. This direct homolytic acylation has no alternative in other synthetic methods; thus the classical eletrophilic acylation, very important in homocyclic aromatic series, does not work with heteroaromatic bases and in any case would yield substituent orientations different from those found in homolytic acylation.

Table 10. Homolytic acylation of protonated heteroaromatic bases

Heteroaromatic compound	Acyl radical	Position of substitution(%)	Yield[1] (%)	Ref.
4-Cyanopyridine	Et-CO	2	57	45,46)
Quinoline	Me CO	2 and 4(20); 2.4(80)	77	45,46)
Quinoline	*p*-Cl-benzoyl	2,4	68[2]	45,46)
4-Cyanoquinoline	Me CO	2(100)	93	45,46)
4-Cyanoquinoline	Benzoyl	2(100)	86	45,46)
4-Cyanoquinoline	*p*-Cl-benzoyl	2(100)	81	45,46)
4-Cyanoquinoline	*m*-Methoxybenzoyl	2(100)	87	45,46)
4-Cyanoquinoline	*m*-Me-benzoyl	2(100)	88	45,46)
2-Cyanoquinoline	Me CO	4(100)	90	45,46)
2-Cyanoquinoline	Benzoyl	4(100)	70	45,46)
4-Cl-quinoline	Me CO	2(100)	71	45,46)
4-Cl-quinoline	*p*-Me-benzoyl	2(100)	67	45,46)
2-Cl-quinoline	Benzoyl	4(100)	80	45,46)
2-Carboxyethyl-quinoline	Me CO	4(100)	79	45,46)
2-Carboxyethyl-quinoline	Benzoyl	4(100)	70	45,46)
2-Methoxyquinoline	Me CO	4(100)	75	45,46)
Acridine	EtCO	9(100)	76	45,46)
Acridine	Benzoyl	9(100)	54	45,46)
Phenantridine	Me CO	9(100)	62	45,46)
Phenantridine	Benzoyl	9(100)	50	45,46)
Pyrazine	EtCO	2.5	47[2]	45,46)
Pyrazine	*p*-Cl-benzoyl	2.5	40[2]	45,46)
Quinoxaline	Me CO	2(100)	70	47)
Quinoxaline	EtCO	2(100)	73	47)
Quinoxaline	*t*-BuCO	2(100)	62	47)
Quinoxaline	Benzoyl	2(100)	55	47)
Quinoxiline	2-Furyl CO	2(100)	51	47)
Benzothiazole	MeCO	2(100)	65	48)
Benzothiazole	Et CO	2(100)	69	48)
Benzothiazole	Benzoyl	2(100)	69	48)
Benzothiazole	*p*-Methoxybenzoyl	2(100)	80	48)
Benzothiazole	2-Furyl CO	2(100)	79	48)

[1]) Based on the used heterocyclic compound; conversions are not generally quantitative.
[2]) Monoacylderivatives are neglected.

The high reactivity of acyl radicals towards protonated heteroaromatic bases is shown by the behavior of the pivalyl radical, which attacks protonated heteroaromatic bases in competition with decarbonylation [Eq. (11)] which is itself a fast reaction.

$$(CH_3)_3C\text{—}\dot{C}O \longrightarrow (CH_3)_3C. + CO \qquad (11)$$

Two sources of acyl radicals proved to be useful for the homolytic acylation: hydrogen abstraction from aldehydes [45] [Eq. (12)] and oxidative dacarboxylation of α-ketoacids [46] [Eq. (13)].

$$R{-}CHO + X\cdot \longrightarrow R{-}\dot{C}O + H{-}X \qquad (12)$$

$$R{-}CO{-}COOH \xrightarrow{-e} R{-}\dot{C}O + CO_2 + H^+ \qquad (13)$$

The ease of the hydrogen abstraction from aldehydes by electrophilic radicals (RO. in particular) is related to the low dissociation energy of the bond RCO—H (87 ± 1 kcal/mol) and to the favorable polar effects, due to the contribution of the polar forms *15* to the transition state

$$R{-}C(=O)H \cdot X \leftrightarrow R{-}\overset{+}{C}O\,\dot{H}\,X^- \leftrightarrow R{-}\dot{C}O + H{-}X\,.$$

15

Decarboxylation of α-ketoacids takes place unter milder conditions than that of aliphatic carboxylic acids, due to the higher stability of acyl radicals compared with alkyl radicals. It was carried out with peroxydisulphate by the silver-catalyzed process of Scheme 12,

$$\begin{aligned} S_2O_8^{2-} + Ag^+ &\longrightarrow SO_4^{-\cdot} + SO_4^{2-} + Ag^{2+} \\ SO_4^{-\cdot} + Ag^+ &\longrightarrow SO_4^{2-} + Ag^{2+} \\ R{-}CO{-}COOH + Ag^{2+} &\longrightarrow R{-}\dot{C}O + CO_2 + H^+ + Ag^+ \end{aligned}$$

Scheme 12

or in absence of catalyst according to the Scheme 13 involving caroxylate ion

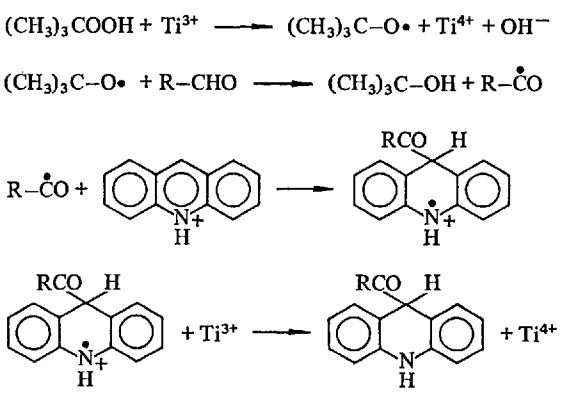
$$\begin{aligned} S_2O_8^{2-} &\longrightarrow 2\,SO_4^{-\cdot} \\ R{-}CO{-}COO^- + SO_4^{-\cdot} &\longrightarrow R{-}\dot{C}O + CO_2 + SO_4^{2-} \end{aligned}$$

Scheme 13

The introduction of an acyl group activates the heteroaromatic ring towards further acylation, which however always takes place exclusively at the positions α and γ to the heterocyclic nitrogen (the protonated nitrogen is by far the main activating factor, which determines the positional selectivity). Thus, if a heterocyclic compound has two reactive positions, it is easy to obtain diacyl derivatives, but only one isomer (for example 2,4-diacylderivatives in the case of quinoline), whereas the monoacylderivatives prevail only at very low conversions. Due to the nucleophilic character of alkyl and acyl radicals, the behavior of homolytic

alkylation and acylation of protonated heteroaromatic bases is therefore opposite to that of the corresponding electrophilic substitutions of homocyclic aromatics as concerns polysubstitution. An alkyl group slightly deactivates the heteroaromatic ring towards further homolytic alkylation so that monosubstitution can be obtained with partial conversion. If the heteroaromatic compound has only one α or γ free position (for example benzothiazole, 2- and 4-substituted quinolines, acridine, phenanthridine etc.), monoacylation occurs also with high conversion. It is possible, however, to obtain monoacylation even if the heterocyclic compound has more free reactive positions, by taking advantage of protonation equilibria of the starting base and the monoacylated products. These latter, being less basic, can undergo hydrolysis under suitable acidity conditions and precipitate from the aqueous solutions (in any case the protonated starting base is more reactive than the unprotonated monoacyl derivative; the activation produced by the protonation of the heterocyclic nitrogen is much higher than that of an acyl group).

With polycyclic heteroaromatic bases, such as acridine, the reaction can lead to dihydroderivatives when the metal salt used in the redox system for generating acyl radicals from aldehydes, has a marked reducing character [46] (Scheme 14).



Scheme 14

The high reactivity of acyl radicals towards protonated heteroaromatic bases allows their presence to be demonstrated in several oxidation [48] and rearrangement processes [50].

C. Homolytic α-Oxyalkylation

α-Oxyalkyl radicals can be easily obtained by hydrogen abstraction from alcohols and ethers. The ease of the abstraction has been related to the resonance stabilization [Eq. (14)], even if some studies [51,52] would appear to exclude this stabilization, and to polar factors [Eq. (15)] when the abstracting species, X·, is an electrophilic radical

$$R{-}O{-}\dot{C}H{-}R \longleftrightarrow R{-}\overset{+}{O}{-}\dot{\underset{-}{C}}H{-}R \qquad (14)$$

$$X \cdot H-\overset{|}{\underset{|}{C}}-O-R \leftrightarrow X^- \dot{H}\overset{|+}{\underset{|}{C}}-O-R \leftrightarrow \overset{|}{\underset{|}{C}}=\overset{+}{O}-R \qquad (15)$$

Oxidative decarboxylation of α-oxy carboxylic acids is another general route for α-oxyalkyl radicals [Eq. (16)]

$$R-O-CH_2-COOH \xrightarrow{-e} R-O-CH_2\cdot + CO_2 + H^+ \qquad (16)$$

α-Oxylalkyl radicals are more nucleophilic than the corresponding alkyl radicals. The high nucleophilicity determines high positional and substrate selectivity, but it also causes limitations in their use owing to the easy oxidability, which seriously competes with the aromatic attack. Thus methanol among the alcohols gives good results (Table 11), while *t*-α-hydroxyalkyl radicals arising from secondary alcohols are preferably oxidized to ketones [Eq. (17)]

$$\overset{OH}{\underset{|}{\overset{|}{R-C}}}-R \xrightarrow{-e} \overset{OH}{\underset{+}{\overset{|}{R-C}}}-R \longrightarrow R-CO-R + H^+ \qquad (17)$$

Probably the low strength of the bonds formed by *t*-hydroxyalkyl radicals makes the aromatic attack reversible and the oxidation of the radical easier.

Table 11. Homolytic hydroxymethylation of protonated heteroaromatic bases by methanol [53]

Heteroaromatic compound	Position of attack	Yield %[1]
Pyridine	2 and 4	40
Quinoline	2 and 4	53
2-Methylquinoline	4	86
4-Methylquinoline	2	43
Isoquinoline	1	31

[1] Based on the used heterocyclic compound; yields based on converted aromatic substrate are always higher.

Cyclic ethers also give good results (Table 12), while acyclic ethers undergo partial β-scission with formation of carbonyl and alkyl derivatives [Eq. (18)]

$$C_2H_5-O-\dot{C}H-CH_3 \longrightarrow CH_3-CH_2\cdot + CH_3-CHO\,. \qquad (18)$$

Thus ethyl ether gives α-ethoxyethylation and also appreciable amounts of ethyl and acetyl derivatives. The ethyl radical arising from Eq. (18) directly attacks the heteroaromatic base, while acetaldehyde acts as a source of acetyl radical.

Table 12. Homolytic α-oxyalkylation of protonated heteroaromatic bases by cyclic ethers [53]

Heteroatomic compound	Ether	Position	Yield[1])
4-Cyanopyridine	Dioxane	2	65
2-Methylquinoline	Dioxane	4	74
4-Methylquinoline	Dioxane	2	68
2-Cyanoquinoline	Dioxane	2	55
Pyrazine	Dioxane	2	68
Quinoxaline	Dioxane	2	56
Quinoxaline	Tetrahydro-furane	2	52
Quinoxaline	1,3-Dioxolane	2	70

[1]) Based on the used aromatic substrate; conversions were not determined

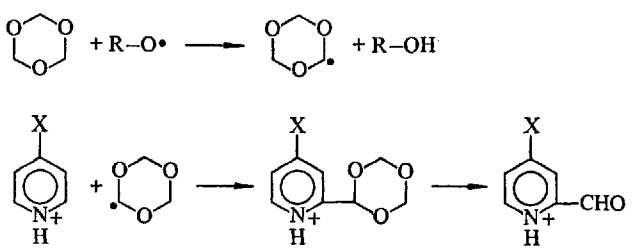
A wide variety of oxidants has been used to produce α-oxy-alkyl radicals from alcohols and ethers: hydrogen peroxide, hydroperoxides, perborate, peroxydicarbonate, peroxydisulphate. This last gives good results; the mechanism of the oxidation is controversial. Electron transfer from oxygen [Eq. (19)] has been proposed on the basis of spin-trapping experiments [54], followed by a hydrogen-transfer process [Eq. (20)]

$$SO_4^{\cdot-} + CH_3OH \longrightarrow SO_4^{2-} + CH_3\overset{+}{O}H \longrightarrow CH_3O\cdot + H^+ \qquad (19)$$

$$CH_3O\cdot + CH_3OH \longrightarrow CH_3OH + \cdot CH_2OH\,. \qquad (20)$$

It has been observed that the evidence is not unambiguous, however, since the spin label may have been formed by the oxidation of the methanol adduct [55].

The oxyalkylation by trioxane provides a direct route to heterocyclic aldehydes [56] (Scheme 15).



Scheme 15

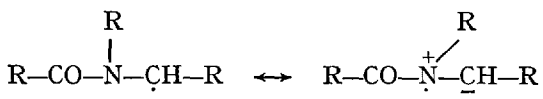
D. Homolytic Amidation and Carboxylation

Carbamoyl and α-N-amidoalkyl radicals can be easily obtained by hydrogen abstraction from formamides and N-alkylamides. They have a close analogy with acyl and α-oxyalkyl radicals. The nucleophilic character of the carbamoyl radical is explained by the fact that it can be considered an acyl radical in which the alkyl or aryl group is substituted by an amino group; it can be related with resonance structures like *16*

$$R_2N{-}\dot{C}=O \quad \longleftrightarrow \quad R_2N{-}\bar{C}=\overset{+}{O}\,.$$

16

The amino group would affect the polar character only by inductive effect owing to the σ nature of the radical. The nucleophilicity of the α-N-amidoalkyl radicals can be explained in the ground state by a conjugative electron-releasing effect (*17*), which causes a higher electron availability on the C-radical, and in transition state by the stability of the corresponding carbonium ion (*18*)



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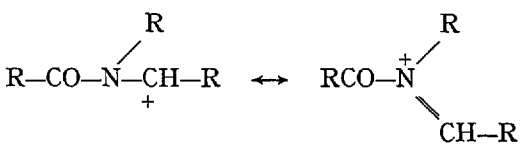

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1. Amidation by Formamide

Formamide is the most simple source of the carbamoyl radical [Eq. (21)]

$$R{-}O\cdot + H{-}CONH_2 \longrightarrow R{-}OH + \cdot CONH_2\,. \qquad (21)$$

Hydroxy and alkoxy radicals, obtained from hydrogen peroxide or alkyl peroxides were used [57,58]. Bond dissociation energies and polar effects preferentially promote the hydrogen abstraction from the C—H bond. However a hydrogen abstraction from the N—H bond would result without consequences because it would give rise to an electrophilic nitrogen-centered radical, unreactive towards protonated heteroaromatic bases.

Some results are shown in Table 13. The variety of heteroaromatic bases which can be used, the high selectivity, the often good yields and the simple experimental conditions contribute to the synthetic interest of this substitution. The polysubstitution by carbamoyl radical has the same characteristics of the acylation because the amido group ($CONH_2$) activates the heteroaromatic ring.

Table 13. Amidation of heterocyclic bases by formamide [58]

Heterocyclic base	Position of attack	Conversion %	Yield %
4-Acetylpyridine	2	46	98[1]
4-Carboxyethylpyridine	2	78	100[1]
4-Cyanopyridine	2	97	100[1]
Pyrazine	2	—	49[2]
Quinoline	2 and 4 (40%) 2,4-disulbstituted (60%)	92	100[1]
Lepidine	2	—	87[2]
Isoquinoline	1	41	61[1]
Acridine	9	97	100[1]
Quinoxaline	2	82	97[1]
Benzothiazole	2	—	68[2]
Benzimidazole	2	45	57[1]

[1] Yield based on converted heterocyclic base.
[2] Yield based on starting heterocyclic base; conversions were not determined.

2. Amidation by N-Alkylformamides

In N-alkylformamides, hydrogen abstraction can involve the formyl C—H bond with formation of carbamoyl radicals or the C—H bonds of the alkyl group with formation of amido-alkyl radicals. Bond dissociation energies and polar effects would preferentially cause the abstraction of an α-hydrogen among the different C—H bonds of the alkyl group. Since both types of radicals, carbamoyl and α-N-amidoalkyl, have nucleophilic character and easily attack protonated heteroaromatic bases, a very important role is played by the nature of the radical source, in order to have a selective and synthetically useful reaction. Two radical sources showed a high selectivity: the redox system *t*-BuOOH/Fe^{2+}, which mainly leads to carbamoyl radicals, and $S_2O_8^{2-}$, which leads to α-N-amidoalkyl radicals. This dramatic difference of selectivity under the same experimental conditions was explained by assuming two different mechanisms [59]; with *t*-BuOOH an actual hydrogen abstraction would occur [Eq. (22)]; with $S_2O_8^{2-}$ the primary process would be an electron transfer [Eq. (23)].

$$(CH_3)_3C{-}O\cdot + H{-}CO{-}N(CH_3)_2 \longrightarrow (CH_3)_3C{-}OH + \cdot CON(CH_3)_2 \qquad (22)$$

$$(CH_3)_2N{-}CHO + SO_4^{-\cdot} \longrightarrow SO_4^{2} + (CH_3)_2\overset{+}{\dot{N}}{-}\dot{C}HO \longrightarrow \dot{C}H_2{-}\underset{\displaystyle CH_3}{\underset{|}{N}}{-}CHO. \qquad (23)$$

The hydrogen abstraction is less selective with other radical sources and both types of radicals are formed in significant amounts, as shown in Table 14.

Table 14. Homolytic amidation ($CONME_2I$) and amidoalkylation ($CH_2N(Me)COHII$) of protonated lepidine by dimethylformamide [59]

Radical source	Position of attack	I %	II %
t-BuOOH + Fe^{2+}	2	97	3
H_2O_2 + Fe^{2+}	2	85	15
S_2O_8 + Fe^{2+}	2	2	98
t-BuOOBu-t	2	33	67
Ph COOCO Ph	2	40	60

3. Amidation by N-Alkylamides Different from Formamides

N-alkylamides different from formamides exclusively give rise to α-N-amidoalkylation. Most of the study was accomplished with N-alkylacetamides because only the N-alkyl groups are involved in the substitution. The C—H bond in α to the carbonyl group can be also abstracted with some ease owing to the resonance stabilization (*19*)

$$R\text{—}\dot{C}H\text{—}CO\text{—}NR_2 \longleftrightarrow R\text{—}CH{=}C(O\cdot)\text{—}NR_2$$

19

but the proximity of the carbonyl group induces electrophilic character to the radical, which is unreactive towards protonated heteroaromatic bases. Some results with acetamides are shown in Table 15.

Table 15. Homolytic α-N-amidoalkylation of protonated heteroaromatic bases by N-alkylacetoamides [58]

Heterocyclic compound	Amide	Position of attack	Yield %
Quinoline	N-methylacetamide	2 and 4	48
Quinoline	N,N-dimethylacetamide	2 and 4	74
Lepidine	N-methylacetamide	2	71
Lepidine	N,N-dimethylacetamide	2	85
Lepidine	N-ethylacetamide	2	62
Lepidine	N,N-dimethylurea	2	38
Quinaldine	N-methylacetamide	4	56
Quinaldine	N,N-dimethylacetamide	4	81
Quinaldine	N-cyclohexylacetamide	4	52
Quinaldine	N-acetylpiperidine	4	37
Benzothiazole	N-methylacetamide	2	55
Benzothiazole	N,N-dimethylacetamide	2	70

4. Carboxylation

Alkoxycarbonyl radicals, ROĊO, have structural features very similar to carbamoyl radicals. The higher electronegativity of the oxygen atom compared with the nitrogen atom makes them somewhat less nucleophilic. Their polar character is however sufficient to determine a high selectivity with consequent synthetic interest, as shown by the results of Table 16, obtained by using ethyl pyruvate and H_2O_2 as radical source [Eq. (24)]

$$CH_3{-}CO{-}COOC_2H_5 + H_2O_2 \longrightarrow CH_3{-}\overset{HO}{\underset{}{\overset{|}{C}}}(OOH){-}COOC_2H_5$$

$$CH_3{-}\overset{HO}{\underset{}{\overset{|}{C}}}(OOH){-}COOC_2H_5 + Fe^{2+} \longrightarrow CH_3COOH + \cdot COOC_2H_5 + Fe^{3+} + OH^- . \qquad (24)$$

Table 16. Homolytic ethoxycarbonylation of protonated heteroaromatic bases by ethyl pyruvate [60]

Heterocyclic compound	Position of attack	Conversion %	Yield %
Quinoline	2(4.5); 4(17.5); 2.4(78)	76	92
Pyrazine	2(48); disubstituted (52)	90	85
Quinoxaline	2(77); 2.3(23)	91	90
Benzothiazole	2(100)	96	85

Other radical sources involve hydrogen abstraction from alkyl formates [Eq. (25)] and oxidation decarboxylation of semiesters of oxalic acid [Eq. (26)]

$$RO\cdot + H{-}COOR \longrightarrow R{-}OH + \cdot COOR \qquad (25)$$

$$HOOC{-}COOR \xrightarrow{-e} H^+ + CO_2 + \cdot COOR . \qquad (26)$$

The alkoxycarbonyl groups, as well as the acyl and amido, activate the heterocyclic ring towards further carboxylation, facilitating polysubstitution if more α and γ positions are free.

E. Structure: Nucleophilicity Relationship of Carbon Free Radicals

The high positional and substrate selectivity of the homolytic substitutions of protonated heteroaromatic bases with nucleophilic carbon free radicals is one of the main factors determining the synthetic success of these reactions. In this section it will be shown that the selectivity is mainly determined by the influence of polar effects. As the extent of these effects is much larger than that previously observed in all the other reactions of the same radicals, these reactions have provided very useful models for determining the structure: nucleophilicity relationship of the most common carbon free radicals.

Particularly suitable models were provided by the homolytic substitutions of 4-substituted pyridines and 2- and 4-substituted quinolines, which are selectively attacked respectively in the positions 2, 4 and 2 by nucleophilic carbon free radicals. The positional selectivity is in fact always determined by the protonated heterocyclic nitrogen, which has a much more activating effect than the common substituents.

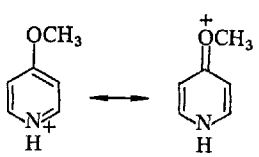
The method, by using these models, is based on the assumption that the radical-stabilizing effects are minimized and the strengths of the bonds formed between the free radicals and the heteroaromatic ring are not substantially affected by the fact that the substituents are in *meta* to the position of attack in the heterocyclic ring. Thus the sequence of the reactivities of the meta positions to the substituents can be considered as best reflecting the effect of the polar nature of the attacking radical.

The results of the Table 17 show the substrate selectivity of the homolytic alkylation of 4-substituted pyridines by the simplest types of alkyl radicals;

Table 17. Relative rates in the homolytic alkylation of protonated 4-X-pyridines [61]

X	K_X/K_H					K_X/K_{Cl}
	Me	*n*-Pr	*n*-Bu	*sec*-Bu	*t*-Bu	Benzyl[41]
CN	12.45	19.70	20.30	259.00	1890	233.5
$COCH_3$	3.60	5.57	5.60	55.60	144	11.5
Cl	2.38	—	—	—	11.12	1
H	1	1	1	1	1	—
CH_3	0.53	0.35	0.32	0.28	0.15	—
OCH_3	0.27	0.12	0.10	0.02	0.0054	—

in all cases the substitution takes place exclusively in position 2. On the basis of the orientation and reactivity, all the radicals of Table 17 have a net nucleophilic character and this character increases from methyl to primary, secondary, tertiary and benzyl radicals. A Hammett correlation was not observed, due to the fact that the methoxy group is deactivating, despite the positive value of its σ_m constant, and chlorine is less activating than would be expected from its σ_m constant. Such behavior is however peculiar to the pyridine ring in reactions with nucleophilic species [61] (ionic and radical). The phenomenon was explained by enhanced conjugation between electron-releasing groups and heterocyclic nitrogen (*20*)



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resulting in higher electron availability in the heteroaromatic ring, which reduces the electron-accepting capacity in the rate-determining step. The strong polar effect of the protonated heterocyclic nitrogen clearly appears from the exceptional selectivity observed with pyrazine in concentrated sulphuric acid, in which both nitrogen atoms are protonated. The change from =CH— to =N— and $=\overset{+}{N}H-$, in going from protonated pyridine to monoprotonated and diprotonated pyrazine, increases in fact the rates of alkylation by *n*-butyl radical 30 and 2,500 times respectively [13]. With the more nucleophilic secondary and tertiary alkyl radicals, the differences of reactivity are too large to permit analogous determinations in strong acidic medium. A Hammett correlation is observed, considering only the electron-withdrawing groups in 4-substituted pyridines and treating an heterocyclic nitrogen atom of pyrazine as a substituent in position 4 of the pyridine ring. The σ_m values obtained for =N— (0.6) and $=\overset{+}{N}H-$ (1.6) agree well with the values obtained from kinetic data of ionic reactions (0.62 for =N— [36] and 1.584 for $=\overset{+}{N}(CH_3)-$ [62]). That indicates that the activation of the heterocyclic nitrogen is due to polar effect, which is strongly enhanced by the protonation.

The good correlations [61] observed between the relative rates of Table 17 and the chemical shifts of the protons in position 2 of protonated 4-substituted pyridines would indicate that the anisotropic contributions and the intermolecular interactions are substantially identical and that the major factor controlling both the chemical reactivity and the relative shielding of the hydrogen nuclei in the *meta* position to the substituent is the electron density in position 2 of the molecule. The slopes of the plots (Table 18) give a measure of the different selectivity, exclusively due to polar effects, and therefore a measure of the relative nucleophilicities of the free radicals involved. This interpretation is further supported by the linear correlations [61] between the relative rates and the pKa of the 4-substituted pyridines.

Table 18. Slopes [61] from correlations of relative rates and chemical shifts

Alkyl radical	Slope
Me	2.224
n-Pr	3.014
n-Bu	3.130
sec-Bu	5.573
t-Bu	7.455
Benzyl	7.494

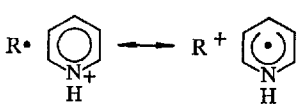
In Table 19, the relative rates, obtained in the alkylation of 3-substituted pyridines by *t*-butyl radical, are reported. The exceptional positional selectivity (only the position 6 is attacked) results from combined polar and steric effects. A satisfying Hammett correlation was observed with σ_p; the value of $\varrho = 5.5$ is of the same order of magnitude of those of nucleophilic aromatic substitutions, indicating a high degree of charge development in the transition state.

Table 19. Relative rates in homolytic t-butylation of 3-(a)- and 4-(b)-X-substituted pyridines, in nucleophilic methoxydechlorination of 4-(c)-X-substituted-2-chloroquinoline and amination of 1-Cl-2-NO_2-4-(d)- and 5-(e)-X-benzenes with piperidine

X	a[63]	b[61]	c[64]	d[65]	e[65]
CN	4380	1890	536	5890	58.5
$COCH_3$	956	144	—	—	—
$COOCH_3$	509	—	—	922	5.3
Cl	10.7	11.1	17.75	6.2	32.3
H	1	1	1	1	1
CH_3	0.2	0.15	0.395	0.15	0.85
OCH_3	—	0.0054	0.219	0.025	4.2

In Table 19 the polar effects of the substituents in *meta* and *para* positions in classical nucleophilic substitutions are also compared with those of the homolytic alkylation of 3- and 4-substituted pyridines by *t*-butyl radical. A very striking feature is the exceptional sensitivity to the polar effects of the substituents, of the same order of magnitude or higher in homolytic alkylation by *t*-butyl radical than in classical nucleophilic substitutions. The contrast is particularly striking with the generalization still accepted that the only factor directing the course of the reactions of alkyl radicals, provided steric and solvent effects do not intervene, would be the relative stability of the reaction intermediates or, more exactly, the incipient radical in the transition state [66]. Interesting is also the difference of selectivity determined by substituents in *meta* and *para* positions in the homolytic *t*-butylation; this difference is in the expected direction, but it is too low in comparison with that of nucleophilic substitutions.

The general behavior was explained by a mechanistic picture involving a transition state similar to a charge-transfer complex [40,61,63] (*21*).



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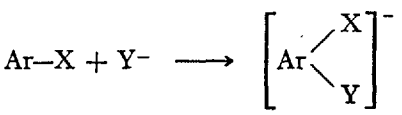
The degree of charge development in the transition state depends on the donor character of the radical and the acceptor character of the aromatic ring, a complete electron-transfer being the limit case. Because a primary valence bond is not developed in the transition state, the whole electron-deficiency of the heterocyclic ring is more important than the specific positional effect of the substituents in determining the reaction rates. The transition state of the nucleophilic substitutions, similar to a σ-complex (*22*), in which a primary valence bond is developed,

can, on the contrary, be stabilized in quite a different way by a substituent depending on its *meta* or *para* position



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That would explain the fact that in nucleophilic substitutions the Hammett correlations fit better with σ_p^-, while in homolytic alkylation, σ_p give the best correlation.

The main problem arising from these results concerns the causes which determine such macroscopic polar effects, which have no precedent of the same order of magnitude in the previously known reactivity of carbon free-radicals.

From the results obtained with a large variety of carbon free radicals, the author has suggested that the following factors would mainly contribute to determining the sensitivity to the polar effects and the relative nucleophilicities of these free-radicals.

1. Polarity of the Radical

The polarity of the free radicals is certainly one of the main factors determining the sensitivity to polar effects. Often the terms of polarity and electrophilicity and nucleophilicity of the free radicals are considered synonymous.

As concerns carbon free radicals, a measure of the polarity can be offered by the ionization potentials. Now the ionization potentials of alkyl radicals with very similar structure correlate [41] well with the slopes of the Table 18, which give a measure of their relative nucleophilicities. The good correlation indicates that actually the ionization potential is one of the main factors responsible for the sensitivity to polar effects, in agreement with a transition state similar to a charge-transfer complex (*21*). Other carbon free radicals with different structures, such as phenyl, benzyl, allyl, vinyl and acyl radicals do not show the same good correlation. It even happens that the sequence of the ionization potentials is the opposite of that of the relative nucleophilicities. This is the case in benzyl and *t*-butyl radicals: the ionization potential of the benzyl radical is higher (7.27 and 6.93 e.v. respectively for $PhCH_2$. and Me_3C.), which however is slightly more nucleophilic (Table 18).

This behavior is, however, not surprising for two reasons: the ionization potentials are determined in gas phase and the reactions take place in polar solvents; moreover there is good evidence that other factors play an important role in determining the sensitivity to polar effects.

The identification of the polarity with electrophilicity and nucleophilicity of the free-radicals must be therefore considered an oversimplification; the most polar radical is not necessarily always the most sensitive to the polar effects.

2. Polarity of the Aromatic Substrate

A transition state similar to a charge-transfer complex (*21*) requires both donor and acceptor character of the two partners. Now the reactions with nucleophilic carbon free radicals either do not occur (for example with *t*-butyl, benzyl, acyl, α-oxyalkyl and α-amidoalkyl radicals), or have a poor interest in benzene series because, in addition to the low selectivity, yields are usually low, due to side reactions which seriously compete with the simple substitution reactions. Thus the homolytic substitution by nucleophilic carbon free radicals does not offer suitable reagent models in benzene series for a satisfactory evaluation of the influence that the structure of the carbon free radical has on the reactivity. Moreover the few quantitative data, available with methyl, cyclopropyl and cyclohexal radicals, indicate that the effect of the substituents in benzene series is not only quantitatively, but also qualitatively different from that in protonated pyridine series. That is clearly shown by the comparison of the results obtained with cyclohexyl and sec-butyl radicals (Table 20), in which the benzene ring is slightly activated by both a strongly electron-withdrawing group (CN) and a strongly electron-releasing group (OCH_3); the protonated pyridine ring, on the contrary, is strongly activated by the cyano group and strongly deactivated by the methoxy group.

Table 20. Relative rates in homolytic cyclohexylation of X-substituted benzenes and butylation of 4-X-substituted pyridines

X	Benzene series cyclohexyl radical [67]	Pyridine series sec-butyl radical [61]
CN	27	259
H	1	1
OCH_3	2.3	0.02

Cyclopropyl radicals show a selectivity substantially identical to that of phenyl radical in benzene series (Table 21); the results of Table 22 indicate that in protonated pyridine series, the selectivity of cyclopropyl radical is much higher than

Table 21. Isomer ratios and relative rates in homolytic phenylation[1] and cyclopropylation [68] of benzene derivatives, C_6H_5—X

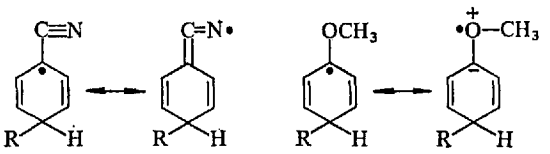
X	Phenylation (%)				Cyclopropylation (%)			
	ortho	*meta*	*para*	K_H^X	*ortho*	*meta*	*para*	K_H^X
CN	60	10	30	3.7	62	11	27	3.6
Cl	50	32	18	1.1	59	27	14	1.8
CH_3	67	19	14	1.2	—	—	—	1.0
Bu(*t*)	31.7	24	49	0.64	2	64	34	0.6
OCH_3	69	18	13	1.7	70	18	12	1.9

Table 22. Isomer ratios and relative rates in homolytic phenylation [69] and cyclopropylation [70] of protonated 4-X-pyridines

X	Phenylation (%)		K_H^X of	Cyclopropylation		$K_{CH_3}^X$
	α	β	α-position	α	β	
CN	62.5	37.5	1.9	100	—	14
Cl	79	21	1.6	—	—	—
H	64.5	13.5	1	—	—	—
CH_3	84	16	0.6	100	—	1
OCH_3	80	20	0.3	—	—	—

that of phenyl radical under the same experimental conditions and with the same radical source.

This dramatic difference of behavior has been interpreted in terms of transition state [61]. The benzene series has not enough electron-deficient character to determine a transition state similar to a charge-transfer complex, so that the reaction rates would be affected more by the stability of the intermediate cyclohexadienyl radicals (*23*, *24*) than by polar effects



23 *24*

In protonated pyridine series, a transition state similar to a charge-transfer complex (*21*) would allow the clear distinguishing even of carbon free radicals differing little in nucleophilicity, such as methyl, cyclopropyl and phenyl radicals.

The polarity of the substrate is therefore not less important than the polarity of the free radical in determining the sensitivity to polar effects and the consequent selectivity and synthetic interest.

3. Strengths of the Bonds Formed between Free Radicals and Aromatic Rings

The strengths of the bonds formed between various carbon free radicals and a heteroaromatic compound are not known, but it can be assumed that the sequence reproduces that of Table 23.

An explanation of the selectivities observed with substituted pyridines, which does not involve polar effects, could be similar to that suggested by Zavitsas *et al.* [73] for the hydrogen abstraction from substituted toluenes. The electron-withdrawing substituents would increase and the electron-releasing substituent would decrease the strength of the bonds formed between the carbon free radicals and the pyridine ring, affecting in this way the reaction rates. There is, however, no evidence supporting such interpretation. The selectivities observed with many

Table 23. Bond dissociation energies of C—H bonds [71]

	$K_{cal/mol}$
Me—H	104
Et—H	98
i-Pr—H	95
t-Bu—H	91
$PhCH_2$—H	85
CH_2=$CHCH_2$—H	85
RCO—H	87 ± 1
HOOC—H	90
$HOCH_2$—H	93
Cyclopropyl—H[72]	100.7
Cyclobutyl—H[72]	95.7
Cyclopentyl-H[72]	94.3
Cyclohexyl-H[72]	94.9
CH_2=CH—H	103
Ph—H	112

carbon free radicals follow often but not always the sequence of the expected strengths of the formed bonds. Thus acyl radicals, which are expected to form weaker bonds than alkylradicals, are much less selective than secondary and tertiary alkyl radicals. Above all, carbon free radicals with electrophilic character, due to the proximity of electron-withdrawing groups (X—$\dot{C}H_2$, X=—CN, —COR, —$\overset{+}{N}H_3$), do not react at all with protonated heteroaromatic bases, thus showing the basic importance of the polar effects. It was suggested [63,70] that the dissociation energy of the bonds formed between carbon free radicals and the heterocyclic ring is actually an important factor responsible for the selectivity observed, but only because it contributes to determining the extent of charge transfer in the transition state. All other conditions being equal, the lower the strength of the bond formed, the more the transition state would be similar to a charge-transfer complex according to the Hammond postulate, and the more sensitive the reaction to polar effects. In this sense, the strength of the bonds formed is one of the factors contributing to the determination of the relative nucleophilicities of the carbon free radicals. Thus the lower dissociation energy expected for the bond formed by the benzyl than by the *t*-butyl radical can be considered one of the factors contributing to determining the sequence of nucleophilicities, which does not follow that of the ionization potentials.

4. Electronic Configuration of Carbon Free Radicals

The hybridization of the carbon free radicals affects their polarity, polarizability and also the strength of the bonds formed. The *s*-electrons are, on the average, closer to the nucleus than *p*-electrons and therefore experience a greater interac-

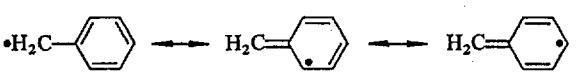
tion with the nucleus, that is, *s*-orbitals have a higher electronegativity than *p*-orbitals. It is therefore easier to remove an electron from a *p*-orbital than from an *s*-orbital of the same quantum number in similar structures. The larger the contribution of *s*-character to the hybrid orbital, the greater the electronegativity of that hybrid orbital and the lower the nucleophilicity of the corresponding radical, if all other conditions are equal. Moreover the greater the *s*-character, the greater the strength of the bonds formed in similar structures.

a) Alkyl and Acyl Radicals. Alkyl and acyl radicals both have a clear-cut nucleophilic character, but their nucleophilicities are determined by different structural causes. The alkyl radicals are generally π-type radicals; the unpaired electron occupies a p orbital, which plays an important role in determining the sensitivity to polar effects. The acyl radicals are σ-type radicals, in which the unpaired electron is located mainly in a hybrid orbital on the carbon atom. Bond strengths (Table 24) indicate that there is no stabilization of the acyl radicals

Table 24. Bond strengths of X—H and Y—H bonds

X	K—H [71] $K_{cal/mol}$	Y	Y—H [74,75] $K_{cal/mol}$
CH_3	104	HCO	87
CH_3CH_2	98	CH_3CO	87
$PhCH_2$	85	PhCO	86.9
$CH_2{=}CHCH_2$	85	$CH_2{=}CHCO$	87.1

due to substitution of a hydrogen atom by a methyl, vinyl or phenyl group, contrary to the behavior of the alkyl radicals. Also the ESR spectrum supports the lack of stabilization of the benzoyl radical due to conjugation of the phenyl group. The major proton hyperfine splitting is due to the *meta* hydrogen atoms; this is in contrast with the familiar *para* > *ortho* > *meta* trend observed with the benzyl π-radical (Table 25), due to the resource structures (*25*, *26*)



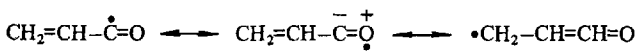
25 *26*

Table 25. Hyperfine coupling constants (*a*) of benzyl [76] and benzoyl[77] radicals

a	$PH\dot{C}H_2$	$Ph\dot{C}O$
a—H	5.17	0.1
a_m—H	1.77	1.16
a_p—H	6.19	0.1

Stabilization of benzoyl and acrylyl radicals could be formally considered in terms of resonance structures (*27—31*)

27 *28* *29*



30 *31*

Actually both thermochemical and ESR data suggest that the stabilization of benzoyl and acrylyl radicals is determined only by conjugation with the lone pair of the oxygen atom (*27, 30*), with no contribution whatsoever from structures *28, 29, 31*. The nucleophilic character of the acyl radicals can be related in the ground state to resonance structures like *27* and *30* and in the transition state (*21*) by the stability of the acyl cations ($R-\overset{+}{C}O$).

The relative rates of acetylation and benzoylation of 2- and 4-substituted quinolines are reported in Tables 26 and 27. The use of quinoline models with only one reactive position is more suitable than that of 4-substituted pyridines because

Table 26. Relative rates of acylation of 2-substituted quinolines [78]

Substituent	Acetylation	Benzoylation
OMe	0.23	0.21
Me	1.00	1.00
H	2.49	2.77
Cl	5.45	5.82
COOEt	11.80	24.20
CN	27.00	48.00

Table 27. Relative rates of acylation of 4-substituted quinolines [78]

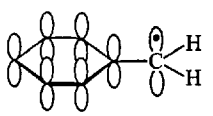
Substituent	Acetylation	Benzoylation
OMe	0.032	—
Me	1.00	1.00
Cl	4.65	4.84
COOEt	16.80	29.50
CN	49.50	129.90

the acyl group activates the pyridine ring towards further acylation so that it is difficult to avoid completely the formation of 2,6-diacylderivatives, even with low conversion of the 4-substituted pyridines.

To correlate the two series of substituted pyridines and quinolines, relative rates of alkylation were determined also with 2- and 4-substituted quinolines. The following sequence of nucleophilicity of alkyl and acyl radicals was obtained: methyl < primary alkyl < acetyl < *m*-chlorobenzoyl < *p*-chlorobenzoyl < *m*-methoxybenzoyl < benzoyl < *p*-methylbenzoyl < *p*-methoxybenzoyl < sec. alkyl < *t*-alkyl < benzyl.

A peculiar characteristic of this sequence is that the change of structure of the acyl radicals has a small effect on its polar character, while the effects are very strong in the alkyl radicals. That is further supported by the low value of ϱ (−0.49) in Hammett correlation of the acylation rates of 4-cyanoquinoline relative to 4-chloroquinoline by *m* and *p*-substituted benzoyl radicals [78].

All the acyl radicals have nucleophilicities between that of a primary and a secondary alkyl radical; *i.e.* the acetyl radical is more nucleophilic than the ethyl radical, but the benzoyl radical is much less nucleophilic than the benzyl radical. The different polarizability of these last two radicals, due to their different configuration, was considered an important factor of this behavior. An incipient positive charge in a transition state similar to a charge-transfer complex (*21*) can be stabilized in the benzyl radical (*32*) by the aromatic orbitals, but not in the benzoyl radical, in which the unpaired electron occupies a hybrid orbital (*33*).



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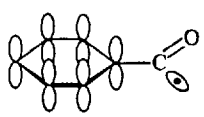


33

Moreover the configuration of alkyl and acyl radicals affects also the strength of the bonds formed by these radicals. The bond-dissociation energy greatly decreases from ethyl to benzyl radicals, while it is constant in acetyl and benzoyl radicals (Table 24). This factor does not therefore affect the selectivity in the acylation, but contributes to determining a greater extent of charge-transfer and a higher nucleophilicity of the benzyl than of the ethyl radical.

b) *α-Alkoxyalkyl and α-Alkoxycarbonyl Radicals.* A hydroxy or alkoxy group bonded to a carbon-centered radical can, in principle, cause two opposite polar effects:

i) An inductive electron-withdrawing polar effect, which decreases the nucleophilicity of the carbon free radical

ii) A conjugative electron-releasing effect, which, in the ground state can be related to the resonance structures of [Eq. (14)], and in the transition state to the stability of the corresponding carbonium ion, $^{+}\dot{C}-O-R$.

The relative rates of oxyalkylation of 4-substituted pyridines by methoxymethyl, $CH_3O\dot{C}H_2$, and phenoxymethyl, $PhO\dot{C}H_2$, radicals are summarized in Table 28, which also gives for comparison the corresponding values obtained with

Table 28. Relative rates for homolytic substitution in the position 2 of protonated 4-X-pyridines with methoxymethyl [70], phenoxymethyl [70], methyl [61] and *n*-propyl [61] radicals

X	$MeO\dot{C}H_2$	$PhO\dot{C}H_2$	Me.	*n*-Pr.
CN	341	164	23.5	56.3
$COCH_3$	90.5	62	7	17.5
CH_3	1	1	1	1

methyl and n-propyl radicals under the same experimental conditions. The substitution of an α-hydrogen atom by an alkoxy group represents a clear-cut increase of nucleophilicity of the alkyl radical. α-Alkoxyalkyls are π-type radicals and the incipient positive charge in a transition state similar to a charger-transfer complex (*21*) can be stabilized by the lone-pair electrons of the oxygen atom. This electron-releasing effect overcomes the inductive electron-withdrawing effect of the alkoxy group resulting in a net increase of the nucleophilic character.

The σ-type ethoxycarbonyl radical is on the contrary less nucleophilic than the acetyl radical (Table 29); in this case the unpaired electron occupies a hybrid orbital and the incipient positive charge in the transition state cannot be stabilized by the lone-pair electron of the alkoxy group, as with the alkoxyalkyl radical, so that only the inductive effect is working and a clean reduction of nucleophilicity is observed. The remarkable fact is therefore that the same substituent, an α-alkoxy group, produces opposite polar effects depending on the electronic configuration of the carbon-centered radical.

Table 29. Relative rates for homolytic substitution in the position 2 of protonated 4-X-pyridines with ethoxy carbonyl [70] and acetyl [56] radicals

X	$EtO\dot{C}O$	$Me\dot{C}O$
CN	18.7	—
$COCH_3$	6.7	20
CH_3	1	1

The strength of the bonds formed can also contribute to this behavior; the alkoxy group increases the stability of the alkyl radicals by the resonance structures [Eq. (14)], decreasing therefore the strength of the bonds formed; that should not occur in the alkoxy carbonyl radicals owing to their different configuration.

c) Cycloalkyl and Bridgehead Carbon Free Radicals. Spectroscopic [79] and chemical [80] evidence indicates that in cyclopropyl, as distinct from other cycloalkyl radicals, the unpaired electron occupies a hybrid orbital. The relative rates of homolytic cycloalkylation of 4-substituted pyridines, summarized in Table 30,

Table 30. Relative rates for homolytic cycloalkylation [70] of protonated 4-X-pyridines

X	Cyclopropyl	Cyclobutyl	Cyclopentyl	Cyclohexyl
CN	13.9	34.2	233	256
$COCH_3$	6.2	13.8	86.4	91.6
CH_3	1	1	1	1

show that the cyclopropyl radical, which has the highest *s* character, is the least nucleophilic among the cycloalkyl radicals; it is even less nucleophilic than the methyl radical.

Alkyl radicals with the odd electron in a hybrid orbital with some *s* character can be also obtained at the bridgehead positions of polycyclic hydrocarbons. In Table 31 the relative rates of alkylation of 4-substituted pyridines by t-butyl and apocamphyl (*34*) radicals are compared.

Table 31. Relative rates for homolytic alkylation of protonated 4-X-pyridines with *t*-butyl [61] and apocamphyl [81] radicals

X	*t*-Butyl	Apocamphyl
CN	1890	10.1
$COCH_3$	144	3.7
Cl	11.1	1.6
H	1	1
CH_3	0.15	0.26
OCH_3	0.0054	0.11

34

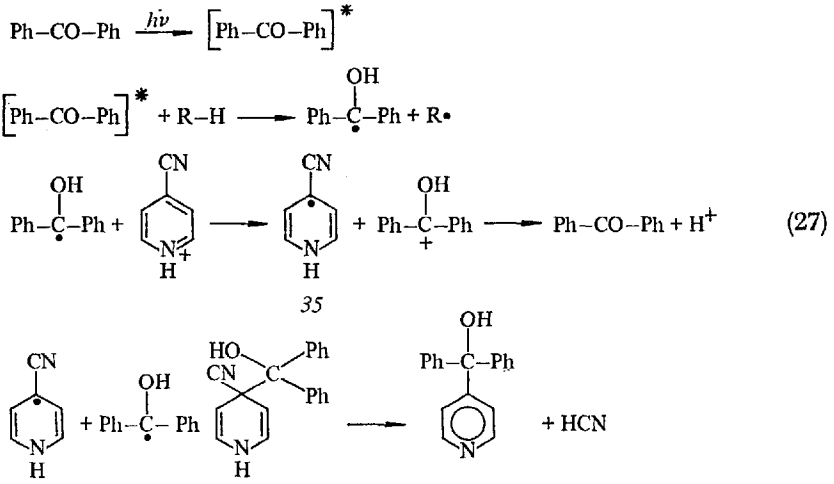
The great difference of selectivity of the two tertiary alkyl radicals must be ascribed to their different configuration; the unpaired electron occupies a p orbital in *t*-butyl and a sp^3 orbital in the apocamphyl radical, affecting in this way the polarity and the polarizability of the radicals and the strength of the bonds formed and therefore their nucleophilic character.

d) Phenyl Radical. Referring to the phenyl radical the factors affecting the nucleophilicity of the carbon free radicals, the very low positional and substrate selectivity (Table 22) can be related to its σ-nature, which determines a low polarizability and polarity (high ionization potential) and a high strength of the bonds formed (Table 23). It results in a very low degree of charge development in the transition state also with protonated heteroaromatic bases.

Thus the arylation cannot be considered as a model of general validity for the homolytic aromatic substitution, not even for substitutions with carbon free radicals.

Two facts strongly support the general mechanism of the reaction of nucleophilic carbon free radicals with protonated heteroaromatics, based on a transition state similar to a charge-transfer complex (*21*).

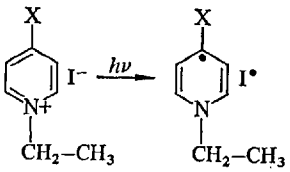
Because the substitution of a hydrogen atom in the methyl radical by a phenyl or alkoxy group strongly increases the nucleophilic character (Tables 17 and 28), the radical $Ph_2\dot{C}$—OH must be considered very strongly nucleophilic. Now chemical and spectroscopic evidence shows that this radical reacts with protonated pyridines or N-methyl pyridinium salts by complete electron transfer. Thus the reaction of protonated 4-cyanopyridine and the radical $Ph_2\dot{C}$—OH is interpreted according to the Scheme 16 [84].



Scheme 16

If the reaction is carried out in the cavity of the ESR instrument the spectrum of *35* or its N-methylderivative is recorded [13]. The complete electron-transfer of [Eq. (27)] is the limit case of the general transition state considered in (*21*).

Another interesting correlation supports the nature of the transition state of these reactions. The charge-transfer transition for pyridinium iodides [Eq. (28)] shows an absorption maximum that is very sensitive to the nature of the substitution on the pyridinium ring [82].



(28)

Variation of the 4-substituent from methyl to cyano changes the position of the charge-transfer band in a given solvent from 3590 to 4912 Å. The high sensitivity of the position of the maximum to the nature of the substituent on the ring implies very strongly that an electron-transfer process is responsible for the absorption band. Table 32 lists charge-transfer absorption bands for various 1-alkyl-4-

Table 32. Charge-transfer bonds for 4-X-substituted pyridinium iodides

X	λmax	εmax	Transition energy Kcal/mol
CH_3	3590	1230	79.64
H	3738	1200	76.49
$COOCH_3$	4489	1230	63.69
CN	4912	922	58.20

substituted pyridinium iodides. Now the energies of the charge-transfer bands (Table 32) correlate very well [83] with the relative rates of the homolytic alkylation (Table 17). This correlation is particularly significant as regards a charge-transfer character of the transition state in the homolytic alkylation of protonated pyridines.

IV. Conclusion

A common aspect characterizing both the homolytic amination and the substitution of protonated hetero-aromatic bases by nucleophilic free radicals is the presence of a nitrogen atom with a positive charge. This presence determines strong polar effects whether it characterizes the radical ($R_2\overset{\cdot}{\underset{+}{N}}H$) or the aromatic substrate (protonated base). The awareness that the global polar effects result from the polar characteristics of both the radical and the substrate has led to new homolytic aromatic substitutions, characterized by high selectivity and versatility. Thus the homolytic substitution acquires a more significant weight in the field of the aromatic substitutions.

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A General Protocol for Systematic Synthesis Design

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Contents

This rather long article introduces a number of relatively new concepts and terms, as well as a detailed procedure for utilizing them for synthesis design. To assist the reader a glossary of terms used is appended at the end and the text itself is divided into two parts, subdivided into labeled sections. The conceptual base is developed first in general terms in the first part (Sections 1—8) while the second part describes their implementation, developing the tools of the protocol and illustrating their practical use with examples. The system may be used to generate synthetic routes for any organic structure without computer assistance, and is completely described in this article.

1. Introduction

Although most areas of organic chemistry have been put on a logical and systematic basis over the years, the important field of organic synthesis design has remained largely undeveloped, an art in the midst of a science. Our minds are not geared to it, our literature is not indexed for it, our starting material catalogs are not even organized for it. Despite many elegant syntheses which have been successfully executed, we can neither clearly define "elegant" nor say whether other routes might have been shorter, cheaper, or easier. The need to impose a systematic structure or new logic form on synthesis design has only become recognized in recent years and it is clear that this goal will be both elusive and intellectually challenging [1].

At present we do not possess the unifying concepts or even conceptual terminology for synthesis design such as lies at the heart of other chemical disciplines like reaction mechanism study. In fact the concepts of reaction mechanism are now so deeply embedded in our thinking that they probably interfere with the development of synthesis design ideas.

It is important to put aside a mechanistic view and return to the 19th century conception of reactions in terms of their *net structural change*. Although mechanistic understanding is always necessary for prediction of reaction success in new compounds, it is not central to the needs of synthesis design, which require simple but systematic description of the structural change a reaction affords in order to cope with the combinatorial complexities implicit in synthesis design.

As a starting point, the information presented to the synthetic c hemist is of two kinds, that of the particular structure of the target compound, and that of the repository of available tools and materials, *i.e.*, the blueprint and the shop. The structural information may be seen in two main categories [18].

Skeleton: Size of the molecule; size and number of rings; relation of rings to chains; number and kind of branch points; symmetry and repeated skeletal units.

Functionality: Number and kind; interrelation on skeleton; stability.

The available tools are also of two kinds: a collection of available starting materials and a collection of possible reactions. It is important that these two large collections be systematically indexed not only for maximum accessibility but also in a common format for easy interrelation. Thus the catalog of starting materials should be organized by the prime structural elements of skeleton and functionality instead of just alphabetically, and the reactions should be ordered in terms of net structural change rather than by starting functionality or reaction mechanism, as is now common. The same dichotomy of skeleton and functionality transfers to reactions as *constructions* (and cleavages) and *refunctionalizations*, respectively, the former building (or altering) skeleton, the latter altering functionality on an unchanged skeleton.

2. Numerical Characterization of Structures and Reactions

A simple but fundamental numerical system suitable for characterizing both structures and reactions has been offered [8] and is summarized in Fig. 1. The system

Single carbon atom:

bond type	number		
C { H, R, Π, Z } F	h		
	σ	—skeletal	$\sigma + f = 4 - h$
	π, z	$f = \pi + z$—functional	
	$\Sigma = 4$		(oxidation state, $x = z - h$)

Structures:	Skeleton	Functionality	
	$\sigma = 0$	$f = 0$ hydrocarbon (saturated)	$f' = 0$
	1 primary	1 R—X, R—OH, etc.	$f' = 1$
	2 secondary	2 R—CHO, R_2CO, etc.	
	3 tertiary	3 R—COOR′, RCN, etc.	
	4 quaternary	4 CO_2, $COCl_2$, etc.	

Reactions:	Construction				Refunctionalization			
	RH	RZ	RΠ	RR	ZZ	HZ	HΠ	ZΠ
(cleavage:	HR,	ZR,	ΠR,	RR)	ΠΠ	ZH	ΠH	ΠZ

Fig. 1. Symbolic characterization of structures and reactions

focuses on characterizing single carbon atoms by four kinds of attachment:

H for hydrogen,
R for single σ-bond to carbon,
Π for π-bond to carbon, and
Z for any bond to hetero-atom;

and the numbers of each kind: h, σ, π and z, respectively, limited by valency to $h + \sigma + \pi + z = 4$. The number σ is the skeletal level of the carbon ($\sigma = 1$, primary or terminal carbon; $\sigma = 2$, secondary, etc.). The functionality level is the sum of carbon-carbon π-bonds (π limited to 2) and attachments to heteroatoms z, symbolized by $f = \pi + z$. This distinction in kind of functionality is denoted by placing one or two bars over the value of f to indicate $\pi = 1$ or 2, respectively. Hence a single carbon site in a molecule may be characterized simply by two digits, σ for the skeletal level and f for the functionality level, such that $\sigma + f = 4 - h$. It may be noted also that the oxidation state of any single carbon is simply given by $x = z - h$.

Reactions may be classified by the kind of attachment gained and the kind lost in the net structural change at a single carbon, the letter for the former placed first and that for the latter placed second, so that there are 16 possible reaction types based on the four kinds of attachment. As examples, the construction reactions are RH, R,Π RZ, implying creation of a carbon-carbon σ-bond at the expense of hydrogen, π-bond (to another carbon), or heteroatom, respectively,

as well as RR, construction of one carbon-carbon σ-bond at the expense of another, as in the migrating carbon of a rearrangement. The cleavage reactions are conversely, HR, ΠR, ZR (and of course RR). More recently the system has been extended [17] to catalog all possible construction reactions in terms of the net structural change on each of the two synthons being linked. This creates the tool to organize available reactions, as required above, and is discussed more fully in Section 11. The same system is easily applied to the cataloguing of available starting materials, as outlined in the Appendix.

3. The Synthesis Tree

A general diagram of the possible synthetic routes to a given target molecule can be constructed with lines indicating converting reactions and points symbolizing intermediates [19], as shown in Fig. 2. The lines converge at the top on the point representing the target molecule and so the diagram is often called *synthesis tree* [20]. In Fig. 2 can be seen the general form of such trees, rapidly expanding outward from the target to many possible intermediates, the complexity of which decreases with distance from the target until intermediates simple enough to be available starting materials begin to appear. Here the tree is contracting again to the ultimate and simplest starting material, carbon itself ("C"). Systems for generating intermediates have commonly started at the target and worked backwards ("retrosynthetically") [4], stepwise, to successive levels of intermediates (cf. Refs. [3–7,11,14,15]) while others [12,13,15,21] have started from available starting materials and worked forward similarly.

Both procedures have disadvantages [12]. The main problem with the first approach is the unmanageably vast number of intermediates rapidly generated, none of which can be safely deleted until each full route is discovered and evaluated, *i.e.*, until available starting materials have been reached in the generation process. The trouble with the second, or forward, approach is that it contains no device to force convergence on the target. A more powerful approach will be a hybrid which sees both starting materials and target together and strikes through the large center part of the tree considering whole multistep sequence units instead of single reactions stepwise.

By any definition [19] the main feature of, and problem with, the synthesis tree is its overwhelming size; the number of routes possible to synthesize a given target is enormous. In fact endless sequences of aimless refunctionalizations make it potentially infinite. Even if only construction reactions are considered, there are two kinds of complexity. First, for any given bond constructed there is a considerable, but finite, number of different chemical construction reactions available to achieve it, delineated in Ref. [17]. Secondly, there is a much greater number of *combinations* of various skeletal bonds in the target which may constitute the set constructed in any synthesis, as enumerated in Ref. [16]. Considering as an example the 21-carbon steroids to be synthesized via six construction steps, there are $6 \times 134{,}596 \simeq 10^8$ possible bond conbinations [16] for construction with up to about 350 different chemical reactions (as defined in Ref. [17]) available for

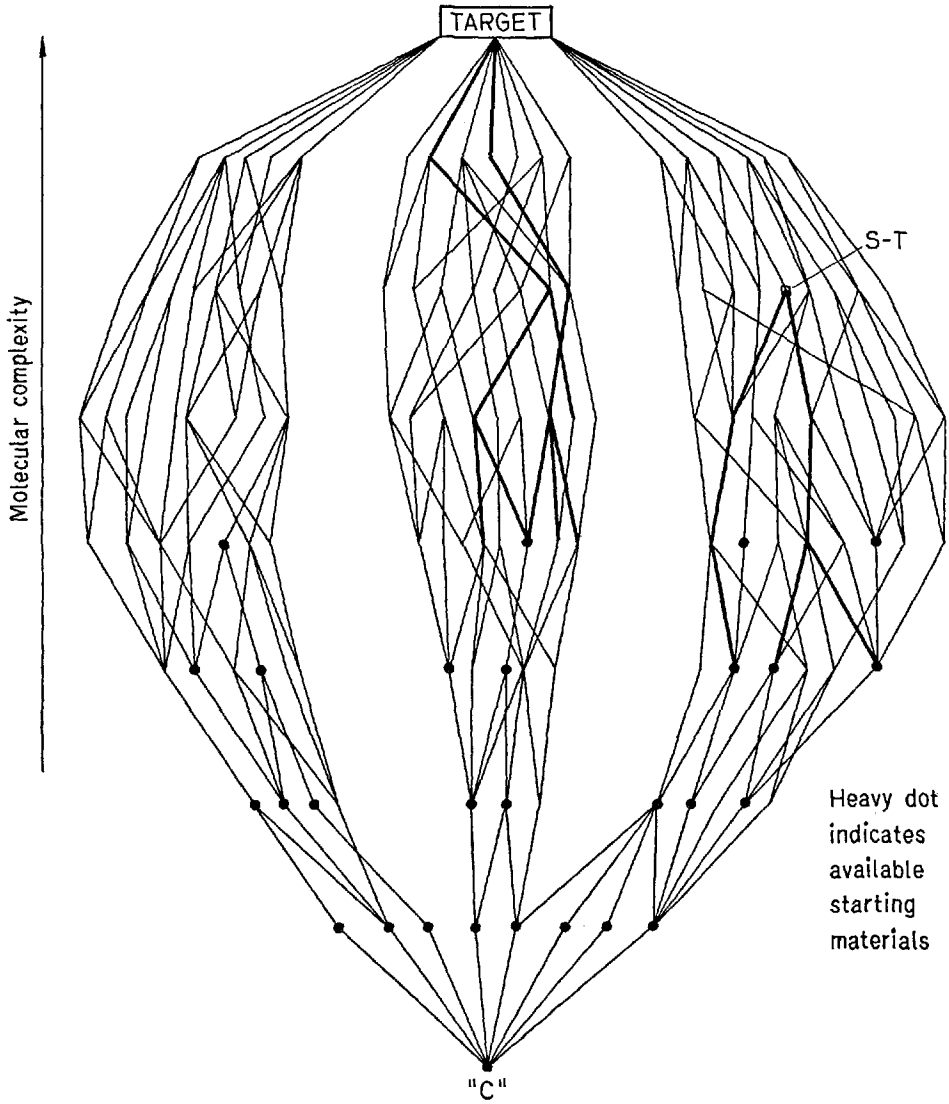


Fig. 2. The synthesis tree

each of the six constructions, or $(350)^6 \times 10^8 \simeq 2 \times 10^{19}$ potential construction sequences, quite apart from attendant refunctionalizations.

1. The first major step toward managing any search system in so large a potential search space is the reduction of bulky molecular information to numbers. The numerical convention must retain the significant information, consolidate trivial distinctions such as minor functionality variants, and also serve to define the problem and its options sharply. This is the intent of Section 2. The tree, however, will still be very large and we must look further for criteria to apply

both to isolate independent sections of search space for separate manipulation and to define criteria for stringent selection of optimal paths. The guide then will be to find all routes that fit these clearly defined criteria and to know clearly not only what routes are found but also the nature of all rejected. In this way there may be confidence that no routes are missed within the limits of the criteria applied.

Hence our primary task is to reduce drastically the effective size of the synthesis tree. Even with this reduction, however, another problem arises. In solving similar search problems in other fields, it is common to generate all routes and apply an efficiency criterion to measure each in order to seek the best routes [12, 21,22]. In our case this requires predicting the yield of each reaction and the overall yield of each route. However the present state of yield prediction in organic chemistry is so crude and uncertain as to make its employment in this way unrealistic. Hence we must seek other criteria and these can be approached in two ways [22]. Since the number of possible reactions is limited, we can hope to decompose the tree into more manageable and independent subtrees for separate examination. Secondly, there must be found a general heuristic basis, other than yield prediction, which allows a stringent selection of a few optimal routes through the tree. Three independent subtrees are illustrated in the generalized synthesis tree in Fig. 2 and the heavy lines to the target in the central subtree (and to a subtarget (S-T) in the righthand subtree) illustrate selected optimal routes.

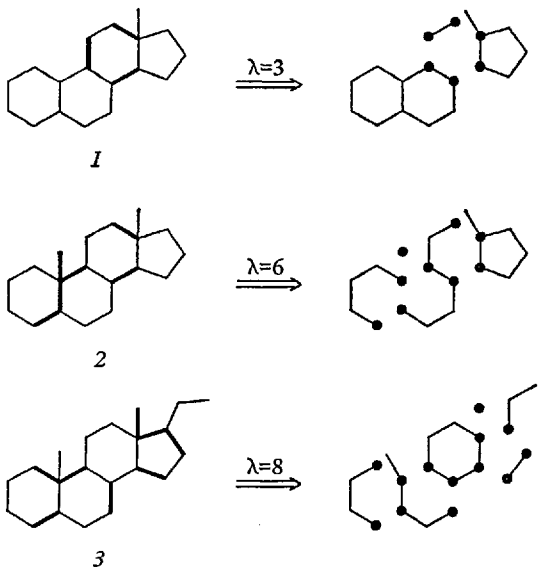
The overall criterion of any synthesis will ultimately be one of economy, and this can take several forms: economy of overall yield; economy of cost; economy of time. If yield prediction is not to be a criterion, then we shall focus on a criterion of time and seek synthetic sequences of the fewest steps.

4. Reducing the Synthesis Tree

The reactions which show real progress forward toward the target are the construction reactions, which build up the skeleton from smaller starting material components. This may be seen by considering an ideal synthesis. Such a synthesis would start from available small molecules so functionalized as to allow successive constructions to link them together without refunctionalizing after any construction, and would lead directly in this way to the target structure, not only its skeleton but also its correctly placed functionality. Such a synthesis is then a sequence of construction steps with no intermediary refunctionalization. It demands that the functionality remaining after one construction is consistent with the requirements for the next. Such a sequence will therefore be termed a *self-consistent sequence*. If available, such a self-consistent sequence would constitute the shortest and most economical synthesis and it would contain only construction reactions. Hence, if we accept as a criterion the selection of only self-consistent sequences, we can reduce the tree drastically, not only by deleting all routes with refunctionalizations but also because self-consistency stringently reduces the choice of possible reactions to succeed each other with self-consistent functionality. This represents indeed a potent heuristic basis for sequence selection (heavy lines in Fig. 2), as required above, by cutting down the chemical options

for doing the successive constructions [23]. Procedures for systematically deriving self-consistent sequences are developed in Section 12.

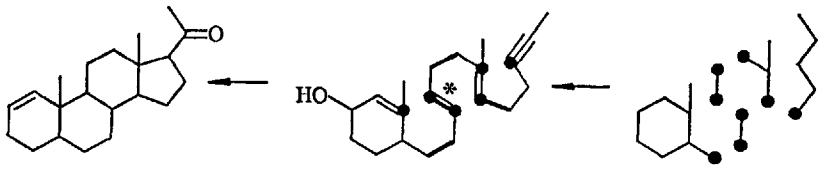
The second source of complexity, that of the many possible combinations of bonds to create [16], may be handled in the other way, *i.e.*, by decomposing the tree into independent subtrees. The simplest gross definition of a particular synthesis is the *bondset*, the set of skeletal bonds or links (λ in number) which are actually constructed in that synthesis [16]. To illustrate this, three steroid syntheses are depicted as bondsets of $\lambda = 3,6$ and 8, respectively, in structures *1*, *2* and *3* [25].



1 *2* *3*

Such a bondset, once defined, implies a multistep sequence passing through the tree from starting materials to target, seeing both at once. The bondset is a skeletal conception and immediately defines the skeletons of the starting materials as well as the sites on each synthon at which construction is to occur (marked as heavy dots in *1*, *2* and *3*), *i.e.*, the *construction sites*.

Each bondset defines an independent subtree of synthetic sequences, all of which construct only that particular set of λ bonds in the target. Each of these subtrees now has significantly fewer synthetic options and each can be manipulated separately and more manageably. Each bondset defines a multistep sequence of constructions for which detailed self-consistent sequences may be selected. Although there are many possible bondsets for any given target [16], only a relatively few are efficient and these may be defined by the application of various heuristics, some already obvious, others waiting to be discerned. Some heuristics may lead only to partial bondsets, but as these often represent an entrée into the difficult central part of the synthesis tree they have special value. The definition of a sub-target on some special grounds (S-T in Fig. 2) illustrates the partial bondset, as in Johnson's recent steroid syntheses [27] (*4*), conceptually based on a linear poly-olefin sub-target itself dictated by biomimetic considerations.



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The first task then is to pick out viable bondsets from the target. This can be done by selecting certain key bonds for construction and then variously assembling them into bondsets of minimal λ for shortest syntheses. Such key bonds may be selected on grounds of either functionality or skeleton, the former having been more widely discussed [4,5,17]. Heuristics for bondset selection both ways are developed below.

A further decomposition of each bondset subtree is now possible by treating separately each synthon defined by a bondset [28]. In the analysis of construction reactions previously developed [17] it was shown that each of the two synthons being linked by a construction can be treated independently, each exhibiting the net structural change of a half-reaction. It will be shown below (Section 12) that this independent treatment of the synthons can be extended to a multistep sequence of half-reactions involving overlapping functionality.

General sequence lists can be developed of all possible self-consistent sequences of half-reactions on one synthon with a given pattern of construction sites. These lists will show the initial and final functionality required on the synthon skeleton and the sequences of self-consistent half-reactions which link them. Since the construction sites for these sequences are fixed in advance by the bondset (see *1*—*4*) one has only to locate the combinations in the general sequence lists which are applicable to the skeletal levels (σ-values) of these sites in order to find all applicable sequences for the synthon. This defines as well particular starting materials (synthon skeleton and defined functionality placed on it initially) and also the functionality borne by that synthon at the end of the sequence, *i.e.*, when it is incorporated in the skeleton of the target. It should be noted here that stringent reduction of the combinatorial options for successive constructions is achieved in two ways. In the first, of course, the criterion of self-consistency puts rigid demands on the possible overlapping functionality serving several successive reactions. In the second, a number of functionalities possible for such general self-consistent sequences are rendered impossible by an unsuitable skeleton in the particular synthon under consideration (*e.g.*, a carbonyl cannot be placed at a tertiary site, etc.). An acceptable sequence must have $f \leq 4\text{-}\sigma$ at each site on the given synthon.

Such a procedure provides a list of possible self-consistent sequences for each synthon, in the form: starting material — half-reaction sequence — final functionalized synthon in target. These options for each synthon are further pruned by availability of starting material, practical viability of sequence, and acceptability of final functionality. They are then paired with the options from the other synthons to yield whole constructions and thus full synthetic routes. The pairing is limited by the fact that generally only half-reactions of opposite polarity are allowed to pair for a viable (*i.e.*, isohypsic) construction [17].

5. Summary of the Basic Protocol

The reductive criteria above resolve themselves into a general protocol for systematic synthesis design, summarized in the following algorithmic form.

1. Select from the target structure prime bonds for construction.
   a) Functionality criteria: pairwise consideration of functionalities and their relative positions on the skeleton (Section 7).
   b) Skeletal (and stereochemical) criteria (Section 8).
2. Combine these bonds into bondsets, adequate to dissect reasonable synthon skeletons but minimal in λ (Section 6).
3. From each bondset isolate the synthon skeletons dissected, noting the pattern of construction sites on each (Section 9).
4. For each synthon skeleton, locate in the general sequence list corresponding to its pattern of construction sites the sequences applicable to the skeletal (σ-) levels of those sites. This defines for each synthon a set of all self-consistent sequences of half-reactions, their particular starting materials and their consequent product functionalities (Section 13).
5. Eliminate for each synthon undesirable sequences
   a) Sequences unsuitable for the synthon skeleton (at sites, other than construction sites, which must bear functionality, $f \leq 4\text{-}\sigma$).
   b) Unavailable starting materials [29].
   c) Unacceptable product functionality for the target structure [30].
   d) Exclusion of certain functionalities in rings (*e.g.*, triple bonds) and certain reactions (cf., Grignard) for cyclizations.
   e) Other criteria, such as implicit refunctionalization or regiospecificity in sequences.
6. Select a prime synthon, with the most construction sites, and match successive constructions serially with the other synthons as dictated by the bondset, accepting only matching half-reactions of opposite polarity (Section 14), to create full synthetic routes.
7. Eliminate matchings in which subsequent constructions on one synthon are not compatible with existing functionality on any other synthon already linked to it.

This protocol will in practice derive a number of self-consistent routes without having applied any judgment of reaction yields. This number will depend much on the particular target and somewhat on the rigor of application of exclusions, especially in 5. and 7. On the other hand, within clearly defined and applied cirteria, this systematic protocol must produce *all* routes and so satisfies the need that all possibilities are known.

Once produced, a final choice remains a matter of practical judgment, which must of course incorporate yield prediction, but reducing the total synthesis tree

to a relatively few options before applying this presently dangerous measure appears much more productive. In the following sections the details of the protocol, and the general sequence lists, are developed and explored with specific directions (and examples) for its practical application to particular targets. In these sections lies also an effort to survey both the extent to which the protocol reduces the synthesis tree and the number of final offered routes to be expected in real cases.

6. Bondsets

The goal here is to define discrete bondsets especially suitable for synthesis. The bondsets define in turn both the starting material skeletons and the particular bonds which will be created. Such bondsets strike through the synthesis tree, seeing both target and starting materials at once, and so provide more perspective than a stepwise approach from either set. The bondsets themselves are assembled by combining various key, or strategic, bonds dictated by considerations of functionality and of skeleton. Some of the bonds in the skeleton may be dictated as strategic from several different criteria and priority should be given to the use of such bonds in assembling the various bondset combinations. The criteria for selecting certain bonds for construction are discussed in Sections 7 and 8 on the dissection of the target structure.

The number of bonds in a bondset (λ) equals the number of construction reactions in the synthetic sequence, and so should be minimal for economy of steps in the synthesis. Since the bondset also defines the synthon skeletons, it follows that any bondset must dissect the target into the skeletons of available starting materials. The number of bonds in any bondset is not fixed, of course, but the larger the acceptable starting synthons, the fewer bonds in the bondset and the fewer construction reactions in the sequence. In order to establish a scale of present practice, a large collection of syntheses [24,31] was surveyed in the terms of Ref. [16], summarized in these equations.

$b_0 = n_0 + r_0 - 1$

$\lambda = k + r_0 - r - 1$

n_0/k = average synthon size

λ/b_0 = construction ratio

b_0 = C—C single (σ-)bonds in target

n_0 = number of carbons in target

r_0 = number of carbocyclic rings in target

r = number of carbocyclic rings in starting materials

k = number of synthons

λ = number of bonds constructed (bondset)

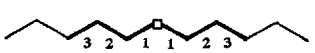
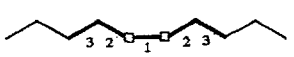
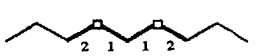
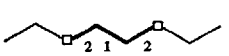
Synthons actually used [24,31] are predominantly acyclic unbranched skeletons of four carbons or less, or aromatic derivatives. The average size of starting materials is n_0/k and amounts to an overall average of 4.0 carbons in the examples surveyed. The bondset size, as a proportion of the total bonds (construction ratio) is λ/b_0 and averages to 0.24, or a tradition of constructing one bond in four in the various structures synthesized. Since these molecules have commonly 15—25

carbons, this represents bondsets of 4–7 constructions. Furthermore, there is a rough inverse correlation between average synthon size (n_0/k) and the size of the bondset (λ/b_0), which emphasizes the importance of large synthons in minimizing the number of constructions necessary.

7. Dissection by Functionality

Functionality, and its position on the target skeleton, is the common heuristic basis for deriving synthetic routes [5] and the main guide in the automated systems of Corey [4,11] and Wipke [14]. In this approach the functional groups on the target structure are examined pairwise [4] (or singly) to dictate the last synthesis step as a construction yielding the particular paired functionalized sites of the target as product. The procedure has also been systematized and explored [17] in the numerical format [8] used here. Implicit in the approach is the definition of a particular skeletal bond to be constructed, defined by the functional group (or pair of groups) examined. Without consideration of the detailed functional groups required, the actual bonds so selected for construction may be summarized (Table 1) as a function simply of the position of functionalized sites on the target skeleton. There are eleven different relative positions of final functionality and bond constructed, with examples of particular reactions for achieving each illustrated in Table 1.

Table 1. Construction of bonds dictated by product functionality

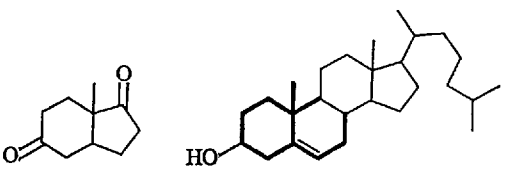
Molecular form[1])	Common examples[2])
Single functionality:	
	(1) Grignard addition; activated anion alkylation (2) Enolate alkylation; Grignard + epoxide (3) Alkylcuprate conjugate addition
Functional group pairs:	
Functionality span =	
2 	(1) Activated anion addition or acylation (2) Acetylene alkylation (3) Allylic anion alkylation
3 	(1) Claisen condensation; aldol reaction (2) Allylic activated anion alkylation
4 	(1) Enolate or acetylene anion + epoxide (2) Activated anion conjugate addition
5 	(1) Michael addition; Claisen rearrangement

[1]) Boxes indicate functional group sites, heavy bonds those marked for construction. Other functional sites, between the outer ones marked with boxes (in 3–5), are implicitly accepted.

[2]) Examples taken from complete table (≠13), Ref. [17]; activated anion = hetero-atom-stabilized carbanion, as Wittig reagent, nitroalkyl anion, dithiane anion, cyanide ion, etc.; addition = carbonyl and related additions.

All bonds in the target skeleton selected for construction by the target functionality can now be easily tabulated. Some bonds will have a higher priority if the target functionality is exactly correct for certain constructions [30], or if more constructions are available to yield the particular sites of functionality [17]. The general approach of Table 1 ignores details of functionality and focusses only on its position on the skeleton. This approach is easier and more useful. It emphasizes the important synthetic conception that functionality is easier to change at one site than to remove from one site and introduce at another. Hence constructions dictated by Table 1 will produce the right functionalized *sites* but may create somewhat different functionality detail there which will be easily rectified [30]. The actual functionality to result from the constructions will be determined later from the general sequence lists (see protocol step 4; Sections 12 and 13).

This bond selection by functionality is not very stringent. With many moderately functionalized targets a large proportion of all skeletal bonds will be dictated in this way, partly because for n functionalized sites there are $\binom{n}{2}$ functionality pairs and partly because there are several bonds dictated for construction by any given functional group or any pair (Table 1). As illustration, application of functionality dissection from Table 1 dictates all skeletal bonds as construction candidates in 3-methylcyclohexanone or in *5*, and in cholesterol (*6*) points to the eleven bonds marked in boldface for construction.



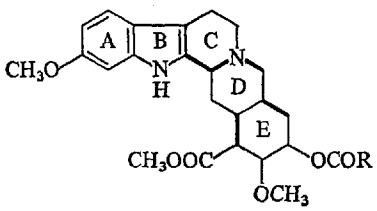
5 *6*

The functionality approach to target dissection is only used here to define certain bonds as construction candidates for formulation into discrete bondsets, along with bonds selected on skeletal grounds. However, it has always been discussed previously as the basis for a stepwise approach to synthetic routes, working backward from the target [3–7,11,14]. In this approach the target functionality determines the last bond constructed and the substrates for it, and these are then considered again as targets for penultimate constructions, etc. This approach has obvious problems of generating too many intermediates and so being forced into pruning by yield prediction, and of being blind to potential starting materials until the end. The full bondset is only revealed piecemeal as the derivation proceeds since each successive bond dissected is only determined by the functionality remaining from the previous dissection. Apart from these a more subtle problem arises in cases with very limited functionality (cf., cholesterol, *6*) or functionality only at one extreme of the skeleton, for which the stepwise functionality approach will generate too long a sequence, dissecting back into the unfunctionalized part too slowly and deriving too many small synthons, and too many construction steps, for economy. Finally, saturated hydrocarbons cannot even be approached in this way unless dummy functional groups are carried and

there is no functionality basis for assigning these. (If dummy functionality can serve in those obvious cases, it may also be useful for functionalized targets and removed at the end, but again there is no basis for assigning such evanescent functions.) All of these problems call for an alternative and complementary approach to target dissection which is based on the skeleton, rather than the functionality, of the target.

8. Dissection by Skeleton

Any effort to discern the guiding principles in existing complex syntheses reveals that the functionality approach was often not important to the synthetic conception. Indeed this approach could hardly expect to generate the many different steroid syntheses (cf., *1*—*4*) that have been achieved [26], most of which appear to have derived from skeletal considerations. Woodward's reserpine synthesis [32] was apparently designed around the twin ideas of a convergent synthesis [3] of two chemically different synthons of similar size and the stereochemical control (via *cis*-decalin stereospecificity and flexibility) of the massed asymmetric centers on ring E (*7*), which also dictated the cycloaddition choice of skeletal construction at rings D/E. In a second example, Johnson's synthesis of the sub-target (*4*) [27] appears to have been conceived around the idea of convergent synthesis efficiency [3] operating to join two independent synthons at a central double bond (starred in *4*). Again these approaches are basically skeletal in conception, not primarily related to target functionality.



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Certain considerations of the skeleton define particular bonds as candidates for construction. A set of seven such skeletal criteria are listed here and discussed below. A number are obviously a part of current synthetic practice, often used intuitively. They deserve specific definition, however, as a basis for further systematic exploration, and more heuristic criteria of this kind are needed for the future [10].

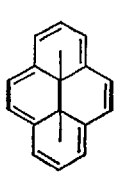
1. Presence of the skeletons of available starting materials.
2. Division into two (or three) similar-sized synthon skeletons for convergent synthesis efficiency.
3. Bond pairs for annelation (double construction: affixation + cyclization).

4. Multiple affixation: presence of several like groups which could be introduced simultaneously.
5. Presence of skeletal features with limited synthetic choices.
   a) Quaternary (and tertiary) centers.
   b) Small (3- and 4-membered) rings.
6. Strategic ring disconnections in polycyclic skeletons.
7. Stereochemical features.

Some of these criteria lead to the selection of individual bonds, some to sets of bonds, *i.e.*, partial bondsets. The latter themselves define partial sequences, back from the target, up from starting materials, or simply a multistep sequence in the midst of the synthesis tree. Such partial bondsets can be examined separately for their partial solutions from the general sequence lists, defining a set of partial sequences to be examined further: starting materials, reaction steps, and products, as with full bondsets. Also some of the criteria define not only certain bonds but something about the order of constructions as well.

The first criterion implies the recognition of large particular skeletal units, of aromatic rings, or of simple appendage skeletons known to be available as starting materials [29]. This is a potent criterion where large units are recognized, as the use of monoterpenes to start sesquiterpene syntheses, the relatively easy availability of tryptamines in indole alkaloid syntheses (cf., *7*), naphthalenes in steroid syntheses (cf., *1*), etc. Once recognized, such a skeleton of an available starting material dictates that all other bonds linked to it in the target skeleton be dissected as a partial bondset (cf., two bonds in *1*, three in *7*).

The convergent synthesis [3] (#2) demands two (or three) synthons of similar size so that they may be separately constructed in parallel, then linked. The criterion implies selection of bonds at/or near the center of the skeleton such as to divide the skeleton into separate component synthons, as in *4*. The halves may be sought so as to incorporate different kinds of chemistry (as in *7*) or to be equivalent or symmetrical as in Boeckelheide's synthesis [33] of the rigid, large aromatic monocycle, *8*, or Barton's synthesis [34] of usnic acid, *9*. Furthermore, the criterion also places demands on the *order* of constructions in the bondset since those bonds selected for the convergency are to be constructed last.



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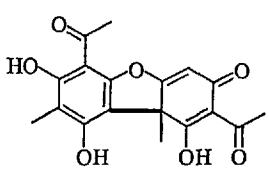

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Operations that construct two or more bonds at once (#3,4) are of special importance for efficiency. Annelation reactions are of this class. Annelations may be annotated [16] by the number of ring atoms in each of the two synthons forming

the ring (of size, ϱ), *i.e.*, $(m+n)$-annelations, with $m+n=\varrho$. Annelations in common use include cycloadditions [cyclopropanations $=(1+2)$; Diels-Alder $=(2+4)$] and Robinson $(2+4)$-annelation or $(3+3)$-annelation. A systematic survey of all possible annelations on a skeleton can be made [35], but a number of useful ones can easily be picked out by visual inspection (cf., rings C in *2*, A and B in *3*, and E in *7*). Multiple affixations of identical units ($\neq 4$) may be illustrated by attack of alkyl (often methyl) Grignard reagents on esters (or polyketones), or double alkylation of active methylenes. Both kinds of multiple constructions ($\neq 3,4$) define partial bondsets.

Since available starting materials are commonly unbranched, tertiary and, more often, quaternary carbons in the target skeleton will usually have to be constructed. Thus this consideration ($\neq 5$a) directs selection of bonds linked to sites of $\sigma=3$ and 4. Furthermore, construction of bonds forming quaternary carbons is quite limited in chemical possibilities (cf., discussion in Ref. [36]) and will be critical in limiting sequences derived from bondsets containing them. Similarly ($\neq 5$b), few starting materials contain small rings and their construction options are limited. Hence bonds in such rings are selected, as are bonds in other strained systems ($\neq 5$c), and the nature of the skeleton containing them may often dictate construction of some particular bonds.

Corey's analysis [10] of polycyclic systems and strategic bond disconnections directed by maximizing simplification of intermediates is an example of the definition of new heuristics for skeletal dissection ($\neq 6$). This analysis directs the selection of particular bonds for construction. His rules also derive in part from stereochemical considerations ($\neq 7$). A further treatment of rules for bond selection via stereochemistry would be valuable.

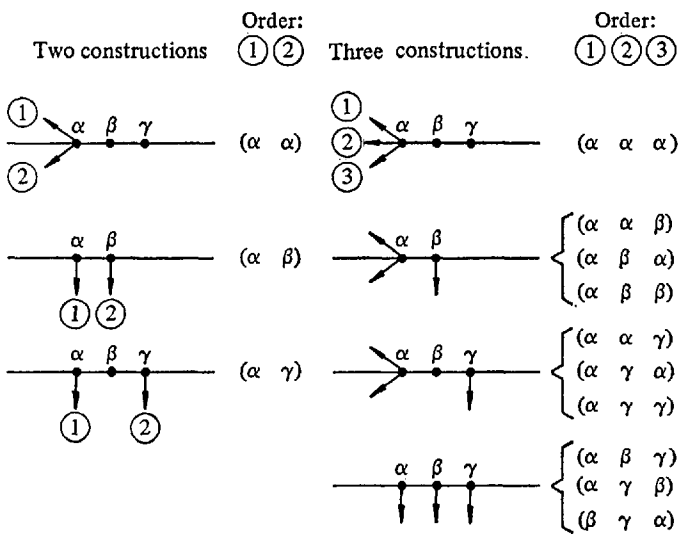
The need for stereocontrol often severely limits the choice (and sequence) of available constructions and dictates the construction of particular bonds by particular reactions, generally for bonds linked to asymmetric sites in the skeleton. Alternatively, there may be cases in which an asymmetric center is desired from the outset in the starting material (*e.g.*, to avoid later resolution); hence bonds to that site are omitted in bond selection. As with convergency selection, bonds selected on grounds of polycyclic disconnection and stereochemistry also have limits on their place in the sequence order.

The chief problem with a purely skeletal approach to target dissection lies in the fact that it is blind to target functionality. Thus for any bond selected for construction on skeletal grounds a large variety of different functionalized sites can then be assigned to the synthons to activate these constructions, leaving functionality at many places on the created target skeleton at the end of the synthesis. Some of these resultant functions may occupy sites functionalized in the target, and be easily convertible to the desired groups, but many will turn up as dummy functions which must be removed afterwards. Clearly then, any optimal use of the skeleton approach must incorporate information on the location of targest functionality to guide and limit the assignment of acceptable activating functionality needed to construct the bonds selected on skeletal grounds. The place for this limitation in the protocol comes with the assignment of activating functionality on the separate synthons by the general sequence lists.

9. Synthons: Patterns of Construction Sites

A given bondset defines the synthon skeletons and the location of construction sites on each one. Synthons will rarely exhibit more than three sites each, a general supposition confirmed by the bondsets of known syntheses [24,32,37]. This implies that any synthon may engage in self-consistent sequences of up to three construction halfreactions [17] at those sites. (With more than one construction at single sites there could be even longer sequences for one synthon, but this is likely to be rare). Furthermore, it is common for the construction sites to appear close together on the synthon skeleton, usually no more than three carbons apart; this is the *site span* (SS) of the synthon — the separation of sites on its skeleton — and will generally have values of 1, 2 or 3. Finally we must consider the order in which the half-reactions at the construction sites occur. For an n-step sequence there are $n!$ orders possible (2 orders for 2 half-reactions, 6 orders for 3).

We may therefore define *pattern* of construction sites on any synthon as their relative placement or location and the order in which they undergo construction half-reactions. The limits accepted above, which will include nearly all cases, allow for 13 possible patterns,[38] summarized and annotated in Fig. 3. The strand



Possible σ-blocks: [a]

$(\alpha\alpha)$: σ_α = 0 1 2

$(\alpha\beta)$ $\sigma_\alpha\,\sigma_\beta$ = 11 12 13 / 21 22 23 / 31 32 33

$(\alpha\gamma)$ $(\sigma_\alpha\,\sigma_\gamma)$

$(\alpha\alpha\alpha)$: σ_α = 0 1

$(\alpha\alpha\beta)$ etc. $\sigma_\alpha\,\sigma_\beta$ = 11 12 13 / 21 22 23

$(\alpha\alpha\gamma)$ etc. $(\sigma_\alpha\,\sigma_\gamma)$

$(\alpha\beta\gamma)$ etc. $\sigma_\alpha\,\sigma_\beta\,\sigma_\gamma$ = $12x$ $13x$ / $22x$ $23x$ / $32x$ $33x$ ($x = \sigma_\gamma = 1,2,3$)

[a] Acceptable combinations of σ at the construction sites for each of the seven families, the σ-values being those of the *substrate* in construction.

Fig. 3. Sequence patterns: construction sites and construction order on synthon

of carbons through the site span is labeled α,β,γ from the left, and since any pattern of more than one site can be laid on a real synthon in two ways (right-to-left or left-to-right) all the patterns except ($\alpha\alpha$) and ($\alpha\alpha\alpha$) represent two orders each. Thus the ($\alpha\beta$)-pattern also includes the ($\beta\alpha$) order and for three reactions, ($\gamma\alpha\alpha$)≡($\alpha\gamma\gamma$), ($\beta\alpha\gamma$)≡($\beta\gamma\alpha$), etc. Thus there are $n!$=6 orders for three reactions but only three patterns need be distinguished. For the sake of consistency the patterns are labeled wherever possible, *i.e.*, all but ($\beta\gamma\alpha$), with the left-hand site labeled α and undergoing the first construction of the sequence. [For this reason the labels of ($\alpha\beta\beta$) and ($\alpha\gamma\gamma$) are used in Fig. 3 although the diagrams imply the equivalent ($\beta\alpha\alpha$) and ($\gamma\alpha\alpha$) labels.]

In the present protocol we start with synthon skeletons marked with construction sites. On these skeletons we must now place the functionality appropriate for activating construction half-reactions in a self-consistent sequence for these sites. The numerical codification of individual half-reactions [17] (summarized below in Section 11) defines a reactive strand of up to three functionalized carbons out from the construction site in the substrate as well as the net change in that functionality as the construction occurs. Thus except for a terminal, or primary, construction site (σ=1) there is a question as to which strand of carbons out from the site shall be selected to bear the activating functionality. For secondary (σ=2) construction sites on a synthon there are two choices for the reactive strand, and for tertiary (σ=3) sites there are three strands out from the site which might bear the activating functionality. Taken with the many different functionality strands for the various half-reactions, the possible combinations of placement choices for them about several construction sites proliferate excessively; for a synthon with three separate secondary sites to undergo construction, *e.g.* ($\alpha\beta\gamma$), there are 2^3=8 ways to lay on the skeleton the reactive strands of functionality needed to initiate these constructions.

10. Functional Overlap

Skeletal dissection creates a synthetic problem because it is unresponsive to target functionality. This can produce an undesirable proliferation of structures with the skeleton of the target but incorrect or incorrectly placed functional groups, and many with excess (or "dummy") functional groups which activated earlier construction but must be removed at the end. Linked with this is the need to avoid excessive functionality in the intermediates also. The more functionality present the more the possibility exists of undesired alternative courses of reaction during the constructions. Finally, the need to minimize functionality extends back to the starting materials, since most available compounds have relatively simple functionality. In view of these considerations, then, we must focus the selection of sequences and of starting materials both to orient and to minimize functionality placement on the given skeleton. In the present protocol we impose functionality on the skeleton to activate each construction. In order to achieve the desired focussing of selection we must then seek *maximum overlap* of these imposed functionalities both with the target and with each other.

10.1. Functional Overlap with Target

The choice in the last section as to which strands out from construction sites may bear activating functionality will obviously be made in terms of which carbons of that synthon are functionalized in the target. Although some bonds of a bondset may be selected on functionality grounds (Section 7), we are formally dealing at this point in the protocol with a synthon skeleton marked only by its construction sites. If the carbons functionalized in the target are also marked, we can select only strands containing these carbons when laying on the requisite reactive strands for the sites. Thus, when there is a choice reactive strands for constructions are selected to overlap with target functionality sites.

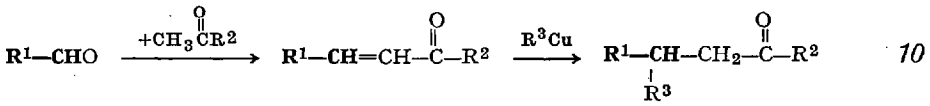
10.2. Internal Function Overlap

To minimize functionality en route the self-consistent sequences should utilize the same functional groups for each step as much as possible. This demands maximum functional overlap of the reactive strands for each successive half-reaction on the synthon. It is indeed the application of this criterion of maximum functional overlap that creates the stringent reduction in choices for the self-consistent sequences since the functionality left by one half-reaction must be that required for the next when the reactive strands for the two overlap. Overlap can be total or partial, as explored in Section 12, but clearly the farther apart the construction sites on a synthon the less overlap there can be for the reactive strands of the two successive half-reactions, and consequently the less effective the reduction in the number of choices of available sequences. This is another reason for not considering construction spans over three in the patterns of Fig. 3. Construction sites beyond a span of three are considered separately in the protocol.

The second criterion of maximum overlap is easily applied in general to simplify placement of functionality on the construction site patterns of Fig. 3. If the functional groups activating each half-reaction are to overlap maximally it is clear that, whatever branching may exist on real synthons, a linear strand of functionality passing through all construction sites will bear all the functional groups necessary for the successive half-reactions in each case. This functionalized linear strand may extend one or even two carbons beyond the sites at either end but any branching of the functionality strand must result in less overlap. These criteria now allow the generation of the most viable self-consistent sequences, to be incorporated into general sequence lists for each of the 13 patterns. This is considered after description of the nature of the reactive strands for half-reactions in the following section. With that tool in hand more specific application of overlap criteria to the particular half-reactions is possible for the several patterns, as well as an appraisal of the significant reduction in choices effected.

The overlap described above is *internal overlap* in that the overlapping strands of the two successive half-reactions all lie on the synthon itself. *External overlap* is also possible, in which the bond created to the partner synthon in the first construction becomes a part of the reactive strand for the second construction. As an illustration, two successive constructions ($\alpha\alpha$) occur at the aldehyde carbon

of an aldehyde undergoing first an aldol condensation with a methyl ketone followed by a conjugate addition (*10*). The three-carbon reactive strand for the second



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(conjugate addition) construction does not fully lie on the original aldehyde synthon skeleton **(boldface type in 10)** but incorporates the bond formed in the first (aldol) construction and two carbons of the methyl ketone, the first partner synthon. In order to maintain the independence of one synthon from the others for the protocol, the possibilities for external overlap must be included in the sequence list for any synthon and formulated independently of the involved partner. In the development of general sequence lists in Section 12, this will be shown to be possible.

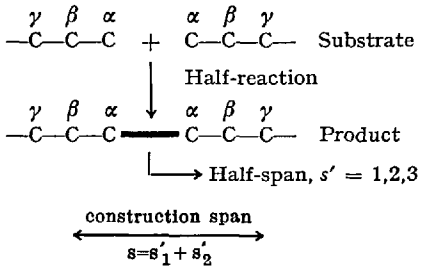
11. Coding System for Half-Reactions

In order to derive general sequence lists we must be able to express the necessary functionality which is to lie on the linear strand of carbons passing through the construction sites on any of these 13 synthon patterns of Fig. 3. This can be done by a linear list of f-values for the involved carbons, first as starting materials, then as products. The basis for this lies in the codification of the involved functionality in construction reactions, developed in Ref. [17] and summarized in this section.

Construction reactions consist of the linking of two synthons, each involving obligatory activating functionality on a strand (linear chain) of up to three carbon atoms from the constructed link (Fig. 4), referred to as the *reactive strand*. These atoms are labeled α,β,γ out from that link on each synthon, the α-carbon being the construction site. The particular functionalities of substrates and products for each synthon are specifically related for any given construction reaction. Each partial synthon (α,β,γ carbons only) undergoes a *half-reaction* and each construction half-reaction is characterized by the net structural change relating substrate and product for that partial synthon. The actual synthon may exhibit branching on the α,β,γ carbons, simply expressed as the σ-values of those carbons [39], and the skeletal part of the net structural change is only $\Delta\sigma_\alpha = 1$. The main part of the net structural change is in functionality, defined by an *f-list* of up to three digits, $f_\alpha f_\beta f_\gamma$; *f*-lists are used to express the requisite substrate functionality as well as the product functionality with the change expressed by Δf for each of the involved carbons (α,β,γ).

The *half-span* (s') of a half-reaction is the number of carbons from the constructing bond to the outermost obligatory function, *i.e.*, values of $s' = 1, 2$, or 3. The construction span, $s = s'_1 + s'_2$, is the length of the whole product strand, incorporating the constructed link, between the outermost functionalized carbon sites of the two linked synthons [40]. Also useful for generalizing or organizing *f*-lists are the less specific *f'*-lists of *f'*-values which are either 0 or 1 to denote the

Generalized Construction Reaction:



Half-reaction Labels:

Polarity:	⊖	⊕*		
f_α (Substrate)	RH	RF: RZ	RF: RΠ	
0	A	– –	– –	
1	B	1	$\bar{1}$	$\bar{1}'$
2	C	2	$\bar{2}$	$\bar{2}'$
3	D	3	– –	– –
4	— —	4	– –	– –
Δf_α	0	– 1	– 1	– 1
Δf_β	0	0	– 1	0
Δf_γ	0	0	0	0

(* Two RΠ reactions are ⊖: $\bar{1}'_2$ and $\bar{2}'_2$)

Half-spans	Possible f'-lists	
$s' = 1$	000	100
$s' = 2$	010	110
$s' = 3$	001	(101)
	011	111

Example: Michael Additions ($A_2 \cdot \bar{1}_3$ and $\bar{1}'_2 \cdot \bar{1}_3$)

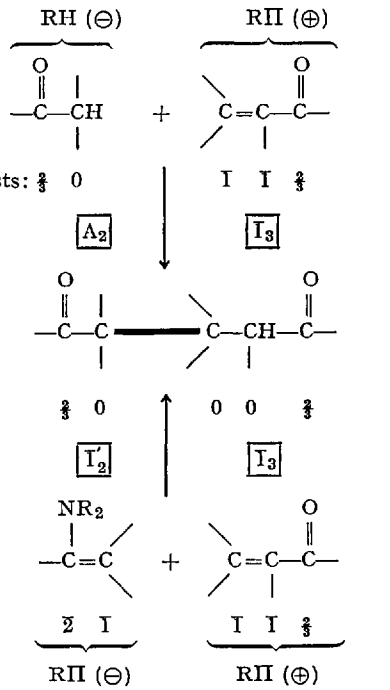


Fig. 4. Summary of reaction codification [17]

presence or absence, respectively, of any functionality at a carbon site ($f' = 0$ for $f = 0$; $f' = 1$ for $f = 1, 2, 3, 4$). The eight possible f'-lists for reactive strands are shown in Fig. 4; one of these (101) is without any real examples [17]. In practice the number of digits used in an f-list (or f'-list) defining a given half-reaction is only that of the half-span, $s' = 1$, 2 or 3.

This codification logically defines all possible constructions, not merely those currently known in chemistry, because all possible mathematical combinations of f-lists may be generated (there are 40 possible f-lists for half-reaction products [17]. The half-reactions are divided by type into RH and RF(= RZ and RΠ) and into related polarity types, ⊖ and ⊕. Half-reactions of ⊖ polarity are oxidative constructions, and essentially nucleophilic, while those of ⊕ polarity are reductive, essentially electrophilic (although polarity definition does not require mechanistic

understanding but only oxidation state change) [17]. Half-reactions are defined by the *f*-lists for substrate and product and annotated with a simple two-character code of symbol and subscript, the subscript denoting the half-span, s'. The symbol denotes α-carbon functionality (f_α) in the substrate, using a capital letter (A—D) for RH half-reactions and a number (1—4) for RF half-reactions, distinguishing RΠ from RZ by placing a bar over the symbol for RΠ half-reactions (to imply the π-bond broken). The relation between substrate and product (net functional change) is specified by Δf at three sites depending on the type of half-reactions. These net changes, as well as the reaction symbols and polarities, are summarized in the table of labels in Fig. 4, which also distinguishes R*II* reactions by the change at the other π-bond carbon, *i.e.*, Δf_β, using a prime for those of $\Delta f_\beta = 0$. Examples are shown in Fig. 4 as the Michael additions $A_2 \cdot \bar{1}_3$ and $\bar{1}_2' \cdot \bar{1}_3$, both of construction span, $s = 5 = 2 + 3$, the half-spans of each half-reaction seen as their label subscripts. The common notation $\frac{2}{3}$ indicates $f = 2$ or 3. Any construction half-reaction can be written in the Fig. 4 format and its *f*-lists and label determined; a number

Table 2. Selected construction reactions

Half-reactions		Full reactions	
Grignard reactions	A_1	Grignard additions	$A_1 \cdot 2_1$
Wittig reactions	B_1	Wittig reactions	$B_1 \cdot 2_1$
Dithianes	C_1	Enolate alkylations	$A_2 \cdot 1_1$
Enolates	A_2	Aldol condensations	$A_2 \cdot 2_1$
Friedel-Crafts reactions	$\bar{B}_2$	Claisen condensations	$A_2 \cdot 3_1$
Alkylations	1_1	Grignard carbonations	$A_1 \cdot 4_1$
Epoxide openings	1_2	Michael additions	$A_2 \cdot \bar{1}_3$
Carbonyl additions	2_1	Conjugate additions/CN^-	$D_1 \cdot \bar{1}_3$
Acylations	3_1	Conjugate additions of alkyl copper	$A_1 \cdot \bar{1}_3$
Conjugate additions:		Alkyne alkylations	$C_2 \cdot 1_1$
to carbonyl	$\bar{1}_3$	Benzoin condensations	$C_1 \cdot 2_1$
to acetylenic carbonyl	$\bar{\bar{2}}_3$	Pinacol reductions	$2_1 \cdot 2_1$
to nitro, sulfonyl	$\bar{1}_2$	Acetylenic couplings	$C_2 \cdot C_2$
Addition-eliminations:		Claisen rearrangements	$\bar{1}_2' \cdot \bar{1}_3'$
to unsatd. carbonyl	2_3	Fischer indole synthesis	$A_2 \cdot \bar{B}_2$
to unsatd. sulfonyl	2_2		
Electrophilic additions	$\bar{1}_2'$		

of common examples are labeled in Table 2 [17]. Although the notation is initially unfamiliar, it is basically very simple and easy to familiarize and use. The groupings also closely parallel ordinary half-reaction descriptions (see Table 2). Since it derives systematically from structural fundamentals, the reaction code also affords confidence that it includes all possible options.

Armed with this codification scheme, we can assemble a masterlist of half-reactions, shown as Table 3 [41]. This table is the basis for the derivation of general sequence lists. It also represents the "sequence list" for a one-construction

Table 3. Masterlist of construction half-reactions

	⊖ Polarity			⊕ Polarity		
σ-Block	Substrate $\alpha\beta\gamma$	Half-reaction Label	Product $\alpha\beta\gamma$	Substrate $\alpha\beta\gamma$	Half-reaction Label	Product $\alpha\beta\gamma$
$\sigma_\alpha \leq 3$	**0**·	A_1	0·	$\overline{1}\overline{1}$	$\overline{1}_2$	**00**
	1·		0·	$\overline{1}\mathbf{2}$		**01**
	$\overline{1}\overline{1}$	$\overline{1}_2'$	01	$\overline{\frac{2}{3}}\mathbf{3}$–		**02**–
	$\overline{1}\frac{2}{3}$		$0\frac{2}{3}$	$\overline{1}\overline{1}\frac{2}{3}$	$\overline{1}_3$	$\mathbf{00}\frac{2}{3}$
	$\mathbf{0}\overline{1}\overline{1}$	A_3	$0\overline{1}\overline{1}$	$\overline{1}\mathbf{2}\frac{2}{3}$		$\mathbf{01}\frac{2}{3}$
	$\mathbf{1}\overline{1}\overline{1}$		$0\overline{1}\overline{1}$	$\overline{1}\overline{1}\mathbf{1}$	$\overline{1}_3'$	$\mathbf{0}\overline{1}\overline{1}$
	$\overline{1}\overline{1}\mathbf{0}$		$0\overline{1}\overline{1}$	$\overline{1}\mathbf{2}\mathbf{1}$		$\mathbf{02}\overline{1}$
	$\mathbf{0}\frac{2}{3}$	A_2	$0\frac{2}{3}$			
	$\mathbf{1}\frac{2}{3}$		$0\frac{2}{3}$			
	$\overline{1}\frac{2}{3}$		$0\frac{2}{3}$			
	$\mathbf{0}\overline{\overline{22}}$	A_3	$0\overline{\overline{22}}$			
	$\mathbf{1}\overline{\overline{22}}$		$0\overline{\overline{22}}$			
$\sigma_\alpha \leq 2$	**1**·	B_1	**1**·	**1**	$\mathbf{1}_1$	**0**
	1·		$\overline{1}$·	**2**	$\mathbf{2}_1$	**1**
	$\mathbf{1}\overline{1}$	B_2	$\overline{1}\overline{1}$	**2**		$\overline{1}$
	$\overline{2}\mathbf{1}$		$\overline{1}\overline{1}$	**11**	$\mathbf{1}_2$	**01**
	$\mathbf{1}\frac{2}{3}$		$\overline{1}\frac{2}{3}$	$\overline{2}\frac{2}{3}$	$\mathbf{2}_2$	$\overline{1}\frac{2}{3}$
	$\mathbf{0}\overline{1}\overline{1}$	A_3	$\overline{1}\overline{1}\mathbf{0}$	$\overline{\mathbf{22}}$	$\overline{\mathbf{2}}_2$	$\overline{\mathbf{11}}$
	$\overline{1}\overline{1}\mathbf{0}$		$\overline{1}\overline{1}\mathbf{0}$	$\overline{2}\mathbf{3}$–		$\overline{1}\mathbf{2}$–
	$\mathbf{1}\overline{1}\overline{1}$	B_3	$1\overline{1}\overline{1}$	$\mathbf{21}\frac{2}{3}$	$\mathbf{2}_3$	$\overline{1}\overline{1}\frac{2}{3}$
	$\overline{2}\mathbf{1}\mathbf{0}$		$1\overline{1}\overline{1}$	$\overline{\mathbf{22}}\frac{2}{3}$		$\overline{1}\mathbf{2}\frac{2}{3}$
	$\mathbf{1}\overline{1}\overline{1}$		$\overline{1}\overline{1}\overline{1}$	$\overline{\overline{22}}\frac{2}{3}$	$\overline{\mathbf{2}}_3$	$\overline{1}\overline{1}\frac{2}{3}$
	$\overline{2}\mathbf{1}\mathbf{0}$		$\overline{1}\overline{1}\overline{1}$			
	$\mathbf{0}\frac{2}{3}$	A_2	$\overline{1}\frac{2}{3}$			
	$\mathbf{1}\frac{2}{3}$	B_2	$1\frac{2}{3}$			
	$\mathbf{1}\frac{2}{3}$		$\overline{1}\frac{2}{3}$			
	$\overline{2}\frac{2}{3}$	$\overline{2}_2'$	$\overline{1}\frac{2}{3}$			
	$\overline{2}\frac{2}{3}$		$0\frac{2}{3}$			
$\sigma_\alpha \leq 1$	**1**·	B_1	$\overline{2}$·	$\underline{3}$	$\mathbf{3}_1$	$\underline{\mathbf{2}}$
	2	C_1	**2**	$\underline{\overline{3}}\frac{2}{3}$	$\mathbf{3}_2$	$\underline{\overline{2}}\frac{2}{3}$
	2		$\overline{2}$			
	$\mathbf{1}\overline{1}$	B_3	$\overline{2}\mathbf{1}\mathbf{0}$			
	$\overline{2}\mathbf{1}\mathbf{0}$		$\overline{2}\mathbf{1}\mathbf{0}$			
	$\mathbf{1}\overline{1}$		$\overline{2}\overline{1}$			
	$\overline{2}\mathbf{1}\mathbf{0}$		$\overline{2}\overline{1}$			
	$\mathbf{1}\frac{2}{3}$	B_2	$\overline{2}\frac{2}{3}$			
	$\overline{2}\frac{2}{3}$	C_2	$\overline{\overline{2}}\frac{2}{3}$			
$\sigma_\alpha = 0$	**2**–	C_1	$\overline{\mathbf{3}}$–	4–	$\mathbf{4}_1$	**3**–
	3–	D_1	**3**–			
	3–		$\overline{\mathbf{3}}$–			

Notes: Taken from Table 8, Ref.[17] — see discussion there for any apparent anomalies. Carbons bearing obligatory hydrogen shown in boldface in substrate and product *f*-lists.

"sequence" itself and is presented in the same format as the multistep sequences to be derived below, showing substrate functionality, half-reaction label and product functionality. The masterlist includes 25 half-reaction labels and, with their variations,[41] 60 detailed substrate-product pairs or actual half-reactions.

The masterlist is divided by reaction polarity as well as by the acceptable skeletal level of the α-carbon (the construction site). Thus cyanide ion as nucleophile (D_1) cannot be used to attach a chain of carbons in one construction; it is limited to $\sigma = 1$ by its necessary functionality ($f = 3$). Similarly, carbonyl addition (2_1) cannot be a half-reaction of a tertiary construction site on a synthon. This division of the masterlist by substrate σ-values allows quick matching with any real synthon having a known σ-value at the construction site. For economy in the table, each half-reaction shown for any σ-value in Table 3 can be used in particular cases for sites of that σ-value or lower (with the proviso that one-carbon synthons, $\sigma = 0$, can only utilize $s' = 1$ half-reactions, of course). A dash in the f-list indicates the impossibility of a β- or γ-carbon, hence no indicated functionality, as in D_1.

12. General Sequence Lists

The masterlist of individual half-reactions in Table 3 may now be used to derive all possible pairs of two successive, self-consistent half-reactions for each of the three two-construction patterns in Fig. 3. The products of these pairs will in turn constitute substrates for a third successive self-consistent half-reaction to give sequence lists for each of the derived three-construction patterns. In this way general sequence lists for each of the 13 patterns will be obtained, containing all possible self-consistent sequences. The generation of these lists is now simply a mechanical mathematical exercise, unprejudiced by chemical preconceptions. Like the masterlist itself they will include sequences of dubious practicality and even presently unknown chemical detail, but they must include all possible sequences derived from the masterlist reactions [42]. These lists can also serve to stimulate study of potentially useful construction sequences which are not currently practical.

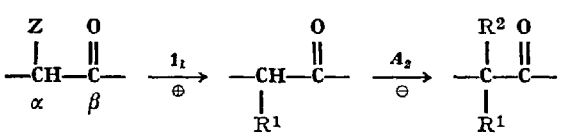
The general sequence lists will take the form of an ordered table of possible product f-lists, preceded by the requisite substrate f-lists and half-reaction sequences for each one, as in the format of Table 3. For any given synthon skeleton marked with a particular pattern of construction sites, the general sequence list for that pattern will provide all the possible product functionalities the skeleton may bear, as well as the starting materials required to produce it and the sequence of 2—3 self-consistent half-reactions which are to be utilized in each case, with the reaction polarities needed to match partner synthons for each construction. This allows all product f-lists to be compared quickly with the f-list for that synthon in the target (protocol step 5b) and also provides the full structures of required starting materials to compare (protocol step 5c) with the catalog of available compounds. (The cataloguing of available starting materials by size, skeleton and functionality f-list is described in the Appendix.)

Mechanical generation of sequences is simply a matter of examining every product *f*-list in the masterlist (Table 3) and ascertaining whether it may act as a substrate *f*-list for a subsequent half-reaction at the site required. Samples of this generation for two-construction patterns are shown in Fig. 5, first as sequence lists, then some examples spelled out in fuller structures. It may be noted here how much more articulation is required to write the fuller structures, but how little more significant information they contain. The final sequence lists generated are presented at the end of the text and are even shorter in that the intermediate *f*-list is omitted since it is readily derivable from the substrate-sequence-product information. The fully articulated structures below in Fig. 5 are easily derived from the sequence lists above, as may be ascertained from the given examples.

Certain skeletal conditions are implied by the requisite functionality for any half-reaction or sequence. This can be seen clearly in the fuller structures at the bottom of Fig. 5, in which the "extra" bonds on the synthon leading to no specific atoms are understood to be single bonds to carbon or hydrogen. The number of allowed attachments of the given carbons to other skeletal carbons is implicit in this and may be expressed by the allowed σ-values of any given carbon in the part structure of the synthon shown. For any construction site the maximum allowed σ-value is a function of the *f*-value of the substrate at that site and the *h*-value, if there are obligatory hydrogens (especially RH half-reactions; see boldface in Table 3), *i.e.*, $\sigma_{max} = 4\text{-}f\text{-}h$. The maximum σ-values for each construction site

Fig. 5. Examples of two-construction sequences

Example	Pattern	σ-Block	Substrate	Reaction ①	Intermediate	Reaction ②	Product	Polarity sequence
			$\alpha\beta\gamma$	—	$\alpha\beta\gamma$		$\alpha\beta\gamma$	
1.	$(\alpha\alpha)$	1	3	3_1	2	2_1	1	+ +
2.		2	12	1_1	02	A_2	02	+ −
3.		2	$\overline{2}$13	2_3	$\overline{1}$13	$\overline{1}_3$	003	+ +
4.		1	$\overline{\overline{2}}$2	C_2	22	$\overline{2}'_2$	02	− −
5.		2	$\overline{1}$2	$\overline{1}'_2$	02	A_2	02	− −
6.	$(\alpha\beta)$	33	$\overline{1}$12	$\overline{1}_3$	002	A_2	002	+ −
7.		32	$\overline{1}$21	$\overline{1}'_3$	0$\overline{2}$1	$\overline{B}_2$	0$\overline{1}$1	+ −
8.		12	31	3_1	21	B_2	2$\overline{1}$	+ −
9.	$(\alpha\gamma)$	22	$\overline{\overline{2}}$2	$\overline{2}_3$	$\overline{1}$12	2_1	$\overline{1}$1$\overline{1}$	+ +
10.		23	2$\overline{1}$0	B_3	1$\overline{1}$	$\overline{1}'_3$	$\overline{1}$10	− +

2. 

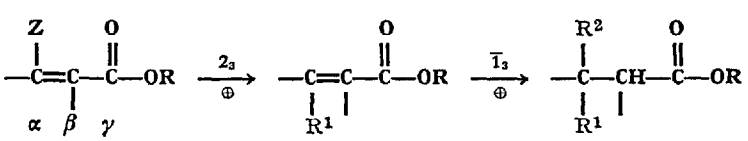
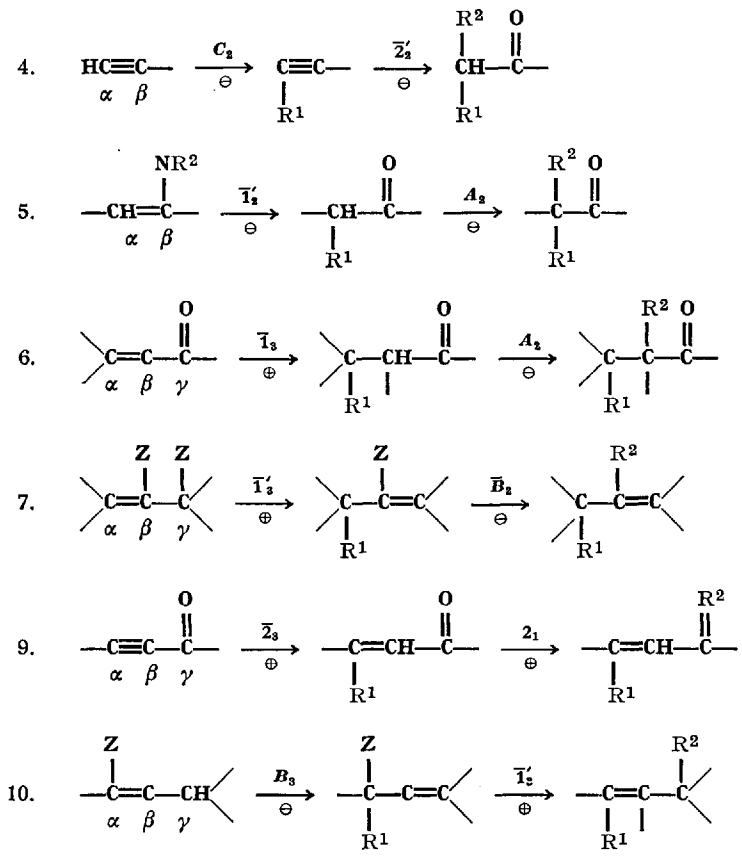
3. 

Fig. 5. (continued)



are written as an ordered σ-list and called the *σ-block*, characteristic of both the half-reaction sequence and the pattern used. The possible σ-blocks for the 13 patterns are appended to Fig. 3. The half-reactions of the masterlist (Table 3) are also grouped into "σ-blocks", simply of σ_α.

The σ-blocks are used to divide the general sequence lists into blocks of sequences for which that σ-list represents the maximum allowed skeletal articulation in any acceptable synthon skeleton. This simplifies searching the lists for particular synthons, since only the sequences included in σ-blocks equal to or larger than the σ-list of sites on the given synthon will fit. The minimum σ-values are of course $\sigma = 1$ for a site at the end of the strand of obligatory functionality in the f-list and $\sigma = 2$ for a site within that strand.

The reactions sampled in Fig. 5 are all cases of internal overlap, for all the overlapping functions needed to activate the two successive constructions are contained internally, *i.e.*, within the carbon strand of the synthon skeleton. The cases of *external overlap* (Section 10) need to be defined and added in order to produce the full sequence lists for the 13 patterns. These will be cases like *10* in

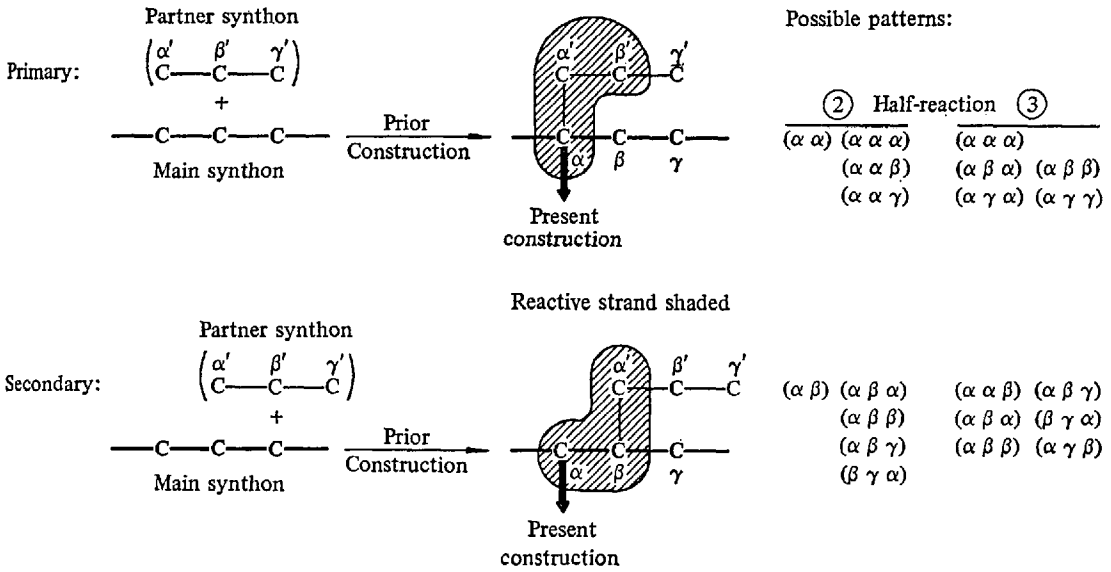


Fig. 6. External overlap

which the reactive strand for the second construction overlaps the bond constructed in the first, and so bears some requisite functionality left on the partner synthon from the previous construction.

The possible situations in which external overlap can occur are analyzed in Fig. 6, which shows that there are two kinds of external overlap. In *primary overlap* the previous construction was at the same site as the one under consideration. Hence only the α-carbon of the synthon is now part of the reactive strand for the new half-reaction, the rest of the strand lying across the previously constructed bond into the product f-list of the previous partner synthon, as in *10*. Thus primary overlap can involve only half-reactions of $s' = 2$ or 3. With *secondary overlap* the prior construction has occurred at the β-carbon of the present reactive strand and allows external overlap to involve only the first (α') carbon of the prior partner synthon and so only present half-reactions of $s' = 3$.

These two kinds of external overlap are characteristic of particular patterns, such as ($\boldsymbol{\alpha\alpha}$) for primary overlap and ($\boldsymbol{\alpha\beta}$) for secondary, with ($\boldsymbol{\alpha\gamma}$) offering no option for external overlap. The kind of external overlap available to each pattern is set out in Fig. 6. Primary overlap usually arises either with α-functionality of 0 (requiring partner activation for A_2 or A_3) or a double bond extending over the previously constructed link (as in *10*). With secondary overlap the main synthon either exhibits a double bond at $\alpha\beta$ (requiring γ-activation) or a double bond over the previously constructed link at β. The possible substrates for external overlap are, therefore, the normal $s' = 2$ or 3 f-lists truncated after f_α for primary, after f_β for secondary, overlap, the remainder of the strand being found on the partner synthon. In order to recognize f-lists on the main synthon which will serve as reactive strands if coupled to a suitable joined partner synthon, we can gather all

Table 4. Half-reactions with external overlap

Partner sets	Substrates $\alpha\beta\gamma$	Products:	σ-Blocks (Max σ_α): 3 $\alpha\beta\gamma$	2 $\alpha\beta\gamma$		1 $\alpha\beta\gamma$
Primary:						
J,K,M	0	A_2A_3	0	A_2A_3	$\bar{1}$	
J	1			A_3	$\bar{1}$	
F,G,H,I,L	$\bar{1}$	$A_3\bar{1}_2\bar{1}_3\bar{1}'_2\bar{1}'_3$	0	$A_3\bar{B}_2$	$\bar{1}$	
K	$\bar{1}\bar{1}$	A_2	00			
F,G,I,L	$\bar{2}$			B_3	1	B_3 $\bar{2}$
				$\bar{B}_2B_32_3\bar{2}_3$	$\bar{1}$	
Secondary:						
F	$0\bar{1}$	A_3	$0\bar{1}$	A_3	$\bar{1}\bar{1}$	
F	$1\bar{1}$	A_3	$0\bar{1}$	A_3	$\bar{1}\bar{1}$	
				B_3	$1\bar{1}$	B_3 $\bar{2}\bar{1}$
				B_3	$\bar{1}\bar{1}$	B_3 $\bar{2}\bar{1}$
O,E	$\bar{1}\bar{1}$	$A_3\bar{1}'_3$	$0\bar{1}$	A_3	$\bar{1}\bar{1}$	
E	$\bar{1}\bar{2}$	$\bar{1}'_3$	$0\bar{2}$			
K,O	$2\bar{1}$			2_3	$\bar{1}\bar{1}$	
				B_3	$1\bar{1}$	B_3 $\bar{2}\bar{1}$
				B_3	$\bar{1}\bar{1}$	B_3 $\bar{2}\bar{1}$

Partner sets (available functionality in prior product, to activate external overlap)

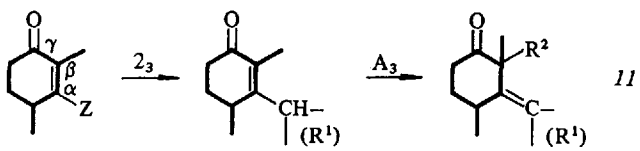
Partner synthon:

Set	Prior product $\alpha\beta\gamma$	From *half-reactions* —	+
O	0	$A_1A_1A_1\bar{1}'_2\bar{2}'_3$	$1_1\bar{1}_2\bar{1}_3\bar{1}'_3$
E	1	$B_1(B_2B_3)$	
F	$\bar{1}$		
G	$\bar{1}0$	B_1	2_1
H	$\bar{1}1$	—	
I	$\bar{1}\frac{2}{3}$	A_2B_2	
J	$\bar{1}\bar{1}$	$\bar{B}_2$	$\bar{2}_2(2_3,\bar{2}_3)$
K	$\frac{2}{3}$	C_1	3_1
L	$\bar{2}$	$B_1B_2B_3C_1$	—
M	$\bar{2}\bar{2}$	C_2	3_2

such truncated *f*-lists. These are collected, as both the substrate and product functionality which appears on the main synthon, in Table 4, and they offer a set of acceptable sequences to be added to those of the masterlist when seeking the second or third half-reaction in a sequence [43]. At the bottom of Table 4 is a guide to the restrictions placed on the possible half-reactions of the previous partner in order to leave the functionality needed for the external overlap.

Thus the strands in Table 4 are incomplete and can only activate construction when taken together with functionality provided by a prior construction partner.

The main consequence of this analysis is that sequences for a synthon may still be listed independently of the construction partners but that the nature of the given synthon *f*-lists and half-reactions fully defines the requirements that must be laid on the prior partner if an external overlap sequence is to succeed. Hence it is enough in the general sequence lists to indicate which sequences invoke external overlap in order to define completely the limitations imposed on the prior partner reactions. By way of illustration the aldehyde synthon in *10* is simply written as $f=2 \rightarrow 0(2_1\bar{1}_3)$ with external overlap (primary) in the (***αα***) pattern list; this implies $2 \rightarrow \bar{1}$ in the first (2_1) half-reaction and the second ($\bar{1}_3$) is external overlap using the $\bar{1}$ as substrate as listed in Table 4. The implication is that the first construction partner, which must have ⊖ polarity, used an A_2 or B_2 half-reaction. The example in 11 lists the main synthon (boldface in *11*) with (***αβ***) pattern and secondary overlap, simply as $(\bar{2}\bar{1}2)2_3A_3 \rightarrow (\bar{1}02)$, *i.e.*, (substrate *f*-list at ***αβγ***) sequence of two successive self-consistent half-reactions → (product *f*-list at ***αβγ***), the italics indicating the secondary overlap of the first construction link to



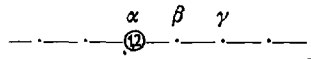
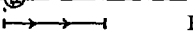
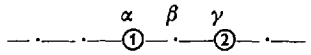
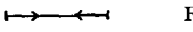
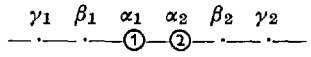
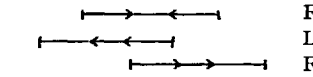
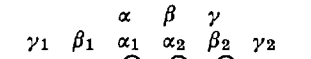
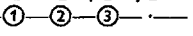
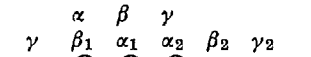
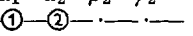
11

(αβγ): $(\bar{2}\bar{1}2)$ $(\bar{1}\bar{1}2)$ $(\bar{1}02)$

R^1 in activating the second (A_3) half-reaction; the sequence can be found in the 23 *σ*-block of the (***αβ***) pattern sequence list.

For the generation of the sequence lists now there remains the problem of defining only the sequences with maximum overlap. Continuing the discussion in Section 10, we must now examine the various choices for laying on reactive strands in the 13 patterns so as to achieve maximum overlap and to minimize excess functionality. Clearly the maximum overlap for (***αα***) will result from the reactive strands of both half-reactions taken to the right of their common site of construction. This yields full overlap and a maximum functionality span (FS) of 3 if at least one half-reaction has $s'=3$. The same is true of (***ααα***) with all three half-reactions overlapping to the right of the site. Thus the only sequences accepted into the lists for (***αα***) and (***ααα***) patterns are those with all reactive strands oriented to the same side of the ***α*** construction site, *i.e.*, functionalizing the same carbons for each successive construction.

Similarly, the (***αγ***) pattern will exhibit overlap only with the first half-reaction (at ***α***) to the right and the second (at *γ*) to the left. This again yields a full functionality span of 3 for the (***αγ***) pattern. For both patterns the functionality placed by acceptable sequences will appear at ***α,β,γ***. The locations of these functionalized carbons are shown in Fig. 7 as a bar indicating the extent and position of the *functionality span* (*FS*) below the strand of the synthon skeleton marked with the construction sites and their site span (*SS*). The directions of the reactive strands of the successive half-reactions are also indicated as lying to right (R) or left (L) of their respective construction sites. Hence in all lists for patterns (***αα***) and (***αγ***)

Two constructions	Strand of construction sites and overlapping functional span	Derived patterns for three constructions		
($\alpha\alpha$)	($SS = 1$): 	($\alpha\alpha\alpha$)	($\alpha\alpha\beta$)	($\alpha\alpha\gamma$)
	($FS = 3$):  RR			
($\alpha\gamma$)	($SS = 3$): 	($\alpha\gamma\alpha$)	($\alpha\gamma\beta$)	($\alpha\gamma\gamma$)
	($FS = 3$):  RL			
($\alpha\beta$)	($SS = 2$): 	($\alpha\beta\alpha$)	($\alpha\beta\beta$)	
	($FS = 4$):  RL, LL, RR			
	($SS = 3$): 	($\alpha\beta\gamma$)		
	($FS = 3$): 			
	($SS = 3$): 	($\beta\gamma\alpha$)		
	($FS = 3$): 			

SS = Site span; FS = overlapping functional span; R = Right, L = left (directions of reactive spans from construction sites); construction sites circled with numbers showing order of reaction.

Fig. 7. Functional spans used for sequence lists

and their derived three-construction patterns the requisite functionality will always be found on the span of the α,β,γ carbons.

The ($\alpha\beta$) pattern is more complex. If the functionality span were limited to the site span (SS = 2), half-reactions of $s' = 3$ would be omitted. To include these obliges acceptance of a functionality span of 4 and reactive strands for each site either to right or left. Hence the two reactive strands can be RL, RR, or RL with maximum $FS = 4$ in three ways, but the fourth combination, LR, results in no overlap at all and is omitted. To encompass these variants the synthon strand cannot simply be labeled α,β,γ as before, but is labeled $\gamma_1\beta_1\alpha_1\alpha_2\beta_2\gamma_2$ over the six accessible carbons, four of which may be functionalized in three ways, with α_1 and α_2 the first and second construction sites, respectively, as illustrated in Fig. 7.

With this definition of functionality span in ($\alpha\beta$) all sequences used are overlapping except the simplest, *i.e.*, $s_1' = s_2' = 1$, and these simple non-overlap sequences are all added to the list. The wider site span of the ($\alpha\gamma$) pattern results in more non-overlap sequences: if one half-span is $s' = 1$, and the other $s' \leq 2$, there is no overlap even though all functionality lies within the functionality span accepted, *i.e.*, α,β,γ. Hence these non-overlap sequences are also included in the list, as in (120) $1_1A_2 \rightarrow$ (020), *i.e.*, **CX–CO–CH** $\xrightarrow{1_1\,A_2}$ **R–C–CO–C–**R′.

The three-construction sequences are derived from two-construction sequences by accepting the product *f*-list of two constructions as the substrate for a third.

The derived patterns are assembled in Fig. 7 at the right. From ($\alpha\alpha$), ($\alpha\alpha\alpha$) fully overlaps but ($\alpha\alpha\beta$) will have no overlap for the third reaction if $s_1' = s_2' = 1$. As with the non-overlap case in ($\alpha\beta$) these must be separately generated by adding to these ($\alpha\alpha$) products (with $FS = 1$) all possible β-functionalities to make non-overlap substrates for the third half-reaction. ($\alpha\alpha\gamma$) is similarly parallel to ($\alpha\gamma$) and non-overlap cases must be created by adding all possible γ- or β,γ-functionality to the parent ($\alpha\alpha$) sequences of $FS = 1$ or 2. In extending ($\alpha\gamma$) to its three derived patterns, ($\alpha\gamma\alpha$), ($\alpha\gamma\beta$) and ($\alpha\gamma\gamma$), all non-overlaps have already been included in ($\alpha\gamma$) and no added functionalities are required. All six of these derived three-construction sequences will have $FS = 3$, their functionality fitting onto the α,β,γ strand; in all cases the reactive strand for the third half-reaction also lies on this strand.

Again, three-construction sequences derived from ($\alpha\beta$) are less simple. The ($\alpha\beta\alpha$) and ($\alpha\beta\beta$) patterns utilize only the two construction sites of the parent ($\alpha\beta$) and have the same three functionality spans of $FS = 4$. In creating these lists all cases of ($\alpha\beta$) product *f*-lists which acted as substrates for a third half-reaction were used and no new functionality was added. However, the last two patterns have again a site span of three and so are parallel to the ($\alpha\gamma$) and its derived patterns. Like these other patterns, the functionality span was limited to the site span ($FS = SS = 3$) as shown at the bottom of Fig. 7 and only ($\alpha\beta$) product *f*-lists within that span were used to generate the sequence lists for ($\alpha\beta\gamma$) and ($\beta\gamma\alpha$). New functional groups were added at β_2 for ($\alpha\beta\gamma$) and at β_1 for ($\beta\gamma\alpha$) if there was no present indicated functionality there in the ($\alpha\beta$) product as third-construction substrate, *i.e.*, for ($\alpha\beta$) products with $FS = 2$ only. This parallels the addition of extra functionality described for ($\alpha\alpha\beta$) and ($\alpha\alpha\gamma$) patterns above.

In this way the 13 general sequence lists were mechanically generated, with no judgments made as to chemical practicality, in order to see all possibilities that could arise from applying these few simple and clearly defined criteria and overlap limitations [44]. A key feature of the criteria of self-consistent sequences with maximum overlap is the expectation that they will result in a stringent reduction of possible sequences, and hence a significant pruning of the synthesis tree. It is important, therefore, to examine the extent of this reduction. There are 60 half-reactions and so there should be $(60)^2 = 3600$ two-construction sequences possible without this reduction, and four times this number (14,400) if all options of strands both left and right are allowed. For three constructions there are $(60)^3 =$ 216,000 and eight times as many (1,728,000) with right-left placement options. Thus without these stringent criteria acting to reduce the number of possible sequences this approach would be unmanageable. The reductions amount to a selection of particular favored (short) routes through the synthesis tree, and the resulting selection is severe.

There are only 237 sequences (substrates and two successive half-reactions) for the ($\alpha\alpha$) pattern which emerge from application of the criteria and lead to only 30 different product *f*-lists. This represents a selection of 237/14,400 or 1.65%. The other two-construction sequence patterns list 396 sequences (2.75%) for ($\alpha\beta$) and 503 (3.49%) for ($\alpha\gamma$) with less overlap. Indeed the latter two contain a large proportion of non-overlap sequences, as noted above, which rapidly swells the total; the non-overlaps for ($\alpha\beta$), for example, are the $s_1' = s_2' = 1$ sequences,

amounting to $10 \times 10 = 100$ of the total 396 sequences, since there are ten half-reactions of $s' = 1$, although a few are disallowed [44]; for ($\alpha\gamma$) more than half of the sequences (327) are non-overlaps. The extent of external overlap possibility may be seen in that there are 98 such sequences in the total of 237 for ($\alpha\alpha$) and 64/396 for ($\alpha\beta$). For the three-construction sequences the selection is even stronger, as may be expected for the greater stringency of the self-consistency criterion applied twice. The ($\alpha\alpha\alpha$) pattern is the most severe with only 531 sequences, or 0.03% of 1,728,000, leading to 14 product f-lists. These enumerations are displayed in Table 5 and show under 1% selection for most three-construction sequences. The stringency of selection also shows in the products. The number of possible f-lists for a three-carbon strand ($f_\alpha f_\beta f_\gamma$) is 175 if all f-values of 0,1,2 and all barred combinations of them ($\bar{1}2$, $1\bar{2}$, $\bar{2}\bar{2}$, etc.) are allowed. The number of actual product f-lists which emerge is much less (Table 5), showing restrictions on possible target functionality resulting from self-consistent construction sequences. Self-consistent sequences, therefore, will not produce all possible targets.

Parenthetically, these enumerations also indicate the importance of separate consideration of each synthon, using only half-reaction sequences. There are 40 $\ominus$ and 20 $\oplus$ half-reactions in the masterlist, or 800 possible isohypsic ($\oplus$ $\ominus$) combinations for one construction. Since some combinations are unreal [17], this figure is actually reduced to only 350. Two successive full constructions then represents $(350)^2 = 122{,}500$ combinations and a sequence of three has 42,875,000.

Table 5. Enumeration of general sequence lists

Pattern	Number of sequences	Number of products[1]
($\alpha\alpha$)	237	34(30)
($\alpha\alpha\alpha$)	531	15(14)
($\alpha\alpha\beta$)	823	65(49)
($\alpha\alpha\gamma$)	1879	91(58)
($\alpha\beta$)	396	132(104)
($\alpha\beta\alpha$)	1313	116(100)
($\alpha\beta\beta$)	1159	88(80)
($\alpha\beta\gamma$)	936	181(90)
($\beta\gamma\alpha$)	1085	221(93)
($\alpha\gamma$)	503	128(86)
($\alpha\gamma\alpha$)	1621	82(63)
($\alpha\gamma\beta$)	1506	175(95)
($\alpha\gamma\gamma$)	1589	84(56)

[1] The total number of products in the list is shown first and in parentheses the number of different products (no duplication).

Thus the combinations are already much reduced on separate consideration of one synthon and its half-reaction sequences only. If considerable selection is then achieved on each separate synthon and its sequences, the combinations of full constructions possible when they are finally matched into whole construction routes will be far fewer.

Thus the complete sequence lists are generated and displayed at the end of the text. They constitute a huge number of synthetic reaction combinations which are dramatically reduced in representation by including only synthetically significant information, the net structural changes defined by the numerical convention. Without this convention the lists would require many volumes of written structures to reproduce, as may be seen by expanding any list item into a fully written structural sequence (cf., the examples of Fig. 5 or *11* in the text). With a little practice this becomes an easy process and also clearly demonstrates that the spatial condensation afforded by the numerical convention sacrifices very little significant information.

13. Practical Use of Sequence Lists

Although the foregoing explanations of sequence list generation are rather complex, the practical use of these lists is simple. The protocol calls for assembling several bondsets from bonds selected as good candidates for construction, and then considering these bondsets separately. The bondset in turn reveals the skeletons of the starting materials and these synthon skeletons are then each overlaid with the functionality required to achieve self-consistent construction sequences all possible ways. The criteria of maximum functional overlap (Section 10) are applied to focus choices in order to avoid excess proliferation of functionality, and this focus is already included in the given sequence lists, as described in Section 12. The sequence lists now offer all sequences within these criteria, and those appropriate to the given synthon skeleton and its pattern of construction sites may be withdrawn from the list for consideration.

The general sequence lists are presented as an ordered listing of product *f*-lists, with the several half-reaction sequences leading to each and the substrate *f*-lists required to initiate each of these sequences. The sequence lists are organized by products in order to compare quickly with given target functionality. They could also be re-organized into another set by substrate *f*-lists, showing all sequences and products arising from each substrate, if it were more useful to focus selection on available starting materials. The lists are further divided into σ-blocks indicating the maximum synthon σ-value allowed by sequences in that block for each construction site. Thus only those σ-blocks with σ-values equal to or greater than those in the given synthon may be used to provide valid sequences.

In each block the products are ordered by increasing functionality level in the *f*-list. Those products with fewer functionalized positions than the full functionality span allowed for the pattern (Fig. 7) are listed first. This allows their quick isolation for use on synthon skeletons whose carbons also do not cover the full functionality span. Thus only example 1 in Fig. 5 could be used with a one-

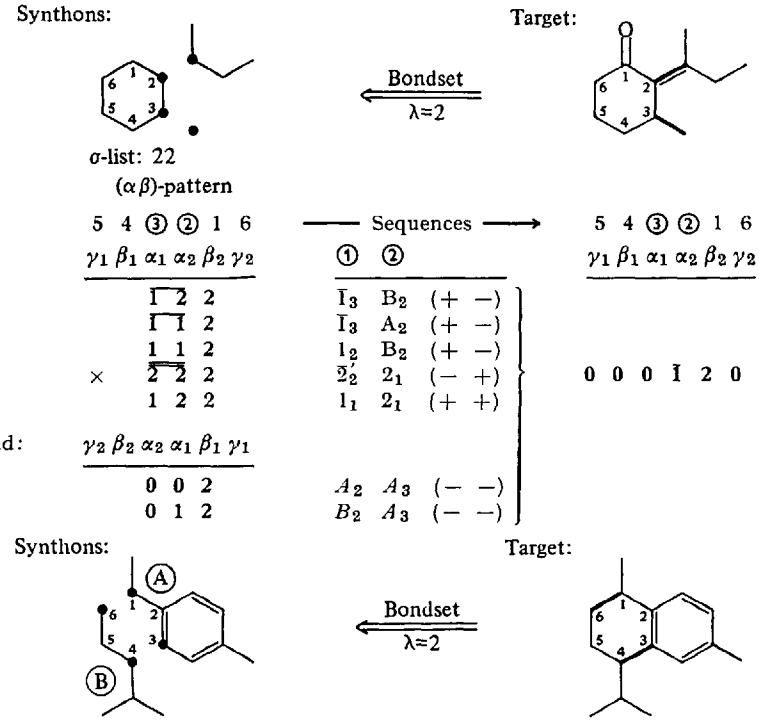
carbon synthon, and its place in the ($\alpha\alpha$) sequence list is quickly seen by inspection among products with only one-digit *f*-lists. In general the *f*-values at the construction sites are the same for all the products in one block and equal to (3—σ), the σ being the substrate value at the site shown in the σ-list defining the block (2—σ if two constructions at the site). In those cases with lesser *f*-values there must be an obligatory hydrogen appearing at the site in one half-reaction. Hence certain product *f*-lists turn up not only in their expected block but also in lower blocks, although always formed there by different sequences.

The procedure for using the sequence lists is as follows. One synthon is selected as the prime synthon for consideration first, preferably the one with most construction sites. The synthon skeleton is numbered as desired and its product *f*-list entered below the numbers. The construction sites are marked and their pattern noted. The σ-list of the construction sites on the synthon is also noted and all σ-blocks of that list or higher are then valid sources of sequences. Within these blocks on the sequence list for the given pattern are now located all sequences yielding an acceptable product *f*-list, usually the *f*-list of the synthon as it appears in the target. The general sequence lists must always be applied to the synthon skeleton in two ways: left-to-right and right-to-left, reflecting reversed orders of constructions.

The process may be illustrated with the two simple examples of Fig. 8. In the first the bondset was chosen to afford an unbranched cyclohexane derivative as starting material and yields that prime synthon in the ($\alpha\beta$) pattern with a σ-list of 22 for the construction sites. The atom numbering is superimposed on the strand of the ($\alpha\beta$) pattern used in the sequence list ($\gamma_1\beta_1\alpha_1\alpha_2\beta_2\gamma_2$) and the target functionality entered for each position. A list of starting materials, similarly numbered, is now culled from σ-blocks 33,32,23 and 22 of the ($\alpha\beta$) sequence list and entered as *f*-lists with corresponding two-construction sequences. Two lists are collected for the reversed orders, *i.e.* $\alpha = C$—3, $\beta = C$—2 or $\alpha = C$—2, $\beta = C$—3, with five examples found for the first order and two for the second, leading to the target functionality of $2\bar{1}0$ for carbons 1,2,3. The second (reverse) order is written backwards in the example. The polarities of the sequences are shown in parentheses. Each of the seven sequences may easily be written out in full from the collected list, sequence 2 ($\bar{1}_3A_2$) illustrated in *12* with the intermediate derived by consulting the masterlist for the product of $\bar{1}_3$ and substrate of A_2. Sequences 4 and 5 arise from the ($\alpha\beta$) product entry $0\bar{1}$ (in σ-block 22) which demands no functionality at β_1 ($= C$—1); hence the target functionality is entered there as extraneous and carried along unused. Sequence 4 also illustrates that other restrictions (protocol step 5d) may serve to eliminate sequences, here one requiring a triple bond in a ring in the starting material. Sequences 6 and 7 show external overlap; in the former the first half-reaction (A_2) leads to a double bond across the construction link (intermediate *f*-list $0\bar{1}2$) and this is then used in an A_3 half-reaction (secondary overlap) to yield an identically functionalized product. Thus the partner half-reaction for the first construction is restricted to SET F, $\oplus$ polarity, *i.e.*, only a 2_1 half-reaction (Table 4). Such restrictions and the remaining protocol steps (matching the other synthons) are discussed below.

In the second example, a hydrocarbon, the bondset was selected to yield a large but simple aromatic starting material and one with symmetry to avoid

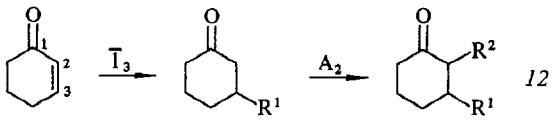
Fig. 8. Examples of sequence list use



S.M.-Ⓐ αβγ (1–3) γβα (3–1) Atoms: 1 2 3	—— Sequences ——→ (1–3)	(3–1)	Target 1 2 3 | 4 5 6	←—— Sequences —— (6–4)	(4–6)	S.M.-Ⓑ αβγ (4–6) γβα (6–4) 4 5 6
0 1̄ 1̄	$A_3A_3/A_3\bar{B}_2$	$A_3A_3/\bar{B}_2A_3$	0 1̄ 1̄ | 0 0 0	$A_3\bar{I}_2$	$A_3\bar{I}_2$	0 1̄ 1̄
0 1̄ 2	—	$\bar{B}_2A_3/B_3\bar{I}_3'$		A_1A_1/A_1I_1	A_1A_1/I_1A_1	1 0 1
1 1̄ 1̄	$I_1A_3/I_1\bar{B}_2$	$\bar{B}_2I_1/\bar{I}_3'A_3$		I_1A_1/I_1I_1	A_1I_1/I_1I_1	—
	$A_3A_3/A_3\bar{B}_2$	$\bar{B}_2A_3$		$A_3\bar{I}_2$	$A_3\bar{I}_2$	1̄ 1̄ 0
1 1̄ 2	$I_1\bar{B}_2$	$\bar{B}_2I_1/\bar{B}_2A_3$		$\bar{I}_3'\bar{I}_2/\bar{I}_2I_1$	$I_1\bar{I}_2$	1 1̄ 1̄
				$I_1\bar{I}_2$	$\bar{I}_3'\bar{I}_2/\bar{I}_2I_1$	1̄ 1̄ 1
1 1̄ 1̄	$B_3\bar{B}_2$	$\bar{B}_2B_3$ {1 1̄ 1̄		$B_3\bar{I}_2$	—	0 1̄ 2
1 1̄ 2	—	$\bar{B}_2B_3$ {Ī 1̄ 1̄	0 0 Ī	B_1A_1/B_1I_1	A_1B_1/I_1B_1	1 0 1
2 1̄ 1̄	$2_1\bar{B}_2$	$\bar{B}_22_1$		$2_1A_1/2_1I_1$	A_12_1/I_12_1	1 0 2
2 1̄ 2	$2_1\bar{B}_2$	$\bar{B}_22_1/2_32_1$		$B_3\bar{I}_2$	$\bar{I}_2B_1$	1̄ 1̄ 1
				$2_1\bar{I}_2$	$\bar{I}_32_1$	1̄ 1̄ 2

Polarity Matching to Target f-list 0 1̄ 1̄ 0 0 0 or 1 1̄ 0 0 0:

						Combinations: (1–3)(6–4)	(2–1)(4–6)
(− −)	5	7	(+ +)	4	4	20	28
(− +)	0	5	(+ −)	1	1	0	5
(+ −)	5	1	(− +)	3	3	15	3
(+ +)	0	1	(− −)	1	1	0	1
Totals	10	14		9	9	35	37

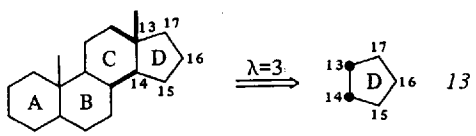


12

$f_3f_2f_1=$ $\bar{1}\bar{1}2$ 002 002

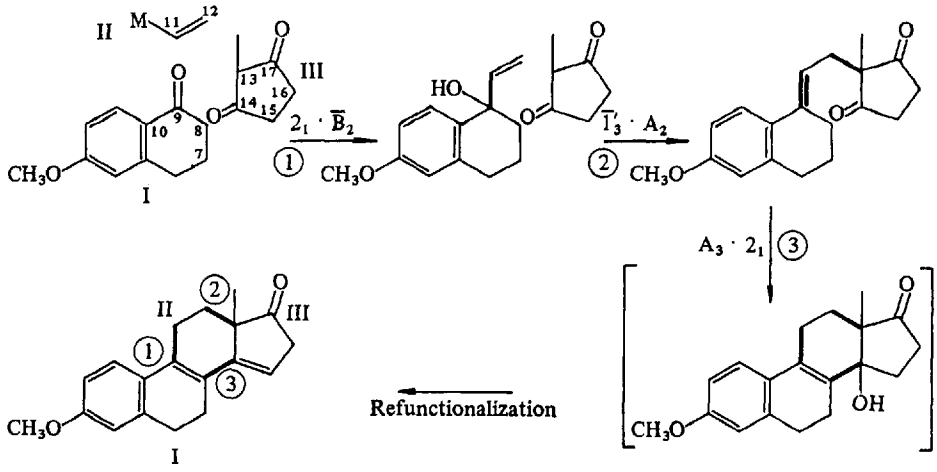
problems of regiospecificity (the two ortho positions are equivalent, one a construction site). Both synthons exhibit the (*aγ*) pattern and sequences in both directions for that pattern are collected for each synthon; in separate columns. Thus the (1—3) column for the aromatic synthon (A) refers to construction at C—1 followed by C—3 and (3—1) refers to the reverse order. A number of sequences were further eliminated by consideration of only aromatic starting materials, hence those with barred f-values for C—2 and C—3. The σ-list for this synthon (A) is again 22 and sequences are found only in σ-blocks 33, 32, 23, 22. Furthermore, the σ_β value is not in the σ-blocks, which refer only to construction sites, but $\sigma=3$ at C—2 and this will further eliminate any products or starting materials with $f>1$ at C—2. Other products may be deemed acceptable even though they will require a final refunctionalization. As illustration, the sequences leading to ($1\bar{1}\bar{1}$) and ($\bar{1}\bar{1}\bar{1}$) products were also collected. After the constructions are complete these will require hydrogenation to the saturated target. The possible sequences for synthon-B, to unfunctionalized product (**000**), are collected in the right column.

Use of sequence lists to formulate the constructions for a partial bondset may be illustrated with the annelation of steroid ring C by a D-ring synthon *13*. The



13

possible patterns are (***aaβ***) and (***aβa***) starting with C—13 and (***aββ***) starting with C—14, and in each case the choice of whether the angular methyl is to be attached by the first or second of the constructions at C—13. If it is the first, it provides only SET 0 (Table 4) for subsequent external overlaps. Various possible product *f*-lists can be searched depending on the desired functionality in the final steroid. Conversely, particular starting materials, like cyclopentadiene, can be systematically sought for all possible products; in the case of cyclopentadiene the ***aβγ*** strand for the (***aaβ***) pattern is C—13, 14, 15 and would include starting material *f*-lists of ($0\bar{1}\bar{1}$) and ($\bar{1}\bar{1}$) with the second double bond carried as extraneous. Alternatively, a functionality like ketone at C—17 might be deemed a desirable product and would also be carried as extraneous in the (***aaβ***) pattern. In this way systematic searches for various particular conditions may be carried out. The (***aaβ***) pattern produces the sequence $A_2A_22_1$ from *f*-list (**02**)≡C—13—14, which if used with the extraneous C—17 ketone added affords the Torgov steroid synthesis (see *1*) [25] from cyclopentane-1,3-dione, shown in Fig. 9 and discussed in Section 14.



Starting Materials:

	I				II		III					— Reactions →	①	②	③
Atoms:	7	8	9	10	11	12	13	14	15	16	17				
σ=	2	2	2	3	1	1	3	2	2	2	2				
I	f=	0	0	2	Ī								$2_1\oplus$		$A_3\ominus$
II						1̄1̄							$\bar{B}_2\ominus$	$\bar{I}'_3\oplus$	
III							0	2	0	0	2			$A_2\ominus$	$2_1\oplus$

Product:

7	8	9	10	11	12	13	14	15	16	17
2	3	3	3	2	2	4	3	2	2	2
0	1̄1̄	Ī	0	0	0	1	0	0	2	

Fig. 9. The Torgov steroid synthesis

As a final example, consider the bondset shown in Fig. 10 for prostaglandin E_1, containing a (2 + 3)-annelation and an affixation of the lower linear side chain. The prime synthon is II with three construction sites and σ-list 221. All three patterns (***αβγ***), (***αγβ***) and (***βγα***) may be used, both for C—8=***α*** and for C—13=***α***. Some 188 sequences emerge to the target *f*-list (**00Ī**) from all six orders, and eight samples are shown in Fig. 10. For synthon I, however, only eight (***αγ***) sequences (both orders) lead to (**201**) in the target and eight more to (**101**) which needs a final refunctionalization. Synthon III is limited to the 2_1 half-reaction to form the double bond if *f*=**1** at C—15 (RH half-reactions eliminate at C—15) [44]; the A_2 and B_2 half-reactions offer ⊖ polarity but an altered product at C—15. Matching these separate sets of sequences is discussed in the next section.

Thus the general sequence lists offer all posssible sequences within their defined limits of self-consistency and maximum overlap. The number of sequences so obtained will depend on the nature of the particular synthons, but often too many sequences are produced and further restrictive conditions must be applied to narrow the selection. These are outlined in steps 5—7 of the protocol, discussed in the next section. Some of these conditions, such as limits placed on acceptable functionality for starting materials and products, have already been applied in the examples.

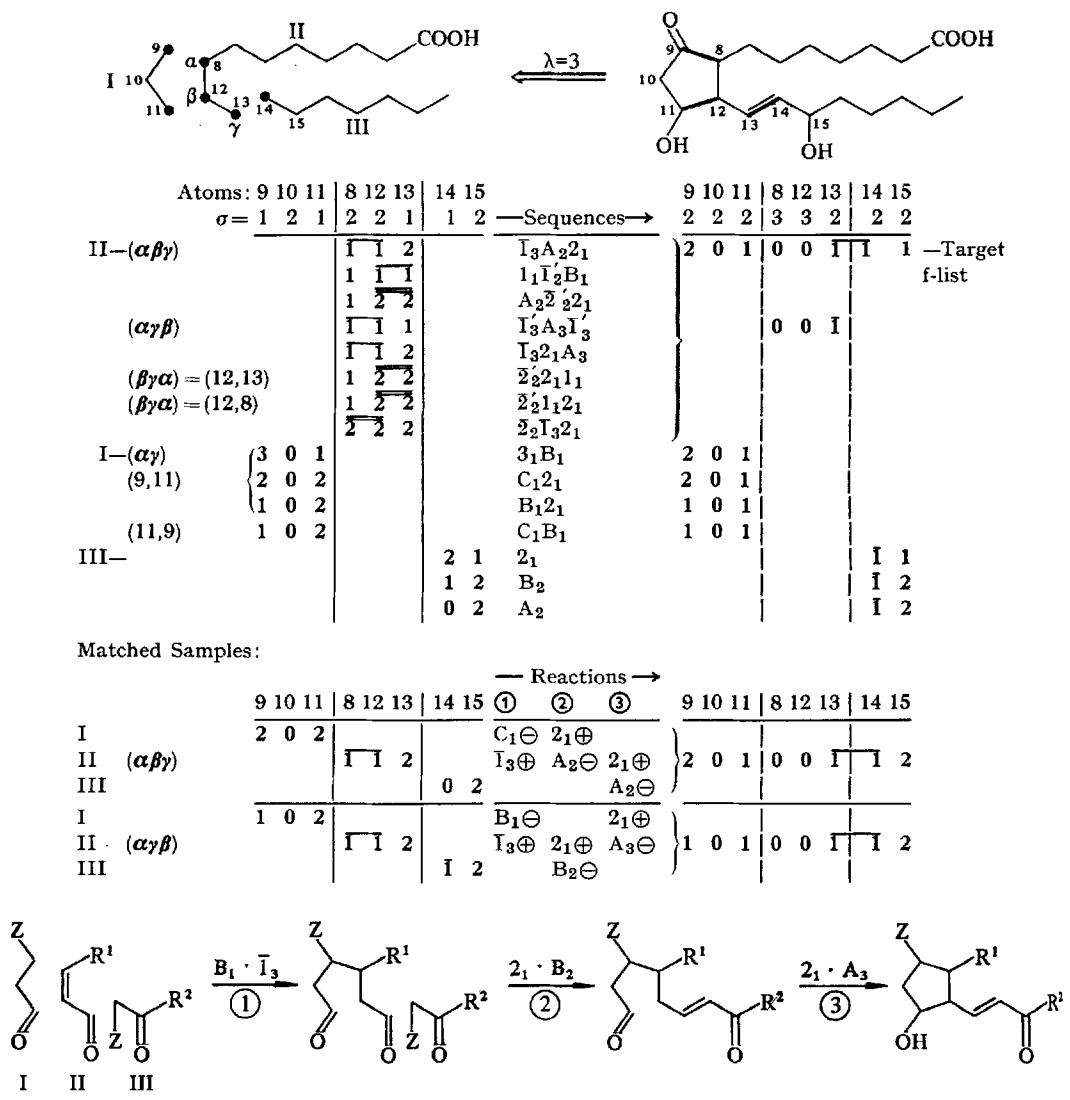


Fig. 10. Sample sequences to protaglandin E_1

14. Final Protocol Steps for Route Selection

Step 5 in the protocol consists of eliminating undesirable sequences found in the selection provided by the general sequence lists. The lists already provide exclusion of reactions inappropriate for the skeletal level of the construction sites on the given synthon, through the use of the σ-blocks. Sequences inappropriate to the

other involved synthon carbons are also easily eliminated (step 5a) by accepting no sequences with substrate or product *f*-lists containing *f*-values greater than $4-\sigma$ at each synthon carbon or requiring a functionalized carbon where no carbon exists in the given synthon.

The imposition of requirements on product *f*-lists (step 5b) and substrate *f*-lists (step 5c) reflects the focussing of the natural proliferation of possible functionality to that of the target and of the available starting materials. The method is heavily oriented to skeletal dissection up to this point, offering all functional variants for assembling given skeletons and so obtains compensation by these important functionality selection steps, at both ends of the synthesis route, target and starting materials. The target functionality is a single *f*-list, but there are thousands of available starting materials and these should be indexed in a catalog by skeletons and *f*-lists. The basis for organizing known starting materials in this compatible format is described in the Appendix.

Finally many half-reactions and sequences are not practical in particular cases. The difference in cyclic and acyclic situations is one such case. Certain half-reactions, notably A_1, C_2 and 3_3, and in some instances 2_2 and 2_3, are usually unsuitable for cyclization, while others require triply-bonded substrates which cannot be accommodated in common rings, as noted in the first example of Fig. 8, sequence 4. The most common problem that rises, however, is that available chemical methods do not presently exist for executing the change demanded by the sequence, either in that other functionality present in the *f*-lists will not tolerate the required conditions for a given half-reaction or that the regiospecificity implicit in the combination of particular synthon and listed sequence is mechanistically unacceptable. At present these will be spotted easily by the experienced chemist and eliminated, but much can be done in future development of the system to eliminate such sequences automatically and systematically.

Certain half-reactions imply a regiospecificity which is often not warranted when applied to particular synthon skeletons. All $s'=1$ half-reactions are of course regiospecific as involving only one carbon and most $s'=3$ half-reactions are clearly directive owing to functional asymmetry, but $s'=2$ half-reactions with symmetrical substrate functionality are not. These are essentially those with substrate *f*-lists of **11**, $\overline{\mathbf{11}}$, or $\overline{\overline{\mathbf{22}}}$, *i.e.*, 1_2,$\bar{B}_2$, $\bar{1}_2$, $\bar{1}_2'$, $\bar{2}_2$ and $\bar{2}_2'$ with minimum *f*-lists. A major synthetic problem of regiospecificity is the A_2 reaction when either CH adjacent to ketone may act as enolate, and the A_3 reaction, also with tautomerically equivalent α- and γ-carbons, has the same problem. In many such functionally symmetrical cases it is skeletal asymmetry which offers regiospecificity, and this is simply expressed in the different σ-values of the two carbons competing for the construction.

As this information is given in the synthon, it can be mechanically applied to evaluate half-reactions offered by the sequence lists. Thus, in epoxide opening (1_2) the site of lower σ should be preferred for most RH partner half-reactions, *i.e.*, a specification of $\sigma_\alpha < \sigma_\beta$. A similar Markownikoff specification can also be laid on the $\bar{B}_2$ and $\bar{1}_2'$ half-reactions from substrate ($\overline{\mathbf{11}}$), at least when isolated from other functionality, and similar σ-preference is often valid for the A_2 reaction from (**020**). The presence of adjacent functionality in particular *f*-lists may

also influence regiospecificity, especially with adjacent carbonyl, and such cases could similarly be reduced to mechanical selection.

The A_3 reaction, (and of course A_2) is given strong regiospecificity if sited next to a carbonyl and sequences may often be legitimized by the addition of an otherwise extraneous carbonyl adjacent (on a β-carbon) [17]. A second way of providing this functional asymmetry to ensure regiospecificity is through external overlap, in which a prior partner is selected to provide the extra functional group (*e.g.*, carbonyl). In this way an $\bar{1}_2$ reaction from ($\overline{11}$) becomes $\bar{1}_3$ if there is secondary overlap with a prior construction leaving carbonyl on the partner synthon, an A_1 half-reaction can become A_2 or A_3 with prior construction affording $f=2$ or $\overline{11}$ respectively on the partner synthon and so change reaction demands.

Finally cyclization reactions can be noted as providing preferential ring-size regiospecificity for a number of these otherwise ambiguous substrates. All of the considerations are capable of mechanical application to the process of sequence selection, *i.e.*, of eliminating sequences (step 5d) and so pruning the list offered, but without resorting to yield prediction.

Another important factor in this selection of sequences is refunctionalization. If sequences are selected yielding product *f*-lists different from target, refunctionalization must of course take place as separate operations at the end of the synthetic route, and this will be accorded lower priority on grounds of economy. The basic condition of sequence selection in the lists is self-consistency, implying that a product of one construction is ready to undergo the next construction without refunctionalization intervening. This condition is rarely met in practice, and indeed is often not met by the sequence lists. Many sequences contain *implicit refunctionalizations*, owing to a central feature of the initial definition [8], namely the consolidation of all heteroatoms as Z. Thus an alcohol left from aldehyde addition (2_1) is not distinguished from the bromide or tosylate required for an alkylation (1_1) in the next construction. There is an implicit $Z \rightarrow Z'$ refunctionalization step which is not registered in the *f*-list by definition.

Such successive half-reactions are not properly self-consistent, and a tally of such combinations could be made and used mechanically to discard certain sequences from a derived set if a criterion of true self-consistency is desired [45]. On the other hand many of the refunctionalization steps in the actual syntheses surveyed [24,31] are of exactly this kind, *i.e.*, derivatization of alcohols to mesylates, acetates, etc., ketone-ketal protective interconversions, ester-acid interconversions, etc. Thus, although the self-consistency criterion was applied for reasons of efficiency and does strongly reduce the tree, the fact that the original definition of Z is broad allows a generous amount of implicit refunctionalization in practice. Furthermore, it should be possible to tabulate which of the pairs of successive half-reactions require it and which do not so that its exclusion can be a matter of choice.

When the sequences for each synthon have been pruned to a minimum by these considerations for step 5, they are ready for combination into full construction reactions, by matching the half-reactions of each of the two synthons involved in each construction (protocol step 6). The importance of eliminating undesirable sequences prior to matching will be evident since the number of combinations will be the product of the number of sequences chosen for each synthon. This is,

however, much reduced in several ways, the chief one being the selection of matching half-reactions of opposite polarity only.

For two general synthons combining there are up to 60 half-reactions each (dependent on σ-values) or 3600 possible matchings but this is reduced to $40\ominus \times 20\oplus = 800$ combinations of opposite polarity. This is reduced further by a number of half-reactions creating double bonds at the construction link, which require a similar half-reaction in the partner, lowering possible combinations to 350 [17]. The construction at C—2 in example I, Fig. 8, shows this, as does the C—13—14 construction in prostaglandin (Fig. 10). There are in the former case in fact only the $B_1\ominus$ and $2_1\oplus$ options for the 4-carbon synthon to yield target functionality and only $A_1\ominus$ and $1_1\oplus$ for the methyl synthon, hence only six possible synthetic routes after matching. In prostaglandin synthon III also only one $\oplus$ (2_1) and two $\ominus$ (A_2,B_2) half-reactions can yield the double bond as well as functionality on only C—14,15 of that synthon. In example II, Fig. 8, the polarity matchings yield 35 synthetic routes for one order of constructions and 37 for the reverse, or 72 syntheses to two functionalized variants of the target. There are similarly $8+9=17$ syntheses to the target with the 1—6 double bond. The number of syntheses for the bondset of prostaglandin in Fig. 10 will be composed of polarity matchings for 188 sequences on synthon I (but reduced by the above sequence eliminations of protocol step 5), 8 or 16 sequences for synthon II and 3 for synthon III. This would be $188 \times 16 \times 3 = 4524$ synthetic routes without polarity matching but still in the hundreds with matching. Indeed many of these are seen to be only minor variations, but this combinatorial proliferation nevertheless puts an especial premium on examination of the viability of the separate half-reaction sequences before matching.

In any case, if the protocol aims for discovery of all sequences within the defined criteria, any published synthesis from this bondset should turn up, and indeed one combination here has been successfully executed by Corey and his group [46]; this synthesis is outlined at the bottom of Fig. 10 and is written directly as derived from the *f*-lists in the second matched sample above it. In the actual work, the C—9—Z was a nitro-carbanion (B_1), the C—13—Z was $\ddot{C}^{\ominus}$—$P\emptyset_3^{\oplus}$ for the B_2 reaction of synthon III and implicit refunctionalization occurs in protection and release of the C—11 aldehyde as acetal before construction 3. The first matched sample shown is an ($\alpha\beta\gamma$) pattern of otherwise very similar chemistry for comparison.

The Torgov steroid synthesis (Fig. 9) illustrates a number of the ideas presented here, and represents a particularly efficient self-consistent route. The bondset *1* satisfies several skeletal criteria (Section 6): the large and available starting material skeleton of naphthalene is recognized as is the need to create the quaternary center, and the bondset also serves to cut the skeleton into roughly equal halves. The average synthon size (n_0/k) is $18/3=6$ and the construction ration (λ/b_0) $=3/20=0.15$, both ratios more favorable than the average values of 4 and 0.24, respectively, and so indicative of relative efficiency. The half-reactions are annotated and matched by polarity. In construction 2 the $\bar{1}_3'$ represents an external (secondary) overlap on synthon II with its attendant functionality change on the prior partner synthon I. The ketone at C—17 (cf., *13*) was added for reasons of desired product functionality to synthon III, delivering at the

same time the necessary regiospecificity to the half-reaction A_2 on that synthon. Regiospecificity for the final A_3 half-reaction is seen to arise from ring-size demands in cyclization.

15. Conclusion

The intent of this exposition has been to delineate a protocol, or stepwise procedure, for analyzing a target skeleton and arriving at a number of specific routes for its synthesis. Disallowing yield prediction as too imprecise for discrimination among millions of alternatives, the protocol seeks instead to locate the shortest routes with least chance of deflective side reactions. As such it cannot hope to single out a "best route", but it does provide confidence that within clearly defined limits it examines *all* routes, and so allows the user to know exactly what kinds of syntheses it produces and what it does not. The protocol is largely free of detailed bias concerning practical viability of the sequences produced. In general the numbers of routes produced are not excessive, but the final practical selection among them remains a matter for chemical experience and, implicitly, yield prediction. However, such prediction is only made on the few candidates left after stringent selections made on other, more reliable bases.

The aim throughout has been to develop a system which encompasses all possibilities within clearly defined limits. A clearer perspective on the scope of the procedure can be obtained by summarizing these limits.

a) The initial consolidation of reactions into a numerical code not only simplifies the sorting but also condenses synthetically trivial functionality distinctions into a sharp definition. This leaves many options to the laboratory in such matters as the practical choice of ester vs. nitrile, choice of leaving groups or carbanion-stabilizing groups (Z), etc. However, the consolidation chosen largely parallels the common expectation of such choice flexibility to meet experimental exigencies.

b) The selection of the 60 construction half-reactions is quite specific as to detailed functionality required and limitations placed on added, extraneous functionality in the obligatory strand. The number is open to user alteration but exclusion or inclusion of any possible half-reaction is clear.

c) The general sequence lists developed from the half-reactions demand self-consistency and clear restrictions on functionality placement via the criterion of maximum overlap, specified for each pattern.

Probably the least mechanical and easily defined operation is the initial choice of bondsets as a starting point for the protocol. Criteria for bond selection on grounds of both target functionality and target skeleton are applied but the procedure is still somewhat arbitrary and in need of sharper definition. In view of the enormous size of the synthesis tree this is probably inevitable, but it may be noted that it is no more arbitrary than the "traditional" description of stepwise retrosynthetic development from target functionality. In that procedure a bondset is also ultimately defined in steps, of course, by the constructions selected from the functionality each time. Such a procedure in fact misses many

routes involving dummy functionality, which will, however, appear in the protocol offered here.

Finally there are imposed limitations in the present method in that certain important areas are not covered at all, although they can presumably be added in future development. This is so because the present protocol only derives direct routes of single sequential constructions and offers no consideration of indirect routes, those which involve cleavages of C—C bonds or skeletal rearrangements (RR reactions with concurrent cleavage and construction) [8]. Nearly thirty of the hundred syntheses in Ref. [24] and most of the newer prostaglandin syntheses to date [47] exhibit such cleavages and/or rearrangements. Cleavages (and rearrangements) can certainly be formulated in the same numerical format as constructions, so that it should be possible to expand the present system by their inclusion under acceptable, defined restrictions. In particular, an examination of the cleavage reactions in known syntheses shows many to be merely decarboxylations. Thus carboxyl groups could be alternatively regarded in certain contexts as functionalities (Z), particularly when used simply, as in β-keto-esters, to gain reactivity or regioselectivity, and are skeletally extraneous. Rearrangements, on the other hand, link functional change to three carbons in a triangle and such triangles can be set up by closing any 3-strand in the target skeleton with a bond intended for cleavage [16]. This allows rearrangement options to be systematically explored under the restrictions of the net structural changes of known (or knowable) rearrangement reactions, involving a skeletal triangle unit for *f*-listing.

Furthermore, the single sequential constructions derived in this protocol will miss some concerted two-construction reactions, most notably cycloadditions like the Diels-Alder reaction. These are simply special cases of annelation. Annelations are of central importance to the synthesis of cyclic molecules since they are the family of reactions creating rings from separate, smaller starting materials (see Section 8, item 3, and Ref.[16]). They deserve separate special treatment as linked pairs of two successive half-reactions on two synthons. This could derive special exhaustive sequence lists for annelations, both those already buried in the present sequence lists and the important cycloadditions, as *f*-lists of net structural change.

The system as defined is also flexible with respect to future development in incorporating presently excluded options. Since all possible target *f*-lists are not produced by the self-consistent sequences of the lists, there must be occasions which demand refunctionalization. At present these are assumed to occur at the end of the route, following full skeletal construction, but it is equally efficient and more flexible to allow them en route as well. It is possible to systematize refunctionalization in the same format as constructions (cf., Table 3), perhaps including the $Z \rightarrow Z'$ reactions implicit in the present sequences [45]. With this added tool the self-consistency criterion could be made less inflexible by allowing certain specified refunctionalizations to intervene among constructions, with a view to exploring the expansion of options this will produce.

Development of the system to incorporate a more definitive handling of stereochemistry is a clear need, but the necessary heuristic treatment of the relation of stereochemistry to synthesis design has not yet been explicitly formulated, (see, however, Ref. [10]). The view implicit in the present protocol is that stereo-

chemistry is of secondary importance to the main theme of skeleton building and appears here largely as the selection, from those derived by the sequence lists, of the sequences amenable to stereocontrol.

The half-reactions formulated here in the masterlist, and used in the general sequence lists, have value for the synthetic chemist not only in clarifying our sense of definition of construction reactions but also in pointing out deficiencies in our practical collection of viable reactions. A check on the frequency of appearance of the various half-reactions in the general sequence lists can show which are most important and lead to reexamination of those with practical limitations. In particular substitutions and nucleophilic or electrophilic additions to simple, unactivated olefins, (respectively B_2, $\bar{1}_2$ and $\bar{1}'_2$) seem to need better implementation, perhaps through organometallic mediation.

The computer has not been employed here primarily because of the philosophy that the development of a framework of logic must precede mechanization of its use. It was also seen as an ideal from the beginning to be able to create tools simple enough for the chemist to use without resorting to computer help, although the complexity of the problem always made that ideal unlikely. The protocol and its general sequence lists can indeed be used by hand, but their linear, numerical format at the same time ideally suits them for computerization. Future expansion of the system should also now be computerized to handle more expeditiously the exploration of mechanizing refunctionalization, regiospecificity exclusions, and sorting synthons by size, but it may well be that the results of such exploration can be returned to usable form for hand searching.

Used by hand, the protocol is probably more time-consuming than the present, intuitive approach to synthesis design, but the time spent is certainly valuable in offering new structural insights and in satisfying the chemist that shorter schemas are not missed, especially when that time is compared against the man-years of time often required by the actual laboratory execution of a synthesis. Furthermore, the protocol can provide standards against which syntheses derived in the traditional intuitive way may be compared. However, the system offered here is only a beginning and needs extensive use to perceive its strengths and inadequacies for future development. It is not meant to replace art in synthesis but rather to help clarify where real art lies.

The author wishes to express his gratitude to the University of Cape Coast, Ghana, and the U.S. Department of State for a Fulbright visiting professorship which afforded the time and serenity needed to consider the problem, to the Hoffmann-LaRoche Foundation for the financial support of an unrestricted grant, and to numerous friends and audiences who have listened to these ideas and responded constructively over several years.

16. Appendix

Starting Material Catalogs

Although the product *f*-lists offered by the general sequence lists may be assessed by comparison with target functionality, the substrate *f*-lists must be assessed for availability against a starting material catalog. In the introduction above appeared the observation that the tools of the synthetic chemist included a catalog of reactions and a catalog of starting materials. The former is offered in the master-list (Table 3); the latter is only presently available in general as alphabetical lists of names from suppliers. What the synthetic chemist needs is a list subdivided by:

a) synthon size [48];
b) skeleton;
c) locus of functionality on skeleton;
d) nature of functionality.

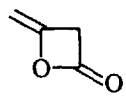
It is possible to formulate a simple cataloguing procedure which is fully compatible with the foregoing discussion, and also easy to learn and use, by describing starting materials with *f*-lists. The *f*-list immediately satisfies requirements c) and d) and the skeletons, usually simple acyclic or monocyclic ones in available starting materials, can be handled with a few superimposed conventions for requirement b). The lists are then ordered in the catalog by a), synthon size [48].

1. A linear chain synthon is designated by its *f*-lists; the number of digits is the chain length.
2. A branched chain is designated by the *f*-list of the longest chain or strand with branched chains shown as *f*-lists, from the branch-point, enclosed in parentheses directly following the *f*-value of the branch-point.
3. Two branches from a quaternary carbon are shown serially within the parenthesis, separated by a slash-line.
4. A monocyclic ring is indicated by enclosure of the cycle in brackets. The cycle could be placed in parentheses as long as it stands at chain end since a parenthesis at the end of a chain cannot indicate a branch. However, the distinguishing of monocycles as brackets is more definitive.
5. An aromatic ring will be a 6-digit set in brackets with a bar over all six digits, but unsubstituted phenyl groups can be shown as $\varnothing$.
6. Bicyclics which are not fused or spiro are accommodated by $\neq 4$, but fused bicyclics (not bridged or spiro) are designated with one ring listed in brackets at chain end and the other nested between the two adjacent carbons of the first ring to which they are attached [49].
7. Oxygen atoms in a chain (ethers, esters) are regarded merely as functionality and the chain (or ring) as broken.
8. Nitrogen atoms in a chain or ring should be treated either way (catalogued twice), as functionality (like oxygen) or as part of the skeleton. In the latter case the letter N is inserted as the *f*-value in the *f*-lists and the adjacent carbons are given their normal *f*-values.

Acyclic:

$CH_3CH_2CH_2COOH$
$CH_3CH_2CH_2COOC_2H_5$
$CH_3CH_2CH_2CN$
$CH_3CH_2CH_2CCl_3$
0003

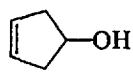
$CH_3COCH_2COOC_2H_5$
0203



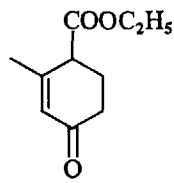
$\bar{1}203$

$(CH_3)_3COH$
01(0)0

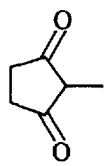
Monocyclic:



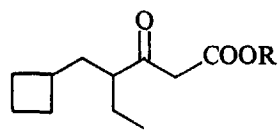
[010$\bar{1}\bar{1}$]



3[0002$\bar{1}\bar{1}$(0)]

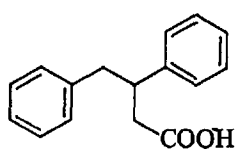


[0020(0)2]

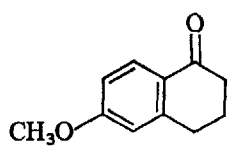


[0000]00(00)203

Bicyclic:

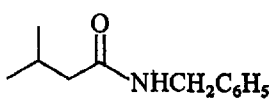


ϕ00(ϕ)03

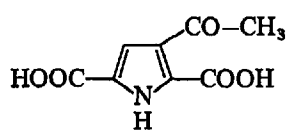


[$\bar{1}\bar{1}\bar{1}$(2000)$\bar{1}\bar{1}\bar{2}$]

Nitrogen:



(a) **00(0)03N1ϕ**
(b) **00(0)03 + 1ϕ**



02[$\bar{1}\bar{1}$(3)N$\bar{1}$(3)$\bar{1}$]
3$\bar{2}\bar{1}\bar{1}$(20)$\bar{2}$3

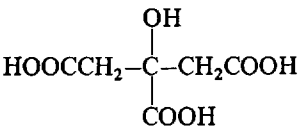
Fig. 11. Examples of annotated starting materials for cataloguing

$CH_3CH_2CH(COOC_2H_5)_2$

$CH_3CH_2CH(CN)COOCH_3$

$CH_3CH_2CH(CCl_3)CN$

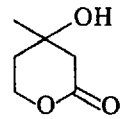
000(3)3



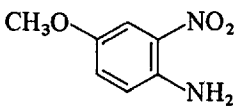
301(3)03

$CH_3CH_2C(CH_2OH)_3$

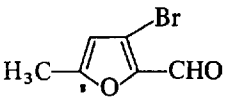
000(1/1)1



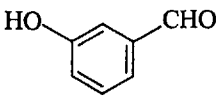
101(0)03



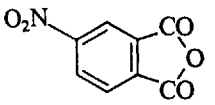
[$\overline{112212}$]



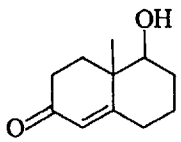
0$\overline{21}\overline{22}$2



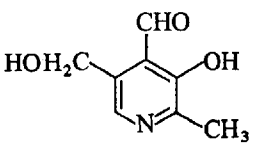
2[$\overline{111121}$]



3[$\overline{111211}$]3



[00$\overline{2}\overline{1}$[0001]0(0)]



0[$\overline{1N11}$(1)$\overline{1}$(2)$\overline{2}$]
02$\overline{21}$(2)$\overline{1}$(1)$\overline{2}$

Cataloguing then proceeds by arranging compounds first by synthon size [48] and subdividing these groups in order of total functionality level $\sum f$, or by number of functionalized sites, as preferred. Final ordering within these subgroups can then proceed by increasing value of the *f*-lists, seen as whole numbers, *i.e.* 0012 before 0021 before 0120 before 1200 before 2100. In this way duplication of entries by reversing the *f*-lists may be avoided (the idea parallels that of IUPAC nomenclature which specifies which chain end begins the numbering).

This *f*-list notation generally reads like linear typed formulas, as in $CH_3CH(CH_3)COCOOH{\equiv}00(0)23$. The σ-values of the various carbons are implicit, those at list ends being terminal ($\sigma = 1$), those in mid-strand secondary ($\sigma = 2$), those before parentheses tertiary ($\sigma = 3$) or quaternary ($\sigma = 4$) if a slash-line appears in the parenthesis. Examples of annotated starting materials are illustrated in Fig. 11. A useful though generalized structure may be drawn for any molecule from its *f*-list coded in this way, just as structures may be drawn from IUPAC names. Considering the number of different starting materials offered for sale in commercial catalogs it is surprising how few different starting materials are used in the many published syntheses surveyed [24], the same favored few in one after another. This seems to imply that synthetic chemists, without catalogs arranged according to their needs, have often employed a rather restricted, commonly familiar set of chemicals. In general available starting materials are skeletally simple, so that it is likely that >90 % of commercial substances can be listed easily without complication by this *f*-list method [49].

17. Glossary

In probing a poorly charted area of concept the development of new terms and the sharper definition of old ones is inescapable but should even so be as minimal as possible. The particular definitions used here are listed below, divided into referent sections.

Structures

Synthon [28]. A synthetic unit of defined skeleton, either linked into a larger skeleton by constructed bonds or unlinked as a starting material with whatever functionality it bears in the situation.

Starting material. Specific structure used as the starting synthon in a synthesis.

Substrate. Relevant part of a synthon before construction.

Product. Relevant part of a synthon after construction.

Target. Full structure of the specific substance for which synthesis is to be designed.

Parts of Structures

Bondset. A set of λ bonds or links in the target skeleton to be constructed in a synthesis; the bondset defines the synthons.

Construction Sites. The carbons of a synthon skeleton at which construction occurs, defined by the bondset.

Pattern. The arrangement of construction sites on a synthon and the order of their construction. Indicated with Greek letters in parentheses, α designating the leftmost site and where possible also the first construction, *i.e.*, all cases in Fig. 3 except ($\beta\gamma\alpha$).

Strand. Any linear chain of carbons in a skeleton defined by the pair of terminal carbons. The reactive strand of a half-reaction constitutes the carbons bearing the obligatory functionality which defines the particular half-reaction.

Span. The number of carbons in a strand.

Functionality Span (*FS*). The number of carbons between, and including, any pair of functionalized carbons.

Construction Span(s). The span of outermost obligatory functions in a construction ($2 \leq s \leq 6$).

Half-span(s'). The span on one synthon from the bond constructed to the outermost obligatory function ($1 \leq s' \leq 3$).

Site Span (*SS*). The span of construction sites on the synthon skeleton. Taken here as limited to three sites, this is the span of the strand joining them in the synthon.

Reactions

Construction. Reaction creating a carbon-carbon σ-bond.

Refunctionalization. Reaction changing functionality but creating no carbon-carbon σ-bond, *i.e.*, not affecting the skeleton.

Affixation [16]. Construction linking two separate synthons, unlinked by C—C σ-bond but perhaps linked prior to construction by a heteroatom bond (*e.g.*, Claisen rearrangement).

Cyclization [16]. Construction within one carbon skeleton, to form a carbocyclic ring.

Isohypsic [8]. Reaction with no overall change in oxidation state of the organic participants.

Half-reaction Net structural change in one synthon during construction.

Reaction List. A list of numerical characteristics of the strand of carbons in a reaction or half-reaction, as substrate or product: *f*-list of functionalities (*f*-values); σ-list of skeletal levels (σ-values).

Self-consistent Sequence. A sequence of construction half-reactions on one synthon which requires no intermediate refunctionalization reactions. The functionality left by one construction is consistent with that required for the next.

Overlap. (Functional Overlap). Occupancy of the same strand by the requisite functionality in the half-spans of two successive constructions.

Internal Overlap. Overlap entirely on one synthon.

External Overlap. Overlap on two previously linked synthons across their construction link. Two kinds are distinguished in Fig. 6:

Primary Overlap. Only the α-carbon of the synthon involved in the reactive strand of a half-reaction ($s'=2$ or 3), the rest of the strand lying across a prior construction link at the α-carbon to a prior partner synthon.

Secondary Overlap. The reactive strand of an $s'=3$ half-reaction lying on the α- and β-carbons of the synthon and the γ-carbon across a prior construction link at the β-carbon to a prior partner synthon.

18. General Sequence Lists

The general sequence lists are printed here in a form suitable for use by hand in seeking sets of half-reaction sequences to combine into synthetic routes as described in sections 12—14. The lists are easy to use; familiarity with *f*-lists is easily established in most cases and their translation to real structures on a given synthon skeleton soon becomes a facile mental process. Although many sequences may be offered by the lists for certain cases, many will quickly be seen to be somewhat minor variants of each other and so encompassed as a group for comprehension.

There are 13 general sequence lists, corresponding to the 13 patterns of construction sites delineated in Fig. 7. In use they must be applied to any given synthon skeleton both left-to-right and right-to-left. The *f*-lists of products and starting materials are annotated as a linear strand of three atoms through the construction sites, as $\alpha\beta\gamma$, for all lists except the ($\alpha\beta$) pattern and its derived ($\alpha\beta\alpha$) and ($\alpha\beta\beta$) three-construction patterns. In the $\alpha\beta\gamma$-strand, the α-carbon is understood to be the site of first construction and the sites of subsequent constructions are implicit, in the pattern label, in every case except the ($\beta\gamma\alpha$) pattern which of course has first construction at the β-carbon. In the ($\alpha\beta$) and derived patterns, the products are listed as a six-carbon strand, $\gamma_1\beta_1\alpha_1\alpha_2\beta_2\gamma_2$, for which the α_1-carbon is the first construction site and α_2 the second.

The products are listed in boldface in the right column with corresponding starting materials and sequences to the left, sorted by polarity for the two-construction patterns. The starting materials are shown as boldface *f*-lists in parentheses, each followed by all sequences of half-reaction labels leading to the product at the right; the various sequences are separated by slashes. Sequences exhibiting external overlap are shown in italics and put restrictive demands on the acceptable partner synthon reactions as shown in Table 4. The starting material *f*-lists correspond to those for products, in most lists being $\alpha\beta\gamma$ (or just $\alpha\beta$ or α if less obligatory functionality is specified). In the $\alpha\beta$ pattern, and in ($\alpha\beta\alpha$) and ($\alpha\beta\beta$), only the central four carbons are specified in the starting material *f*-lists, *i.e.*, ($\beta_1\alpha_1\alpha_2\beta_2$); the γ_1 and γ_2 carbons bear the same *f*-value as seen in the corresponding product *f*-list. A notation of x is used for β_1 and/or β_2 when no functionality is specified. Product *f*-lists bearing single barred digits (at a construction site) imply double bonds created across a construction link to another synthon; in matching synthons, the other must be chosen with such a barred *f*-value at its corresponding construction site. In all *f*-lists, $f = 2$ or 3 is consolidated as $^2/_3$ on non-construction sites where $\Delta f = 0$. In two lists, ($\alpha\beta\gamma$) and ($\beta\gamma\alpha$), it is common for the same set of sequences to afford both $f = 1$ and $\bar{1}$ (or 2 and $\bar{2}$) at α- or γ-construction sites and these are consolidated via an asterisk next to the α- or γ-*f*-value.

In deriving three-construction lists from the parent two-construction lists it is common to specify the whole set of sequences leading to the parent two-construction product followed by an entry showing the added third construction half-reaction(s) yielding the specified three-construction product. This is only done, to consolidate the lists, when such a set comprised more than four or five sequences. Hence the two-construction lists, ($\alpha\alpha$), ($\alpha\beta$) and ($\alpha\gamma$), have a left column labeled

"SET" and bearing identification letters for all the sequences leading to the product on that line. When used in three-construction lists, these sequence sets are placed in brackets with the σ-block, product f-list (numbers only) and identification letter of the parent set of sequences and a number showing the number of sequences to be found in that set. Thus in the $(\alpha\gamma\beta)$ pattern may be found $[\text{SET } 21\text{-}122\text{E}]_6$ indicating that the six sequences in σ-block 21 of the parent $(\alpha\gamma)$ pattern leading to that product f-list **122** identified as E (it is $\bar{1}\bar{2}2$) constitute $(\alpha\gamma\beta)$ pattern sequences when the third half-reaction added after the bracket is used to complete the sequence. In some cases of truncated functionality the set description has the necessary added functionality included in parentheses, particularly for $(\alpha\alpha\beta)$ and $(\alpha\alpha\gamma)$ patterns from $(\alpha\alpha)$ products of $FS = 1$. Hence $[\text{SET } 2\text{-}00 + 3]_8$ in $(\alpha\alpha\gamma)$ implies the eight $(\alpha\alpha)$ sequences in σ-block 2 to product f-list **00** with an added carboxyl derivative ($f = 3$) at the γ-carbon. To consolidate listing space, brackets are also used to contain a series of two-construction sequences which all require the same third half-reaction(s). Following all such brackets which denote two-construction sequences are the third half-reactions to be added to the sequence; they are placed after a +-sign and simply listed, without punctuation, as the acceptable half-reactions to complete the several two-construction sequences in the brackets.

The lists are organized first into σ-blocks, which are σ-lists designating the maximum σ-value at each construction site which is permitted in the given synthon. In use the σ-list of the construction sites for a given synthon is first noted and then all σ-blocks of the pattern list are examined, down from the top of the list to, and including, the σ-block equal to that given σ-list. Within the σ-blocks the sequences are organized by product f-lists, first the truncated ones suitable for smaller synthons (obvious by inspection of the lists). Within these groups the product f-lists are arranged by increasing f-values in $\alpha\beta\gamma$ order (or $\alpha_1\alpha_2\beta_1\beta_2$ order for $(\alpha\beta)$ patterns).

($\alpha\alpha$) Pattern

σ-Block	Seq Set	Substrates and Sequences by Polarity — —	— +	+ —	+ +	Product α β γ
2		(0) A_1A_2/A_1A_3	(1) $B_1\bar{I}_2/B_1\bar{I}_3/B_1\bar{I}'_3$	(1) $1_1A_2/1_1A_3$	(2) $2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}'_3$	0
		(1) $B_1A_1/A_1A_2/A_1A_3/B_1\bar{I}'_2$ B_1A_3/B_1A_3		(2) $2_1A_1/2_1\bar{I}'_2/2_1A_2/2_1A_3$		
		($\bar{1}\bar{1}$) ($\bar{2}\bar{1}$) $\bar{B}_2A_2$	($\bar{1}\bar{1}$) ($\bar{2}\bar{1}$) $\bar{B}_2\bar{I}_2$	($\bar{1}\bar{1}$) $\bar{I}_2A_2/\bar{I}_2A_3$ ($\bar{2}\bar{2}$) $\bar{2}_2A_2$	($\bar{2}\bar{2}$) $\bar{2}_2\bar{I}_2$	0 0
		($\bar{1}\bar{1}$) ($\bar{2}\bar{1}$) $\bar{B}_2\bar{I}'_2$	($\bar{1}\bar{2}$) $\bar{B}_2\bar{I}_2$ ($\bar{2}\bar{2}$) $\bar{2}'_2\bar{I}_2$	($\bar{2}\bar{2}$) $\bar{2}_2\bar{I}'_2$	($\bar{2}\bar{2}$) $2_2\bar{I}_2$	0 1
					($\bar{2}\bar{3}$–) $\bar{2}_2\bar{I}_2$	0 1 –
		(0$\frac{2}{3}$) $A_2A_2/A_2A_2/A_2A_3/A_2\bar{I}'_2$	(0$\frac{2}{3}$) $A_2\bar{I}_2/A_2\bar{I}_3/A_2\bar{I}'_3$	(1$\frac{2}{3}$) 1_1A_2		0 $\frac{2}{3}$
		(1$\frac{2}{3}$) $A_2A_2/B_2A_2/B_2A_2$ $A_2A_3/B_2A_3/B_2\bar{I}'_2$	(1$\frac{2}{3}$) $B_2\bar{I}_2/B_2\bar{I}_3/B_2\bar{I}'_3$	(2$\frac{2}{3}$) $2_1A_2/2_1A_2/2_1A_3$		
		($\bar{1}\frac{2}{3}$) $\bar{B}_2\bar{I}'_2/\bar{I}'_2A_2$		(2$\frac{2}{3}$) $2_2\bar{I}'_2$		
		($\bar{2}\frac{2}{3}$) $\bar{2}'_2A_2/\bar{2}'_2\bar{I}'_2$				
		($\bar{I}\frac{2}{3}$) $A_2A_2/\bar{B}_2A_2/A_3A_2$				
	A		($\bar{1}\bar{3}$–) $\bar{B}_2\bar{I}_2$ ($\bar{2}\bar{3}$–) $\bar{2}'_2\bar{I}_2$	($\bar{1}\bar{3}$–) $\bar{I}_2A_2$ ($\bar{2}\bar{3}$–) $\bar{2}_2\bar{I}'_2$	($\bar{2}\bar{3}$–) $2_2\bar{I}_2$	0 2 –
			(0$\bar{1}\bar{1}$) (1$\bar{1}\bar{1}$) ($\bar{1}\bar{1}$0) $A_3\bar{I}_2$			0 0 0
			($\bar{1}\bar{1}\frac{2}{3}$) ($\bar{2}\bar{1}\frac{2}{3}$) $\bar{B}_2\bar{I}_3$	($\bar{1}\bar{1}\frac{2}{3}$) $\bar{I}_3A_2/\bar{I}_3A_3$	($\bar{2}\bar{1}\frac{2}{3}$) $2_3\bar{I}_3$	0 0 $\frac{2}{3}$
				($\bar{2}\bar{1}\frac{2}{3}$) 2_3A_2 ($\bar{2}\bar{2}\frac{2}{3}$) $\bar{2}_3A_2$	($\bar{2}\bar{2}\frac{2}{3}$) $\bar{2}_3\bar{I}_3$	
		(0$\bar{1}\bar{1}$) (1$\bar{1}\bar{1}$) ($\bar{1}\bar{1}$0) $A_3\bar{I}'_2$				0 1 0
	A	(0$\bar{1}\bar{1}$) (1$\bar{1}\bar{1}$) ($\bar{1}\bar{1}$0) A_3A_3	(1$\bar{1}\bar{1}$) ($\bar{2}$10) $B_3\bar{I}_2/B_3\bar{I}_3/B_3\bar{I}'_3$	(1$\bar{1}\bar{1}$) 1_1A_3 ($\bar{1}\bar{1}$1) $\bar{I}'_3A_3$	($\bar{2}\bar{2}$1) $\bar{2}_2\bar{I}'_3$	0 $\bar{1}$ $\bar{1}$
		(1$\bar{1}\bar{1}$) ($\bar{2}$10) $B_3A_3/B_3\bar{I}'_2$	($\bar{1}\bar{1}$1) ($\bar{2}\bar{1}$1) $\bar{B}_2\bar{I}'_3$	(2$\bar{1}\bar{1}$) 2_1A_3 ($\bar{2}\bar{2}$0) $\bar{2}_2A_3$		
			($\bar{1}\bar{2}\frac{2}{3}$) $\bar{B}_2\bar{I}_3$ ($\bar{2}\bar{2}\frac{2}{3}$) $\bar{2}'_2\bar{I}_3$	($\bar{2}\bar{1}\frac{2}{3}$) $2_3\bar{I}'_2$ ($\bar{2}\bar{2}\frac{2}{3}$) $\bar{2}_3\bar{I}'_2$	($\bar{2}\bar{2}\frac{2}{3}$) $2_3\bar{I}_3$	0 1 $\frac{2}{3}$
	A		($\bar{1}$21) $\bar{B}_2\bar{I}'_3$ ($\bar{2}\bar{2}$1) $\bar{2}'_2\bar{I}'_3$		($\bar{2}\bar{2}$1) $2_2\bar{I}'_3$	0 $\bar{2}$ $\bar{1}$
	A	(0$\bar{2}\bar{2}$) (1$\bar{2}\bar{2}$) A_3A_3		(1$\bar{2}\bar{2}$) 1_1A_3 (2$\bar{2}\bar{2}$) 2_1A_3		0 $\bar{2}$ $\bar{2}$

($\alpha\alpha$) **Pattern** (continued)

σ-Block	Set	Substrates and Sequences by Polarity − −	− +	+ −	+ +	Product α β γ
1			(1) $B_1 1_1$		(2) $2_1 1_1$	0
		(1) B_1B_1/B_1B_3 (2) C_1B_3	(2) $C_1 2_1$	(2) 2_1B_1	(3) $3_1 2_1$	1
	A	(0) A_1A_2/A_1A_3	(1) $B_1 2_2/B_1 2_3$	(1) $1_1A_2/1_1A_3$	(3) $3_1 2_1$	$\bar{1}$
		(1) $B_1B_1/A_1A_2/A_1A_3/B_1\bar{B}_2$ B_1A_3/B_1B_3	(2) $C_1 2_1/C_1 2_2/C_1 2_3$	(2) $2_1B_1/2_1A_3/2_1A_3/2_1\bar{B}_2$		
		(2) $C_1\bar{B}_2/C_1B_3$				
					(21) $2_1 1_2$	0 1
		($\bar{2}\frac{2}{3}$) $C_2\bar{2}'_2$	($1\frac{2}{3}$) $B_2 1_1$	($\bar{3}\frac{2}{3}$) $3_2\bar{2}'_2$		0 $\frac{2}{3}$
	A			($\bar{1}\bar{1}$) $\bar{1}_2A_2/\bar{1}_2A_3$		$\bar{1}$ 0
	A	($\bar{1}\bar{1}$) ($\bar{2}\bar{1}$) $\bar{B}_2\bar{B}_2$	($\bar{2}\bar{2}$) $C_2\bar{2}_2$	($\bar{2}\bar{2}$) $\bar{2}_2\bar{B}_2$	($\bar{3}\bar{2}$) $3_2\bar{2}_2$	$\bar{1}\,\bar{1}$
		($1\frac{1}{3}$) B_2B_2/B_2B_3		($2\frac{2}{3}$) 2_1B_2		$1\frac{1}{3}$
	A	($0\frac{2}{3}$) ($1\frac{1}{3}$) A_2A_2/A_2A_3	($1\frac{1}{3}$) $B_2 2_2/B_2 2_3$	($1\frac{1}{3}$) 1_1A_2		$\bar{1}\frac{1}{3}$
		B_2A_3/B_2A_3		($2\frac{2}{3}$) 2_1B_2		
		($1\frac{1}{3}$) $B_2B_2/B_2\bar{B}_2/B_2B_3$				
		($\bar{1}\frac{1}{3}$) $\bar{1}_2A_2/\bar{1}'_2A_3$				
		($\bar{2}\frac{2}{3}$) $\bar{2}'_2A_2/\bar{2}'_2A_3$				
	B			($\bar{1}\bar{3}$–) $\bar{1}_2A_2/\bar{1}_2A_3$		$\bar{1}$ 2 –
	C	($\bar{1}\frac{2}{3}$) $\bar{B}_2\bar{B}_2$ ($\bar{2}\frac{2}{3}$) $C_2\bar{2}'_2/\bar{2}'_2\bar{B}_2$		($\bar{2}\frac{2}{3}$) $2_2\bar{B}_2$ ($\bar{3}\frac{2}{3}$) $3_2\bar{2}'_2$		$\bar{1}\,\bar{1}\frac{2}{3}$
	D		($\bar{2}\bar{3}$–) $C_2\bar{2}_2$		($\bar{3}\bar{3}$–) $3_2\bar{2}_2$	$\bar{1}\,\bar{2}$ –
	A		($1\bar{1}\bar{1}$) ($\bar{2}\bar{1}0$) $B_3 1_1$			0 $\bar{1}\,\bar{1}$
	A			($\bar{1}\bar{1}\frac{2}{3}$) $\bar{1}_3A_2/\bar{1}_3A_3$		$\bar{1}$ 0 $\frac{2}{3}$
	A	($0\bar{1}\bar{1}$) ($1\bar{1}\bar{1}$) ($\bar{1}\bar{1}0$) $A_3A_3/A_3\bar{B}_2$		($\bar{1}\bar{1}1$) $\bar{1}'_3A_3$		$\bar{1}\,\bar{1}$ 0
		($1\bar{1}\bar{1}$) $\bar{2}\bar{1}0$) $B_3\bar{B}_2/B_3A_3$ ($\bar{1}\bar{1}0$) $\bar{B}_2A_3$		($\bar{2}\bar{2}0$) $\bar{2}_2A_3$		

	A	$(1\bar{1}\Gamma)$ $(\bar{2}10)$ B_3B_3/B_3B_3		$(2\Gamma\Gamma)$ 2_1B_3		1 ΓΓ
	B	$(1\bar{1}\Gamma)$ $(\bar{2}10)$ B_3B_3/B_3A_3 $B_3B_3/B_3\bar{B}_2$	$(1\bar{1}\Gamma)$ $(\bar{2}10)$ B_22_2/B_32_3	$(2\Gamma\Gamma)$ 2_1B_3		1 ΓΓ
	A		$(1\bar{1}\frac{1}{2})$ B_32_3 $(\bar{2}\bar{2}\frac{1}{2})$ $C_2\bar{2}_3$	$(2\Gamma\frac{1}{2})$ $2_3\bar{B}_2$ $(\bar{2}\bar{2}\frac{1}{2})$ $\bar{2}_3B_2$	$(\bar{3}\bar{2}\frac{1}{2})$ $3_2\bar{2}_3$	$\Gamma\Gamma\frac{1}{2}$
	A			$(\bar{2}\bar{2}\frac{1}{2})$ $2_3\bar{B}_2$		$\Gamma\bar{2}\frac{1}{2}$
0		(2) C_1C_1	(3) D_13_1	(3) 3_1C_1	(4) 4_13_1	2 – –
	A	(1) B_1B_1/B_1B_3		(2) $2_1B_1/2_1\bar{B}_2/2_1B_3$		$\bar{2}$ – –
		(2) C_1C_1/C_1B_3		(3) 3_1C_1		

($\alpha\alpha\alpha$) Pattern

σ-Block	Sequence Sets	Product α β γ
1	$[\text{SET 1–0}]_2\,[\text{SET 2–0}]_{19} + A_2A_3\,[\text{SET 1–1}]_5 + \text{A}_1\,[\text{SET 1–1A}]_{23} + A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	0
	$(\bar{1}\bar{1})\ \bar{1}_2A_2A_3/\bar{1}_2A_3A_3/\bar{1}_2A_2\bar{1}_2/\bar{1}_2A_3\bar{1}_2/\bar{1}_2A_2\bar{1}'_2/\bar{1}_2A_3\bar{1}'_2/\bar{1}_2A_2\bar{1}_3/\bar{1}_2A_3\bar{1}_3/\bar{1}_2A_2\bar{1}'_3/\bar{1}_2A_3\bar{1}'_3\ [\text{SET 1–11A}]_5 + \bar{1}_2A_2\,[\text{SET 2–00}]_7 + A_2A_3$	0 0
	$(\bar{1}\bar{1})\ (\bar{2}\bar{1})\ \bar{B}_2\bar{B}_2\bar{1}'_2\ (\bar{2}\bar{2})\ \text{C}_2\bar{2}_2\bar{1}'_2/\bar{2}_2\bar{B}_2\bar{1}'_2\ (\bar{3}\bar{2})\ 3_2\bar{2}_2\bar{1}'_2\ (\bar{1}\tfrac{2}{3})\ \bar{B}_2\bar{B}_2\bar{1}_2\ (\bar{2}\tfrac{2}{3})\ \text{C}_2\bar{2}'_2\bar{1}_2/\bar{2}'_2\bar{B}_2\bar{1}_2\ (\bar{2}\tfrac{1}{3})\ 2_2\bar{B}_2\bar{1}_2\ (\bar{3}\tfrac{1}{3})\ 3_2\bar{2}'_2\bar{1}_2$	0 1
	$(\bar{2}\bar{3}\text{–})\ \text{C}_2\bar{2}_2\bar{1}_2\ (\bar{3}\bar{3}\text{–})\ 3_2\bar{2}_2\bar{1}_2$	0 1 –
	$[\text{SET 2–02}]_{28}\,[\text{SET 1–02}]_3\,[\text{SET 1–12}]_3\,[\text{SET 1–12A}]_{19} + \text{A}_2\,[\text{SET 1–12C}]_5 + \bar{1}_2\bar{1}'_2$	0 $\frac{2}{3}$
	$[\text{SET 2–02A}]_5\,[\text{SET 1–12B}]_2 + \text{A}_2\ (\bar{2}\bar{3}\text{–})\ \text{C}_2\bar{2}_2\bar{1}'_2\ (\bar{3}\bar{3}\text{–})\ 3_2\bar{2}_2\bar{1}'_2$	0 2 –
	$[\text{SET 1–110A}]_{13} + \bar{1}_2A_2\ (0\bar{1}\bar{1})\ (1\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ A_3\bar{1}_2A_2/A_3\bar{1}_2A_3$	0 0 0
	$[\text{SET 1–102A}]_2 + A_3\bar{1}_2\bar{1}_3\bar{1}'_2\bar{1}'_3\ (1\bar{1}\tfrac{2}{3})\ \text{B}_3\text{2}_3\bar{1}_3\ (\bar{2}\bar{1}\tfrac{2}{3})\ 2_3\bar{B}_2\bar{1}_3\ (\bar{2}\bar{2}\tfrac{2}{3})\text{C}_2\bar{2}_3\bar{1}_3/\bar{2}_3\bar{B}_2\bar{1}_3\,[\text{SET 2–002}]_8 + A_2A_3\ (\bar{3}\bar{2}\tfrac{2}{3})\ 3_2\bar{2}_3\bar{1}_3$	0 0 $\frac{2}{3}$
	$[\text{SET 1–110A}]_{13} + \bar{1}'_2$	0 1 0
	$(0\bar{1}\bar{1})\ (1\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ \text{A}_3\text{A}_3\text{A}_3/\text{A}_3\bar{\text{B}}_2\text{A}_3\ (1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ \text{B}_3\bar{\text{B}}_2\text{A}_3/\text{B}_3\text{A}_3\text{A}_3/\text{B}_3\text{B}_3\text{A}_3/\text{B}_3\text{l}_1\text{A}_3\ (\bar{1}\bar{1}0)\bar{\text{B}}_2\text{A}_3\text{A}_3\ (\bar{1}\bar{1}1)\ \bar{1}'_3\text{A}_3\text{A}_3\ (\bar{2}\bar{2}0)\ \bar{2}_2\text{A}_3\text{A}_3$ $(2\bar{1}\bar{1})\ 2_1\text{B}_3\text{A}_3\,[\text{SET 1–111B}]_{13} + A_3\bar{1}_2\bar{1}_3\bar{1}'_2\bar{1}'_3$	0 $\bar{1}$ $\bar{1}$
	$(\bar{2}\bar{2}\tfrac{2}{3})\ 2_3\bar{B}_2\bar{1}_3$	0 1 $\frac{2}{3}$
	$(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ \text{A}_3\text{A}_3\text{A}_3\ (1\bar{2}\bar{2})\text{l}_1\text{A}_3\text{A}_3\ (2\bar{2}\bar{2})\ 2_1\text{A}_3\text{A}_3$	0 $\bar{2}$ $\bar{2}$
0	(1) $\text{B}_1\text{B}_1\text{l}_1/B_1B_3\text{l}_1$ (2) $C_1B_3\text{l}_1/\text{C}_1\text{2}_1\text{l}_1/2_1\text{B}_1\text{l}_1$ (3) $3_1\text{2}_1\text{l}_1$	0 – –
	(1) $\text{B}_1\text{B}_1\text{B}_1/B_1B_3B_3$ (2)$C_1B_3B_3/\text{C}_1\text{2}_1\text{B}_1/2_1\text{B}_1\text{B}_1/\text{C}_1\text{C}_1\text{2}_1$ (3) $3_1\text{2}_1\text{B}_1/\text{D}_1\text{3}_1\text{2}_1/3_1\text{C}_1\text{2}_1$ (4) $4_1\text{3}_1\text{2}_1\,[\text{SET 0–2A}]_8 + B_3$	1 – –
	$[\text{SET 1–1}]_5 + \text{B}_1A_3\,[\text{SET 1–1A}]_{22} + \bar{B}_2\,[\text{SET 0–2A}]_8 + \bar{B}_2B_32_22_3$ (2) $\text{C}_1\text{C}_1\text{2}_1$ (3) $\text{D}_1\text{3}_1\text{2}_1/3_1\text{C}_1\text{2}_1$ (4) $4_1\text{3}_1\text{2}_1$	$\bar{1}$ – –

σ-Block	Sequence Sets	Product α β γ
23	$[\text{SET 2-01}]_6 + \text{A}_1$ (21) $2_1\bar{1}_2\text{A}_1/2_1\bar{1}_3\text{A}_1/2_1\bar{1}'_3\text{A}_1$	0 0
	$(\bar{2}\bar{3}\text{–})\ \bar{2}_2\text{I}_2\text{A}_1$	0 0 –
	(0$\bar{1}$) (1$\bar{1}$) $\bar{1}$0) $\text{A}_3\bar{1}'_2\text{A}_1$ $[\text{SET 2-011A}]_{20} + \text{I}_2$	0 0 0
	$[\text{SET 2-011A}]_{20} + \bar{1}'_2$	0 0 1
	$[\text{SET 2-002}]_8$ $[\text{SET 2-012}]_4 + \text{A}_2$	0 0 $\frac{1}{3}$
22	$[\text{SET 2-01}]_6 + 1_1$ (21) $2_1\bar{1}_2 1_1/2_1\bar{1}_3 1_1/2_1\bar{1}'_3 1_1$	0 0
	$(\bar{2}\bar{3}\text{–})\ \bar{2}_1\text{I}_2 1_1$	0 0 –
	$[\text{SET 2-01}]_6 + \text{B}_1$ (21) $2_1\bar{1}_2\text{B}_1/2_1\bar{1}_3\text{B}_1/2_1\bar{1}'_3\text{B}_1$ $[\text{SET 2-02}]_{28} + 2_1$ (12) $A_2A_32_1/1_1A_32_1$ (22) $2_1\bar{1}_22_1/2_1\bar{1}'_22_1/2_1\bar{1}_32_1/2_1\bar{1}'_32_1$	0 1
	($\bar{1}$3–) $\bar{\text{B}}_2\text{I}_22_1/\text{I}_2\text{A}_22_1$ (23–) 2_2I_22_1 ($\bar{2}\bar{3}$–) $\bar{2}_2\text{I}'_22_1/\bar{2}'_2\text{I}_22_1/\bar{2}_2\text{I}_2\text{B}_1$	0 1 –
	$[\text{SET 2-01}]_6 + \text{B}_1$ (21) $2_1\bar{1}_2\text{B}_1/2_1\bar{1}_3\text{B}_1/2_1\bar{1}'_3\text{B}_1$ $[\text{SET 2-02}]_{28} + 2_1$ (12) $A_2A_32_1/1_1A_32_1$ (22) $2_1\bar{1}_22_1/2_1\bar{1}'_22_1/2_1\bar{1}_32_1/2_1\bar{1}'_32_1$	0 $\bar{1}$
	(13–) $\bar{\text{B}}_2\text{I}_22_1/\text{I}_2\text{A}_22_1$ (23–) 2_2I_22_1 ($\bar{2}\bar{3}$–) $2_2\text{I}'_22_1/\bar{2}'_2\text{I}_12_1/\bar{2}_2\text{I}_2\text{B}_1$	0 $\bar{1}$ –
	(0$\bar{1}$) (1$\bar{1}$) ($\bar{1}$0) $\text{A}_3\bar{1}'_21_1$	0 0 0
	(0$\bar{2}\bar{2}$) (1$\bar{2}\bar{2}$) $\text{A}_3\text{A}_3\bar{2}'_2$ (1$\bar{2}\bar{2}$) $1_1\text{A}_3\bar{2}'_2$ (2$\bar{2}\bar{2}$) $2_1\text{A}_3\bar{2}'_2$	0 0 2
	(0$\bar{1}$) (1$\bar{1}$) ($\bar{1}$0) $\text{A}_3\bar{1}'_2\text{B}_1$	0 1 0
	(0$\bar{1}$) (1$\bar{1}$) ($\bar{1}$0) $\text{A}_3\bar{1}'_2\text{B}_1$	0 $\bar{1}$ 0
	$[\text{SET 2-011A}]_{20} + \bar{\text{B}}_2$ $[\text{SET 2-021A}]_3 + \bar{\text{B}}_2$ $[\text{SET 2-022A}]_4 + \bar{2}_2$	0 $\bar{1}$ $\bar{1}$
	($\bar{1}$210) $\bar{\text{B}}_2\text{I}'_3\text{B}_3$ ($\bar{2}\bar{2}$10) $2_2\text{I}'_3\text{B}_3$ ($\bar{2}\bar{2}$10) $\bar{2}'_2\text{I}'_3\text{B}_3$	0 1 $\bar{1}$
	($\bar{1}$210) $\bar{\text{B}}_2\text{I}'_3\text{B}_3$ ($\bar{2}\bar{2}$10) $2_2\text{I}'_3\text{B}_3$ ($\bar{2}\bar{2}$10) $\bar{2}'_2\text{I}'_3\text{B}_3$	0 $\bar{1}$ $\bar{1}$
	($\bar{1}2\frac{1}{3}$) $\bar{\text{B}}_2\text{I}_3\text{B}_2$ ($\bar{2}1\frac{1}{3}$) $2_3\text{I}'_2\text{B}_2$ ($\bar{2}2\frac{1}{3}$) $2_3\bar{1}_3\text{B}_2$ ($\bar{2}\bar{2}\frac{1}{3}$) $\bar{2}'_2\text{I}_3\text{B}_2$	0 1 $\frac{1}{3}$
	$[\text{SET 2-002}]_8 + \text{A}_2$ ($\bar{1}2\frac{1}{3}$) $\bar{\text{B}}_2\text{I}_3\text{B}_2$ ($\bar{2}1\frac{1}{3}$) $2_3\text{I}'_2\text{B}_2$ ($\bar{2}2\frac{1}{3}$) $2_3\bar{1}_3\text{B}_2$ ($\bar{2}\bar{2}\frac{1}{3}$) $\bar{2}'_2\text{I}_3\text{B}_2$	0 $\bar{1}$ $\frac{1}{3}$
	(0$\bar{2}\bar{2}$) (1$\bar{2}\bar{2}$) $\text{A}_3\text{A}_3\bar{2}'_2$ (1$\bar{2}\bar{2}$) $1_1\text{A}_3\bar{2}'_2$ (2$\bar{2}\bar{2}$) $2_1\text{A}_3\bar{2}'_2$	0 $\bar{1}$ 2

($\alpha\alpha\beta$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
21	$[\text{SET 2–02}]_{28} + \text{C}_1$ (12) $A_2A_3\text{C}_1/I_1A_3\text{C}_1$ (22) $2_1\bar{I}_2\text{C}_1/2_1\bar{I}'_2\text{C}_1/2_1\bar{I}_3\text{C}_1/2_1\bar{I}'_3\text{C}_1$ ($\bar{1}\bar{3}$–) $\bar{\text{B}}_2\text{I}_2\text{C}_1/\bar{\text{I}}_2\text{A}_2\text{C}_1$ ($\bar{2}\bar{3}$–) $2_2\text{I}_2\text{C}_1$ ($\bar{2}\bar{3}$–) $\bar{2}_2\bar{\text{I}}'_2\text{C}_1/\bar{2}'_2\bar{\text{I}}_2\text{C}_1$ $[\text{SET 2–03}]_{28} + 3_1$ (13–) $A_2A_33_1/I_1A_33_1$ (23–) $2_1\bar{I}_23_1/2_1\bar{I}'_23_1/2_1\bar{I}_33_1/2_1\bar{I}'_33_1$	0 2 –
	$[\text{SET 2–01}]_6 + \text{B}_1$ (21) $2_1\bar{I}_2\text{B}_1/2_1\bar{I}_3\text{B}_1/2_1\bar{I}'_3\text{B}_1$ ($\bar{2}\bar{3}$–) $\bar{2}_2\bar{\text{I}}'_2\text{C}_1/\bar{2}'_2\bar{\text{I}}_2\text{C}_1/\bar{2}_2\text{I}_2\text{B}_1$ $[\text{SET 2–02}]_{28} + \text{C}_1$ (12) $A_2A_3\text{C}_1/I_1A_3\text{C}_1$ (22) $2_1\bar{I}_2\text{C}_1/2_1\bar{I}'_2\text{C}_1/2_1\bar{I}_3\text{C}_1/2_1\bar{I}'_3\text{C}_1$ ($\bar{1}\bar{3}$–) $\bar{\text{B}}_2\text{I}_2\text{C}_1/\bar{\text{I}}_2\text{A}_2\text{C}_1$ ($\bar{2}\bar{3}$–) $2_2\text{I}_2\text{C}_1$	0 $\bar{2}$ –
13	(21) $2_1\text{I}_2\text{A}_1$ ($\bar{1}\bar{1}$) ($\bar{2}\bar{1}$) $\bar{\text{B}}_2\bar{\text{B}}_2\text{I}_2$ ($\bar{2}\bar{2}$) $\text{C}_2\bar{2}_2\text{I}_2/\bar{2}_2\bar{\text{B}}_2\text{I}_2$ ($\bar{3}\bar{2}$) $3_2\bar{2}_2\text{I}_2$	0 0
	($\bar{1}\bar{1}$) ($\bar{2}\bar{1}$) $\bar{\text{B}}_2\bar{\text{B}}_2\text{I}'_2$ ($\bar{2}\bar{2}$) $\text{C}_2\bar{2}_2\text{I}'_2/\bar{2}_2\bar{\text{B}}_2\text{I}'_2$ ($\bar{3}\bar{2}$) $3_2\bar{2}_2\text{I}'_2$	1 0
	$[\text{SET } \dot{1}\text{–1A} + 0]_{23} + A_3$ ($\bar{1}\bar{1}$) $\bar{I}_2A_2A_3/\bar{I}_2A_3A_3$ $[\text{SET 1–11A}]_5 + A_3\bar{I}'_3$ (31) $3_12_1A_3$	$\bar{\text{I}}$ 0
	$[\text{SET 1–110A}]_{13} + \bar{\text{I}}_2$ (1$\bar{1}\bar{1}$) ($\bar{2}\bar{1}$0) $\text{B}_3\text{l}_1\bar{\text{I}}_2$	0 0 0
	(1$\bar{1}\bar{1}$) ($\bar{2}\bar{1}$0) $\text{B}_3\text{l}_1\bar{\text{I}}'_2$	0 0 1
	(1$\bar{1}\bar{1}$0) ($\bar{2}\bar{1}$00) $\text{B}_3\text{l}_1\text{A}_3$	0 0 $\bar{\text{I}}$
	$[\text{SET 1–112A}]_5 + \text{A}_2\bar{\text{I}}_2$	0 0 $\frac{1}{3}$
	$[\text{SET 1–110A}]_{13} + \bar{\text{I}}'_2$ (1$\bar{1}\bar{1}$) ($\bar{2}\bar{1}$0) $\text{B}_3\text{B}_3\bar{\text{I}}_2$ (2$\bar{1}\bar{1}$) $2_2\text{B}_3\bar{\text{I}}_2$	1 0 0
	$[\text{SET 1–110A}]_{13} + A_3\bar{I}'_3$ $[\text{SET 1–111B}]_{13} + \bar{\text{I}}_2$	$\bar{\text{I}}$ 0 0
	(1$\bar{1}\bar{1}$) $\bar{2}\bar{1}$0)$\text{B}_3\text{B}_3\bar{\text{I}}'_2$ (2$\bar{1}\bar{1}$) $2_1\text{B}_3\bar{\text{I}}'_2$	1 0 1
	$[\text{SET 1–111B}]_{13} + \bar{\text{I}}'_2$	$\bar{\text{I}}$ 0 1
	$[\text{SET 1–111B} + 0]_{13} + \text{A}_3$	$\bar{\text{I}}$ 0 $\bar{\text{I}}$
	$[\text{SET 1–112A}]_5 + \bar{\text{I}}'_2$	1 0 $\frac{1}{3}$
	$[\text{SET 1–112A}]_5 + A_3\bar{I}'_3$ ($\bar{1}\bar{1}\frac{1}{3}$) $\bar{I}_3A_2A_3/\bar{I}_3A_3A_3$	$\bar{\text{I}}$ 0 $\frac{1}{3}$
12	(21) $2_1\text{l}_2\text{l}_1$	0 0
	(12) B_2l_12_1 (21) $2_1\text{l}_2\text{B}_1$ ($\bar{2}\bar{2}$) $\text{C}_2\bar{2}'_22_1$ ($\bar{3}\bar{2}$) $3_2\bar{2}'_22_1$	0 1
	(12) B_2l_12_1 (21) $2_1\text{l}_2\text{B}_1$ ($\bar{2}\bar{2}$) $\text{C}_2\bar{2}'_22_1$ ($\bar{3}\bar{2}$) $3_2\bar{2}'_22_1$	0 $\bar{\text{I}}$
	(31) 3_12_1l_2	1 0

	(31) $3_1 2_1 1_1$	$\bar{1}$ 0
	(12) $B_2 B_2 2_1$ (22) $2_1 B_2 2_1$ (32) $3_1 2_1 2_1$	1 1
	(12) $B_2 B_2 2_1$ (22) $2_1 B_2 2_1$ (32) $3_1 2_1 2_1$	1 $\bar{1}$
	$[\text{SET 1–1A} + 0]_{23} + A_3$ $[\text{SET 1–11A}]_5 + \bar{B}_2 A_3$ ($\bar{1}\bar{1}$) $\bar{I}_2 A_2 A_3/\bar{I}_2 A_3 A_3$ (31) $3_1 2_1 A_3$ $[\text{SET 1–12C}]_5 + \bar{B}_2 2_3$	$\bar{1}\bar{1}$
	($\bar{2}\bar{3}$–) $C_2\bar{2}_2\bar{B}_2/C_2\bar{2}_2 2_3$ ($\bar{3}\bar{3}$–) $3_2\bar{2}_2\bar{B}_2/3_2\bar{2}_2 2_3$	$\bar{1}\bar{1}$ –
	$[\text{SET 1–12A}]_{17} + 2_1$ $[\text{SET 1–12C}]_5 + B_3$ (31) $3_1 2_1 B_3$ (32) $3_1 2_1 2_1$	$\bar{1}$ 1
	($\bar{1}\bar{3}$–) $\bar{I}_2 A_2 2_1/\bar{I}_2 A_3 2_1$ ($\bar{2}\bar{3}$–) $C_2\bar{2}_2 B_3$ ($\bar{3}\bar{3}$–) $3_2\bar{2}_2 B_3$	$\bar{1}$ 1 –
	$[\text{SET 1–12A}]_{17} + 2_1$ $[\text{SET 1–12C}]_5 + B_3$ (31) $3_1 2_1 B_3$ (32) $3_1 2_1 2_1$	$\bar{1}$ $\bar{1}$
	($\bar{1}\bar{3}$–) $\bar{I}_2 A_2 2_1/\bar{I}_2 A_3 2_1$ ($\bar{2}\bar{3}$–) $C_2\bar{2}_2 B_3$ ($\bar{3}\bar{3}$)– $3_2\bar{2}_2 B_3$	$\bar{1}$ $\bar{1}$ –
	($1\bar{1}$) ($\bar{2}\bar{1}0$) $B_3 1_1 \bar{B}_2$	0 $\bar{1}\bar{1}$
	($1\bar{1}\bar{1}0$) ($\bar{2}\bar{1}00$) $B_3 1_1 A_3$	0 $\bar{1}\bar{1}$ 0
	$[\text{SET 1–110A}]_{13} + \bar{B}_2 A_3$	$\bar{1}\bar{1}$ 0
	$[\text{SET 1–111B}]_{13} + \bar{B}_2$	$\bar{1}$ $\bar{1}\bar{1}$
	$[\text{SET 1–111B} + 0]_{13} + A_3$	$\bar{1}$ $\bar{1}\bar{1}$ 0
	$[\text{SET 1–112A}]_5 + \bar{B}_2 A_3$ ($\bar{1}\bar{1}\frac{2}{3}$) $\bar{I}_3 A_2 A_3/\bar{I}_3 A_3 A_3$ ($\bar{2}\bar{2}\frac{2}{3}$) $2_3\bar{B}_2 B_2/2_3\bar{B}_2 2_3$	$\bar{1}\bar{1}$ $\frac{2}{3}$
	($\bar{2}\bar{2}\frac{2}{3}$) $2_3\bar{B}_2 B_3$	$\bar{1}$ 1 $\frac{2}{3}$
	($\bar{2}\bar{2}\frac{2}{3}$) $2_3\bar{B}_2 B_3$	$\bar{1}$ $\bar{1}$ $\frac{2}{3}$
11	(12) $B_2 1_1 C_1$ (13) $B_2 1_1 3_1$ ($\bar{2}\bar{2}$) $C_2\bar{2}'_2 C_1$ ($\bar{2}\bar{3}$) $C_2\bar{2}'_2 3_1$ ($\bar{3}\bar{2}$) $3_2\bar{2}'_2 C_1$ ($\bar{3}\bar{3}$) $3_2\bar{2}'_2 3_1$	0 2 –
	(12) $B_2 1_1 C_1$ (21) $2_1 1_2 B_1$ ($\bar{2}\bar{2}$) $C_2\bar{2}'_2 C_1$ ($\bar{3}\bar{2}$) $3_2\bar{2}'_2 C_1$	0 $\bar{2}$ –
	(12) $B_2 B_2 C_1$ (13) $B_2 B_2 3_1$ (22) $2_1 B_2 C_1$ (23) $2_1 B_2 3_1$ (32) $3_1 2_1 C_1$ (33–) $3_1 2_1 3_1$	1 2 –
	(12) $B_2 B_2 C_1$ (22) $2_1 B_2 C_1$ (32) $3_1 2_1 C_1$	1 $\bar{2}$ –
	$[\text{SET 1–12C}]_5 + B_3$ ($\bar{2}\bar{3}$–) $C_2\bar{2}_2 B_3$ ($\bar{3}\bar{3}$–) $3_2\bar{2}_2 B_3$ (31) $3_1 2_1 B_3$	$\bar{1}$ 2 –
	$[\text{SET 1–12A}]_{17} + C_1$ $[\text{SET 1–13A}]_{17} + 3_1$ ($\bar{1}\bar{3}$–) $\bar{I}_2 A_2 C_1/\bar{I}_2 A_3 C_1$ (32) $3_1 2_1 C_1$ (33–) $3_1 2_1 3_1$	$\bar{1}$ 2 –
	$[\text{SET 1–12A}]_{17} + C_1$ $[\text{SET 1–12C}]_5 + B_3$ ($\bar{1}\bar{3}$–) $\bar{I}_2 A_2 C_1/\bar{I}_2 A_3 C_1$	$\bar{1}$ $\bar{2}$ –
	($\bar{2}\bar{3}$–) $C_2\bar{2}_2 B_3$ (31) $3_1 2_1 B_3$ (32) $3_1 2_1 C_1$ ($\bar{3}\bar{3}$–) $3_2\bar{2}_2 B_3$	

($\alpha\alpha\gamma$) Pattern

σ-Block	Sequence Sets	Product α β γ
23	$[\text{SET 2-011A}]_{20}$ $[(2\bar{1}\bar{1})\ 2_1A_2/2_1A_3/2_1\bar{I}_2'/2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + \bar{I}_2$	0 0 0
	$[\text{SET 2-0}+01]_{19}$ $[(\bar{1}\bar{1}1)\ (2\bar{1}1)\ \bar{B}_2A_2/\bar{B}_2\bar{I}_2$ $(1\bar{1}1)\ \bar{I}_2A_2/\bar{I}_2A_3$ $(\bar{2}\bar{2}1)\ \bar{2}_2A_2/\bar{2}_2\bar{I}_2] + A_1$	
	$[\text{SET 2-011A}]_{20}$ $[(2\bar{1}\bar{1})\ 2_1A_2/2_1A_3/2_1\bar{I}_2'/2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + \bar{I}_2'$	0 1 0
	$[(1\bar{2}1)\ \bar{B}_2\bar{I}_3'\ (2\bar{2}1)\ 2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'$ $(\bar{2}\bar{2}1)\ 2_2\bar{I}_3'$ $(\bar{2}\bar{2}1)\ \bar{2}_2'\bar{I}_3'] + \bar{I}_2$	
	$[\text{SET 2-02}+0]_{28}$ $[(120)\ 1_1A_3$ $(220)\ 2_1\bar{I}_2'/2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + A_2$ $[(1\bar{2}1)\ \bar{B}_2\bar{I}_3'$ $(\bar{2}\bar{2}1)\ \bar{2}_2'\bar{I}_3'$ $(\bar{2}\bar{2}1)\ 2_2\bar{I}_3'$ $(2\bar{2}\bar{1})\ 2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + \bar{I}_2'$	0 2 0
22	$[\text{SET 2-0}+01]_{19}$ $[(\bar{1}\bar{1}1)\ (2\bar{1}1)\ \bar{B}_2A_2/\bar{B}_2\bar{I}_2$ $(1\bar{1}1)\ \bar{I}_2A_2/\bar{I}_2A_3$ $(\bar{2}\bar{2}1)\ \bar{2}_2A_2/\bar{2}_2\bar{I}_2] + 1_1$	0 0 0
	$[(\bar{1}\bar{1}1)\ (2\bar{1}1)\ \bar{B}_2\bar{I}_2'$ $(1\bar{2}1)\ \bar{B}_2\bar{I}_2$ $(\bar{2}\bar{2}1)\ \bar{2}_2'\bar{I}_2/\bar{2}_2\bar{I}_2'$ $(2\bar{2}1)\ 2_2\bar{I}_2$ $(211)\ 2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + 1_2$	0 1 0
	$[(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3A_3$ $(1\bar{2}\bar{2})\ 1_1A_3$ $(2\bar{2}\bar{2})\ 2_1A_3/2_1A_3/2_1\bar{I}_2'/2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + \bar{2}_2'$	0 2 0
	$[\text{SET 2-0}+01]_{19}$ $[\text{SET 2-00}+1]_8 + B_1$ $[\text{SET 2-002}]_8$ $[\text{SET 2-0}+02]_{19} + 2_1$ $(1\bar{1}2)\ (2\bar{1}2)\ \bar{B}_2A_22_1$	0 0 1
	$[\text{SET 2-0}+01]_{19}$ $[\text{SET 2-00}+1]_8 + B_1$ $[\text{SET 2-002}]_8$ $[\text{SET 2-0}+02]_{19} + 2_1$ $(1\bar{1}2)\ (2\bar{1}2)\ \bar{B}_2A_22_1$	0 0 $\bar{1}$
	$[(1\bar{1}2)\ (2\bar{1}2)\ \bar{B}_2\bar{I}_2'$ $(1\bar{2}2)\ \bar{B}_2\bar{I}_3$ $(\bar{2}\bar{2}2)\ \bar{2}_2'\bar{I}_3/\bar{2}_2\bar{I}_2'$ $(2\bar{1}2)\ 2_3\bar{I}_2'$ $(\bar{2}\bar{2}2)\ 2_2\bar{I}_3] + 2_1$	0 1 1
	$[(1\bar{1}2)\ (2\bar{1}2)\ \bar{B}_2\bar{I}_2'$ $(1\bar{2}2)\ \bar{B}_2\bar{I}_3$ $(\bar{2}\bar{2}2)\ \bar{2}_2'\bar{I}_3/\bar{2}_2\bar{I}_2'$ $(2\bar{1}2)\ 2_3\bar{I}_2'$ $(\bar{2}\bar{2}2)\ 2_2\bar{I}_3] + 2_1$	0 1 $\bar{1}$
	$[\text{SET 2-011A}]_{20}$ $[(2\bar{1}\bar{1})\ 2_1A_2/2_1A_3/2_1\bar{I}_2'/2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + \bar{B}_2A_3$ $[(2\bar{1}\bar{2})\ 2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + \bar{B}_2$	0 $\bar{1}$ $\bar{1}$
	$[(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3A_3$ $(1\bar{2}\bar{2})\ 1_1A_3$ $(2\bar{2}\bar{2})\ 2_1A_3/2_1A_3/2_1\bar{I}_2'/2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + \bar{2}_2$	
	$[\text{SET 2-02}+1]_{29}$ $[(121)\ 1_1A_3$ $(221)\ 2_1\bar{I}_2'/2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + B_2$ $[\text{SET 2-02}+2]_{29} + 2_1$	0 2 1
	$[\text{SET 2-02}+1]_{29}$ $[(121)\ 1_1A_3$ $(221)\ 2_1\bar{I}_2'/2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + B_2$ $[\text{SET 2-02}+2]_{29} + 2_1$	0 2 $\bar{1}$
	$[(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3A_3$ $(1\bar{2}\bar{2})\ 1_1A_3$ $(2\bar{2}\bar{2})\ 2_1A_3/2_1A_3/2_1\bar{I}_2'/2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + \bar{2}_2'$	0 $\bar{2}$ $\bar{1}$
	$[(1\bar{2}1)\ \bar{B}_2\bar{I}_3'$ $(\bar{2}\bar{2}1)\ \bar{2}_2'\bar{I}_3'$ $(\bar{2}\bar{2}1)\ 2_2\bar{I}_3'$ $(2\bar{2}\bar{1})\ 2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + \bar{B}_2$ $[(2\bar{2}\bar{2})\ 2_1\bar{I}_2/2_1\bar{I}_3/2_1\bar{I}_3'] + 2_2$	
21	$[\text{SET 2-002}]_8$ $[\text{SET 2-0}+02]_{19} + C_1$ $(1\bar{1}2)\ (2\bar{1}2)\ \bar{B}_2A_2C_1$ $(1\bar{1}3)\ (2\bar{1}3)\ \bar{B}_2A_23_1$	0 0 2
	$[\text{SET 2-003}]_8$ $[\text{SET 2-0}+03]_{19}$ $[\text{SET 2-00}+3]_8 + 3_1$	
	$[\text{SET 2-0}+01]_{19}$ $[\text{SET 2-00}+1]_8 + B_1$ $[\text{SET 2-002}]_8$ $[\text{SET 2-0}+02]_{19} + C_1$ $(1\bar{1}2)\ (2\bar{1}2)\ \bar{B}_2A_2C_1$	0 0 $\bar{2}$

	$[\text{SET 2–012}]_4$ $[(\bar{1}\bar{1}2)\ (\bar{2}\bar{1}2)\ \bar{B}_2\bar{1}'_2\ \ (\bar{2}\bar{2}2)\ \bar{2}_2\bar{1}'_2] + C_1$ $[\text{SET 2–013}]_4$ $[(\bar{1}\bar{1}3)\ (\bar{2}\bar{1}3)\ \bar{B}_2\bar{1}'_2\ \ (\bar{2}\bar{2}3)\ \bar{2}_2\bar{1}'_2] + 3_1$	0 1 2
	$[(\bar{1}\bar{1}2)\ (\bar{2}\bar{1}2)\ \bar{B}_2\bar{1}'_2\ \ (\bar{1}\bar{2}2)\ \bar{B}_2\bar{1}_3\ \ (\bar{2}\bar{2}2)\ \bar{2}'_2\bar{1}_3/\bar{2}_2\bar{1}'_2\ \ (\bar{2}\bar{1}2)\ 2_3\bar{1}'_2\ \ (\bar{2}\bar{2}2)\ 2_3\bar{1}_3] + C_1$	0 1 2
	$[(2\bar{1}\bar{2})\ 2_1\bar{1}_2/2_1\bar{1}_3/2_1\bar{1}'_3] + B_3$	0 $\bar{1}$ 2
	$[\text{SET 2–02+2}]_{29} + C_1$ $[\text{SET 2–02+3}]_{29} + 3_1$	0 2 2
	$[\text{SET 2–02+2}]_{29} + C_1$ $[\text{SET 2–02+1}]_{29}$ $[(121)\ 1_1A_3\ \ (221)\ 2_1\bar{1}'_2/2_1\bar{1}_2/2_1\bar{1}_3/2_1\bar{1}'_3] + B_2$	0 2 2
	$[(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3A_3\ \ (1\bar{2}\bar{2})\ 1_1A_3\ \ (2\bar{2}\bar{2})\ 2_1A_3/2_1A_3/2_1\bar{1}'_2/2_1\bar{1}_2/2_1\bar{1}_3/2_1\bar{1}'_3] + C_2$ $[(2\bar{2}\bar{3})\ 2_1\bar{1}_2/2_1\bar{1}_3/2_1\bar{1}'_3] + 3_2$	0 $\bar{2}$ $\bar{2}$
13	$(101)\ B_1\bar{1}_1A_1\ \ (201)\ 2_1\bar{1}_1A_1\ \ (1\bar{1}\bar{1})\ (2\bar{1}0)\ B_3\bar{1}_1\bar{1}_2\ \ (2\bar{1}\bar{1})\ 2_1\bar{1}_1\bar{1}_2$	0 0 0
	$(1\bar{1}\bar{1})\ (2\bar{1}0)\ B_3\bar{1}_1\bar{1}'_2\ \ (2\bar{1}\bar{1})\ 2_1\bar{1}_1\bar{1}'_2\ \ (2\bar{2}\bar{1})\ 2_1\bar{1}_1\bar{1}_2$	0 1 0
	$(120)\ (121)\ B_2\bar{1}_1A_2\ \ (220)\ (221)\ 2_1\bar{1}_1A_2\ \ (2\bar{2}\bar{1})\ 2_1\bar{1}_1\bar{1}'_2\ \ (\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ C_2\bar{2}'_2A_2\ \ (\bar{3}\bar{2}0)\ (\bar{3}\bar{2}1)\ 3_2\bar{2}'_2A_2$	0 2 0
	$[\text{SET 1–1+01}]_6 + A_1$	1 0 0
	$[\text{SET 1–1A+01}]_{23} + A_1$ $[\text{SET 1–111B}]_{13} + \bar{1}_2$ $(2\bar{1}\bar{1})\ C_12_1\bar{1}_2/C_1\bar{B}_2\bar{1}_2/C_1B_3\bar{1}_2/C_12_2\bar{1}_2/C_12_3\bar{1}_2/2_1\bar{B}_2\bar{1}_2\ \ (3\bar{1}\bar{1})\ 3_12_1\bar{1}_2$	$\bar{1}$ 0 0
	$(\bar{1}\bar{1}1)\ \bar{1}_2A_2A_1/\bar{1}_2A_3A_1$	
	$(2\bar{2}\bar{1})\ C_12_1\bar{1}_2/C_1B_3\bar{1}_2\ \ (3\bar{2}\bar{1})\ 3_12_1\bar{1}_2$	1 1 0
	$[\text{SET 1–111B}]_{13} + \bar{1}'_2\ \ (2\bar{1}\bar{1})\ C_12_1\bar{1}'_2/C_1\bar{B}_2\bar{1}'_2/C_1B_3\bar{1}'_2/C_12_2\bar{1}'_2/C_12_3\bar{1}'_2/2_1\bar{B}_2\bar{1}'_2\ \ (3\bar{1}\bar{1})\ 3_12_1\bar{1}'_2\ \ (2\bar{2}\bar{1})\ C_12_1\bar{1}_2/C_12_2\bar{1}_2/C_12_3\bar{1}_2$	$\bar{1}$ 1 0
	$(3\bar{2}\bar{1})\ 3_12_1\bar{1}_2$	
	$[\text{SET 2–011A}]_{20}\ [\text{SET 1–11A+0}]_5\ [\text{SET 1–11A+1}]_5\ [\text{SET 1–110A}]_{13}\ [\text{SET 1–011A}]_2 + A_3$	$\bar{1}$ $\bar{1}$ 0
	$(2\bar{1}\bar{1})\ 2_1B_3\bar{1}'_3/2_1\bar{1}_2A_3/2_1\bar{1}'_2A_3/2_1\bar{1}_3A_3/2_1\bar{1}'_3A_3/C_1B_3\bar{1}'_3/C_12_1\bar{1}'_3\ [\text{SET 1–111A}]_5 + \bar{1}'_3\ \ (3\bar{1}\bar{1})\ 3_12_1\bar{1}'_3$	
	$(120)\ (121)\ B_2B_2A_2\ \ (220)\ (221)\ C_12_1A_2/2_1B_2A_2\ \ (320)\ (321)\ 3_12_1A_2\ \ (2\bar{2}\bar{1})\ C_12_1\bar{1}'_2/C_1B_3\bar{1}'_2\ \ (3\bar{2}\bar{1})\ 3_12_1\bar{1}'_2$	1 2 0
	$[\text{SET 1–12A+0}]_{20}\ [\text{SET 1–12A+1}]_{20} + A_2$ $(120)\ (121)\ 1_1A_2A_2$ $(220)\ (221)\ C_12_1A_2/C_1\bar{B}_2A_2/C_1B_3A_2/C_12_2A_2/C_12_3A_2/2_1A_3A_2$	$\bar{1}$ 2 0
	$2_1\bar{B}_2A_2\ \ (320)\ (321)\ 3_12_1A_2\ \ (2\bar{2}\bar{1})\ C_12_1\bar{1}'_2/C_12_2\bar{1}'_2/C_12_3\bar{1}'_2\ \ (3\bar{2}\bar{1})\ 3_12_1\bar{1}'_2$	
	$(2\bar{2}\bar{1})\ C_12_1\bar{1}'_3\ \ (3\bar{2}\bar{1})\ 3_12_1\bar{1}'_3$	$\bar{1}$ 2 0
12	$(101)\ B_1\bar{1}_1\bar{1}_1\ \ (201)\ 2_1\bar{1}_1\bar{1}_1$	0 0 0
	$(211)\ 2_1\bar{1}_2\bar{1}_2$	0 1 0
	$(121)\ B_2\bar{1}_1\bar{1}_1\ \ (221)\ 2_1\bar{1}_1\bar{1}_1\ \ (\bar{2}\bar{2}1)\ C_2\bar{2}'_2\bar{1}_1\ \ (2\bar{2}\bar{2})\ 2_1\bar{1}_1\bar{2}'_2\ \ (\bar{3}\bar{2}1)\ 3_2\bar{2}'_2\bar{1}_1$	0 2 0
	$(101)\ B_1\bar{1}_1B_1\ \ (102)\ B_1\bar{1}_1\bar{2}_1\ \ (201)\ 2_1\bar{1}_1B_1\ \ (202)\ 2_1\bar{1}_1\bar{2}_1$	0 0 1

($\alpha\alpha\gamma$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
12	(101) $B_1l_1B_1$ (102) $B_1l_1\bar{2}_1$ (201) $\bar{2}_1l_1B_1$ (202) $\bar{2}_1l_1\bar{2}_1$	0 0 $\bar{1}$
	(212) $\bar{2}_1l_2\bar{2}_1$	0 1 1
	(212) $\bar{2}_1l_2\bar{2}_1$	0 1 $\bar{1}$
	$[\text{SET 1–110A}]_{13}$ $[\text{SET 1–11A}+0]_5$ $[\text{SET 1–11A}+1]_5 + A_3$ (1$\bar{1}\bar{1}$) ($\bar{2}\bar{1}0$) $B_3l_1\bar{B}_2/B_3l_1A_3$ (2$\bar{1}\bar{1}$) $\bar{2}_1l_1\bar{B}_2/\bar{2}_1l_1A_3$ (2$\bar{1}\bar{2}$) $\bar{2}_1l_1\bar{B}_2$ ($2\bar{2}\bar{2}$) $\bar{2}_1l_1\bar{\bar{2}}_2$	0 $\bar{1}$ $\bar{1}$
	(121) $B_2l_1B_2$ (122) $B_2l_1\bar{2}_1$ (221) $\bar{2}_1l_1B_2$ ($\bar{2}\bar{2}1$) $C_2\bar{\bar{2}}'_2B_2$ ($\bar{2}\bar{2}2$) $C_2\bar{\bar{2}}'_22_1$ ($\bar{3}\bar{2}1$) $3_2\bar{\bar{2}}'_2B_2$ ($\bar{3}\bar{2}2$) $3_2\bar{\bar{2}}'_22_1$	0 2 1
	(120) $B_2l_1A_2$ (121) $B_2l_1B_2$ (122) $B_2l_1\bar{2}_1$ (220) $\bar{2}_1l_1A_2$ (221) $\bar{2}_1l_1B_2$ ($\bar{2}\bar{2}0$) $C_2\bar{\bar{2}}'_2A_2$ ($\bar{2}\bar{2}1$) $C_2\bar{\bar{2}}'_2B_2$ ($\bar{2}\bar{2}2$) $C_2\bar{\bar{2}}'_22_1$ ($\bar{3}\bar{2}0$) $3_2\bar{\bar{2}}'_2A_2$ ($\bar{3}\bar{2}1$) $3_2\bar{\bar{2}}'_2B_2$ ($\bar{3}\bar{2}2$) $3_2\bar{\bar{2}}'_22_1$	0 2 $\bar{1}$
	(2$\bar{2}\bar{1}$) $\bar{2}_1l_1\bar{B}_2$ (2$\bar{2}\bar{2}$) $\bar{2}_1l_1\bar{2}_1$ ($2\bar{2}\bar{2}$) $\bar{2}_1l_1\bar{\bar{2}}'_2$	0 $\bar{2}$ $\bar{1}$
	$[\text{SET 1–1}+01]_6 + 1_1$	1 0 0
	$[\text{SET 1–1A}+01]_{23} + 1_1$ ($\bar{1}\bar{1}1$) $\bar{1}_2A_2l_1/\bar{1}_2A_3l_1$	$\bar{1}$ 0 0
	(311) $3_1\bar{2}_1l_2$	1 1 0
	(211) $C_1\bar{2}_1l_2/C_1\bar{2}_2l_2/C_1\bar{2}_3l_2$ (311) $3_1\bar{2}_1l_2$	$\bar{1}$ 1 0
	$[\text{SET 1–11A}+1]_5 + 1_1$	$\bar{1}$ $\bar{1}$ 0
	(121) $B_2B_2l_1$ (221) $C_1\bar{2}_1l_1/\bar{2}_1B_2l_1$ (321) $3_1\bar{2}_1l_1$ ($2\bar{2}\bar{2}$) $C_1\bar{2}_1\bar{\bar{2}}'_2/C_1B_3\bar{\bar{2}}'_2/\bar{2}_1B_3\bar{\bar{2}}'_2$ ($3\bar{2}\bar{2}$) $3_1\bar{2}_1\bar{\bar{2}}'_2$	1 2 0
	$[\text{SET 1–12A}+1]_{19} + 1_1$ (121) $1_1A_3l_1$ (221) $C_1\bar{2}_1l_1/C_1\bar{B}_2l_1/C_1B_3l_1/C_1\bar{2}_2l_1/C_1\bar{2}_3l_1$ (221) $\bar{2}_1\bar{B}_2l_1/\bar{2}_1A_3l_1$ (321) $3_1\bar{2}_1l_1$	$\bar{1}$ 2 0
	$[(0\bar{2}\bar{2})\ A_3A_2/A_3A_3$ (1$\bar{2}\bar{2}$) $A_3A_2/A_3A_3/1_2A_2/1_2A_3$ ($2\bar{2}\bar{2}$) $C_1\bar{2}_1/C_1\bar{2}_2/C_1\bar{2}_3/C_1\bar{B}_2/C_1B_3/\bar{2}_1A_3/\bar{2}_1A_3/\bar{2}_1\bar{B}_2] + \bar{\bar{2}}'_2$ ($3\bar{2}\bar{2}$) $3_1\bar{2}_1\bar{\bar{2}}'_2$	
	$[\text{SET 1–12B}+1]_5 + 1_1$	$\bar{1}$ $\bar{2}$ 0
	$[\text{SET 1–1}+01]_6 + B_1$ $[\text{SET 1–1}+02]_6 + 2_1$	1 0 1
	$[\text{SET 1–1}+01]_6 + B_1$ $[\text{SET 1–1}+02]_6 + 2_1$	1 0 $\bar{1}$
	$[\text{SET 1–1A}+01]_{23} + B_1$ $[\text{SET 1–1A}+02]_{23} + 2_1$ ($\bar{1}\bar{1}1$) $\bar{1}_2A_2B_1/\bar{1}_2A_3B_1$ ($\bar{1}\bar{1}2$) $\bar{1}_3A_2\bar{2}_1/\bar{1}_3A_3\bar{2}_1$	$\bar{1}$ 0 1
	$[\text{SET 1–1A}+01]_{23} + B_1$ $[\text{SET 1–1A}+02]_{23} + 2_1$ ($\bar{1}\bar{1}1$) $\bar{1}_2A_2B_1/\bar{1}_2A_3B_1$ ($\bar{1}\bar{1}2$) $\bar{1}_3A_2\bar{2}_1/\bar{1}_3A_3\bar{2}_1$	$\bar{1}$ 0 $\bar{1}$
	$[\text{SET 1–111A}]_5 + \bar{B}_2$ (2$\bar{1}\bar{1}$) $2_1B_3\bar{B}_2/C_1\bar{2}_1\bar{B}_2/C_1B_3\bar{B}_2$ (2$\bar{1}\bar{2}$) $C_1\bar{2}_1\bar{B}_2/\bar{2}_1B_3\bar{B}_2/C_1B_3\bar{B}_2$ ($2\bar{2}\bar{2}$) $C_1\bar{2}_1\bar{\bar{2}}_2/C_1B_3\bar{\bar{2}}_2/\bar{2}_1B_3\bar{\bar{2}}_2$	1 $\bar{1}$ $\bar{1}$

	$(3\bar{1}\bar{1})\ 3_1 2_1 \bar{B}_2 \quad (3\bar{1}\bar{2})\ 3_1 2_1 \bar{B}_2 \quad (3\bar{2}\bar{2})\ 3_1 2_1 \bar{2}_2$	
	$[\text{SET 1–111B}]_{13} + \bar{B}_2 \quad [(0\bar{1}\bar{1})\ A_3 A_2 / A_3 A_3 \quad (1\bar{1}\bar{1})\ A_3 A_2 / A_3 A_3 / 1_1 A_2 / 1_1 A_3] + \bar{B}_2 \quad [(2\bar{1}\bar{1})\ C_1 2_1 / C_1 2_2 / C_1 2_3 / C_1 \bar{B}_2 / C_1 B_3 / 2_1 A_3 / 2_1 A_3 /$	$\bar{1}\ \bar{1}\ 1$
	$2_1 \bar{B}_2 \quad (2\bar{1}\bar{2})\ C_1 2_1 / C_1 2_2 / C_1 2_3] + \bar{B}_2 \quad (3\bar{1}\bar{1})\ 3_1 2_1 \bar{B}_2 \quad (3\bar{1}\bar{2})\ 3_1 2_1 \bar{B}_2 \quad [(0\bar{2}\bar{2})\ A_3 A_2 / A_3 A_3 \quad (1\bar{2}\bar{2})\ A_3 A_2 / A_3 A_3 / 1_1 A_2 / 1_1 A_3] + \bar{2}_2$	
	$[(2\bar{2}\bar{2})\ C_1 2_1 / C_1 2_2 / C_1 2_3 / C_1 \bar{B}_2 / C_1 B_3 / 2_1 A_3 / 2_1 A_3 / 2_1 \bar{B}_2] + \bar{2}_2$	
	$(\bar{1}\bar{1}1)\ (2\bar{1}1)\ \bar{B}_2 \bar{B}_2 B_3 \quad (2\bar{2}1)\ C_2 \bar{2}_2 B_3 / \bar{2}_2 \bar{B}_2 B_3 \quad (3\bar{2}1)\ 3_2 \bar{2}_2 B_3 \quad [\text{SET 1–112A}]_5 + 2_1$	$\bar{1}\ \bar{1}\ 1$
	$(\bar{1}\bar{1}1)\ (2\bar{1}1)\ \bar{B}_2 \bar{B}_2 B_3 \quad (2\bar{2}1)\ C_2 \bar{2}_2 B_3 / \bar{2}_2 \bar{B}_2 B_3 \quad (3\bar{2}1)\ 3_2 \bar{2}_2 B_3 \quad [\text{SET 1–112A}]_5 + 2_1$	$\bar{1}\ \bar{1}\ \bar{1}$
	$(121)\ B_2 B_2 B_2 \quad (122)\ B_2 B_2 2_1 \quad (221)\ 2_1 B_2 B_2 / C_1 2_1 B_2 \quad (222)\ 2_1 B_2 2_1 \quad (321)\ 3_1 2_1 B_2$	1 2 1
	$(120)\ B_2 B_2 A_2 \quad (121)\ B_2 B_2 A_2 / B_2 B_2 B_2 \quad (122)\ B_2 B_2 2_1 \quad (220)\ C_1 2_1 A_2 / 2_1 B_2 A_2$	1 2 $\bar{1}$
	$(221)\ C_1 2_1 A_2 / C_1 2_1 B_2 / 2_1 B_2 A_2 / 2_1 B_2 B_2 \quad (222)\ 2_1 B_2 2_1 \quad (320)\ 3_1 2_1 A_2 \quad (321)\ 3_1 2_1 A_2 / 3_1 2_1 A_2$	
	$(2\bar{2}\bar{1})\ C_1 2_1 \bar{B}_2 \quad (2\bar{2}\bar{2})\ C_1 2_1 2_2 \quad (3\bar{2}\bar{1})\ 3_1 2_1 \bar{B}_2 \quad (3\bar{2}\bar{2})\ 3_1 2_1 2_2 \quad (2\bar{2}\bar{2})\ C_1 2_1 \bar{2}_2' / C_1 B_3 \bar{2}_2' / 2_1 B_3 \bar{2}_2' \quad (3\bar{2}\bar{2})\ 3_1 2_1 \bar{2}_2'$	1 $\bar{2}$ $\bar{1}$
	$[\text{SET 1–12A} + 1]_{19} + B_2 \quad [\text{SET 1–12A} + 2]_{19} + 2_1 \quad (121)\ 1_1 A_3 B_2 \quad (122)\ 1_1 A_3 2_1$	$\bar{1}$ 2 1
	$(221)\ C_1 2_1 B_2 / C_1 \bar{B}_2 B_2 / C_1 B_3 B_2 / C_1 2_2 B_2 / C_1 2_3 B_2 / 2_1 A_3 B_2 / 2_1 \bar{B}_2 B_2 \quad (321)\ 3_1 2_1 B_2$	
	$(222)\ C_1 2_1 2_1 / C_1 \bar{B}_2 2_1 / C_1 B_3 2_1 / C_1 2_2 2_1 / C_1 2_3 2_1 / 2_1 A_3 2_1 / 2_1 \bar{B}_2 2_1 \quad (322)\ 3_1 2_1 2_1$	
	(Same set as for Product $\bar{1}21$ above) and: $[\text{SET 1–12A} + 0]_{19} + A_1 \quad (120) 1_1 A_3 A_2$	$\bar{1}$ 2 $\bar{1}$
	$(220)\ C_1 2_1 A_2 / C_1 \bar{B}_2 A_2 / C_1 B_3 A_2 / C_1 2_2 A_2 / C_1 2_3 A_2 / 2_1 A_3 A_2 / 2_1 \bar{B}_2 A_2 \quad (320)\ 3_1 2_1 A_2$	
	$(2\bar{2}\bar{1})\ C_1 2_1 \bar{B}_2 / C_1 2_2 \bar{B}_2 / C_1 2_3 \bar{B}_2 \quad (2\bar{2}\bar{2})\ C_1 2_1 2_2 / C_1 2_2 2_2 / C_1 2_3 2_2 \quad (3\bar{2}\bar{1})\ 3_1 2_1 \bar{B}_2 \quad (3\bar{2}\bar{2})\ 3_1 2_1 2_2 \quad [(0\bar{2}\bar{2})\ A_3 A_2 / A_3 A_3$	$\bar{1}$ $\bar{2}$ $\bar{1}$
	$(1\bar{2}\bar{2})\ A_3 A_2 / A_3 A_3 / 1_1 A_2 / 1_1 A_3 \quad (2\bar{2}\bar{2})\ C_1 2_1 / C_1 2_2 / C_1 2_3 / C_1 \bar{B}_2 / C_1 B_3 / 2_1 A_3 / 2_1 A_3 / 2_1 \bar{B}_2] + \bar{2}_2'$	
	$(\bar{1}\bar{2}2)\ \bar{B}_2 \bar{B}_2 2_1 \quad (\bar{2}\bar{2}2)\ 2_3 \bar{B}_2 2_1 \quad (\bar{2}\bar{2}\bar{2})\ C_2 \bar{2}_2' 2_1 / \bar{2}_2' \bar{B}_2 2_1 \quad (\bar{3}\bar{2}2)\ 3_2 \bar{2}_2' 2_1$	$\bar{1}$ $\bar{2}$ 1
	$(\bar{1}\bar{2}2)\ \bar{B}_2 \bar{B}_2 2_1 \quad (\bar{2}\bar{2}2)\ 2_3 \bar{B}_2 2_1 \quad (\bar{2}\bar{2}\bar{2})\ C_2 \bar{2}_2' 2_1 / \bar{2}_2' \bar{B}_2 2_1 \quad (\bar{3}\bar{2}2)\ 3_2 \bar{2}_2' 2_1$	$\bar{1}$ $\bar{2}$ $\bar{1}$
11	$(102)\ B_1 1_1 C_1 \quad (103)\ B_1 1_1 3_1 \quad (202)\ 2_1 1_1 C_1 \quad (203)\ 2_1 1_1 3_1$	0 0 2
	$(101)\ B_1 1_1 B_1 \quad (102)\ B_1 1_1 C_1 \quad (201)\ 2_1 1_1 B_1 \quad (202)\ 2_1 1_1 C_1$	0 0 $\bar{2}$
	$(212)\ 2_1 1_2 C_1 \quad (213)\ 2_1 1_2 3_1$	0 1 2
	$(212)\ 2_1 1_2 C_1$	0 1 $\bar{2}$
	$(\bar{1}\bar{1}1)\ (2\bar{1}1)\ \bar{B}_2 \bar{B}_2 B_3 \quad (2\bar{1}\bar{2})\ 2_1 1_1 B_3 \quad (2\bar{2}\bar{1})\ C_2 \bar{2}_2 B_3 / \bar{2}_2 \bar{B}_2 B_3 \quad (3\bar{2}1)\ 3_2 \bar{2}_2 B_3$	0 $\bar{1}$ $\bar{2}$
	$(122)\ B_2 1_1 C_1 \quad (123)\ B_2 1_1 3_1 \quad (2\bar{2}\bar{2})\ C_2 \bar{2}_2' C_1 \quad (2\bar{2}3)\ C_2 \bar{2}_2' 3_1 \quad (3\bar{2}\bar{2})\ 3_2 \bar{2}_2' C_1 \quad (3\bar{2}3)\ 3_2 \bar{2}_2' 3_1$	0 2 2

***(αaγ)* Pattern** (continued)

σ-Block	Sequence Sets	Product α β γ
11	(122) $B_2l_1C_1$ (221) $2_1l_1B_2$ ($\bar{2}\bar{2}2$) $C_2\bar{2}_2'C_1$ ($\bar{3}\bar{2}2$) $3_2\bar{2}_2'C_1$	0 2 2
	($2\bar{2}\bar{2}$) $2_1l_1C_2$ ($2\bar{2}\bar{3}$) $2_1l_13_2$	0 2 3
	$[SET\ 1\text{–}1+02]_6+C_1$ $[SET\ 1\text{–}1+03]_6+3_1$	1 0 2
	$[SET\ 1\text{–}1+01]_6+B_1$ $[SET\ 1\text{–}1+02]_6+C_1$	1 0 3
	$[SET\ 1\text{–}1A+02]_{23}+C_1$ $[SET\ 1\text{–}1A+03]_{23}+3_1$ ($\bar{1}\bar{1}2$) $\bar{I}_3A_2C_1/\bar{I}_3A_3C_1$ ($\bar{1}\bar{1}3$) $\bar{I}_3A_23_1/\bar{I}_3A_33_1$	1 0 2
	$[SET\ 1\text{–}1A+01]_{23}+B_1$ $[SET\ 1\text{–}1A+02]_{23}+C_1$ ($\bar{1}\bar{1}1$) $\bar{I}_2A_2B_1/\bar{I}_2A_3B_1$ ($\bar{1}\bar{1}2$) $\bar{I}_3A_2C_1/\bar{I}_3A_3C_1$	1 0 3
	$[SET\ 1\text{–}112A]_5+C_1$ $[SET\ 1\text{–}113A]_5+3_1$	1 1 2
	$[SET\ 1\text{–}112A]_5+C_1$ $[(2\bar{1}\bar{2})2_1l_1$ ($\bar{1}\bar{1}1$) ($2\bar{1}1$) $\bar{B}_2\bar{B}_2$ ($\bar{2}\bar{2}1$) $C_22_2/\bar{2}_2\bar{B}_2$ ($\bar{3}\bar{2}1$) $3_2\bar{2}_2]+B_3$	1 1 3
	(122) $B_2B_2C_2$ (123) $B_2B_23_1$ (222) $2_1B_2C_1$ (223) $2_1B_23_1$	1 2 2
	(121) $B_2B_2B_2$ (122) $B_2B_2C_2$ (221) $2_1B_2B_2/C_12_1B_2$ (222) $2_1B_2C_1$ (321) $3_12_1B_2$	1 2 3
	$[(2\bar{2}\bar{2})\ C_12_1/C_1B_3/2_1B_3$ ($3\bar{2}\bar{2}$) $3_12_1]+C_2$ $[(2\bar{2}\bar{3})\ C_12_1/C_1B_3/2_1B_3$ ($3\bar{2}\bar{3}$)$3_12_1]+3_2$	1 2 3
	$[SET\ 1\text{–}12A+2]_{19}+C_1$ $[SET\ 1\text{–}12A+3]_{19}+3_1$	1 2 2
	$[SET\ 1\text{–}12A+1]_{19}+B_2$ $[SET\ 1\text{–}12A+2]_{19}+C_1$ (121) $I_1A_3B_2$	1 2 3
	$[(0\bar{2}\bar{2})\ A_3A_2/A_3A_3$ ($1\bar{2}\bar{2}$) $A_3A_2/A_3A_3/I_1A_2/I_1A_3$ ($2\bar{2}\bar{2}$) $C_12_1/C_12_2/C_12_3/C_1\bar{B}_2/C_1B_3/2_1A_3/2_1A_3/2_1\bar{B}_2]+C_2$	1 3 3
	$[(0\bar{2}\bar{3})\ A_3A_2/A_3A_3$ ($1\bar{2}\bar{3}$) $A_3A_2/A_3A_3/I_1A_2/I_1A_3$ ($2\bar{2}\bar{3}$) $C_12_1/C_12_2/C_12_3/C_1\bar{B}_2/C_1B_3/2_1A_3/2_1A_3/2_1\bar{B}_2]+3_2$	
	($\bar{1}\bar{2}2$) $\bar{B}_2\bar{B}_2C_1$ ($\bar{2}\bar{2}2$) $2_3\bar{B}_2C_1$ ($\bar{2}\bar{2}2$) $C_2\bar{2}_2'C_1/\bar{2}_2'\bar{B}_2C_1$ ($\bar{3}\bar{2}2$)$3_2\bar{2}_2'C_1$	1 2 2
	($\bar{1}\bar{2}3$) $\bar{B}_2\bar{B}_23_1$ ($\bar{2}\bar{2}3$)$2_3\bar{B}_23_1$ ($\bar{2}\bar{2}3$) $C_2\bar{2}_2'3_1/\bar{2}_2'\bar{B}_23_1$ ($\bar{3}\bar{2}3$) $3_2\bar{2}_2'3_1$	
	($\bar{1}\bar{2}2$) $\bar{B}_2\bar{B}_2C_1$ ($\bar{2}\bar{2}2$) $2_3\bar{B}_2C_1$ ($\bar{2}\bar{2}2$) $C_2\bar{2}_2'C_1/\bar{2}_2'\bar{B}_2C_1$ ($\bar{3}\bar{2}2$) $3_2\bar{2}_2'C_1$	1 2 2

($\alpha\beta$) Pattern

σ-Block	Set	Substrates and Sequences by Polarity ——	— +	+ —	+ +	Product $\gamma_1\beta_1\alpha_1$	$\alpha_2\beta_2\gamma_2$
33		$(x\bar{1}\bar{1}x)\ \bar{1}'_2A_1$				0	0
			$(x0\bar{1}\bar{1})\ (x\bar{1}\bar{1}0)\ (x1\bar{1}\bar{1})\ A_3\bar{1}_2$		$(x\bar{1}\bar{1}1)\ \bar{1}'_3\bar{1}_2$	0	0 0
	A		$(x0\bar{1}\bar{1})\ (x\bar{1}\bar{1}0)\ (x1\bar{1}\bar{1})\ A_3\bar{1}_3$		$(x\bar{1}\bar{1}1)\ \bar{1}'_3\bar{1}_3$	0	0 0 $\frac{1}{2}$
		$(x0\bar{1}\bar{1})\ (x\bar{1}\bar{1}0)\ (x1\bar{1}\bar{1})\ A_3\bar{1}'_2$		$(x\bar{1}\bar{1}1)\ \bar{1}'_3\bar{1}'_2$		0	0 1
	A	$(x0\bar{1}\bar{1})\ (x\bar{1}\bar{1}0)\ (x1\bar{1}\bar{1})\ A_3A_3$		$(x\bar{1}\bar{1}1)\ \bar{1}'_3A_3$	$(x\bar{1}\bar{1}1)\ \bar{1}'_3\bar{1}'_3$	0	0 $\bar{1}\bar{1}$
		$(x\bar{1}\bar{1}\bar{1})\ \bar{1}'_2A_3$		$(x\bar{1}\bar{1}\bar{1})\ \bar{1}_2A_3$			
				$(x\bar{1}\bar{1}\frac{1}{2})\ \bar{1}_3A_2$		0	0 $\frac{1}{2}$
	A	$(x\bar{1}\bar{1}\bar{2})\ \bar{1}'_2A_3$		$(x\bar{1}\bar{1}\bar{2})\ \bar{1}_2A_3$		0	0 $\bar{2}\bar{2}$
32			$(x\bar{1}\bar{1}x)\ \bar{1}'_2\bar{1}_1$	$(x\bar{1}\bar{2}x)\ \bar{1}_2A_1$	$(x\bar{1}\bar{2}x)\ \bar{1}_2\bar{1}_1$	0	0
		$(x\bar{1}\bar{1}x)\ \bar{1}'_2B_1$	$(x02x)\ (x12x)\ A_22_1\ (x\bar{1}\bar{2}x)\ \bar{1}'_22_1$	$(x\bar{1}\bar{2}x)\ \bar{1}_2B_1$		0	1
		$(x\bar{1}\bar{1}x)\ \bar{1}'_2B_1$	$(x02x)\ (x12x)\ A_22_1\ (x\bar{1}\bar{2}x)\ \bar{1}'_22_1$	$(x\bar{1}\bar{2}x)\ \bar{1}_2B_1$		0	$\bar{1}$
			$(x\bar{1}\bar{1}1)\ \bar{1}'_2\bar{1}_2$		$(x\bar{1}\bar{2}1)\ \bar{1}_2\bar{1}_2$	0	0 1
	A			$(x\bar{1}\bar{2}\bar{1})\ \bar{1}_2A_3$		0	0 $\bar{1}\bar{1}$
		$(x0\bar{2}\bar{2})\ (x1\bar{2}\bar{2})\ A_3\bar{2}'_2$		$(x\bar{1}\bar{2}\frac{1}{2})\ \bar{1}_3A_2$	$(x\bar{1}\bar{2}\frac{1}{2})\ \bar{1}_3\bar{1}_1$	0	0 $\frac{1}{2}$
		$(x0\bar{1}\bar{1})\ (x\bar{1}\bar{1}0)\ (x1\bar{1}\bar{1})\ A_3\bar{B}_2$	$(x0\bar{2}\bar{2})\ (x1\bar{2}\bar{2})\ A_3\bar{2}_2$	$(x\bar{1}\bar{1}1)\ (x\bar{1}\bar{2}1)\ \bar{1}'_3\bar{B}_2$		0	$\bar{1}\bar{1}$
	A	$(x0\bar{1}\bar{1})\ (x\bar{1}\bar{1}0)\ (x1\bar{1}\bar{1})\ A_3A_3$		$(x\bar{1}\bar{1}\bar{1})\ (x\bar{1}\bar{2}\bar{1})\ \bar{1}_2A_3\ (x\bar{1}\bar{1}1)$		0	$\bar{1}\bar{1}$ 0
				$(x\bar{1}\bar{2}1)\ \bar{1}'_3A_3$			
	B	$(x\bar{1}\bar{1}\bar{1})\ \bar{1}'_2B_3$		$(x\bar{1}\bar{2}1)\ \bar{1}'_3B_3\ (x\bar{1}\bar{2}\bar{1})\ \bar{1}_2B_3$		0	1 $\bar{1}\bar{1}$
	C	$(x\bar{1}\bar{1}\bar{1})\ \bar{1}'_2B_3$		$(x\bar{1}\bar{2}1)\ \bar{1}'_3B_3\ (x\bar{1}\bar{2}\bar{1})\ \bar{1}_2B_3$		0	$\bar{1}$ $\bar{1}\bar{1}$
	D				$(x\bar{1}\bar{2}1)\ \bar{1}'_32_3$	0	$\bar{1}\bar{1}$ $\frac{1}{2}$
				$(x\bar{1}\bar{2}\frac{1}{2})\ \bar{1}_3B_2$		0	1 $\frac{1}{2}$

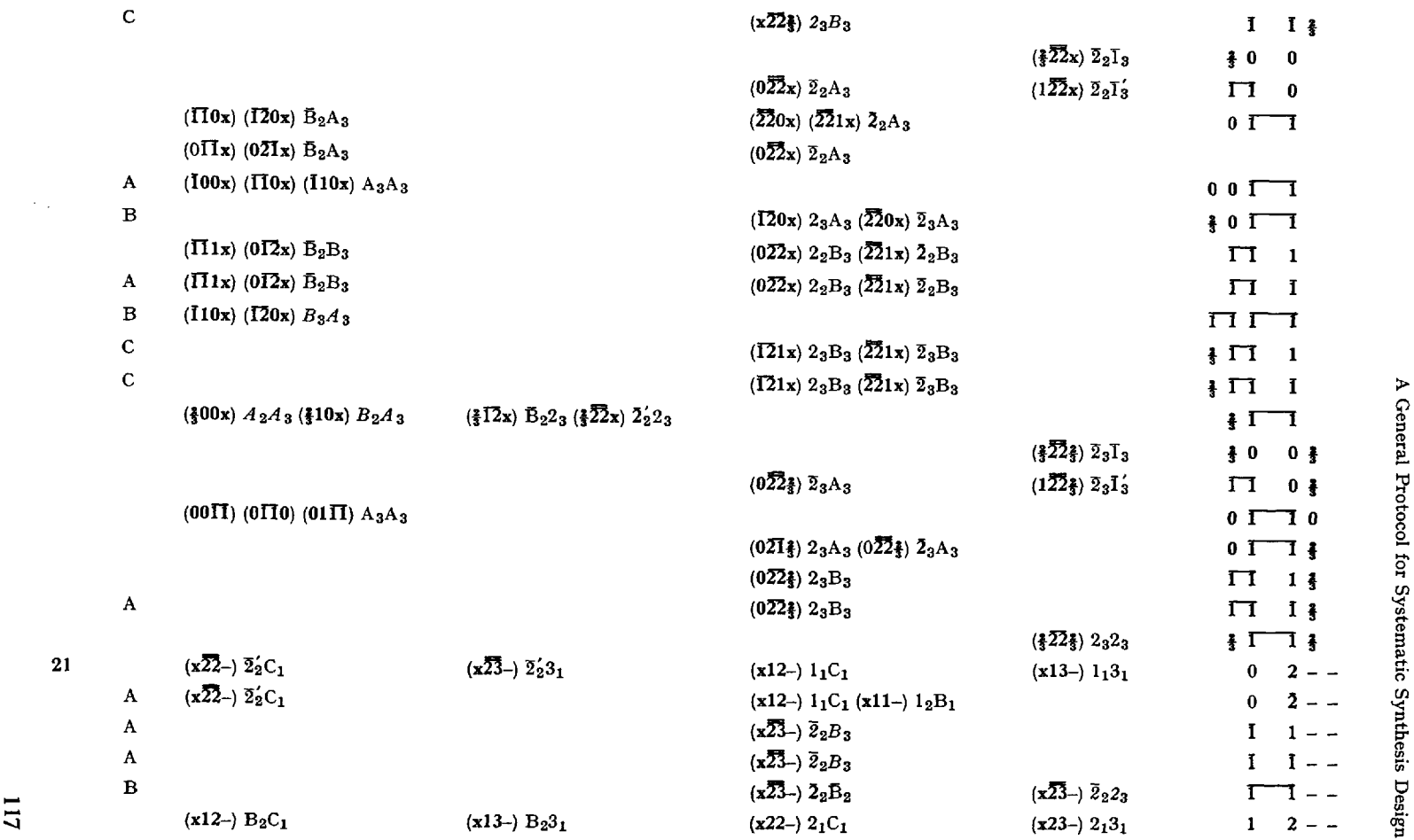
($\alpha\beta$) Pattern (continued)

-σ Block	Set	Substrates and Sequences by Polarity — —	— +	+ —	+ +	Product $\gamma_1\beta_1\alpha_1$	$\alpha_2\beta_2\gamma_2$
32	A			(x$\bar{1}$2$\frac{1}{3}$) $\bar{1}_3B_2$(x$\bar{1}\bar{1}\frac{1}{3}$) $\bar{1}_3A_2$		0	$\bar{1}$ $\frac{1}{3}$
	B	(x0$\bar{2}\bar{2}$) (x1$\bar{2}\bar{2}$) $A_3\bar{2}'_2$				0	$\bar{1}$ $\bar{2}$
			($\bar{1}\bar{1}$2x) $A_2$2$_1$			0 0	1
	A		($\bar{1}\bar{1}$2x) $A_2$2$_1$			0 0	$\bar{1}$
31					(x$\bar{1}$3–) $\bar{1}_2$2$_1$	0	1 – –
	A				(x$\bar{1}$3–) $\bar{1}_2$2$_1$	0	$\bar{1}$ – –
		(x02–) (x12–) A_2C_1	(x03–) (x13–) $A_2$3$_1$	(x$\bar{1}$3–) $\bar{1}_2C_1$		0	2 – –
		(x$\bar{1}$2–) $\bar{1}'_2C_1$	(x$\bar{1}$3–) $\bar{1}'_2$3$_1$				
	A	(x02–) (x12–) A_2C_1		(x$\bar{1}$2–) $\bar{1}_2B_1$		0	2 – –
		(x$\bar{1}\bar{1}$–) $\bar{1}'_2B_1$(x$\bar{1}$2–) $\bar{1}'_2C_1$		(x$\bar{1}$3–) $\bar{1}_2C_1$			
		($\bar{1}\bar{1}$2–) A_2C_1	($\bar{1}\bar{1}$3–) $A_2$3$_1$			0 0	2 – –
	A	($\bar{1}\bar{1}$2–) A_2C_1				0 0	2 – –
23			(x$\bar{1}\bar{1}$x) (x$\bar{2}\bar{1}$x) $\bar{B}_2\bar{1}_2$	(x11x) 1_2A_1		0	0
		(x$\bar{1}\bar{1}$x) (x$\bar{2}\bar{1}$x) $\bar{B}_2\bar{1}'_2$				1	0
	A	(x10x) B_1A_3 (x$\bar{1}\bar{1}$x)	(x$\bar{1}\bar{1}$x) (x$\bar{2}\bar{1}$x) $\bar{B}_2\bar{1}'_3$	(x20x) (x21x) 2_1A_3		$\bar{1}$	0
		(x$\bar{2}\bar{1}$x) $\bar{B}_2A_3$					
			(x0$\bar{1}\bar{1}$) (x$\bar{1}\bar{1}$0) (x1$\bar{1}\bar{1}$) $A_3\bar{1}_2$			0	0 0
			(x11$\bar{1}$) 1_2A_3			0	0 $\bar{1}$ $\bar{1}$
		(x$\bar{1}\bar{1}\frac{1}{3}$) (x$\bar{2}\bar{1}\frac{1}{3}$) $\bar{B}_2A_2$		(x11$\frac{1}{3}$) 1_2A_2 (x$\bar{2}\bar{1}\frac{1}{3}$) 2_3A_2	(x$\bar{2}\bar{1}\frac{1}{3}$) $2_3\bar{1}_2$	0	0 $\frac{1}{3}$
	A			(x11$\bar{2}$) 1_2A_3		0	0 $\bar{2}$ $\bar{2}$
		(x0$\bar{1}\bar{1}$) (x$\bar{1}\bar{1}$0) (x1$\bar{1}\bar{1}$) $A_3\bar{1}'_2$	(x1$\bar{1}\bar{1}$) (x$\bar{2}\bar{1}$0) $B_3\bar{1}_2$			1	0 0
	A	(x0$\bar{1}\bar{1}$) (x$\bar{1}\bar{1}$0) (x1$\bar{1}\bar{1}$) A_3A_3	(x1$\bar{1}\bar{1}$) (x$\bar{2}\bar{1}$0) $B_3\bar{1}_2$			$\bar{1}$	0 0
			(x0$\bar{1}\bar{1}$) (x$\bar{1}\bar{1}$0) (x1$\bar{1}\bar{1}$) $A_3\bar{1}'_3$				

B		(x1$\bar{1}\bar{1}$) (x2$\bar{1}$0) B_3I_3			1	0	0	$\frac{2}{3}$
		(x1$\bar{1}\bar{1}$) (x$\bar{2}$1̄0) $B_3\bar{I}_3$			$\bar{1}$	0	0	$\frac{2}{3}$
	(x1$\bar{1}\bar{1}$) (x2$\bar{1}$0) B_3I_2'				1	0	1	
	(x1$\bar{1}\bar{1}$) (x$\bar{2}$1̄0) $B_3\bar{I}_2'$				$\bar{1}$	0	1	
			(x2$\bar{1}\frac{2}{3}$) $2_3I_2'$		1	0	$\frac{2}{3}$	
A			(x2$\bar{1}\frac{2}{3}$) 2_3A_3	(x$\bar{2}$1̄$\frac{2}{3}$) $2_3\bar{I}_3'$	$\bar{1}$	0	$\frac{2}{3}$	
		($\frac{2}{3}\bar{1}\bar{1}$x) ($\frac{2}{3}2\bar{1}$x) $\bar{B}_2I_3$			$\frac{2}{3}$	0	0	
A	($\bar{1}\bar{1}$0x) (0$\bar{1}\bar{1}$x) $\bar{B}_2A_3$	(1$\bar{1}\bar{1}$x) $\bar{B}_2I_3'$	($\bar{2}\bar{2}$0x) ($\bar{2}\bar{2}$1x) $\bar{2}_2A_3$		$\bar{1}\bar{1}$	0		
	($\bar{1}$2̄0x) (0$\bar{2}\bar{1}$x) $\bar{B}_2A_3$							
B	($\bar{1}$00x) ($\bar{1}\bar{1}$0x) ($\bar{1}$10x) A_3A_3				0	$\bar{1}\bar{1}$	0	
C	($\bar{1}$10x) ($\bar{1}$2̄0x) B_3A_3				$\bar{1}\bar{1}$	$\bar{1}$	0	
D			($\bar{1}$2̄0x) 2_3A_3 ($\bar{2}\bar{2}$0x) $\bar{2}_3A_3$		$\frac{2}{3}$	$\bar{1}\bar{1}$	0	
	($\frac{2}{3}$00x) A_2A_3 ($\frac{2}{3}$10x) B_2A_3				$\frac{2}{3}$	$\bar{1}$	0	
		($\frac{2}{3}$0$\bar{1}\bar{1}$) ($\frac{2}{3}\bar{1}\bar{1}$0) A_3I_3			$\frac{2}{3}$	0	0	0
				($\frac{2}{3}\bar{2}\bar{1}\frac{2}{3}$) 2_3I_3	$\frac{2}{3}$	0	0	$\frac{2}{3}$
A	(00$\bar{1}\bar{1}$) (0$\bar{1}\bar{1}$0) (01$\bar{1}\bar{1}$) A_3A_3				$\bar{1}\bar{1}$	0	0	
A			(0$\bar{2}\bar{1}\frac{2}{3}$) 2_3A_3	(1$\bar{2}\bar{1}\frac{2}{3}$) $2_3\bar{I}_3'$	$\bar{1}\bar{1}$	0	$\frac{2}{3}$	
				(x11x) 1_21_1 (x$\bar{2}\bar{2}$x) $\bar{2}_2\bar{I}_2$	0	0		
		(x$\bar{2}\bar{2}$x) $\bar{2}_2'2_1$	(x11x) 1_2B_1	(x12x) 1_12_1	0	1		
A		(x$\bar{2}\bar{2}$x) $\bar{2}_2'2_1$	(x11x) 1_2B_1	(x12x) 1_12_1	0	$\bar{1}$		
			(x$\bar{2}\bar{2}$x) $\bar{2}_2I_2'$	(x21x) 2_11_2	1	0		
A			(x$\bar{2}\bar{2}$x) $\bar{2}_2A_3$	(x21x) 2_11_1 (x$\bar{2}\bar{2}$x) $\bar{2}_2\bar{I}_3'$	$\bar{1}$	0		

($\alpha\beta$) Pattern (continued)

σ-Block	Set	Substrates and Sequences by Polarity — —	— +	+ −	+ +	Product $\gamma_1\beta_1\alpha_1$	$\alpha_2\beta_2\gamma_2$
22			(x12x) $B_2 2_1$		(x22x) $2_1 2_1$	1	1
	A		(x12x) $B_2 2_1$		(x22x) $2_1 2_1$	1	$\bar{1}$
	B	(x$\bar{1}$2x) $\bar{B}_2 B_3$ (x$\bar{\bar{2}}\bar{2}$x) $\bar{2}'_2 B_3$	(x02x) $A_2 2_1$ (x12x) $B_2 2_1$	(x21x) $2_1 B_3$ (x$\bar{2}$2x) $2_2 B_3$	(x22x) $2_1 2_1$	$\bar{1}$	1
	C	(x$\bar{1}$2x) $\bar{B}_2 B_3$ (x$\bar{\bar{2}}\bar{2}$x) $\bar{2}'_2 B_3$	(x02x) $A_2 2_1$ (x12x) $B_2 2_1$	(x21x) $2_1 B_3$ (x$\bar{2}$2x) $2_2 B_3$	(x22x) $2_1 2_1$	$\bar{1}$	$\bar{1}$
	D	(x10x) $B_1 A_3$	(x$\bar{1}$2x) $\bar{B}_2 2_3$	(x20x) (x21x) $2_1 A_3$	(x$\bar{2}\bar{2}$x) $2_2 2_3$	$\bar{1}$	1
		(x$\bar{1}\bar{1}$x) (x$\bar{2}\bar{1}$x) $\bar{B}_2 A_3$	(x$\bar{\bar{2}}\bar{2}$x) $\bar{2}'_2 2_3$	(x$\bar{2}\bar{2}$x) $2_2 \bar{B}_2$			
		(x$\bar{1}\bar{1}$x) (x$\bar{1}$2x) (x$\bar{2}\bar{1}$x) $\bar{B}_2 \bar{B}_2$		(x$\bar{\bar{2}}\bar{2}$x) $\bar{2}_2 \bar{B}_2 / \bar{2}_2 A_3$			
					(x111) $1_2 1_2$	0	0 1
				(x$\bar{\bar{2}}\bar{2}\frac{2}{3}$) $\bar{2}_3 A_2$	(x$\bar{\bar{2}}\bar{2}\frac{2}{3}$) $\bar{2}_3 \bar{1}_2$	0	0 $\frac{2}{3}$
	A			(x11$\bar{1}$) $1_2 A_3$		0	$\bar{1}$ 1 0
	B			(x11$\bar{1}$) $1_2 B_3$		0	1 $\bar{1}$ 1
	C			(x11$\bar{1}$) $1_2 B_3$		0	$\bar{1}$ $\bar{1}$ 1
				(x11$\frac{2}{3}$) $1_2 B_2$		0	1 $\frac{2}{3}$
	A			(x11$\frac{2}{3}$) $1_2 B_2$		0	$\bar{1}$ $\frac{2}{3}$
				(x$\bar{\bar{2}}\bar{2}\frac{2}{3}$) $2_3 \bar{1}'_2$		1	0 $\frac{2}{3}$
	A			(x$\bar{\bar{2}}\bar{2}\frac{2}{3}$) $\bar{2}_3 A_3$	(x$\bar{\bar{2}}\bar{2}\frac{2}{3}$) $\bar{2}_3 \bar{1}'_3$	$\bar{1}$	0 $\frac{2}{3}$
		(x0$\bar{1}\bar{1}$) (x$\bar{1}$10) (x1$\bar{1}\bar{1}$) $A_3 \bar{B}_2 / A_3 A_3$				$\bar{1}$	$\bar{1}$ 0
		(x1$\bar{1}$1) (x$\bar{2}$10) $B_3 \bar{B}_2$				1	$\bar{1}$ 1
		(x1$\bar{1}$1) (x$\bar{2}$10) $B_3 \bar{B}_2$				$\bar{1}$	$\bar{1}$ 1
	A			(x$\bar{2}\bar{1}\frac{2}{3}$) $2_3 A_3 / 2_3 \bar{B}_2$ (x$\bar{2}\bar{2}\frac{2}{3}$) $2_3 \bar{B}_2$	(x$\bar{2}\bar{2}\frac{2}{3}$) $2_3 2_3$	$\bar{1}$	$\bar{1}$ $\frac{2}{3}$
				(x$\bar{\bar{2}}\bar{2}\frac{2}{3}$) $\bar{2}_3 A_3 / \bar{2}_3 \bar{B}_2$			
	B			(x$\bar{2}\bar{2}\frac{2}{3}$) $2_3 B_3$		$\bar{1}$	1 $\frac{2}{3}$


C
(x22⅔) 2₃B₃
1 1 ⅔
(⅔22x) 2̄₂1₃
⅔ 0 0
(022x) 2̄₂A₃
(1̄22x) 2̄₂1′₃
1̄ 1 0
(220x) (221x) 2̄₂A₃
0 1̄ 1
(022x) 2̄₂A₃
A (100x) (110x) (110x) A₃A₃
0 0 1̄ 1
B
(120x) 2₃A₃ (220x) 2̄₃A₃
⅔ 0 1̄ 1
(022x) 2₂B₃ (221x) 2̄₂B₃
1̄ 1 1
A (111x) (012x) B̄₂B₃
(022x) 2₂B₃ (221x) 2̄₂B₃
1̄ 1 1̄
B (110x) (120x) B₃A₃
1̄ 1 1̄ 1̄
C
(121x) 2₃B₃ (221x) 2̄₃B₃
⅔ 1̄ 1 1
C
(121x) 2₃B₃ (221x) 2̄₃B₃
⅔ 1̄ 1 1̄
(⅓00x) A₂A₃ (⅔10x) B₂A₃
(⅓12x) B̄₂2₃ (⅔22x) 2̄′₂2₃
⅔ 1̄ 1 1
(⅔22⅔) 2̄₃1₃
⅔ 0 0 ⅔
(022⅔) 2̄₃A₃
(1̄22⅔) 2̄₃1′₃
1̄ 1 0 ⅔
(00 11) (0 110) (01 11) A₃A₃
0 1̄ 1 0
(021⅔) 2₃A₃ (022⅔) 2̄₃A₃
0 1̄ 1 ⅔
(022⅔) 2₃B₃
1̄ 1 1 ⅔
A
(022⅔) 2₃B₃
1̄ 1 1̄ ⅔
(⅔22⅔) 2₃2₃
⅔ 1̄ 1 ⅔
21 (x22–) 2̄′₂C₁
(x23–) 2̄′₂3₁
(x12–) 1₁C₁
(x13–) 1₁3₁
0 2 – –
A (x22–) 2̄′₂C₁
(x12–) 1₁C₁ (x11–) 1₂B₁
0 2̄ – –
A
(x23–) 2̄₂B₃
1̄ 1 – –
A
(x23–) 2̄₂B₃
1̄ 1̄ – –
B
(x23–) 2̄₂B₂
(x23–) 2̄₂2₃
1̄ 1 – –
(x12–) B₂C₁
(x13–) B₂3₁
(x22–) 2₁C₁
(x23–) 2₁3₁
1 2 – –

($\alpha\beta$) Pattern (continued)

σ-Block	Set	Substrates and Sequences by Polarity − −	− +	+ −	+ +	Product $\gamma_1\beta_1\alpha_1$	$\alpha_2\beta_2\gamma_2$
21	A	(x12–) B_2C_1		(x22–) 2_1C_1		1	$\bar{2}$ – –
	B	(x02–) A_2C_1 (x12–) B_2C_1	(x03–) A_23_1 (013–) B_23_1	(x22–) 2_1C_1	(x23–) 2_13_1	$\bar{1}$	2 – –
	C	(x02–) A_2C_1 (x12–) B_2C_1		(x22–) 2_1C_1 (x21–) 2_1B_3		$\bar{1}$	$\bar{2}$ – –
		(x$\bar{1}\bar{2}$–) $\bar{B}_2B_3$ (x$\bar{2}\bar{2}$–) $\bar{2}_2B_3$		(x$\bar{2}\bar{2}$–) 2_2B_3 (x$\bar{2}\bar{3}$–) $\bar{2}_2B_3$			
	D	(x$\bar{1}\bar{2}$–) $\bar{B}_2B_3$ (x$\bar{2}\bar{2}$–) $\bar{2}'_2B_3$		(x$\bar{2}\bar{2}$–) 2_2B_3 (x$\bar{2}\bar{3}$–) $\bar{2}_2B_3$		$\overline{1\ 2}$	– –
				(x21–) 2_1B_3			
	A				($\frac{1}{2}\bar{2}\bar{3}$–) $\bar{2}_22_3$	$\frac{1}{2}\ \overline{1\ 1}$	– –
	A	($\bar{1}\bar{1}$1–) (0$\bar{1}\bar{2}$–) $\bar{B}_2B_3$		($\bar{2}\bar{2}$1–) (0$\bar{2}\bar{3}$–) $\bar{2}_2B_3$		0 $\overline{1\ 2}$	– –
		(0$\bar{2}\bar{2}$–) $\bar{2}'_2B_3$		(0$\bar{2}\bar{2}$–) 2_2B_3			
	B			($\bar{1}$21–) 2_3B_3 ($\bar{2}\bar{2}$1–) $\bar{2}_3B_3$		$\frac{1}{2}$ 0 $\overline{1\ 2}$	– –
	A	($\bar{1}\bar{1}$1–) (0$\bar{1}\bar{2}$–) $\bar{B}_2B_3$		($\bar{2}\bar{2}$1–) (0$\bar{2}\bar{3}$–) $\bar{2}_2B_3$		$\overline{1\ 1}$	$\bar{2}$ – –
		(0$\bar{2}\bar{2}$–) $\bar{2}'_2B_3$		(0$\bar{2}\bar{2}$–) 2_2B_3			
	B			($\bar{1}$21–) 2_3B_3 ($\bar{2}\bar{2}$1–) $\bar{2}_3B_3$		$\frac{1}{2}\ \overline{1\ 1}$	$\bar{2}$ – –
13		(–20x) (–21x) C_1A_2		(–30x) (–31x) 3_1A_2		– – 2	0
			(–1$\bar{1}\bar{1}$) (–$\bar{2}$10) B_3I_2			– – 1	0 0
		(–1$\bar{1}\bar{1}$) (–$\bar{2}$10) $B_3I'_2$		(–3$\bar{1}\bar{1}$) 3_1A_2		– – 2	0 0
		(–2$\bar{1}\bar{1}$) C_1A_2					
	A		(–1$\bar{1}\bar{1}$) (–$\bar{2}$10) $B_3I_2/B_3\bar{I}'_3$			– – $\bar{2}$	0 0
	B		(–1$\bar{1}\bar{1}$) (–$\bar{2}$10) B_3I_3			– – $\bar{2}$	0 0 $\frac{1}{2}$
	A	(–1$\bar{1}\bar{1}$) (–$\bar{2}$10) $B_3I'_2$				– – $\bar{2}$	0 1
12			(–$\bar{2}\bar{2}$x) $C_2\bar{2}_2$		(–$\bar{3}\bar{2}$x) $3_2\bar{2}_2$	– – $\overline{1\ 1}$	
		(–$\bar{2}\bar{2}$x) $C_2\bar{2}'_2$	(–21x) C_1l_1	(–$\bar{3}\bar{2}$x) $3_2\bar{2}'_2$	(–31x) 3_1l_1	– – 2	0
		(–21x) C_1B_2	(–22x) C_12_1	(–31x) 3_1B_2	(–32x) 3_12_1	– – 2	1

	A	(–20x) C_1A_2 (–21x) C_1B_2	(–22x) C_12_1	(–30x) 3_1A_2 (–31x) 3_1B_2	(–32x) 3_12_1	– – 2 $\bar{1}$
	B	(–21x) C_1B_1	(–12x) B_22_1 (–22x) C_12_1			– – $\bar{2}$ 1
	C	(–21x) C_1B_1	(–12x) B_22_1 (–22x) C_12_1			– – $\bar{2}$ $\bar{1}$
	D	(–$\bar{2}\bar{2}$x) $C_2\bar{2}'_2$		(–$\bar{3}\bar{2}$x) $3_2\bar{2}'_2$		– – 2 $\bar{1}$
		(–1$\bar{1}\bar{1}$) (–$\bar{2}\bar{1}$0) $B_3\bar{B}_2$				– – 2 $\bar{1}$ 0
		(–1$\bar{1}\bar{1}$) (–$\bar{2}\bar{1}$0) $B_3\bar{B}_2$				– – $\bar{2}$ $\bar{1}$ $\bar{1}$
11		(–22–) C_1C_1	(–23–) C_13_1	(–32–) 3_1C_1	(–33–) 3_13_1	– – 2 2 – –
	A	(–21–) C_1B_2 (–22–) C_1C_1		(–32–) 3_1C_1 (–31–) 3_1B_2		– – 2 $\bar{2}$ – –
	B	(–12–) B_2C_1 (–22–) C_1C_1	(–13–) B_23_1	(–32–) 3_1C_1		– – $\bar{2}$ 2 – –
	C	(–12–) B_2C_1 (–22–) C_1C_1				– – $\bar{2}$ $\bar{2}$ – –
	D	(–$\bar{2}\bar{2}$–) C_2C_2	(–$\bar{2}\bar{3}$–) C_23_2	(–$\bar{3}\bar{2}$–) 3_2C_2	(–$\bar{3}\bar{3}$–) 3_23_2	– – $\bar{2}$ $\bar{2}$ – –

σ-Block	Sequence Sets	Product $\gamma_1\beta_1\alpha_1$ $\alpha_2\beta_2\gamma_2$
23	$[(x\bar{1}\bar{1}x)\ \bar{1}'_2A_1/\bar{B}_2\bar{1}_2\quad(x\bar{2}\bar{1}x)\ \bar{B}_2\bar{1}_2\quad(x11x)\ 1_2A_1]+A_2A_3\quad(x\bar{1}\bar{1}x)\ (x\bar{2}\bar{1}x)\ \bar{B}_2\bar{1}'_2A_1$	0 0
	$[\text{SET 23–x10xA}]_7+A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	
	$[\text{SET 33–x000}]_4\,[\text{SET 23–x000}]_3+A_2A_3\quad[\text{SET 23–x100}]_5+A_1\quad[\text{SET 23–x100A}]_8+A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	0 0 0
	$[\text{SET 33–x000A}]_4+A_2A_3\quad(x1\bar{1}\bar{1})\ (x\bar{2}\bar{1}0)\ B_3\bar{1}_3A_1\quad(\text{SET 23–x100B})_2+A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	0 0 0 $\frac{1}{3}$
	$[(x\bar{1}\bar{1}1)\ \bar{1}'_21_2\quad(x\bar{1}\bar{2}1)\ \bar{1}_21_2]+A_2A_3\quad(x1\bar{1}\bar{1})\ (x\bar{2}\bar{1}0)\ B_3\bar{1}'_2A_1\quad[\text{SET 23–x101}]_2+A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	0 0 1
	$[\text{SET 33–x001A}]_7\quad[(x11\bar{1})\ 1_2A_3]+A_2A_3$	0 0 $\overline{1\ 1}$
	$[\text{SET 23–x002}]_5\quad[(x\bar{1}\bar{1}\tfrac{1}{3})\ \bar{1}_3A_2]+A_2A_3\quad(x\bar{2}\bar{1}\tfrac{1}{3})\ 2_3\bar{1}'_2A_1\quad[(x\bar{2}\bar{1}\tfrac{1}{3})\ 2_3A_3/2_3\bar{1}'_3]+A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	0 0 $\frac{1}{3}$
	$[(x\bar{1}\bar{1}\bar{2})\ \bar{1}'_2A_3/\bar{1}_2A_3\quad(x11\bar{2})\ 1_2A_3]+A_2A_3$	0 0 $\overline{2\ 2}$
	$[\text{SET 23–110xA}]_7+\bar{1}_2A_2$	0 0 0
	$[(\bar{1}00x)\ (\bar{1}\bar{1}0x)\ (\bar{1}10x)\ A_3A_3]+\bar{1}_2A_2$	0 0 0 0
	$[(\bar{1}\bar{2}0x)\ 2_3A_3\quad(\bar{2}\bar{2}0x)\ \bar{2}_3A_3]+\bar{1}_3A_2$	$\frac{1}{3}$ 0 0 0
	$[\text{SET 23–110xA}]_7+\bar{1}'_2$	1 0 0
	$(\bar{1}00x)\ (\bar{1}\bar{1}0x)\ (\bar{1}10x)\ A_3A_3\bar{1}'_2$	0 1 0 0
	$(\bar{1}\bar{2}0x)\ 2_3A_3\bar{1}'_2\quad(\bar{2}\bar{2}0x)\ \bar{2}_3A_3\bar{1}'_2$	$\frac{1}{3}$ 1 0 0
	$(\bar{1}00x)\ (\bar{1}\bar{1}0x)\ (\bar{1}10x)\ A_3A_3A_3\quad[(\bar{1}10x)\ (\bar{1}\bar{2}0x)\ B_3A_3]+A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	$\overline{1\ 1}$ 0 0
	$(\tfrac{1}{3}\bar{1}\bar{1}x)\ (\tfrac{1}{3}\bar{2}\bar{1}x)\ \bar{B}_2\bar{1}_3A_2\quad[(\tfrac{1}{3}00x)\ A_2A_3\quad(\tfrac{1}{3}10x)\ B_2A_3]+A_2A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	$\frac{1}{3}$ 0 0
	$[(00\bar{1}\bar{1})\ (0\bar{1}\bar{1}0)\ (01\bar{1}\bar{1})\ A_3A_3]+\bar{1}_2A_2$	0 0 0 0
	$[(0\bar{2}\bar{1}\tfrac{1}{3})\ 2_3A_3\quad(1\bar{2}\bar{1}\tfrac{1}{3})\ 2_3\bar{1}'_3]+\bar{1}_2A_2$	0 0 0 $\frac{1}{3}$
	$(\tfrac{1}{3}0\bar{1}\bar{1})\ (\tfrac{1}{3}\bar{1}\bar{1}0)\ A_3\bar{1}_3A_2$	$\frac{1}{3}$ 0 0 0
	$(\tfrac{1}{3}\bar{2}\bar{1}\tfrac{1}{3})\ 2_3\bar{1}_3A_2$	$\frac{1}{3}$ 0 0 $\frac{1}{3}$

22	(x21x) $2_1 1_2 A_1$ (x$\overline{22}$x) $\bar{2}_2 \bar{1}'_2 A_1$ [SET 22–x10xA]$_3 + A_3 \bar{1}_2 \bar{1}'_2 \bar{1}_3 \bar{1}'_3$	0 0
	[(x11x) $1_2 1_1$ (x$\bar{1}$1x) $\bar{1}'_2 1_1$ (x$\bar{1}$2x) $\bar{1}_2 A_1/\bar{1}_2 1_1$ (x$\overline{22}$x) $\bar{2}_2 \bar{1}_2$] $+ A_2 A_3$ [SET 22–x11xD]$_{14} + \bar{1}_2 A_2$	
	[SET 22–x11xD]$_{14} + \bar{1}'_2$ [SET 22–x11xB]$_7 + \bar{1}_2 \bar{1}'_2 \bar{1}_3 \bar{1}'_3$	0 1
	[SET 32–x01x]$_5$ [SET 22–x01xA]$_3$ [SET 22–x11xA]$_3 + A_3$	0 $\bar{1}$
	[SET 22–x11xC]$_7 + A_3 \bar{1}_2 \bar{1}'_2 \bar{1}_3 \bar{1}'_3$ [SET 22–x11xD]$_{14} + A_3 \bar{1}'_3$	
	[(x0$\bar{1}$1) (x$\bar{1}$10) (x1$\bar{1}$$\bar{1}$) $A_3 \bar{B}_2 / A_3 A_3$] $+ \bar{1}_2 A_2$	0 0 0
	[(x111) $1_2 1_2$ (x$\bar{1}$11) $\bar{1}'_2 1_2$ (x$\bar{1}$21) $\bar{1}_2 1_2$] $+ A_2 A_3$	0 0 1
	[(x$\bar{1}$2$\bar{1}$) $\bar{1}_2 A_3$] $+ A_2 A_3$	0 0 $\bar{1}\bar{1}$
	[SET 32–x002]$_3$ [SET 22–x002]$_2 + A_2 A_3$ [SET 22–x112A]$_6 + \bar{1}_3 A_2$ [(x$\overline{22}\frac{1}{3}$) $2_3 A_3 / \bar{2}_3 \bar{1}'_3$] $+ A_3 \bar{1}_2 \bar{1}'_2 \bar{1}_3 \bar{1}'_3$	0 0 $\frac{1}{3}$
	(x0$\bar{1}$$\bar{1}$) (x$\bar{1}$10) (x1$\bar{1}$$\bar{1}$) $A_3 \bar{B}_2 \bar{1}'_2 / A_3 A_3 \bar{1}'_2$	0 1 0
	[(x0$\bar{1}$1) (x$\bar{1}$10) (x1$\bar{1}$$\bar{1}$) $A_3 \bar{B}_2 / A_3 A_3$] $+ \bar{1}'_3$	0 $\bar{1}$ 0
	[(x11$\bar{1}$) $1_2 B_3$ (x$\bar{1}$$\bar{1}$$\bar{1}$) $\bar{1}'_2 B_3$ (x$\bar{1}$21) $\bar{1}'_3 B_3$ (x$\bar{1}$2$\bar{1}$) $\bar{1}_2 B_3$] $+ A_3$	0 $\bar{1}$ $\bar{1}\bar{1}$
	[SET 32–x011]$_7$ [SET 22–x110]$_6$ [(x1$\bar{1}$$\bar{1}$) (x2$\bar{1}$0) $B_3 \bar{B}_2$] $+ A_3$ [(x1$\bar{1}$$\bar{1}$) (x2$\bar{1}$0) $B_3 \bar{B}_2$] $+ A_3 \bar{1}_2 \bar{1}'_2 \bar{1}_3 \bar{1}'_3$	0 $\bar{1}\bar{1}$
	[SET 32–x011A]$_7 + A_3$ (x11$\bar{1}$) $1_2 A_3 A_3$	0 $\bar{1}\bar{1}$ 0
	(x$\bar{1}$21) $\bar{1}'_3 A_3 A_3$	0 $\bar{1}\bar{1}$ $\frac{1}{3}$
	(x$\overline{22}\frac{1}{3}$) $2_3 B_3 \bar{1}_2 / 2_3 B_3 \bar{1}'_2 / 2_3 B_3 \bar{1}_3 / 2_3 B_3 \bar{1}'_3$ [SET 22–x112A]$_6 + \bar{1}'_2$	0 1 $\frac{1}{3}$
	(x$\overline{22}\frac{1}{3}$) $2_3 B_3 \bar{1}_2 / 2_3 B_3 \bar{1}'_2 / 2_3 B_3 \bar{1}_3 / 2_3 B_3 \bar{1}'_3$ [SET 22–x112A]$_6 + \bar{1}'_3$	0 $\bar{1}$ $\frac{1}{3}$
	[SET 22–x112A]$_4$ [(x11$\frac{1}{3}$) $1_2 B_2$ (x$\bar{1}$2$\frac{1}{3}$) $\bar{1}_3 B_2$ (x$\bar{1}\bar{1}\frac{1}{3}$) $\bar{1}_3 A_2$ (x$\overline{22}\frac{1}{3}$) $2_3 B_3$] $+ A_3$	
	[SET 22–011x]$_2$ [SET 22–110x]$_7 + \bar{1}_2 A_2$	0 0 0
	[SET 22–011xA]$_3 + \bar{1}_2 A_2$	0 0 0 0
	($\bar{1}$20x) $2_3 A_3 \bar{1}_2$ ($\overline{22}$0x) $\bar{2}_3 A_3 \bar{1}_2$	$\frac{1}{3}$ 0 0 0
	(0$\overline{22}$x) $\bar{2}_2 A_3 \bar{1}'_2$ (1$\overline{22}$)x $\bar{2}_2 \bar{1}'_3 \bar{1}'_2$	1 0 0
	($\bar{1}$10x) ($\bar{1}$20x) $B_3 A_3 \bar{1}_2 / B_3 A_3 A_2$	$\bar{1}\bar{1}$ 0 0
	($\frac{1}{3}\overline{22}$x) $\bar{2}_2 \bar{1}_3 A_2$ [SET 22–211x]$_4 + A_2 \bar{1}_2$	$\frac{1}{3}$ 0 0
	[SET 22–011x]$_7 + \bar{1}'_2$ [SET 22–111x]$_4 + \bar{1}_2$	0 0 1

($\alpha\beta\alpha$) Pattern (continued)

σ-Block	Sequence Sets	Product $\gamma_1\beta_1\alpha_1$ $\alpha_2\beta_2\gamma_2$
22	(Ī00x) (Ī$\bar{1}$0x) (Ī10x) $A_3A_3\bar{I}_2'$	0 0 0 1
	$[(\bar{I}\bar{1}2x)\ A_2 2_1] + A_3$ [SET 22–011x]$_7 + A_3\bar{I}_3'$ [SET 22–111xA]$_4 + \bar{I}_2$	0 0 Ī
	$[(\bar{I}00x)\ (\bar{I}\bar{1}0x)\ \bar{1}10x)\ A_3A_3] + A_3\bar{I}_3$	0 0 0 Ī
	(Ī$\bar{2}$0x) $2_3A_3\bar{I}_2'$ (Ī$\bar{2}$1x) $2_3B_3\bar{I}_3$ ($\bar{2}\bar{2}$0x) $\bar{2}_3A_3\bar{I}_2'$ ($\bar{2}\bar{2}$1x) $\bar{2}_3B_3\bar{I}_3$	$\frac{1}{3}$ 0 0 1
	$[(\bar{I}\bar{2}0x)\ 2_3A_3$ ($\bar{2}\bar{2}$0x) $\bar{2}_3A_3] + A_3\bar{I}_3'$ (Ī$\bar{2}$1x) $2_3B_3\bar{I}_3$ ($\bar{2}\bar{2}$1x) $\bar{2}_3B_3\bar{I}_3$	$\frac{1}{3}$ 0 0 Ī
	(Ī$\bar{1}$1x) (0Ī$\bar{2}$x) $\bar{B}_2B_3\bar{I}_2'$ (0$\bar{2}\bar{2}$x) $2_2B_3\bar{I}_2'$ ($\bar{2}\bar{2}$Īx) $\bar{2}_2B_3\bar{I}_2'$	1 0 1
	(Ī10x) (Ī$\bar{2}$0x) $B_3A_3\bar{I}_2'$	Ī$\bar{1}$ 0 1
	(Ī$\bar{2}$1x) $2_3B_3\bar{I}_2'$ ($\bar{2}\bar{2}$1)x $\bar{2}_3B_3\bar{I}_2'$	$\frac{1}{3}$ 1 0 1
	(Ī$\bar{1}$1x) (0Ī$\bar{2}$x) $\bar{B}_2B_3\bar{I}_2'$ (0$\bar{2}\bar{2}$x) $2_2B_3\bar{I}_2'$ ($\bar{2}\bar{2}$1x) $\bar{2}_2B_3\bar{I}_2'$	1 0 Ī
	(Ī10x) (Ī$\bar{2}$0x) $B_3A_3A_3/B_3A_3\bar{I}_3'$	Ī$\bar{1}$ 0 Ī
	(Ī$\bar{2}$1x) $2_3B_3\bar{I}_2'$ ($\bar{2}\bar{2}$1x) $\bar{2}_3B_3\bar{I}_2'$	$\frac{1}{3}$ 1 0 Ī
	[SET 22–211x]$_4 + \bar{I}_2'$	$\frac{1}{3}$ 0 1
	[SET 22–211x]$_4 + A_3\bar{I}_3'$	$\frac{1}{3}$ 0 Ī
	$[(00\bar{1}\bar{1})\ (0\bar{1}\bar{1}0)\ (01\bar{1}\bar{1})\ A_3A_3] + \bar{I}_2A_2$	0 0 0 0
	$[(0\bar{2}\bar{2}\frac{2}{3})\ \bar{2}_3A_3$ ($1\bar{2}\bar{2}\frac{2}{3}$) $\bar{2}_3\bar{I}_3'] + \bar{I}_2A_2$ [(0$\bar{2}\bar{1}\frac{1}{3}$) 2_3A_3 (0$\bar{2}\bar{2}\frac{2}{3}$) $\bar{2}_3A_3] + \bar{I}_3A_2$	0 0 0 $\frac{1}{3}$
	(0$\bar{2}\bar{2}\frac{2}{3}$) $\bar{2}_3A_3\bar{I}_2'$ ($1\bar{2}\bar{2}\frac{2}{3}$) $\bar{2}_3\bar{I}_3'\bar{I}_2'$	1 0 0 $\frac{1}{3}$
	($\frac{1}{3}\bar{2}\bar{2}\frac{2}{3}$) $2_32_3\bar{I}_3/2_32_3A_2$ ($\frac{1}{3}\bar{2}\bar{2}\frac{2}{3}$)$\bar{2}_3\bar{I}_3A_2$	$\frac{1}{3}$ 0 0 $\frac{1}{3}$
	$(00\bar{1}\bar{1})\ (0\bar{1}\bar{1}0)\ (01\bar{1}\bar{1})\ A_3A_3\bar{I}_2'$	0 0 1 0
	$(00\bar{1}\bar{1})\ (0\bar{1}\bar{1}0)\ (01\bar{1}\bar{1})\ A_3A_3A_3$	0 0 Ī$\bar{1}$
	(0$\bar{2}\bar{1}\frac{1}{3}$) $2_3A_3\bar{I}_2'$ (0$\bar{2}\bar{2}\frac{2}{3}$) $2_3B_3I_2$ (0$\bar{2}\bar{2}\frac{2}{3}$) $\bar{2}_3A_3\bar{I}_2'$	0 0 1 $\frac{1}{3}$
	$[(0\bar{2}\bar{2}\frac{2}{3})\ 2_3B_3] + \bar{I}_2A_2$	0 0 Ī $\frac{1}{3}$
	(0$\bar{2}\bar{2}\frac{2}{3}$) $2_3B_3\bar{I}_2'$	1 0 1 $\frac{1}{3}$
	(0$\bar{2}\bar{2}\frac{2}{3}$) $2_3B_3\bar{I}_2'$	1 0 Ī $\frac{1}{3}$

	$(\frac{1}{2}\overline{22}\frac{1}{2})\ 2_3 2_3 \bar{1}'_2$	$\frac{1}{2}\ 0\ 1\ \frac{1}{2}$
	$[(\frac{1}{2}\overline{22}\frac{1}{2})\ 2_3 2_3] + A_3 \bar{1}'_3$	$\frac{1}{2}\ 0\ \bar{1}\ \frac{1}{2}$
21	$[(x\overline{23}\text{–})\ \bar{2}_2 B_2/\bar{2}_2 2_3] + 1_2 A_2$	$0\ 0\ -\ -$
	$(x\overline{23}\text{–})\ \bar{2}_2 B_2 \bar{1}'_2/\bar{2}_2 2_3 \bar{1}'_2 \quad [(x\overline{23}\text{–})\ \bar{2}_2 B_3] + \bar{1}_2 \bar{1}'_2 \bar{1}_3 \bar{1}'_3 \quad [\text{SET 21–x12–D}]_5 + 1_2$	$0\ 1\ -\ -$
	$[(x\overline{23}\text{–})\ \bar{2}_2 B_2/\bar{2}_2 2_3] + A_3 \bar{1}'_3 \quad [(x\overline{23}\text{–})\ \bar{2}_2 B_3] + \bar{1}_2 \bar{1}'_2 \bar{1}_3 \bar{1}'_3$	$0\ \bar{1}\ -\ -$
	$[\text{SET 31–x02–}]_7\ [\text{SET 21–x02–}]_4\ [\text{SET 21–x12–}]_4 + A_2 \quad [\text{SET 21–x12–B}]_6 + A_2 A_3 \bar{1}_2 \bar{1}'_2 \bar{1}_3 \bar{1}'_3 \quad [\text{SET 21–x12–D}]_5 + 1'_2$	$0\ 2\ -\ -$
	$[\text{SET 21–x12–C}]_8 + \bar{1}_2 \bar{1}'_2 \bar{1}_3 \bar{1}'_3 \quad [\text{SET 21–x12–D}]_5 + \bar{1}'_3$	$0\ \bar{2}\ -\ -$
	$(\frac{1}{2}\overline{23}\text{–})\ \bar{2}_2 2_3 A_2/\bar{2}_2 2_3 1_2$	$\frac{1}{2}\ 0\ 0\ -\ -$
	$(\bar{1}\bar{1}1\text{–})\ (\bar{2}10\text{–})\ \bar{B}_2 B_3 1_2 \quad (0\overline{22}\text{–})\ 2_2 B_3 1_2 \quad (0\overline{22}\text{–})\ \bar{2}'_2 B_3 1_2 \quad (0\overline{23}\text{–})\ (\overline{22}1\text{–})\ \bar{2}_2 B_3 1_2$	$0\ 0\ 1\ -\ -$
	$(\bar{1}21\text{–})\ 2_3 B_3 1_2 \quad (\overline{22}1\text{–})\ \bar{2}_3 B_3 1_2$	$\frac{1}{2}\ 0\ 0\ 1\ -\ -$
	$(\frac{1}{2}\overline{23}\text{–})\ \bar{2}_2 2_3 \bar{1}'_2$	$\frac{1}{2}\ 0\ 1\ -\ -$
	$[(\frac{1}{2}\overline{23}\text{–})\ \bar{2}_2 2_3] + A_3 \bar{1}'_3$	$\frac{1}{2}\ 0\ \bar{1}\ -\ -$
	$(\bar{1}\bar{1}2\text{–})\ A_2 C_1 A_2 \quad (\bar{1}\bar{1}3\text{–})\ A_2 3_1 A_2 \quad [\text{SET 21–012–A}]_6 + 1'_2$	$0\ 0\ 2\ -\ -$
	$\bar{1}21\text{–})\ 2_3 B_3 1'_2 \quad (\overline{22}1\text{–})\ \bar{2}_3 B_3 1'_2$	$\frac{1}{2}\ 0\ 0\ 2\ -\ -$
	$[\text{SET 21–012–A}]_6 + \bar{1}'_3 \quad [\text{SET 21–112–A}]_6 + 1_2$	$0\ 0\ \bar{2}\ -\ -$
	$[(\bar{1}21\text{–})\ 2_3 B_3 \quad (\overline{22}1\text{–})\ \bar{2}_3 B_3] + 1_3 \bar{1}'_3$	$\frac{1}{2}\ 0\ 0\ \bar{2}\ -\ -$
	$[\text{SET 21–112–A}]_6 + 1'_2$	$1\ 0\ \bar{2}\ -\ -$
	$(\bar{1}21\text{–})\ 2_3 B_3 1'_2 \quad (\overline{22}1\text{–})\ \bar{2}_3 B_3 1'_2$	$\frac{1}{2}\ 1\ 0\ \bar{2}\ -\ -$
13	$(x\bar{1}\bar{1}x)\ (x\bar{2}1x)\ \bar{B}_2 1'_2 1_1$	$-\ -\ 0\ 0$
	$(x\bar{1}\bar{1}x)\ (x\bar{2}1x)\ \bar{B}_2 1'_2 B_1 \quad (\text{–}20x)\ (\text{–}21x)\ C_1 A_2 2_1 \quad (\text{–}30x)\ \text{–}31x)\ 3_1 A_2 2_1$	$-\ -\ 1\ 0$
	$[(x\bar{1}\bar{1}x)\ (x\bar{2}1x)\ \bar{B}_2 1'_2] + B_1 A_3 \quad (\text{–}20x)\ (\text{–}21x)\ C_1 A_2 2_1 \quad (\text{–}30x)\ (\text{–}31x)\ 3_1 A_2 2_1 \quad [\text{SET 23–x10xA}]_7 + A_3 \bar{B}_2$	$-\ -\ \bar{1}\ 0$
	$[\text{SET 23–x100}]_5 + 1_1 \quad [\text{SET 23–x100A}]_8 + A_3 \bar{B}_2$	$-\ -\ 0\ 0\ 0$
	$(\text{–}1\bar{1}\bar{1})\ (\text{–}\bar{2}10)\ B_3 1_3 1_1$	$-\ -\ 0\ 0\ 0\ \frac{1}{2}$
	$(\text{–}1\bar{1}\bar{1})\ (\text{–}\bar{2}10)\ B_3 1'_2 1_1$	$-\ -\ 0\ 0\ 1$
	$[\text{SET 23–x100}]_5 + B_1 \quad [\text{SET 13–200}]_4 + 2_1 \quad [(\text{–}1\bar{1}\bar{1})\ (\text{–}\bar{2}10)\ B_3 1_2 / B_3 \bar{1}'_3] + B_3$	$-\ -\ 1\ 0\ 0$

($\alpha\beta\alpha$) Pattern (continued)

σ-Block		Product $\gamma_1\beta_1\alpha_1$ $\alpha_2\beta_2\gamma_2$
13	$[(-1\bar{1}\bar{1})\ (-\bar{2}10)\ B_3\bar{1}_3] + B_1B_3$	− − 1 0 0 ½
	$[\text{SET } 23\text{–x}100]_5 + B_1A_3$ $[\text{SET } 13\text{–}200]_4 + 2_1$ $[(-1\bar{1}\bar{1})\ (-\bar{2}10)\ B_3\bar{1}_2/B_3\bar{1}'_3] + B_3\bar{B}_22_22_3$	− − Ī 0 0
	$[(-1\bar{1}\bar{1})\ (-\bar{2}10)\ B_3\bar{1}_3] + B_1A_3B_3\bar{B}_22_22_3$	− − Ī 0 0 ½
	$[(-1\bar{1}\bar{1})\ (-\bar{2}10)\ B_3\bar{1}'_2] + B_1B_3$	− − 1 0 1
	$[(-1\bar{1}\bar{1})\ (-\bar{2}10)\ B_3\bar{1}'_2] + B_1A_3B_3\bar{B}_22_22_3$	− − Ī 0 1
12	$(-\bar{2}\bar{2}\mathbf{x})\ \bar{2}_2\bar{1}'_21_1$ $(-2\mathbf{1}\mathbf{x})\ 2_11_21_1$ $[(-\bar{2}\bar{2}\mathbf{x})\ C_2\bar{2}_2$ $(-\bar{3}\bar{2}\mathbf{x})\ 3_2\bar{2}_2] + \bar{1}_2A_2$	− − 0 0
	$(-1\mathbf{2}\mathbf{x})\ B_22_11_2$ $(-2\mathbf{2}\mathbf{x})\ 2_12_11_2$ $(-\bar{2}\bar{2}\mathbf{x})\ C_2\bar{2}_2\bar{1}'_2$ $(-\bar{3}\bar{2}\mathbf{x})\ 3_2\bar{2}_2\bar{1}'_2$	− − 0 1
	$[(-\bar{2}\bar{2}\mathbf{x})\ C_2\bar{2}_2$ $(-\bar{3}\bar{2}\mathbf{x})\ 3_2\bar{2}_2] + A_3\bar{1}'_3$	− − 0 Ī
	$[(-\bar{2}\bar{2}\mathbf{x})\ \bar{2}_2\bar{1}'_2$ $(-2\mathbf{1}\mathbf{x})\ 2_11_2] + B_1A_3$ $(-\bar{2}\bar{2}\mathbf{x})\ C_2\bar{2}'_22_1$ $(-3\mathbf{1}\mathbf{x})\ 3_11_12_1$ $(-\bar{3}\bar{2}\mathbf{x})\ 3_2\bar{2}'_22_1$	− − 1 0
	$(-2\mathbf{1}\mathbf{x})\ 2_11_2B_1$ $(-\bar{2}\bar{2}\mathbf{x})\ 2_2\bar{1}'_2B_1/C_2\bar{2}'_22_1$ $(-3\mathbf{1}\mathbf{x})\ 3_11_12_1$ $(-\bar{3}\bar{2}\mathbf{x})\ 3_2\bar{2}'_22_1$ $[\text{SET } 22\text{–x}10\text{xA}]_3 + A_3\bar{B}_2$	− − Ī 0
	$(-2\mathbf{1}\mathbf{x})\ C_1B_22_1$ $(-2\mathbf{2}\mathbf{x})\ C_12_12_1$ $(-3\mathbf{1}\mathbf{x})\ 3_1B_22_1$ $(-3\mathbf{2}\mathbf{x})\ 3_12_12_1$	− − 1 1
	$[\text{SET } 22\text{–x}11\text{xA}]_2\,[\text{SET } 12\text{–}21\text{xC}]_3\,[\text{SET } 12\text{–}21\text{xD}]_2 + B_3$ $[\text{SET } 12\text{–}21\text{xA}]_6 + 2_1$	− − 1 Ī
	$(-2\mathbf{1}\mathbf{x})\ C_1B_22_1$ $(-2\mathbf{2}\mathbf{x})\ C_12_12_1$ $(-3\mathbf{1}\mathbf{x})\ 3_1B_22_1$ $(-3\mathbf{2}\mathbf{x})\ 3_12_12_1$ $[\text{SET } 12\text{–}21\text{xB}]_3 + 2_22_3$	− − Ī 1
	$[\text{SET } 22\text{–x}11\text{xA}]_2\,[\text{SET } 12\text{–}21\text{xD}]_2 + B_3$ $[\text{SET } 22\text{–x}11\text{xC}]_7 + A_3\bar{B}_2$ $[\text{SET } 12\text{–}21\text{xC}]_3 + B_3\bar{B}_22_22_3$ $[\text{SET } 12\text{–}21\text{xA}]_6 + 2_1$	− − Ī Ī
	$[\text{SET } 32\text{–x}01\text{x}]_5\,[\text{SET } 22\text{–x}01\text{xA}]_3\,[(\mathbf{x}1\mathbf{2}\mathbf{x})\ B_22_1$ $(\mathbf{x}2\mathbf{2}\mathbf{x})\ 2_12_1] + A_3$	− − 1 1
	$[\text{SET } 22\text{–x}11\text{xD}]_{14} + \bar{B}_2A_3$ $[(-\bar{2}\bar{2}\mathbf{x})\ C_2\bar{2}'_2$ $(-\bar{3}\bar{2}\mathbf{x})\ 3_2\bar{2}'_2] + \bar{B}_22_3$	
	$(-\bar{2}\bar{2}\frac{3}{2})\ \bar{2}_3\bar{1}'_21_1$	− − 0 0 ½
	$(-1\bar{1}\bar{1})\ (-\bar{2}10)\ B_3\bar{B}_2A_3$	− − 0 1 1
	$[(-\bar{2}\bar{2}\frac{3}{2})\ \bar{2}_3\bar{1}'_2] + B_1A_3$	− − 1 0 ½
	$(-\bar{2}\bar{2}\frac{3}{2})\ \bar{2}_3\bar{1}'_2B_1$ $[(-\bar{2}\bar{2}\frac{3}{2})\ \bar{2}_3A_3/\bar{2}_3\bar{1}'_3] + A_3\bar{B}_2$	− − Ī 0 ½
	$[\text{SET } 32\text{–x}011]_7 + A_3$ $[\text{SET } 22\text{–x}110]_6 + \bar{B}_2A_3$ $[(-1\bar{1}\bar{1})\ (-\bar{2}10)\ B_3\bar{B}_2] + \bar{B}_22_3$	1 1 0
	$[\text{SET } 32\text{–x}011\text{A}]_7 + A_3$ $(-11\bar{1})\ 1_2A_3A_3$	− − 1 1 0 0
	$(-\bar{1}\bar{2}1)\ \bar{1}'_32_3A_3$	− − 1 1 0 ½

	$(-1\bar{1}\bar{1})$ $(-\bar{2}\bar{1}0)$ $B_3\bar{B}_2B_3/B_3\bar{B}_2B_3$	– – 1 $\bar{1}$ $\bar{1}$
	$(-1\bar{1}\bar{1})$ $(-\bar{2}\bar{1}0)$ $B_3\bar{B}_2B_3/B_3\bar{B}_2B_3$ $[(-1\bar{1}\bar{1})$ $(-\bar{2}\bar{1}0)$ $B_3\bar{B}_2] + \bar{B}_2 2_2 2_3$	– – $\bar{1}$ $\bar{1}$ $\bar{1}$
	$[(-\bar{1}\bar{1}\bar{1})$ $\bar{1}'_2B_3$ $(-\bar{1}\bar{2}1)$ $\bar{1}'_3B_3$ $(-\bar{1}\bar{2}\bar{1})$ $\bar{1}_2B_3$ $(-11\bar{1})$ $1_2B_3] + A_3$	– – $\bar{1}$ $\bar{1}$ $\bar{1}$
	$(-\bar{2}\bar{2}\frac{1}{3})$ $2_3B_3\bar{B}_2/2_3B_3A_3$	– – $\bar{1}$ $\bar{1}$ $\frac{1}{3}$
	$[(-\bar{1}\bar{2}\frac{1}{3})$ $\bar{1}_3B_2$ $(-\bar{1}\bar{1}\frac{1}{3})$ $\bar{1}_3A_2$ $(-11\frac{1}{3})$ $1_2B_2] + A_3$ $[\text{SET 22-x112A}]_6 + \bar{B}_2A_3$	– – $\bar{1}$ $\bar{1}$ $\frac{1}{3}$
11	$(-\bar{2}\bar{2}–)$ $C_2C_2\bar{2}'_2$ $(-\bar{2}\bar{3}–)$ $C_23_2\bar{2}'_2$ $(-\bar{3}\bar{2}–)$ $3_2C_2\bar{2}'_2$ $(-\bar{3}\bar{3}–)$ $3_23_2\bar{2}'_2$	– – 0 2 – –
	$(-12–)$ $B_2C_1\bar{1}_1$ $(-\bar{2}2–)$ $2_1C_1\bar{1}_1$	– – 0 $\bar{2}$ – –
	$(-\bar{2}\bar{3}–)$ $\bar{2}_2B_3A_3/\bar{2}_2B_3\bar{B}_2$	– – $\bar{1}$ $\bar{1}$ – –
	$[(-\bar{2}\bar{3}–)$ $\bar{2}_2\bar{B}_2/\bar{2}_22_3] + \bar{B}_2A_3$	– – $\bar{1}$ $\bar{1}$ – –
	$[\text{SET 21-x12-}]_4 + B_2$ $[\text{SET 11-22-}]_4 + 2_1$ $[\text{SET 11-22-B}]_4 + B_3$	– – 1 2 – –
	$[\text{SET 11-22-A}]_4 + 2_1$ $[\text{SET 11-22-C}]_2 + B_3$	– – 1 $\bar{2}$ – –
	$[\text{SET 31-x02-}]_7$ $[\text{SET 21-x02-}]_4 + A_2A_3$ $[\text{SET 21-x12-}]_4 + B_2$	– – $\bar{1}$ 2 – –
	$[\text{SET 21-x12-B}]_6 + A_3$ $[\text{SET 11-22-}]_4 + 2_1$ $[\text{SET 11-22-B}]_4 + \bar{B}_2B_32_22_3$	
	$[\text{SET 11-22-A}]_4 + 2_1$ $[\text{SET 11-22-C}]_2 + B_2\bar{B}_32_22_3$	– – $\bar{1}$ $\bar{2}$ – –
	$[\text{SET 21-x12-D}]_5 + B_2$ $[\text{SET 11-22-D}]_4 + \bar{2}'_2$	– – $\bar{1}$ 2 – –

($\alpha\beta\beta$) Pattern

σ-Block	Sequence Sets	Product $\gamma_1\beta_1\alpha_1$ $\alpha_2\beta_2\gamma_2$
32	$[(\mathbf{x\bar{1}\bar{1}x})\ \bar{1}'_2A_1/\bar{1}'_21_1\ \ (\mathbf{x\bar{1}\bar{2}x})\ \bar{1}_2A_1/\bar{1}_21_1] + A_2A_3\ \ [\text{SET 32–x01x}]_5 + A_1A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	0 0
	$[\text{SET 33–x000}]_4 + A_2A_3\ \ [\text{SET 32–x011}]_7 + \bar{1}_2A_2$	0 0 0
	$[\text{SET 32–x011A}]_7 + \bar{1}_2A_2$	0 0 0 0
	$[\text{SET 33–x000A}]_4 + A_2A_3\ \ [(\mathbf{x\bar{1}\bar{2}1})\ \bar{1}'_32_3] + \bar{1}_3A_2$	0 0 0 $\frac{1}{3}$
	$(\mathbf{x0\bar{2}\bar{2}})\ (\mathbf{x1\bar{2}\bar{2}})\ A_3\bar{2}'_2\bar{1}_2\ \ [\text{SET 32–x011}]_7 + \bar{1}'_2$	0 0 1
	$[\text{SET 32–x011A}]_7 + \bar{1}'_2$	0 0 1 0
	$[\text{SET 33–x001A}]_7\ [\text{SET 32–x011A}]_7\ [\text{SET 32–x011B}]_3 + A_3\ \ (\mathbf{x\bar{1}\bar{2}\bar{1}})\ \bar{1}_2A_3A_3\ \ [\text{SET 32–x011C}]_3 + A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	0 0 $\overline{1\ 1}$
	$(\mathbf{x\bar{1}2\bar{1}})\ \bar{1}'_32_3\bar{1}'_2$	0 0 1 $\frac{1}{3}$
	$(\mathbf{x0\bar{2}\bar{2}})\ (\mathbf{x1\bar{2}\bar{2}})\ A_3\bar{2}'_2\bar{1}'_2/A_3\bar{2}'_2A_2$	0 0 2
	$(\mathbf{x\bar{1}\bar{1}\frac{2}{3}})\ \bar{1}_3A_2A_2\ \ (\mathbf{x\bar{1}\bar{2}\frac{2}{3}})\ \bar{1}_3A_2A_2/\bar{1}_31_1A_2/\bar{1}_3B_2A_2\ \ [(\mathbf{x\bar{1}\bar{1}\frac{2}{3}})\ \bar{1}_3A_2\ \ (\mathbf{x\bar{2}\bar{1}\frac{2}{3}})\ \bar{1}_3B_2] + A_2\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	0 0 $\frac{1}{3}$
	$(\mathbf{x\bar{1}\bar{1}2})\ \bar{1}'_2A_3A_3/\bar{1}_2A_3A_3$	0 0 $\overline{2\ 2}$
	$[(\bar{1}\bar{1}2\text{x})\ A_22_1] + A_1A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	0 0 0
31	$[\text{SET 32–x01x}]_5 + 1_1\ \ [(\mathbf{x\bar{1}3}\text{–})\ \bar{1}_22_1] + A_11_1A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	0 0 – –
	$[\text{SET 32–x01x}]_5 + B_1\ \ (\mathbf{x\bar{1}3}\text{–})\ \bar{1}_22_1B_1\ \ [\text{SET 31–x02–}]_7 + 2_1\ \ [\text{SET 31–x02–A}]_6 + B_3$	0 1 – –
	$[\text{SET 32–x01x}]_5 + B_1\ \ (\mathbf{x\bar{1}3}\text{–})\ \bar{1}_22_1B_1\ \ [\text{SET 32–x01x}]_5\ [(\mathbf{x\bar{1}3}\text{–})\ \bar{1}_22_1] + A_3\bar{B}_2$	0 $\bar{1}$ – –
	$[\text{SET 31–x02x}]_7 + 2_1\ \ [\text{SET 31–x02–A}]_6 + \bar{B}_2B_32_22_3$	
	$(\bar{1}\bar{1}2\text{–})\ A_22_11_1$	0 0 0 – –
	$(\bar{1}\bar{1}2\text{–})\ A_22_1B_1/A_2C_12_1\ \ (\bar{1}\bar{1}3\text{–})\ A_23_12_1\ \ (\bar{1}\bar{1}2\text{–})\ A_2C_1B_3$	0 0 1 – –
	$[(\bar{1}\bar{1}2\text{–})\ A_22_1] + B_1A_3\bar{B}_2\ \ [(\bar{1}\bar{1}2\text{–})\ A_2C_1] + 2_1\bar{B}_2B_32_22_3\ \ (\bar{1}\bar{1}3\text{–})\ A_23_12_1$	0 0 $\bar{1}$ – –
22	$[(\mathbf{x11x})\ 1_2A_1/1_21_1\ \ (\mathbf{x\bar{1}\bar{1}x})\ (\mathbf{x\bar{2}\bar{1}x})\ \bar{B}_2\bar{1}_2\ \ (\mathbf{x\bar{2}\bar{2}x})\ \bar{2}_2\bar{1}_2] + A_2A_3\ \ [\text{SET 22–x11xD}]_{14} + \bar{1}_2A_2$	0 0
	$[(\mathbf{x11x})\ 1_2B_1\ \ (\mathbf{x12x})\ 1_12_1\ \ (\mathbf{x\bar{2}\bar{2}x})\ \bar{2}'_22_1] + A_1A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$	

$[\text{SET 22–x11xA}]_2 + \bar{I}_2\bar{I}'_2\bar{I}_3\bar{I}'_3$ $[\text{SET 22–x11xD}]_{14} + \bar{I}'_2$	1 0
$[\text{SET 23–x10xA}]_7\,[\text{SET 22–x10xA}]_3\,[\text{SET 22–x11xB}]_7 + A_3$	$\bar{1}$ 0
$[\text{SET 22–x11xC}]_7 + A_3\bar{I}_2\bar{I}'_2\bar{I}_3\bar{I}'_3$ $[\text{SET 22–x11xD}]_{14} + A_3\bar{I}'_3$	
$[(\mathbf{x0\bar{1}\bar{1}})\ (\mathbf{x\bar{1}\bar{1}0})\ (\mathbf{x1\bar{1}\bar{1}})\ \text{A}_3\text{I}_2] + A_2A_3$ $[(\mathbf{x0\bar{1}\bar{1}})\ (\mathbf{x\bar{1}\bar{1}0})\ (\mathbf{x1\bar{1}\bar{1}})\ \text{A}_3\bar{\text{B}}_2/A_3A_3] + \bar{\text{I}}_2A_2$	0 0 0
$(\mathbf{x11\bar{1}})\ 1_2\text{A}_3\text{A}_3/1_2\text{B}_3\text{A}_3$ $[(\mathbf{x11\bar{1}})\ 1_2\text{B}_3] + A_3\bar{I}_2\bar{I}'_2\bar{I}_3\bar{I}'_3$	0 0 $\bar{1}\,\bar{1}$
$[\text{SET 23–x002}]_5\,[\text{SET 22–x002}]_2 + \text{A}_2$ $[\text{SET 22–x112A}]_6 + \bar{\text{I}}_2\text{A}_2$ $[(\mathbf{x11\tfrac{\bar{1}}{3}})\ 1_2\text{B}_2] + \text{A}_2A_3\bar{I}_2\bar{I}'_2\bar{I}_3\bar{I}'_3$	0 0 $\frac{\bar{1}}{3}$
$(\mathbf{x11\bar{2}})\ 1_2\text{A}_3\text{A}_3$	0 0 $\bar{2}\,\bar{2}$
$[(\mathbf{x0\bar{1}\bar{1}})\ (\mathbf{x\bar{1}\bar{1}0})\ (\mathbf{x1\bar{1}\bar{1}})\ \text{A}_3\bar{\text{B}}_2/A_3A_3] + \bar{\text{I}}'_2$ $(\mathbf{x1\bar{1}\bar{1}})\ (\mathbf{x\bar{2}\bar{1}0})\ \text{B}_3\bar{\text{B}}_2\text{I}_2$	1 0 0
$[\text{SET 23–x100A}]_8 + A_3$ $[(\mathbf{x0\bar{1}\bar{1}})\ (\mathbf{x\bar{1}\bar{1}0})\ (\mathbf{x1\bar{1}\bar{1}})\ \text{A}_3\bar{\text{B}}_2/A_3A_3] + A_3\bar{I}'_3$ $[(\mathbf{x1\bar{1}\bar{1}})\ (\mathbf{x\bar{2}\bar{1}0})\ \text{B}_3\bar{\text{B}}_2] + \bar{\text{I}}_2A_2$	$\bar{1}$ 0 0
$[(\mathbf{x1\bar{1}\bar{1}})\ (\mathbf{x\bar{2}\bar{1}0})\ \text{B}_3\bar{\text{I}}_3] + A_3$	$\bar{1}$ 0 0 $\frac{\bar{1}}{3}$
$(\mathbf{x1\bar{1}\bar{1}})\ (\mathbf{x\bar{2}\bar{1}0})\ \text{B}_3\bar{\text{B}}_2\text{I}'_2$	1 0 1
$(\mathbf{x1\bar{1}\bar{1}})\ (\mathbf{x\bar{2}\bar{1}0})\ \text{B}_3\bar{\text{B}}_2\text{I}'_2$	$\bar{1}$ 0 1
$[\text{SET 22–112A}]_6 + \bar{\text{I}}'_2$	1 0 $\frac{\bar{1}}{3}$
$[\text{SET 22–112A}]_6 + A_3\bar{I}'_3$ $[(\mathbf{x\bar{2}1\tfrac{\bar{1}}{3}})\ 2_3A_3/2_3\bar{I}'_3$ $(\mathbf{x\bar{2}\bar{2}\tfrac{\bar{1}}{3}})\ 2_3B_3$ $(\mathbf{x\bar{2}\bar{2}\tfrac{\bar{1}}{3}})\ \bar{2}_3A_3/\bar{2}_3\bar{I}'_3] + \text{A}_2$	$\bar{1}$ 0 $\frac{\bar{1}}{3}$
$(\mathbf{x\bar{2}\bar{2}\tfrac{\bar{1}}{3}})\ 2_2B_3A_3/2_2B_3\bar{I}_2/2_2B_3\bar{I}'_2/2_2B_3\bar{I}_3/2_2B_3\bar{I}'_3$	
$(\bar{\mathbf{1}}\mathbf{10x})\ (\bar{\mathbf{1}}\bar{\mathbf{2}}\mathbf{0x})\ B_3A_3\text{I}_2$	$\bar{1}\,\bar{1}$ 0 0
$[(\tfrac{\bar{1}}{3}\bar{\mathbf{1}}\bar{\mathbf{1}}\mathbf{x})(\tfrac{\bar{1}}{3}\bar{\mathbf{2}}\bar{\mathbf{1}}\mathbf{x})\ \bar{\text{B}}_2\text{I}_3$ $(\tfrac{\bar{1}}{3}\bar{\mathbf{2}}\bar{\mathbf{2}}\mathbf{x})\bar{2}_2\text{I}_3] + A_2A_3$ $[\text{SET 22–211x}]_4 + \bar{\text{I}}_3$	$\frac{\bar{1}}{3}$ 0 0
$[\text{SET 23–110xA}]_7\,[\text{SET 22–110x}]_2\,[\text{SET 22–111x}]_4 + \text{A}_3$ $[\text{SET 22–111x}]_4 + A_3\bar{I}_2\bar{I}'_2\bar{I}_3\bar{I}'_3$	$\bar{1}\,\bar{1}$ 0
$(\bar{\mathbf{1}}\mathbf{00x})\ (\bar{\mathbf{1}}\bar{\mathbf{1}}\mathbf{0x})\ (\bar{\mathbf{1}}\mathbf{10x})\ \text{A}_3\text{A}_3\text{A}_3$	0 $\bar{1}\,\bar{1}$ 0
$(\bar{\mathbf{1}}\mathbf{10x})\,(\bar{\mathbf{1}}\bar{\mathbf{2}}\mathbf{0x})\,B_3A_3\text{I}'_2$	$\bar{1}\,\bar{1}$ 1 0
$(\bar{\mathbf{1}}\mathbf{10x})\ (\bar{\mathbf{1}}\bar{\mathbf{2}}\mathbf{0x})\ B_3A_3A_3/B_3A_3\bar{I}'_3$	$\bar{1}\,\bar{1}$ $\bar{1}$ 0
$(\bar{\mathbf{1}}\bar{\mathbf{2}}\mathbf{0x})\ 2_3\text{A}_3\text{A}_3$ $(\bar{\mathbf{2}}\bar{\mathbf{2}}\mathbf{0x})\ \bar{2}_3\text{A}_3\text{A}_3$ $[(\bar{\mathbf{1}}\bar{\mathbf{2}}\mathbf{1x})\ 2_3\text{B}_3$ $(\bar{\mathbf{2}}\bar{\mathbf{2}}\mathbf{1x})\ \bar{2}_3\text{B}_3] + \text{A}_3A_3\bar{I}_2\bar{I}'_2\bar{I}_3\bar{I}'_3$	$\frac{\bar{1}}{3}$ $\bar{1}\,\bar{1}$ 0
$[\text{SET 22–211x}]_4 + \bar{\text{I}}'_2$	$\frac{\bar{1}}{3}$ 1 0
$[\text{SET 22–211x}]_4 + A_3\bar{I}'_3$ $[(\tfrac{\bar{1}}{3}\mathbf{00x})\ A_2A_3$ $(\tfrac{\bar{1}}{3}\mathbf{10x})\ B_2A_3] + A_3$	$\frac{\bar{1}}{3}$ $\bar{1}$ 0
$[(\tfrac{\bar{1}}{3}\mathbf{0\bar{1}\bar{1}})\ (\tfrac{\bar{1}}{3}\bar{\mathbf{1}}\bar{\mathbf{1}}\mathbf{0})\ \text{A}_3\text{I}_3] + A_2A_3$	$\frac{\bar{1}}{3}$ 0 0 0

($\alpha\beta\beta$) Pattern (continued)

σ-Block	Sequence Sets	Product $\gamma_1\beta_1\alpha_1$	$\alpha_2\beta_2\gamma_2$
22	$(\frac{4}{3}\overline{2}1\frac{4}{3})$ $2_3\bar{1}_3A_2$ $(\frac{4}{3}\overline{2}2\frac{4}{3})$ $2_32_3A_2/2_32_3\bar{1}_3$ $(\frac{4}{3}\overline{2}2\frac{4}{3})$ $\bar{2}_3\bar{1}_3A_2$	$\frac{4}{3}$ 0	0 $\frac{4}{3}$
	$(00\overline{1}\overline{1})$ $(0\overline{1}\overline{1}0)$ $(01\overline{1}\overline{1})$ $A_3A_3A_3$	$\overline{1}\overline{1}$ 0	0 0
	$(0\overline{2}1\frac{4}{3})$ $2_3A_3A_3$ $(1\overline{2}1\frac{4}{3})$ $2_3\bar{1}'_3A_3$ $(0\overline{2}2\frac{4}{3})$ $2_3B_3A_2$ $(0\overline{2}2\frac{4}{3})$ $\bar{2}_3A_3A_3$ $(1\overline{2}2)\frac{4}{3}$ $\bar{2}_3\bar{1}'_3A_2$	$\overline{1}\overline{1}$ 0	$\frac{4}{3}$
	$[(0\overline{2}2\frac{4}{3})$ $2_3B_3]+A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$		
	$(\frac{4}{3}\overline{2}2\frac{4}{3})$ $2_32_3\bar{1}'_2$	$\frac{4}{3}$ 1	0 $\frac{4}{3}$
	$[(\frac{4}{3}\overline{2}2\frac{4}{3})$ $2_32_3]+A_3\bar{1}'_3$	$\frac{4}{3}$ $\bar{1}$	0 $\frac{4}{3}$
21	(x11–) $1_2B_11_1$ (x12–) $1_12_11_1$ (x$\overline{22}$–) $\bar{2}'_22_11_1$ [(x$\overline{23}$–) $\bar{2}_2\bar{B}_2/\bar{2}_22_3]+\bar{1}_2A_2$	0	0 – –
	(x11–) $1_2B_1B_1$ (x12–) $1_12_1B_1/1_1C_12_1$ (x13–) $1_13_12_1$ (x$\overline{22}$–) $\bar{2}'_22_1B_1/\bar{2}'_2C_12_1$ (x$\overline{23}$–) $\bar{2}'_23_12_1$	0	1 – –
	[(x11–) 1_2B_1 (x12–) 1_1C_1 (x$\overline{22}$–) $\bar{2}'_2C_1]+B_3$		
	(x11–) $1_2B_1B_1$ (x12–) $1_12_1B_1/1_1C_12_1$ (x13–) $1_13_12_1$ (x$\overline{22}$–) $\bar{2}'_22_1B_1/\bar{2}'_2C_12_1$ (x$\overline{23}$–) $\bar{2}'_23_12_1$	0	$\bar{1}$ – –
	[(x11–) 1_2B_1 (x12–) 1_1C_1 (x$\overline{22}$–) $\bar{2}'_2C_1]+\bar{B}_2B_32_22_3$ [(x11–) 1_2B_1 (x12–) 1_12_1 (x$\overline{22}$–) $\bar{2}'_22_1]+A_3\bar{B}_2$		
	(x12–) $B_22_11_2$ (x22–) $2_12_11_2$ (x$\overline{23}$–) $\bar{2}_2\bar{B}_2\bar{1}'_2/\bar{2}_22_3\bar{1}'_2$	1	0 – –
	[SET 22–x11xB]$_7+1_1$ [(x$\overline{23}$–) $\bar{2}_2B_3]+1_1A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3$ [(x$\overline{23}$–) $\bar{2}_2\bar{B}_2/\bar{2}_22_3]+A_3\bar{1}'_3$	$\bar{1}$ 0	
	(x12–) $B_2C_12_1$ (x13–) $B_23_12_1$ (x22–) $2_1C_12_1$ (x23–) $2_13_12_1$	1	1 – –
	(x12–) $B_2C_12_1$ (x13–) $B_23_12_1$ (x22–) $2_1C_12_1$ (x23–) $2_13_12_1$ [(x12–) B_2C_1 (x22–) $2_1C_1]+2_22_3$	1	$\bar{1}$ – –
	[SET 22–x11xB]$_7+B_3$ [SET 21–x12–B]$_6+2_1$	$\bar{1}$	1 – –
	[SET 21–x12–C]$_8$ [SET 21–x12–D]$_5$ [(x$\overline{23}$–) $\bar{2}_2B_3]+B_3$		
	[SET 22–x11xB]$_7$ [SET 21–x12–D]$_5$ [(x$\overline{23}$–) $\bar{2}_2B_3]+B_3$ [SET 21–x12–B]$_6+2_1$	$\bar{1}$	$\bar{1}$ – –
	[(x$\overline{23}$–) $\bar{2}_2B_3]$ [SET 22–x11xC]$_7+A_3\bar{B}_2$ [SET 21–x12–C]$_8+\bar{B}_2B_32_22_3$		
	[SET 23–x10xA]$_7$ [SET 22–x10x]$_3$ [(x$\overline{23}$–) $\bar{2}_2B_3]+A_3$	$\overline{1}\overline{1}$	– –
	[SET 22–x11xD]$_{14}$ [(x$\overline{23}$–) $\bar{2}_2\bar{B}_2/\bar{2}_22_3]+\bar{B}_2A_3$ [SET 21–x12–D]$_5+\bar{B}_22_3$		
	[($\frac{4}{3}\overline{2}3$–) $\bar{2}_22_3]+\bar{1}_3A_2$	$\frac{4}{3}$ 0	0 – –
	[SET 22–111x]$_4+1_1$	$\overline{1}\overline{1}$ 0	– –

	$(\bar{1}\bar{2}1\text{–})\ 2_3B_3l_1\quad(\bar{2}\bar{2}1\text{–})\ \bar{2}_3B_3l_1$	$\frac{2}{3}\ \bar{1}\ \bar{1}\ 0\ -\ -$
	$(\frac{2}{3}\bar{2}\bar{3}\text{–})\ \bar{2}_2 2_3 \bar{1}'_2$	$\frac{2}{3}\ 1\ 0\ -\ -$
	$[(\frac{2}{3}\bar{2}\bar{3}\text{–})\ \bar{2}_2 2_3] + A_3\bar{1}'_3$	$\frac{2}{3}\ \bar{1}\ 0\ -\ -$
	$[\text{SET 23–110A}]_7\ [\text{SET 22–110}]_2\ [\text{SET 22–111x}]_4 + A_3\quad [\text{SET 21–012–A}]_6 + \bar{B}_2 2_3$	$0\ \bar{1}\ \bar{1}\ -\ -$
	$(\bar{1}00\text{–})\ (\bar{1}\bar{1}0\text{–})\ (\bar{1}10\text{–})\ A_3A_3A_3$	$0\ 0\ \bar{1}\ \bar{1}\ -\ -$
	$(\bar{1}\bar{2}0\text{–})\ 2_3A_3A_3\quad(\bar{2}\bar{2}0\text{–})\ \bar{2}_3A_3A_3\quad[(\bar{1}\bar{2}1\text{–})\ 2_3B_3\quad(\bar{2}\bar{2}1)\ \bar{2}_3B_3] + \bar{B}_2 2_3$	$\frac{2}{3}\ 0\ \bar{1}\ \bar{1}\ -\ -$
	$[\text{SET 21–012–A}]_6 + B_3\quad[\text{SET 21–112–A}]_6 + B_3$	$\bar{1}\ \bar{1}\ 1\ -\ -$
	$[\text{SET 21–012–A}]_6 + B_3\quad[\text{SET 21–112–A}]_6 + \bar{B}_2 B_3 2_2 2_3\quad[\text{SET 22–111xA}]_4 + A_3\bar{B}_2$	$\bar{1}\ \bar{1}\ \bar{1}\ -\ -$
	$(\bar{1}10\text{–})\ (\bar{1}\bar{2}0\text{–})\ B_3A_3A_3/B_3A_3\bar{B}_2$	$\bar{1}\ \bar{1}\ \bar{1}\ -\ -$
	$[(\bar{1}\bar{2}1\text{–})\ 2_3B_3\quad(\bar{2}\bar{2}1\text{–})\ \bar{2}_3B_3] + B_3B_3$	$\frac{2}{3}\ \bar{1}\ \bar{1}\ 1\ -\ -$
	$[(\bar{1}\bar{2}1\text{–})\ 2_3B_3\quad(\bar{2}\bar{2}1\text{–})\ \bar{2}_3B_3] + B_3A_3\bar{B}_2B_3 2_2 2_3$	$\frac{2}{3}\ \bar{1}\ \bar{1}\ \bar{1}\ -\ -$
	$[(\frac{2}{3}00)\ A_2A_3\quad(\frac{2}{3}\bar{1}0\text{–})\ B_2A_3\quad(\frac{2}{3}\bar{1}\bar{2}\text{–})\ \bar{B}_2 2_3\quad(\frac{2}{3}\bar{2}\bar{2}\text{–})\ \bar{2}'_2 2_3\quad(\frac{2}{3}\bar{2}\bar{3}\text{–})\ \bar{2}_2 2_3] + \bar{B}_2 A_3$	$\frac{2}{3}\ \bar{1}\ \bar{1}\ -\ -$
12	$[(-\bar{2}\bar{2}x)\ C_2\bar{2}_2\quad(-\bar{3}\bar{2}x)\ 3_2\bar{2}_2] + \bar{1}_2A_2$	$-\ -\ 0\ 0$
	$[(-\bar{2}\bar{2}x)\ C_2\bar{2}_2\quad(-\bar{3}\bar{2}x)\ 3_2\bar{2}_2] + A_3\bar{1}'_3$	$-\ -\ 0\ \bar{1}$
	$(-\bar{2}\bar{2}x)\ C_2\bar{2}_2\bar{1}'_2/C_2\bar{2}'_2\bar{1}_2\quad(-\bar{3}\bar{2}x)\ 3_2\bar{2}_2\bar{1}'_2/3_2\bar{2}'_2\bar{1}_2$	$-\ -\ 1\ 0$
	$[\text{SET 13–20x}]_4\ [\text{SET 12–20x}]_3\ [\text{SET 12–21x}]_4 + A_2\quad(-\bar{2}\bar{2}x)\ C_2\bar{2}'_2\bar{1}'_2$	$-\ -\ 2\ 0$
	$[\text{SET 12–21xA}]_6 + A_2A_3\bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3\quad(-\bar{3}\bar{2}x)\ 3_2\bar{2}'_2\bar{1}'_2$	
	$[\text{SET 12–21xC}]_3 + \bar{1}_2\bar{1}'_2\bar{1}_3\bar{1}'_3\quad[(-\bar{2}\bar{2}x)\ C_2\bar{2}'_2\quad(-\bar{3}\bar{2}x)\ 3_2\bar{2}'_2] + \bar{1}'_3$	$-\ -\ \bar{2}\ 0$
	$(-1\bar{1}\bar{1})\ (-\bar{2}\bar{1}0)\ B_3\bar{B}_2\bar{1}_2$	$-\ -\ 1\ 0\ 0$
	$(-1\bar{1}\bar{1})\ (-\bar{2}\bar{1}0)\ B_3\bar{B}_2A_2/B_3\bar{B}_2\bar{1}'_2\quad(-2\bar{1}\bar{1})\ C_1A_2A_2\quad(-3\bar{1}\bar{1})\ 3_1A_2A_2$	$-\ -\ 2\ 0\ 0$
	$[(-1\bar{1}\bar{1})\ (-\bar{2}\bar{1}0)\ B_3\bar{B}_2] + \bar{1}_2\bar{1}'_3$	$-\ -\ \bar{2}\ 0\ 0$
	$(-1\bar{1}\bar{1})\ (-\bar{2}\bar{1}0)\ B_3\bar{B}_2\bar{1}'_2$	$-\ -\ \bar{2}\ 0\ 1$
11	$[(-\bar{2}\bar{2}\text{–})\ C_2\bar{2}_2\quad(-\bar{3}\bar{2}\text{–})\ 3_2\bar{2}_2] + \bar{B}_2A_3\quad[\text{SET 11–22–D}]_4 + \bar{2}_2$	$-\ -\ \bar{1}\ \bar{1}\ -\ -$
	$(-\bar{2}\bar{2}\text{–})\ C_2C_2\bar{2}'_2\quad(-\bar{2}\bar{3}\text{–})C_23_2\bar{2}'_2\quad(-\bar{3}\bar{2}\text{–})\ 3_2C_2\bar{2}'_2\quad(-\bar{3}\bar{3}\text{–})\ 3_23_2\bar{2}'_2$	$-\ -\ 2\ 0\ -\ -$
	$(-21\text{–})\ C_1B_2l_1\ (-22\text{–})\ C_12_1l_1\quad(-31\text{–})\ 3_1B_2l_1\quad(-32\text{–})\ 3_12_1l_1$	

($\alpha\beta\beta$) Pattern (continued)

σ-Block	Sequence Sets	Product $\gamma_1\beta_1\alpha_1$ $\alpha_2\beta_2\gamma_2$
11	(–21–) $C_1B_1l_1$ (–12–) $B_2\bar{2}_1l_1$ (–22–) $C_1\bar{2}_1l_1$	– – $\bar{2}$ 0 – –
	$[\text{SET 12–21x}]_4 + B_2$ $[\text{SET 11–22–}]_4 + 2_1$ $[\text{SET 11–22–A}]_4 + B_3$	– – 2 1 – –
	$[\text{SET 12–21x}]_4 + B_2$ $[\text{SET 11–22–}]_4 + 2_1$ $[\text{SET 11–22–A}]_4 + \bar{B}_2B_3\bar{2}_2\bar{2}_3$ $[\text{SET 12–21xA}]_6 + A_3\bar{B}_2$	– – 2 $\bar{1}$ – –
	[(–12–) B_2C_1 (–22–) C_1C_1] + $2_2\bar{2}_3$ (–31–) $3_1l_1A_2$ (–20–) (–21–) $C_1A_2A_2$ (–$\bar{2}\bar{2}$–) $C_2\bar{2}'_2A_2$ (–30–) (–31–) $3_1A_2A_2$ (–$\bar{3}\bar{2}$–) $3_2\bar{2}'_2A_2$	
	(–12–) $B_2C_1\bar{2}_1$ (–22–) $C_2C_2\bar{2}_1$ (–13–) $B_2\bar{3}_1\bar{2}_1$ (–32–) $\bar{3}_1C_1\bar{2}_1$	– – $\bar{2}$ 1 – –
	(–12–) $B_2C_1\bar{2}_1$ (–22–) $C_2C_2\bar{2}_1$ (–13–) $B_2\bar{3}_1\bar{2}_1$ (–32–) $\bar{3}_1C_1\bar{2}_1$	– – 2 $\bar{1}$ – –
	(–$\bar{2}\bar{2}$–) $C_2C_2\bar{2}'_2/C_2\bar{2}'_2\bar{B}_2$ (–$\bar{2}\bar{3}$–) $C_2\bar{3}_2\bar{2}'_2$ (–$\bar{3}\bar{2}$–) $3_2C_2\bar{2}'_2/3_2\bar{2}'_2\bar{B}_2$ (–$\bar{3}\bar{3}$–) $3_2\bar{3}_2\bar{2}'_2$	– – $\bar{2}$ $\bar{1}$ – –

($\alpha\beta\gamma$) Pattern

σ-Block	Sequence Sets	Product α β γ
I. $\sigma_\beta = 3$		
333	$(0\bar{1}\bar{1})$ $(\bar{1}\bar{1}0)$ $(1\bar{1}\bar{1})$ $A_3\bar{I}'_2A_1$ $(\bar{1}\bar{1}1)$ $\bar{I}'_3\bar{I}'_2A_1$	0 0 0
332	$(0\bar{1}\bar{1})$ $(\bar{1}\bar{1}0)$ $(1\bar{1}\bar{1})$ $A_3\bar{I}'_21_1$ $(\bar{1}\bar{1}1)$ $\bar{I}'_3\bar{I}'_21_1$	0 0 0
	(102) $A_1A_22_1$ $(0\bar{1}\bar{1})$ $(\bar{1}\bar{1}0)$ $(1\bar{1}\bar{1})$ $A_3\bar{I}'_2B_1$ $(\bar{1}\bar{1}1)$ $\bar{I}'_3\bar{I}'_2B_1$ $(\bar{1}\bar{1}2)$ $\bar{I}'_2A_22_1/\bar{I}_3A_22_1$	0 0 1*
331	(102) $A_1A_2C_1$ (103) $A_1A_23_1$ $(\bar{1}\bar{1}2)$ $\bar{I}'_2A_2C_1/\bar{I}_3A_2C_1$ $(\bar{1}\bar{1}3)$ $\bar{I}'_2A_23_1/\bar{I}_3A_23_1$	0 0 2
	(102) $A_1A_2C_1$ $(0\bar{1}\bar{1})$ $(\bar{1}\bar{1}0)$ $(1\bar{1}\bar{1})$ $A_3\bar{I}'_2B_1$ $(\bar{1}\bar{1}1)$ $\bar{I}'_3\bar{I}'_2B_1$ $(\bar{1}\bar{1}2)$ $\bar{I}'_2A_2C_1/\bar{I}_3A_2C_1$	0 0 $\bar{2}$
233	$(1\bar{1}\bar{1})$ $1_1\bar{I}'_2A_1$ $(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{B}_2\bar{I}_2A_1$	0 0 0
	$(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{B}_2\bar{I}'_2A_1$ $(1\bar{1}\bar{1})$ $(\bar{2}\bar{1}0)$ $B_3\bar{I}'_2A_1$ $(2\bar{1}\bar{1})$ $2_1\bar{I}'_2A_1$	1 0 0
	$(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{B}_2\bar{I}'_3A_1$ $(1\bar{1}\bar{1})$ $(\bar{2}\bar{1}0)$ $B_3\bar{I}'_2A_1$ $(2\bar{1}\bar{1})$ $2_1\bar{I}'_2A_1$	$\bar{1}$ 0 0
232	$(1\bar{1}\bar{1})$ $1_1\bar{I}'_21_1$ $(1\bar{1}\bar{2})$ $1_1\bar{I}_2A_1/1_1\bar{I}_21_1$ $(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{B}_2\bar{I}_21_1$	0 0 0
	(102) $1_1A_22_1$ (112) $1_2A_22_1$ $(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{B}_2\bar{I}_2B_1$ $(\bar{1}\bar{1}2)$ $(\bar{2}\bar{1}2)$ $\bar{B}_2\bar{I}_22_1/\bar{B}_2A_22_1$ $(1\bar{1}\bar{1})$ $1_1\bar{I}'_2B_1$ $(1\bar{1}\bar{2})1_1\bar{I}_2B_1/1_1\bar{I}'_22_1$ $(\bar{2}\bar{1}2)$ $2_3A_22_1/2_3\bar{I}_22_1$	0 0 1*
	$(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{B}_2\bar{I}'_21_1$ $(1\bar{1}\bar{1})$ $(\bar{2}\bar{1}0)$ $B_3\bar{I}'_21_1$ $(2\bar{1}\bar{1})$ $2_1\bar{I}'_21_1$ $(2\bar{1}\bar{2})$ $2_1\bar{I}_2A_1/2_1\bar{I}_21_1$	1 0 0
	$(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{B}_2\bar{I}'_3A_1$ $(1\bar{1}\bar{1})$ $(\bar{2}\bar{1}0)$ $B_3\bar{I}'_21_1$ $(2\bar{1}\bar{1})$ $2_1\bar{I}'_21_1$ $(2\bar{1}\bar{2})$ $2_1\bar{I}_2A_1/2_1\bar{I}_21_1$	$\bar{1}$ 0 0
	$(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{B}_2\bar{I}'_2B_1$ $(1\bar{1}\bar{1})$ $(\bar{2}\bar{1}0)$ $B_3\bar{I}'_2B_1$ $(\bar{1}\bar{1}2)$ $(\bar{2}\bar{1}2)$ $B_2\bar{I}'_22_1$ $(\bar{2}\bar{1}2)$ $2_3\bar{I}'_22_1$ $(2\bar{1}\bar{1})$ $2_1\bar{I}'_2B_1$ $(2\bar{1}\bar{2})$ $2_1\bar{I}_2B_1/2_1\bar{I}'_22_1$	1 0 1*
	(102) $B_1A_22_1$ $(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{B}_2\bar{I}'_3B_1$ $(1\bar{1}\bar{1})$ $(\bar{2}\bar{1}0)$ $B_3\bar{I}'_2B_1$ $(\bar{1}\bar{1}2)$ $(\bar{2}\bar{1}2)$ $\bar{B}_2A_32_1/\bar{B}_2\bar{I}'_32_1$ (202) $2_1A_22_1$ $(2\bar{1}\bar{1})$ $2_1\bar{I}'_2B_1$ $(2\bar{1}\bar{2})$ $2_1\bar{I}_2B_1/2_1\bar{I}'_22_1$ (212) $2_1A_32_1$ $(\bar{2}\bar{1}2)$ $2_3A_32_1/2_3\bar{I}'_32_1$	$\bar{1}$ 0 1*
231	$(1\bar{1}\bar{3})$ $1_1\bar{I}_22_1$	0 0 1*
	(103) $1_1A_23_1$ (113) $1_2A_23_1$ $(1\bar{1}\bar{3})1_1\bar{I}'_23_1$ $(\bar{1}\bar{1}3)$ $(\bar{2}\bar{1}3)$ $\bar{B}_2\bar{I}_23_1/\bar{B}_2A_23_1$ $(\bar{2}\bar{1}3)$ $2_3A_23_1/2_3\bar{I}_23_1$	0 0 2
	(102) $1_1A_2C_1$ (112) $1_2A_2C_1$ $(1\bar{1}\bar{2})$ $1_1\bar{I}'_2C_1$ $(1\bar{1}\bar{3})$ $1_1\bar{I}_2C_1$ $(\bar{1}\bar{1}2)$ $(\bar{2}\bar{1}2)$ $\bar{B}_2\bar{I}_2C_1/\bar{B}_2A_2C_1$ $(\bar{2}\bar{1}2)$ $2_3A_2C_1/2_3\bar{I}_2C_1$	0 0 2*
	$(1\bar{1}\bar{1})$ $1_1\bar{I}'_2B_1$ $(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{B}_2\bar{I}_2B_1$ $(1\bar{1}\bar{2})$ $1_1\bar{I}_2B_1$	0 0 $\bar{2}$

($\alpha\beta\gamma$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
231	$(2\bar{1}\bar{3})\ 2_1\bar{1}_2 2_1$	*1 0 1*
	$(\bar{1}\bar{1}3)\ (2\bar{1}3)\ \bar{B}_2\bar{1}'_2 3_1 \quad (2\bar{1}\bar{3})\ 2_1\bar{1}'_2 3_1 \quad (\bar{2}\bar{1}3)\ 2_3\bar{1}'_2 3_1$	1 0 2
	$(\bar{1}\bar{1}2)\ (2\bar{1}2)\ \bar{B}_2\bar{1}'_2 C_1 \quad (2\bar{1}\bar{2})\ 2_1\bar{1}'_2 C_1 \quad (\bar{2}\bar{1}2)\ 2_3\bar{1}'_2 C_1 \quad (2\bar{1}\bar{3})\ 2_1\bar{1}_2 C_1$	1 0 2*
	$(\bar{1}\bar{1}1)\ (2\bar{1}1)\ \bar{B}_2\bar{1}'_2 B_1 \quad (1\bar{1}\bar{1})\ (2\bar{1}0)\ B_3\bar{1}'_2 B_1 \quad (2\bar{1}\bar{1})\ 2_1\bar{1}'_2 B_1 \quad (2\bar{1}\bar{2})\ 2_1\bar{1}_2 B_1$	1 0 $\bar{2}$
	$(103)\ B_1A_2 3_1 \quad (203)\ 2_1A_2 3_1 \quad (213)\ 2_1A_3 3_1 \quad (\bar{1}\bar{1}3)\ (2\bar{1}3)\ \bar{B}_2A_3 3_1/\bar{B}_2\bar{1}'_3 3_1 \quad (2\bar{1}\bar{3})\ 2_1\bar{1}'_2 3_1 \quad (\bar{2}\bar{1}3)\ 2_3A_3 3_1/2_3\bar{1}'_3 3_1$	$\bar{1}$ 0 2
	$(102)\ B_1A_2C_1 \quad (202)\ 2_1A_2C_1 \quad (212)\ 2_1A_3C_1 \quad (\bar{1}\bar{1}2)\ (2\bar{1}2)\ \bar{B}_2A_3C_1/\bar{B}_2\bar{1}'_3C_1 \quad (2\bar{1}\bar{2})\ 2_1\bar{1}'_2C_1 \quad (2\bar{1}\bar{3})\ 2_1\bar{1}_2C_1 \quad (\bar{2}\bar{1}2)\ 2_3A_3C_1/2_3\bar{1}'_3C_1$	$\bar{1}$ 0 2*
	$(\bar{1}\bar{1}1)\ (2\bar{1}1)\ \bar{B}_2\bar{1}'_3B_1 \quad (1\bar{1}\bar{1})\ (2\bar{1}0)\ B_3\bar{1}'_2B_1 \quad (2\bar{1}\bar{1})\ 2_1\bar{1}'_2B_1 \quad (2\bar{1}\bar{2})\ 2_1\bar{1}_2B_1$	$\bar{1}$ 0 $\bar{2}$
133	$(2\bar{1}\bar{1})\ C_1\bar{1}'_2A_1 \quad (3\bar{1}\bar{1})\ 3_1\bar{1}'_2A_1$	2 0 0
	$(1\bar{1}\bar{1})\ (2\bar{1}0)\ B_3\bar{1}'_2A_1 \quad (2\bar{1}\bar{1})\ C_1\bar{1}'_2A_1$	$\bar{2}$ 0 0
132	$(2\bar{1}\bar{1})\ C_1\bar{1}'_2 1_1 \quad (2\bar{1}\bar{2})\ C_1\bar{1}_2 1_1/C_1\bar{1}_2A_1 \quad (3\bar{1}\bar{1})\ 3_1\bar{1}'_2 1_1 \quad (3\bar{1}\bar{2})\ 3_1\bar{1}_2 1_1/3_1\bar{1}_2A_1$	2 0 0
	$(1\bar{1}\bar{1})\ (2\bar{1}0)\ B_3\bar{1}'_2 1_1 \quad (2\bar{1}\bar{1})\ C_1\bar{1}'_2 1_1 \quad (2\bar{1}\bar{2})\ C_1\bar{1}_2 1_1/C_1\bar{1}_2A_1$	$\bar{2}$ 0 0
	$[(2\bar{1}\bar{1})\ C_1\bar{1}'_2 \quad (2\bar{1}\bar{2})\ C_1\bar{1}_2 \quad (3\bar{1}\bar{1})\ 3_1\bar{1}'_2 \quad (3\bar{1}\bar{2})\ 3_1\bar{1}_2] + B_1 \quad (202)\ (212)\ C_1A_2 2_1 \quad (302)\ (312)\ 3_1A_2 2_1 \quad (2\bar{1}\bar{2})\ C_1\bar{1}'_2 2_1 \quad (3\bar{1}\bar{2})\ 3_1\bar{1}'_2 2_1$	2 0 1*
	$[(2\bar{1}\bar{1})\ C_1\bar{1}'_2 \quad (2\bar{1}\bar{2})\ C_1\bar{1}_2 \quad (1\bar{1}\bar{1})\ (2\bar{1}0)\ B_3\bar{1}'_2] + B_1 \quad [(102)\ B_1A_2 \quad (202)\ (212)\ C_1A_2 \quad (2\bar{1}\bar{2})\ C_1\bar{1}'_2] + 2_1$	$\bar{2}$ 0 1*
131	$(2\bar{1}\bar{3})\ C_1\bar{1}_2 2_1 \quad (3\bar{1}\bar{3})\ 3_1\bar{1}_2 2_1$	2 0 1*
	$(2\bar{1}\bar{3})\ C_1\bar{1}_2 2_1$	$\bar{2}$ 0 1*
	$[(202)\ (212)\ C_1A_2 \quad (302)\ (312)\ 3_1A_2 \quad (2\bar{1}\bar{2})\ C_1\bar{1}'_2 \quad (3\bar{1}\bar{2})\ 3_1\bar{1}'_2 \quad (2\bar{1}\bar{3})\ C_1\bar{1}_2 \quad (3\bar{1}\bar{3})\ 3_1\bar{1}_3] + C_1$	2 0 2*
	$[(203)\ (213)\ C_1A_2 \quad (303)\ (313)\ 3_1A_2 \quad (2\bar{1}\bar{3})\ C_1\bar{1}'_2 \quad (3\bar{1}\bar{3})\ 3_1\bar{1}'_2] + 3_1$	2 0 2
	$[(2\bar{1}\bar{1})\ C_1\bar{1}'_2 \quad (3\bar{1}\bar{1})\ 3_1\bar{1}'_2 \quad (2\bar{1}\bar{2})\ C_1\bar{1}_2 \quad (3\bar{1}\bar{2})\ 3_1\bar{1}_2] + B_1$	2 0 $\bar{2}$
	$(2\bar{1}\bar{2})\ C_1\bar{1}'_2C_1 \quad (2\bar{1}\bar{3})\ C_1\bar{1}_2C_1/C_1\bar{1}'_2 3_1$	$\bar{2}$ 0 2
	$(1\bar{1}\bar{1})\ (2\bar{1}0)\ B_3\bar{1}'_2B_1 \quad (2\bar{1}\bar{1})\ C_1\bar{1}'_2B_1 \quad (2\bar{1}\bar{2})\ C_1\bar{1}_2B_1/C_1\bar{1}'_2C_1 \quad (2\bar{1}\bar{3})\ C_1\bar{1}_2C_1$	$\bar{2}$ 0 $\bar{2}$
II. $\sigma_\beta = 2$		
323	$(\bar{1}\bar{1}1)\ \bar{1}'_2 1_2 A_1 \quad (\bar{1}\bar{2}1)\ \bar{1}_2 1_2 A_1 \quad [(0\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ (1\bar{1}\bar{1})\ A_3\bar{B}_2 \quad (\bar{1}\bar{1}1)\ (\bar{1}\bar{2}1)\ \bar{1}'_3\bar{B}_2] + \bar{1}_2$	0 0 0
	$(0\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ (1\bar{1}\bar{1})\ A_3\bar{B}_2\bar{1}'_2 \quad (\bar{1}\bar{1}1)\ (\bar{1}\bar{2}1)\ \bar{1}'_3\bar{B}_2\bar{1}'_2$	0 1 0

	$[(\bar{1}\bar{1}0)\ \bar{1}'_2B_1\quad(\bar{1}\bar{2}0)\ \bar{1}_2B_1\quad(020)\ (021)\ (120)\ (121)\ A_22_1\quad(\bar{1}\bar{2}0)\ (\bar{1}\bar{2}1)\ \bar{1}'_22_1]+A_3\quad[(0\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ (1\bar{1}\bar{1})\ A_3\bar{B}_2\quad(\bar{1}\bar{1}1)\ (\bar{1}\bar{2}1)\ \bar{1}'_3\bar{B}_2]+A_3\bar{1}'_3$	0 Ī 0
322	$(\bar{1}\bar{1}1)\ \bar{1}'_21_21_1\quad(\bar{1}\bar{2}1)\ \bar{1}_21_21_1\quad(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}_2\bar{1}_2$	0 0 0
	$(\bar{1}\bar{1}1)\ \bar{1}'_21_2B_1\quad(\bar{1}\bar{2}1)\ \bar{1}_21_2B_1\quad[(\bar{1}\bar{1}2)\ \bar{1}'_21_1\quad(\bar{1}\bar{2}2)\ \bar{1}_3A_2/\bar{1}_31_1\quad(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}'_2]+2_1$	0 0 1*
	$(021)\ (121)\ A_22_11_2\quad(\bar{1}\bar{2}1)\ \bar{1}'_22_11_2\quad(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}_2\bar{1}'_2$	0 1 0
	$(021)\ (121)\ A_22_11_1\quad(\bar{1}\bar{2}1)\ \bar{1}'_22_11_1\quad[(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})]+A_3\bar{1}'_3$	0 Ī 0
	$(022)\ (122)\ A_22_12_1\quad(\bar{1}\bar{1}2)\ \bar{1}'_2B_22_1\quad(\bar{1}\bar{2}2)\ \bar{1}_3B_22_1/\bar{1}'_22_12_1$	0 1 1*
	$[(021)\ (121)\ A_22_1\quad(\bar{1}\bar{2}1)\ \bar{1}'_22_1]+B_3\quad[(022)\ (122)\ A_22_1\quad(\bar{1}\bar{1}2)\ \bar{1}_3A_2/\bar{1}'_2B_2\quad(\bar{1}\bar{2}2)\ \bar{1}'_22_1/\bar{1}_3B_2\quad(102)\ A_1A_2]+2_1$	0 Ī 1*
	$[(020)\ (021)\ (120)\ (121)\ A_22_1\quad(\bar{1}\bar{1}0)\ \bar{1}'_2B_1\quad(\bar{1}\bar{2}0)\ (\bar{1}\bar{2}1)\ \bar{1}'_22_1\quad(\bar{1}\bar{2}0)\ \bar{1}_2B_1]+A_3$	0 $\bar{1}\bar{1}$
	$[(0\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ (1\bar{1}\bar{1})\ A_3\bar{B}_2\quad(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}_2\quad(\bar{1}\bar{1}1)\ (\bar{1}\bar{2}1)\ \bar{1}'_3\bar{B}_2]+\bar{B}_2\quad[(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}'_2]+\bar{B}_22_3$	
321	$[(\bar{1}\bar{1}2)\ \bar{1}'_21_1\quad(\bar{1}\bar{2}2)\ \bar{1}_3A_2/\bar{1}_31_1\quad(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}'_2]+C_1\quad[(\bar{1}\bar{1}3)\ \bar{1}'_21_1\quad(\bar{1}\bar{2}3)\ \bar{1}_3A_2/\bar{1}_31_1]+3_1$	0 0 2
	$[(\bar{1}\bar{1}2)\ \bar{1}'_21_1\quad(\bar{1}\bar{2}2)\ \bar{1}_3A_2/\bar{1}_31_1\quad(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}'_2]+C_1\quad(\bar{1}\bar{1}1)\ \bar{1}'_21_2B_1\quad(\bar{1}\bar{2}1)\ \bar{1}_21_2B_1$	0 0 $\bar{2}$
	$[(022)\ (122)\ A_22_1\quad(\bar{1}\bar{1}2)\ \bar{1}'_2B_2\quad(\bar{1}\bar{2}2)\ \bar{1}'_22_1/\bar{1}_3B_2]+C_1\quad[(023)\ (123)\ A_22_1\quad(\bar{1}\bar{1}3)\ \bar{1}'_2B_2\quad(\bar{1}\bar{2}3)\ \bar{1}'_22_1/\bar{1}_3B_2]+3_1$	0 1 2
	$[(022)\ (122)\ A_22_1\quad(\bar{1}\bar{1}2)\ \bar{1}'_2B_2\quad(\bar{1}\bar{2}2)\ \bar{1}'_22_1/\bar{1}_3B_2]+C_1$	0 1 $\bar{2}$
	$[(103)\ A_1A_2\quad(023)\ (123)\ A_22_1\quad(\bar{1}\bar{1}3)\ \bar{1}_3A_2/\bar{1}'_2B_2\quad(\bar{1}\bar{2}3)\ \bar{1}'_22_1/\bar{1}_3B_2]+3_1$	0 Ī 2
	$[(102)\ A_1A_2\quad(022)\ (122)\ A_22_1\quad(\bar{1}\bar{1}2)\ \bar{1}_3A_2/\bar{1}'_2B_2\quad(\bar{1}\bar{2}2)\ \bar{1}'_22_1/\bar{1}_3B_2]+C_1$	0 Ī 2*
	$[(021)\ (121)\ A_22_1\quad(\bar{1}\bar{2}1)\ \bar{1}'_22_1]+B_3$	0 Ī $\bar{2}$
	$[(021)\ (121)\ A_22_1\quad(\bar{1}\bar{2}1)\ \bar{1}'_22_1]+B_3$	0 $\bar{1}\bar{2}$
223	$(111)\ 1_21_2A_1\quad(\bar{2}\bar{2}1)\ \bar{2}_3\bar{1}_2A_1\quad(1\bar{1}\bar{1})\ (1\bar{2}\bar{1})\ 1_1\bar{B}_2\bar{1}_2$	0 0 0
	$(1\bar{1}\bar{1})\ (\bar{1}\bar{2}1)\ 1_1\bar{B}_2\bar{1}'_2$	0 1 0
	$[(110)\ 1_2B_1\quad(120)\ (121)\ 1_12_1\quad(\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ \bar{2}_2\bar{B}_2]+A_3\quad[(1\bar{1}\bar{1})\ (1\bar{2}\bar{1})\ 1_1\bar{B}_2]+\bar{1}'_3$	0 Ī 0
	$(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2\bar{1}_2\quad(211)\ 2_11_2A_1\quad(\bar{2}\bar{2}1)\ \bar{2}_2\bar{1}'_2A_1\quad(2\bar{1}\bar{1})\ (2\bar{2}\bar{1})\ 2_1\bar{B}_2\bar{1}_2$	1 0 0
	$(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2\bar{1}_2\quad(211)\ 2_11_2A_1\quad(\bar{2}\bar{2}1)\ \bar{2}_2\bar{1}'_3A_1\quad(2\bar{1}\bar{1})\ (2\bar{2}\bar{1})\ 2_1\bar{B}_2\bar{1}_2$	Ī 0 0
	$(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2\bar{1}'_2\quad(2\bar{1}\bar{1})\ (2\bar{2}\bar{1})\ 2_1\bar{B}_2\bar{1}'_2$	1 1 0
	$[(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2\quad(120)\ (121)\ B_22_1\quad(220)\ (221)\ 2_12_1]+A_3\quad[(2\bar{1}\bar{1})\ (2\bar{2}\bar{1})\ 2_1\bar{B}_2]+A_3\bar{1}'_3$	1 Ī 0
	$(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2\bar{1}'_2\quad(2\bar{1}\bar{1})\ (2\bar{2}\bar{1})\ 2_1\bar{B}_2\bar{1}'_2$	Ī 1 0

($\alpha\beta\gamma$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
223	$[(020)\ (021)\ A_2 2_1\ \ (120)\ (121)\ B_2 2_1\ \ (210)\ 2_1 B_3\ \ (220)\ (221)\ 2_1 2_1\ \ (\bar{1}\bar{2}0)\ \bar{B}_2 B_3\ \ (\bar{2}\bar{2}0)\ 2'_2 B_3] + A_3$	$\bar{1}\ \bar{1}\ 0$
	$(\bar{2}\bar{2}0)\ 2_2 B_3 A_3\ \ [(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2\ \ (2\bar{1}\bar{1})\ (2\bar{2}\bar{1})\ 2_1\bar{B}_2] + A_3\bar{1}'_3$	
	$(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3 B_2\bar{1}'_3\ \ [(100)\ B_1 A_3\ \ (0\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ (1\bar{1}\bar{1})\ A_3\bar{B}_2/A_3 A_3\ \ (\bar{1}\bar{1}0)\ (\bar{2}\bar{1}0)\ \bar{B}_2 A_3/\bar{B}_2\bar{B}_2] + A_3$	$\bar{1}\ \bar{1}\ 0$
	$[(1\bar{1}\bar{1})\ (1\bar{2}\bar{1})\ 1_1\bar{B}_2\ \ (\bar{1}\bar{1}1)\ (\bar{1}\bar{2}1)\ \bar{1}'_3\bar{B}_2\ \ (\bar{1}\bar{2}0)\ \bar{B}_2\bar{B}_2\ \ (\bar{1}\bar{2}0)\ (\bar{1}\bar{2}1)\ \bar{B}_2 2_3\ \ (200)\ (210)\ 2_1 A_3] + A_3$	
	$[(\bar{2}\bar{2}0)\ 2_2\bar{B}_2\ \ (\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ 2_2 2_3\ \ (\bar{2}\bar{2}0)\ \bar{2}_2\bar{B}_2/\bar{2}_2 A_3\ \ (\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ \bar{2}'_2 2_3] + A_3$	
222	$(111)\ 1_2 1_2 1_1\ \ (1\bar{2}\bar{2})\ 1_1\bar{2}_1 1_2\ \ (\bar{2}\bar{2}1)\ \bar{2}_2 1_2 1_1$	0 0 0
	$(111)\ 1_2 1_2 B_1\ \ (112)\ 1_2 1_1 2_1\ \ (1\bar{2}\bar{2})\ 1_1\bar{2}'_2 2_1\ \ (\bar{2}\bar{2}1)\ \bar{2}_2 1_2 B_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_3 A_2 2_1/\bar{2}_3 1_2 2_1$	0 0 1*
	$(121)\ 1_1 2_1 1_2\ \ (1\bar{2}\bar{2})\ 1_1\bar{2}_2 1'_2\ \ (\bar{2}\bar{2}1)\ \bar{2}'_2 2_1 1_2$	0 1 0
	$(121)\ 1_1 2_1 1_1\ \ [(1\bar{2}\bar{2})\ 1_1\bar{2}_2] + \bar{1}'_3\ \ (\bar{2}\bar{2}1)\ \bar{2}'_2 2_1 1_1$	0 $\bar{1}$ 0
	$(112)\ 1_2 B_2 2_1\ \ (122)\ 1_1 2_1 2_1\ \ (\bar{2}\bar{2}2)\ \bar{2}'_2 2_1 2_1$	0 1 1*
	$[(112)\ 1_2 B_2\ \ (122)\ 1_1 2_1\ \ (\bar{2}\bar{2}2)\ \bar{2}'_2 2_1] + 2_1\ \ [(121)\ 1_1 2_1\ \ (\bar{2}\bar{2}1)\ \bar{2}'_2 2_1] + B_3$	0 $\bar{1}$ 1*
	$[(1\bar{1}\bar{1})\ (1\bar{2}\bar{1})\ 1_1\bar{B}_2\ \ (1\bar{2}\bar{2})\ 1_1\bar{2}_2] + \bar{B}_2 A_3\ \ [(110)\ 1_2 B_1\ \ (120)\ (121)\ 1_1 2_1\ \ (\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ \bar{2}'_2 2_1] + A_3$	0 $\bar{1}$ $\bar{1}$
	$[(100)\ B_1 A_3\ \ (0\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ (1\bar{1}\bar{1})\ A_3\bar{B}_2/A_3 A_3\ \ (\bar{1}\bar{1}0)\ (\bar{2}\bar{1}0)\ \bar{B}_2 A_3/\bar{B}_2\bar{B}_2] + A_3$	
	$[(1\bar{1}\bar{1})\ (1\bar{2}\bar{1})\ 1_1\bar{B}_2\ \ (\bar{1}\bar{1}1)\ (\bar{1}\bar{2}1)\ \bar{1}'_3\bar{B}_2\ \ (\bar{1}\bar{2}0)\ \bar{B}_2\bar{B}_2\ \ (\bar{1}\bar{2}0)\ (\bar{1}\bar{2}1)\ \bar{B}_2 2_3\ \ (200)\ (210)\ 2_1 A_3] + A_3$	
	$[(\bar{2}\bar{2}0)\ 2_2\bar{B}_2\ \ (\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ 2_2 2_3\ \ (\bar{2}\bar{2}0)\ \bar{2}_2\bar{B}_2/\bar{2}_2 A_3\ \ (\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ \bar{2}'_2 2_3] + A_3$	
	$(211)\ 2_1 1_2 1_1\ \ (\bar{2}\bar{2}1)\ \bar{2}_2 1'_2 1_1\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2 1_2$	1 0 0
	$(211)\ 2_1 1_2 1_1\ \ (\bar{2}\bar{2}1)\ \bar{2}_2\bar{1}'_3 1_1\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2 1_2$	$\bar{1}$ 0 0
	$(211)\ 2_1 1_2 B_1\ \ (212)\ 2_1 1_2 2_1\ \ (\bar{2}\bar{2}1)\ \bar{2}_2 1'_2 B_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_3 1'_2 2_1\ \ (2\bar{2}\bar{2}) 2_1\bar{2}'_2 2_1$	1 0 1*
	$[(211)\ 2_1 1_1\ \ (\bar{2}\bar{2}1)\ \bar{2}_2\bar{1}'_3] + B_1\ \ [(212)\ 2_1 1_2\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}'_2\ \ (\bar{2}\bar{2}2)\ \bar{2}_3 A_3/\bar{2}_3\bar{1}'_3] + 2_1$	$\bar{1}$ 0 1*
	$(121)\ B_2 2_1 1_2\ \ (221)\ 2_1 2_1 1_2\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2 1'_2$	1 1 0
	$[(2\bar{2}\bar{2})\ 2_1\bar{2}_2] + A_3\bar{1}'_3$	1 $\bar{1}$ 0
	$(021)\ A_2 2_1 1_2\ \ (121)\ B_2 2_1 1_2\ \ (221)\ 2_1 2_1 1_2\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2 1'_2$	$\bar{1}$ 1 0
	$[(2\bar{2}\bar{2})\ 2_1\bar{2}_2] + A_3\bar{1}'_3$	$\bar{1}$ $\bar{1}$ 0

	$[(0\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ (1\bar{1}\bar{1})\ A_3\bar{B}_2\ \ (\bar{1}\bar{1}1)\ (\bar{1}\bar{2}1)\ \bar{1}_3'\bar{B}_2\ \ (0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}_2\ \ (1\bar{2}\bar{2})\ 1_1\bar{2}_2] + A_3$	$\bar{1}\ \bar{1}$ **0**
	$(122)\ B_2 2_1 2_1\ \ (222)\ 2_1 2_1 2_1$	**1 1 1***
	$(122)\ B_2 2_1 2_1\ \ (222)\ 2_1 2_1 2_1\ \ [(120)\ (121)\ B_2 2_1\ \ (220)\ (221)\ 2_1 2_1\ \ (2\bar{2}\bar{2})\ 2_1 2_2\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2] + B_3$	**1 Ī 1***
	$[(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2] + \bar{B}_2 A_3\ \ [(120)\ (121)\ B_2 2_1\ \ (220)\ (221)\ 2_1 2_1] + A_3$	**1** $\bar{1}\ \bar{1}$
	$[(022)\ A_2 2_1\ \ (122)\ B_2 2_1\ \ (\bar{1}\bar{2}2)\ \bar{B}_2 B_3\ \ (212)\ 2_1 B_2\ \ (222)\ 2_1 2_1\ \ (\bar{2}\bar{2}2)\ 2_3 B_3\ \ (\bar{2}\bar{2}2)\ \bar{2}_2' B_3] + 2_1$	**Ī 1 1***
	$[(021)\ A_2 2_1\ \ (121)\ B_2 2_1\ \ (221)\ 2_1 2_1\ \ (2\bar{1}\bar{2})\ 2_1\bar{B}_2\ \ (2\bar{2}\bar{2})\ 2_1 2_2\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2] + B_3$	**Ī Ī 1***
	$[(102)\ B_1 A_2\ \ (202)\ 2_1 A_2\ \ (212)\ 2_1 B_2\ \ (022)\ A_2 2_1\ \ (122)\ B_2 2_1\ \ (222)\ 2_1 2_1] + 2_1$	
	$[(\bar{1}\bar{2}2)\ \bar{B}_2 B_3\ \ (\bar{2}\bar{2}2)\ 2_3 B_3\ \ (\bar{2}\bar{2}2)\ \bar{2}_2' B_3] + 2_1$	
	$[(020)\ (021)\ A_2 2_1\ \ (120)\ (121)\ B_2 2_1\ \ (220)\ (221)\ 2_1 2_1\ \ (210)\ 2_1 B_3\ \ (\bar{1}\bar{2}0)\ \bar{B}_2 B_3\ \ (\bar{2}\bar{2}0)\ 2_3 B_3\ \ (\bar{2}\bar{2}0)\ \bar{2}_2' B_3] + A_3$	**Ī** $\bar{1}\ \bar{1}$
	$[(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2\ \ (2\bar{1}\bar{1})\ (2\bar{2}\bar{1})\ 2_1\bar{B}_2\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2] + \bar{B}_2 A_3$	
	$[(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}_2'\ \ (1\bar{1}\bar{2})\ 1_1\bar{B}_2\ \ (\bar{1}\bar{2}1)\ \bar{B}_2 2_3\ \ (1\bar{2}\bar{2})\ 1_1 2_2\ \ (1\bar{2}\bar{2})\ 1_1\bar{2}_2'\ \ (\bar{2}\bar{2}1)\ 2_2 2_3\ \ (\bar{2}\bar{2}1)\ \bar{2}_2' 2_3] + B_3$	$\bar{1}\ \bar{1}$ **1***
	$[(102)\ B_1 A_3\ \ (202)\ (212)\ 2_1 A_3\ \ (\bar{1}\bar{1}2)\ (\bar{2}\bar{1}2)\ \bar{B}_2\bar{B}_2/\bar{B}_2 A_3\ \ (\bar{1}\bar{2}2)\ \bar{B}_2\bar{B}_2/\bar{B}_2 2_3] + 2_1$	
	$[(\bar{2}\bar{1}2)\ 2_3 A_3/2_3\bar{B}_2\ \ (\bar{2}\bar{2}2)\ 2_3\bar{B}_2/2_3 2_3\ \ (\bar{2}\bar{2}2)\ \bar{2}_3\bar{B}_2/\bar{2}_3 A_3/\bar{2}_2' 2_3] + 2_1$	
221	$(112)\ 1_2 1_1 C_1\ \ (113)\ 1_2 1_1 3_1\ \ (1\bar{2}\bar{2})\ 1_1\bar{2}_2' C_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_3 A_2 C_1/\bar{2}_3 I_2 C_1\ \ (\bar{2}\bar{2}3)\ \bar{2}_3 A_2 3_1/\bar{2}_3 I_2 3_1$	**0 0 2**
	$(111)\ 1_2 1_2 B_1\ \ (112)\ 1_2 1_1 C_1\ \ (1\bar{2}\bar{2})\ 1_1\bar{2}_2' C_1\ \ (\bar{2}\bar{2}1)\ \bar{2}_2 I_2 B_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_3 A_2 C_1/\bar{2}_3 I_2 C_1$	**0 0 2̄**
	$(112)\ 1_2 B_2 C_1\ \ (113)\ 1_2 B_2 3_1\ \ (122)\ 1_1 2_1 C_1\ \ (123)\ 1_1 2_1 3_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_2' 2_1 C_1\ \ (\bar{2}\bar{2}3)\ \bar{2}_2' 2_1 3_1$	**0 1 2**
	$(112)\ 1_2 B_2 C_1\ \ (122)\ 1_1 2_1 C_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_2' 2_1 C_1$	**0 1 2̄**
	$(112)\ 1_2 B_2 C_1\ \ (113)\ 1_2 B_2 3_1\ \ (122)\ 1_1 2_1 C_1\ \ (123)\ 1_1 2_1 3_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_2' 2_1 C_1\ \ (\bar{2}\bar{2}3)\ \bar{2}_2' 2_1 3_1$	**0 Ī 2**
	$(112)\ 1_2 B_2 C_1\ \ [(121) 1_1 2_1\ \ (\bar{2}\bar{2}1)\ \bar{2}_2' 2_1] + B_3\ \ (122)\ 1_1 2_1 C_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_2' 2_1 C_1$	**0 Ī 2̄**
	$[(121)\ 1_1 2_1\ \ (\bar{2}\bar{2}1)\ \bar{2}_2' 2_1] + B_3\ \ [(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}_2'\ \ (1\bar{1}\bar{2})\ 1_1\bar{B}_2\ \ (\bar{1}\bar{2}1)\ \bar{B}_2 2_3] + B_3$	**0** $\bar{1}\ \bar{2}$
	$[(1\bar{2}\bar{2})\ 1_1 2_1\ \ (1\bar{2}\bar{2})\ 1_1\bar{2}_2'\ \ (\bar{2}\bar{2}1)\ 2_2 2_3\ \ (\bar{2}\bar{2}1)\ \bar{2}_2' 2_3\ \ (1\bar{2}\bar{3})\ 1_1\bar{2}_2] + B_3$	
	$(212)\ 2_1 1_2 C_1\ \ (213)\ 2_1 1_2 3_1\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2' C_1\ \ (2\bar{2}\bar{3})\ 2_1\bar{2}_2' 3_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_3 I_2' C_1\ \ (\bar{2}\bar{2}3)\ \bar{2}_3 I_2' 3_1$	**1 0 2**
	$(211)\ 2_1 1_2 B_1\ \ (212)\ 2_1 1_2 C_1\ \ (\bar{2}\bar{2}1)\ \bar{2}_2 I_2' B_1\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2' C_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_3 I_2' C_1$	**1 0 2̄**
	$[(212)\ 2_1 1_1\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2'\ \ (\bar{2}\bar{2}2)\ \bar{2}_3 A_3/2_3\bar{I}_3']\ +\ C_1\ \ [(213)\ 2_1 1_1\ \ (2\bar{2}\bar{3})\ 2_1\bar{2}_2'\ \ (\bar{2}\bar{2}3)\ \bar{2}_3 A_3/\bar{2}_3\bar{I}_3'] + 3_1$	**Ī 0 2**
	$[(212)\ 2_1 1_1\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2'\ \ (\bar{2}\bar{2}2)\ \bar{2}_3 A_3/2_3\bar{I}_3']\ +\ C_1\ \ (211)\ 2_1 1_1 B_1\ \ (\bar{2}\bar{2}1)\ \bar{2}_2\bar{I}_3' B_1$	**Ī 0 2̄**

($\alpha\beta\gamma$) Pattern (continued)

σ-Block	Sequence Sets	Product α	β	γ
221	$[(2\bar{2}\bar{3})\ 2_1\bar{2}_2] + B_3$	*1	$\bar{1}$	1*
	$[(1\bar{2}\bar{3})\ 1_1\bar{2}_2] + B_3$	$\bar{1}\,\bar{1}$		1*
	(122) $B_2 2_1 C_1$ (123) $B_2 2_1 3_1$ (222) $2_1 2_1 C_1$ (223) $2_1 2_1 3_1$	1	1	2
	(122) $B_2 2_1 C_1$ (222) $2_1 2_1 C_1$	1	1	$\bar{2}$
	(122) $B_2 2_1 C_1$ (123) $B_2 2_1 3_1$ (222) $2_1 2_1 C_1$ (223) $2_1 2_1 3_1$	1	$\bar{1}$	2
	(121) $B_2 2_1 B_1$ (122) $B_2 2_1 C_1$ (221) $2_1 2_1 B_1$ (222) $2_1 2_1 C_1$ $[(2\bar{2}\bar{2})\ 2_1 2_2$ $(2\bar{2}\bar{2})\ 2_1\bar{2}_2$ $(2\bar{2}\bar{3})\ 2_1\bar{2}_2] + B_3$	1	$\bar{1}$	$\bar{2}$
	$[(121)\ B_2 2_1$ (221) $2_1 2_1 B_1$ $(2\bar{2}\bar{2})\ 2_1 2_2$ $(2\bar{2}\bar{2})\ 2_1\bar{2}_2$ $(2\bar{2}\bar{3})\ 2_1\bar{2}_2] + B_3$	1	$\bar{1}\,\bar{2}$	
	$[(022)\ A_2 2_1$ (122) $B_2 2_1$ $(\bar{1}\bar{2}2)\ \bar{B}_2 B_3$ (212) $2_1 B_2$ (222) $2_1 2_1$ $(\bar{2}\bar{2}2)\ 2_3 B_3$ $(\bar{2}\bar{2}2)\ \bar{2}'_2 B_3] + C_1$	$\bar{1}$	1	2*
	$[(023)\ A_2 2_1$ (123) $B_2 2_1$ $(\bar{1}\bar{2}3)\ \bar{B}_2 B_3$ (213) $2_1 B_2$ (223) $2_1 2_1$ $(\bar{2}\bar{2}3)\ 2_3 B_3$ $(\bar{2}\bar{2}3)\ \bar{2}'_2 B_3] + 3_1$	$\bar{1}$	1	2
	$[(102)\ B_1 A_2$ (202) $2_1 A_2$ (212) $2_1 B_2$ (022) $A_2 2_1$ (122) $B_2 2_1$ (222) $2_1 2_1] + C_1$	$\bar{1}$	$\bar{1}$	2*
	$[(\bar{1}\bar{2}2)\ \bar{B}_2 B_3$ $(\bar{2}\bar{2}2)\ 2_3 B_3$ $(\bar{2}\bar{2}2)\ \bar{2}'_2 B_3] + C_1$			
	$[(103)\ B_1 A_1$ (203) $2_1 A_2$ (213) $2_1 B_2$ (023) $A_2 2_1$ (123) $B_2 2_1$ (223) $2_1 2_1] + 3_1$	$\bar{1}$	$\bar{1}$	2
	$[(\bar{1}\bar{2}3)\ \bar{B}_2 B_3$ $(\bar{2}\bar{2}3)\ 2_3 B_3$ $(\bar{2}\bar{2}3)\ \bar{2}'_2 B_3] + 3_1$			
	$[(021)\ A_2 2_1$ (121) $B_2 2_1$ (221) $2_1 2_1$ $(2\bar{1}\bar{2})\ 2_1\bar{B}_2$ $(2\bar{2}\bar{2})\ 2_1 2_2$ $(2\bar{2}\bar{2})\ 2_1\bar{2}_2$ $(2\bar{2}\bar{3})\ 2_1\bar{2}_2] + B_3$	$\bar{1}$	$\bar{1}$	$\bar{2}$
	$[(021)\ A_2 2_1$ (121) $B_2 2_1$ (221) $2_1 2_1$ $(2\bar{1}\bar{2})\ 2_1\bar{B}_2$ $(2\bar{2}\bar{2})\ 2_1 2_2$ $(2\bar{2}\bar{2})\ 2_1\bar{2}_2$ $(2\bar{2}\bar{3})\ 2_1\bar{2}_2] + B_3$	$\bar{1}$	$\bar{1}\,\bar{2}$	
	$[(102)\ B_1 A_3$ (202) (212) $2_1 A_3$ $(\bar{1}\bar{1}2)$ $(\bar{2}\bar{1}2)\ \bar{B}_2\bar{B}_2/\bar{B}_2 A_3$ $(\bar{1}\bar{2}2)\ \bar{B}_2\bar{B}_2/\bar{B}_2 2_3] + C_1$	$\bar{1}\,\bar{1}$		2*
	$[(\bar{2}\bar{1}2)\ 2_3 A_3/2_3\bar{B}_2$ $(\bar{2}\bar{2}2)\ 2_3\bar{B}_2/2_3 2_3$ $(\bar{2}\bar{2}2)\ \bar{2}_3\bar{B}_2/\bar{2}_3 A_3/\bar{2}'_2 2_3] + C_1$			
	$[(103)\ B_1 A_3$ (203) (213) $2_1 A_3$ $(\bar{1}\bar{1}3)$ $(\bar{2}\bar{1}3)\ \bar{B}_2\bar{B}_2/\bar{B}_2 A_3$ $(\bar{1}\bar{2}3)\ \bar{B}_2\bar{B}_2/\bar{B}_2 2_3] + 3_1$	$\bar{1}\,\bar{1}$		2
	$[(\bar{2}\bar{1}3)\ 2_3 A_3/2_3\bar{B}_2$ $(\bar{2}\bar{2}3)\ 2_3\bar{B}_2/2_3 2_3$ $(\bar{2}\bar{2}3)\ \bar{2}_3\bar{B}_2/\bar{2}_3 A_3/\bar{2}'_2 2_3] + 3_1$			
	$[(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}'_2$ $(1\bar{1}\bar{2})\ 1_1\bar{B}_2$ $(\bar{1}\bar{2}1)\ \bar{B}_2 2_3$ $(1\bar{2}\bar{2})\ 1_1 2_1$ $(1\bar{2}\bar{2})\ 1_1\bar{2}'_2] + B_3$	$\bar{1}\,\bar{1}$		$\bar{2}$
	$[(1\bar{2}\bar{3})\ 1_1\bar{2}_2$ $(\bar{2}\bar{2}1)\ 2_2 2_3$ $(\bar{2}\bar{2}1)\ \bar{2}'_2 2_3] + B_3$			
123	$(\bar{2}\bar{2}0)$ $(\bar{2}\bar{2}1)\ C_2\bar{2}_2 A_3$ $(\bar{3}\bar{2}0)$ $(\bar{3}\bar{2}1)\ 3_2\bar{2}_2 A_3$	$\bar{1}\,\bar{1}$		0
	$[(211)\ C_1 1_2$ (311) $3_1 1_2$ $(\bar{2}\bar{2}1)\ C_2\bar{2}'_2$ $(\bar{3}\bar{2}1)\ 3_2\bar{2}'_2] + A_1$ $[(2\bar{1}\bar{1})$ $(2\bar{2}\bar{1})\ C_1\bar{B}_2$ $(3\bar{1}\bar{1})$ $(3\bar{2}\bar{1})\ 3_1\bar{B}_2] + I_3$	2	0	0

	$[(2\bar{1}\bar{1})\ (2\bar{2}\bar{1})\ C_1\bar{B}_2 \quad (3\bar{1}\bar{1})\ (3\bar{2}\bar{1})\ 3_1\bar{B}_2] + \bar{1}'_2$	2 1 0
	$[(200)\ C_1A_2 \quad (210)\ C_1B_2 \quad (220)\ (221)\ C_12_1 \quad (300)\ 3_1A_2 \quad (310)\ 3_1B_2 \quad (320)\ (321)\ 3_22_1] + A_3$	2 $\bar{1}$ 0
	$[(2\bar{1}\bar{1})\ (2\bar{2}\bar{1})\ C_1\bar{B}_2 \quad (3\bar{1}\bar{1})\ (3\bar{2}\bar{1})\ 3_1\bar{B}_2] + A_3\bar{1}'_3$	
	$(1\bar{1}\bar{1})\ (2\bar{1}0)\ B_3\bar{B}_2\bar{1}_2 \quad (211)\ C_1\bar{1}_2A_1$	$\bar{2}$ 0 0
	$(1\bar{1}\bar{1})\ (2\bar{1}0)\ B_3\bar{B}_2\bar{1}'_2$	$\bar{2}$ 1 0
	$[(1\bar{1}\bar{1})\ (2\bar{1}0)\ B_3\bar{B}_2] + A_3\bar{1}'_3 \quad [(210)\ C_1B_1 \quad (120)\ (121)\ B_22_1 \quad (220)\ (221)\ C_12_1] + A_3$	$\bar{2}$ $\bar{1}$ 0
122	$(\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ C_2\bar{2}_2A_3 \quad (\bar{3}\bar{2}0)\ (\bar{3}\bar{2}1)\ 3_2\bar{2}_2A_3$	0 $\bar{1}\bar{1}$
	$(\bar{2}\bar{2}1)\ C_2\bar{2}_2\bar{1}_1 \quad (\bar{3}\bar{2}1)\ 3_2\bar{2}_2\bar{1}_1$	$\bar{1}\bar{1}$ 0
	$(\bar{2}\bar{2}1)\ C_2\bar{2}_2B_3 \quad (\bar{3}\bar{2}1)\ 3_2\bar{2}_2B_3$	$\bar{1}\bar{1}$ 1*
	$(211)\ C_1\bar{1}_2\bar{1}_1 \quad (311)\ 3_1\bar{1}_2\bar{1}_1 \quad (\bar{2}\bar{2}1)\ C_2\bar{2}'_2\bar{1}_1 \quad (\bar{3}\bar{2}1)\ 3_2\bar{2}'_2\bar{1}_1 \quad (2\bar{2}\bar{2})\ C_1\bar{2}_2\bar{1}_3 \quad (3\bar{2}\bar{2})\ 3_1\bar{2}_2\bar{1}_3$	2 0 0
	$(211)\ C_1\bar{1}_2\bar{1}_1 \quad (1\bar{2}\bar{2})\ B_1\bar{2}_2\bar{1}_2 \quad (2\bar{2}\bar{2})\ C_1\bar{2}_2\bar{1}_3$	$\bar{2}$ 0 0
	$[(211)\ C_1\bar{1}_2 \quad (311)\ 3_1\bar{1}_2 \quad (\bar{2}\bar{2}1)\ C_2\bar{2}'_2 \quad (\bar{3}\bar{2}1)\ 3_2\bar{2}'_2] + B_1$	2 0 1*
	$[(212)\ C_1\bar{1}_1 \quad (312)\ 3_1\bar{1}_1 \quad (\bar{2}\bar{2}2)\ C_2\bar{2}'_2 \quad (\bar{3}\bar{2}2)\ 3_2\bar{2}'_2 \quad (2\bar{2}\bar{2})\ C_1\bar{2}'_2 \quad (3\bar{2}\bar{2})\ 3_1\bar{2}'_2] + 2_1$	
	$(211)\ C_1\bar{1}_2B_1 \quad (1\bar{2}\bar{2})\ B_1\bar{2}'_22_1 \quad (2\bar{2}\bar{2})\ C_1\bar{2}'_22_1$	$\bar{2}$ 0 1*
	$(221)\ C_12_1\bar{1}_2 \quad (321)\ 3_12_1\bar{1}_2 \quad (2\bar{2}\bar{2})\ C_1\bar{2}_2\bar{1}'_2 \quad (3\bar{2}\bar{2})\ 3_1\bar{2}_2\bar{1}'_2$	2 1 0
	$(221)\ C_12_1\bar{1}_1 \quad (321)\ 3_12_1\bar{1}_1 \quad [(2\bar{2}\bar{2})\ C_1\bar{2}_2 \quad (3\bar{2}\bar{2})\ 3_1\bar{2}_2] + A_3\bar{1}'_3$	2 $\bar{1}$ 0
	$(121)\ B_22_1\bar{1}_2 \quad (221)\ C_12_1\bar{1}_2 \quad (1\bar{2}\bar{2})\ B_1\bar{2}_2\bar{1}'_2 \quad (2\bar{2}\bar{2})\ C_1\bar{2}_2\bar{1}'_2$	$\bar{2}$ 1 0
	$(121)\ B_22_1\bar{1}_1 \quad (221)\ C_12_1\bar{1}_1 \quad [(1\bar{2}\bar{2})\ B_1\bar{2}_2 \quad (2\bar{2}\bar{2})\ C_2\bar{2}_2] + A_3\bar{1}'_3$	$\bar{2}$ $\bar{1}$ 0
	$(212)\ C_1B_22_1 \quad (222)\ C_12_12_1 \quad (312)\ 3_1B_22_1 \quad (322)\ 3_12_12_1$	2 1 1*
	$[(221)\ C_12_1 \quad (321)\ 3_12_1 \quad (2\bar{1}\bar{2})\ C_1\bar{B}_2 \quad (3\bar{1}\bar{2})\ 3_1\bar{B}_2 \quad (2\bar{2}\bar{2})\ C_12_2 \quad (3\bar{2}\bar{2})\ 3_12_2 \quad (2\bar{2}\bar{2})\ C_1\bar{2}'_2 \quad (3\bar{2}\bar{2})\ 3_1\bar{2}'_2] + B_3$	2 $\bar{1}$ 1*
	$[(202)\ C_1A_2 \quad (212)\ C_1B_2 \quad (222)\ C_12_1 \quad (302)\ 3_1A_2 \quad (312)\ 3_1B_2 \quad (322)\ 3_12_1] + 2_1$	
	$[(200)\ C_1A_2 \quad (210)\ C_1B_2 \quad (220)\ (221)\ C_12_1 \quad (300)\ 3_1A_2 \quad (310)\ 3_1B_2 \quad (320)\ (321)\ 3_12_1] + A_3$	2 $\bar{1}\bar{1}$
	$[(2\bar{1}\bar{2})\ C_1\bar{B}_2 \quad (3\bar{1}\bar{2})\ 3_1\bar{B}_2 \quad (2\bar{2}\bar{2})\ C_12_2 \quad (3\bar{2}\bar{2})\ 3_12_2 \quad (2\bar{2}\bar{2})\ C_1\bar{2}'_2 \quad (3\bar{2}\bar{2})\ 3_1\bar{2}'_2] + 2_3\bar{B}_2$	
	$[(2\bar{1}\bar{1})\ (2\bar{2}\bar{1})\ C_1\bar{B}_2 \quad (3\bar{1}\bar{1})\ (3\bar{2}\bar{1})\ 3_1\bar{B}_2] + \bar{B}_2A_3$	
	$(122)\ B_22_12_1 \quad (212)\ C_1B_22_1 \quad (222)\ C_12_12_1$	$\bar{2}$ 1 1*

($\alpha\beta\gamma$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
122	$[(121)\ B_2 2_1\ \ (221)\ C_1 2_1\ \ (1\bar{2}\bar{2})\ B_1\bar{2}'_2\ \ (2\bar{2}2)\ C_1 2_2\ \ (2\bar{2}\bar{2})\ C_1\bar{2}'_2] + B_3\ \ [(122)\ B_2 2_1\ \ (212)\ C_1 B_2\ \ (222)\ C_1 2_1] + 2_1$	2 1 1*
	$[(120)\ (121)\ B_2 2_1\ \ (220)\ (221)\ C_1 2_1\ \ (212)\ C_1 B_1] + A_3\ \ [(1\bar{1}1)\ (\bar{2}10)\ B_3\bar{B}_2\ \ (1\bar{2}\bar{2})\ B_1\bar{2}_2\ \ (2\bar{2}\bar{2})\ C_1\bar{2}_2] + \bar{B}_2 A_3$	2 1 1
	$(\bar{2}\bar{2}2)\ C_2\bar{2}'_2 2_1\ \ (\bar{3}\bar{2}2)\ 3_2\bar{2}'_2 2_1$	
121	$(\bar{2}\bar{2}1)\ C_2\bar{2}_2 B_3\ \ (\bar{3}\bar{2}1)\ 3_2\bar{2}_2 B_3$	0 1 2
	$(\bar{2}\bar{2}1)\ C_2\bar{2}_2 B_3\ \ (\bar{3}\bar{2}1)\ 3_2\bar{2}_2 B_3$	1 1 2
	$[(213)\ C_1 1_1\ \ (313)\ 3_1 1_1\ \ (\bar{2}\bar{2}3)\ C_2\bar{2}'_2\ \ (\bar{3}\bar{2}3)\ 3_2\bar{2}'_2\ \ (2\bar{2}\bar{3})\ C_1\bar{2}'_2\ \ (3\bar{2}\bar{3})\ 3_1\bar{2}'_2] + 3_1$	2 0 2
	$[(212)\ C_1 1_1\ \ (312)\ 3_1 1_1\ \ (\bar{2}\bar{2}2)\ C_2\bar{2}'_2\ \ (\bar{3}\bar{2}2)\ 3_2\bar{2}'_2\ \ (2\bar{2}\bar{2})\ C_1\bar{2}'_2\ \ (3\bar{2}\bar{2})\ 3_1\bar{2}'_2] + C_1$	2 0 2*
	$[(211)\ C_1 1_2\ \ (311)\ 3_1 1_2\ \ (\bar{2}\bar{2}1)\ C_2\bar{2}'_2\ \ (\bar{3}\bar{2}1)\ 3_2\bar{2}'_2] + B_1$	2 0 2
	$[(1\bar{2}\bar{2})\ B_1\bar{2}'_2\ \ (2\bar{2}\bar{2})\ C_1\bar{2}'_2] + C_1\ \ [(1\bar{2}\bar{3})\ B_1\bar{2}'_2\ \ (2\bar{2}\bar{3})\ C_1\bar{2}'_2] + 3_1$	2 0 2
	$(211)\ C_1 1_2 B_1\ \ (1\bar{2}\bar{2})\ B_1\bar{2}'_2 C_1\ \ (2\bar{2}\bar{2})\ C_1\bar{2}'_2 C_1$	2 0 2
	$[(2\bar{2}\bar{3})\ C_1\bar{2}_2\ \ (3\bar{2}\bar{3})\ 3_1\bar{2}_2] + B_3$	2 1 1*
	$[(1\bar{2}\bar{3})\ B_1\bar{2}_2\ \ (2\bar{2}\bar{3})\ C_1\bar{2}_2] + B_3$	2 1 1*
	$(213)\ C_1 B_2 3_1\ \ (223)\ C_1 2_1 3_1\ \ (313)\ 3_1 B_2 3_1\ \ (323)\ 3_1 2_1 3_1$	2 1 2
	$(212)\ C_1 B_2 C_1\ \ (222)\ C_1 2_1 C_1\ \ (312)\ 3_1 B_2 C_1\ \ (322)\ 3_1 2_1 C_1$	2 1 2*
	$[(203)\ C_1 A_2\ \ (213)\ C_1 B_2\ \ (223)\ C_1 2_1\ \ (303)\ 3_1 A_2\ \ (313)\ 3_1 B_2\ \ (323)\ 3_1 2_1] + 3_1$	2 1 2
	$[(202)\ C_1 A_2\ \ (212)\ C_1 B_2\ \ (222)\ C_1 2_1\ \ (302)\ 3_1 A_2\ \ (312)\ 3_1 B_2\ \ (322)\ 3_1 2_1] + C_1$	2 1 2*
	$[(221)\ C_1 2_1\ \ (321)\ 3_1 2_1\ \ (2\bar{1}\bar{2})\ C_1\bar{B}_2\ \ (3\bar{1}\bar{2})\ 3_1\bar{B}_2\ \ (2\bar{2}\bar{2})\ C_1 2_2\ \ (3\bar{2}\bar{2})\ 3_1 2_2] + B_3$	2 1 2
	$[(2\bar{2}\bar{2})\ C_1\bar{2}'_2\ \ (3\bar{2}\bar{2})\ 3_1\bar{2}'_2\ \ (2\bar{2}\bar{3})\ C_1\bar{2}_2\ \ (3\bar{2}\bar{3})\ 3_1\bar{2}_2] + B_3$	
	$[(221)\ C_1 2_1\ \ (321)\ 3_1 2_1\ \ (2\bar{1}\bar{2})\ C_1\bar{B}_2\ \ (3\bar{1}\bar{2})\ 3_1\bar{B}_2\ \ (2\bar{2}\bar{2})\ C_1 2_2\ \ (3\bar{2}\bar{2})\ 3_1 2_2] + B_3$	2 1 2
	$[(2\bar{2}\bar{2})\ C_1\bar{2}'_2\ \ (3\bar{2}\bar{2})\ 3_1\bar{2}'_2\ \ (2\bar{2}\bar{3})\ C_1\bar{2}_2\ \ (3\bar{2}\bar{3})\ 3_1\bar{2}_2] + B_3$	
	$(123)\ B_2 2_1 3_1\ \ (213)\ C_1 B_2 3_1\ \ (223)\ C_1 2_1 3_1$	2 1 2
	$(122)\ B_2 2_1 C_1\ \ (212)\ C_1 B_2 C_1\ \ (222)\ C_1 2_1 C_1$	2 1 2*
	$(123)\ B_2 2_1 3_1\ \ (213)\ C_1 B_2 3_1\ \ (223)\ C_1 2_1 3_1$	2 1 2

(122) $B_2 2_1 C_1$ (212) $C_1 B_2 C_1$ (222) $C_1 2_1 C_1$	2 I 2*
[(121) $B_2 2_1$ (221) $C_1 2_1$ (1$\bar{2}$2) $B_1 \bar{2}'_2$ (1$\bar{2}\bar{3}$) $B_1 \bar{3}_2$ (2$\bar{2}$2) $C_1 2_2$ (2$\bar{2}\bar{2}$) $C_1 \bar{2}'_2$ (2$\bar{2}\bar{3}$) $C_1 \bar{2}_2$] + B_3	2 I 2
[(121) $B_2 2_1$ (221) $C_1 2_1$ (1$\bar{2}$2) $B_1 \bar{2}'_2$ (1$\bar{2}\bar{3}$) $B_1 \bar{2}_2$ (2$\bar{2}$2) $C_1 2_2$ (2$\bar{2}\bar{2}$) $C_1 \bar{2}'_2$ (2$\bar{2}\bar{3}$) $C_1 \bar{2}_2$] + B_3	2 I 2
(2$\bar{2}$2) $C_2 \bar{2}'_2 C_1$ (2$\bar{2}\bar{3}$) $C_2 \bar{2}'_2 3_1$ (3$\bar{2}$2) $3_2 \bar{2}'_2 C_1$ (3$\bar{2}\bar{3}$) $3_2 \bar{2}'_2 3_1$	2 I 2
(2$\bar{2}$2) $C_2 \bar{2}'_2 C_1$ (3$\bar{2}$2) $3_2 \bar{2}'_2 C_1$	2 I 2

σ-Block	($\beta\gamma\alpha$) Pattern Sequence Sets	Product α β γ
I. $\sigma_\beta = 3$		
333	$(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}'_2A_1A_1$	0 0 0
332	$(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}'_2l_1A_1$ $(1\bar{1}\bar{2})$ $\bar{1}_2A_1A_1/\bar{1}_2l_1A_1$	0 0 0
	$(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}'_2B_1A_1$ $(1\bar{1}\bar{2})$ $\bar{1}'_22_1A_1/\bar{1}_2B_1A_1$ $(\bar{1}\bar{1}2)$ $\bar{1}'_22_1A_1$	0 0 1 *
331	$(1\bar{1}\bar{3})$ $\bar{1}_22_1A_1$	0 0 1 *
	$(1\bar{1}\bar{2})$ $(\bar{1}\bar{1}2)$ $\bar{1}'_2C_1A_1$ $(1\bar{1}\bar{3})$ $(\bar{1}\bar{1}3)$ $\bar{1}'_23_1A_1$ $(1\bar{1}\bar{3})$ $\bar{1}_2C_1A_1$	0 0 2
	$(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}'_2B_1A_1$ $(1\bar{1}\bar{2})$ $(\bar{1}\bar{1}2)$ $\bar{1}'_2C_1A_1$ $(1\bar{1}\bar{2})$ $\bar{1}_2B_1A_1$ $(1\bar{1}\bar{3})$ $\bar{1}_2C_1A_1$	0 0 $\bar{2}$
233	$(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}'_2A_1l_1$ $(\bar{2}\bar{1}1)$ $\bar{1}_2A_1A_1/\bar{1}_2A_1l_1$	0 0 0
	$(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}'_2A_1B_1$ $(2\bar{1}\bar{1})$ $(\bar{2}\bar{1}1)$ $\bar{1}'_2A_12_1$ $(\bar{2}\bar{1}1)$ $\bar{1}_2A_1B_1$	*1 0 0
232	$(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}'_2l_1l_1$ $(1\bar{1}\bar{2})$ $\bar{1}_2A_1l_1/\bar{1}_2l_1l_1$ $(\bar{2}\bar{1}1)$ $\bar{1}_2l_1A_1/\bar{1}_2l_1l_1$	0 0 0
	$(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}'_2B_1l_1$ $(1\bar{1}\bar{2})$ $\bar{1}'_22_1l_1/\bar{1}_2B_1l_1$ $(\bar{1}\bar{1}2)$ $\bar{1}'_22_1l_1$ $(\bar{2}\bar{1}1)$ $\bar{1}_2B_1A_1/\bar{1}_2B_1l_1$ $(\bar{2}\bar{1}2)$ $\bar{1}_22_1A_1/\bar{1}_22_1l_1$	0 0 1 *
	$(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}'_2l_1B_1$ $(1\bar{1}\bar{2})$ $\bar{1}_2A_1B_1/\bar{1}_2l_1B_1$ $(2\bar{1}\bar{1})$ $(\bar{2}\bar{1}1)$ $\bar{1}'_2l_12_1$ $(\bar{2}\bar{1}1)$ $\bar{1}_2l_1B_1$ $(2\bar{1}\bar{2})$ $\bar{1}_2A_12_1/\bar{1}_2l_12_1$	*1 0 0
	$(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}_2B_1B_1$ $(1\bar{1}\bar{2})$ $\bar{1}'_22_1B_1/\bar{1}_2B_1B_1$ $(\bar{1}\bar{1}2)$ $\bar{1}'_22_1B_1$ (202) (212) $A_22_12_1$ $(2\bar{1}\bar{1})$ $(\bar{2}\bar{1}1)$ $\bar{1}'_2B_1B_1$ $(\bar{2}\bar{1}1)$ $\bar{1}_2B_1B_1$ $(2\bar{1}\bar{2})$ $\bar{1}'_22_12_1/\bar{1}_2B_12_1$ $(\bar{2}\bar{1}2)$ $\bar{1}_22_1B_1/\bar{1}'_22_12_1$	*1 0 1 *
231	$(1\bar{1}\bar{3})$ $\bar{1}_22_1l_1$	0 0 1 *
	$(1\bar{1}\bar{2})$ $(\bar{1}\bar{1}2)$ $\bar{1}'_2C_1l_1$ $(1\bar{1}\bar{3})$ $(\bar{1}\bar{1}3)$ $\bar{1}'_23_1l_1$ $(1\bar{1}\bar{3})$ $\bar{1}_2C_1l_1$ $(\bar{2}\bar{1}2)$ $\bar{1}_2C_1A_1/\bar{1}_2C_1l_1$ $(\bar{2}\bar{1}3)$ $\bar{1}_23_1A_1/\bar{1}_23_1l_1$	0 0 2
	$[(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}'_2B_1$ $(1\bar{1}\bar{2})$ $(\bar{1}\bar{1}2)$ $\bar{1}'_2C_1$ $(1\bar{1}\bar{2})$ $\bar{1}_2B_1$ $(1\bar{1}\bar{3})$ $\bar{1}_2C_1$ $(\bar{2}\bar{1}1)$ $\bar{1}_2B_1$ $(\bar{2}\bar{1}2)$ $\bar{1}_2C_1] + l_1$ $[(\bar{2}\bar{1}1)$ $\bar{1}_2B_1$ $(\bar{2}\bar{1}2)$ $\bar{1}_2C_1] + A_1$	0 0 $\bar{2}$
	$(1\bar{1}\bar{3})$ $\bar{1}_22_1B_1$ $(2\bar{1}\bar{3})$ $\bar{1}_22_12_1$	*1 0 1 *
	$[(1\bar{1}\bar{2})$ $(\bar{1}\bar{1}2)$ $\bar{1}'_2C_1$ $(1\bar{1}\bar{3})$ $(\bar{1}\bar{1}3)$ $\bar{1}'_23_1$ $(1\bar{1}\bar{3})$ $\bar{1}_2C_1$ $(\bar{2}\bar{1}2)$ $\bar{1}_2C_1$ $(\bar{2}\bar{1}3)$ $\bar{1}_23_1] + B_1$	*1 0 2
	$[(202)$ (212) A_2C_1 (203) (213) A_23_1 $(2\bar{1}\bar{2})$ $(\bar{2}\bar{1}2)$ $\bar{1}'_2C_1$ $(2\bar{1}\bar{3})$ $(\bar{2}\bar{1}3)$ $\bar{1}'_23_1$ $(2\bar{1}\bar{3})$ $\bar{1}_2C_1] + 2_1$	
	$[(1\bar{1}\bar{1})$ $(\bar{1}\bar{1}1)$ $\bar{1}'_2B_1$ $(1\bar{1}\bar{2})$ $\bar{1}\bar{1}2)$ $\bar{1}'_2C_1$ $(2\bar{1}\bar{2})$ $\bar{1}_2B_1$ $(1\bar{1}\bar{3})$ $\bar{1}_2C_1$ $(\bar{2}\bar{1}1)$ $\bar{1}_2B_1$ $(\bar{2}\bar{1}2)$ $\bar{1}_2C_1] + B_1$	*1 0 $\bar{2}$
	$[(202)$ (212) A_2C_1 $(2\bar{1}\bar{1})$ $(\bar{2}\bar{1}1)$ $\bar{1}'_2B_1$ $(2\bar{1}\bar{2})$ $(\bar{2}\bar{1}2)$ $\bar{1}'_2C_1$ $(2\bar{1}\bar{2})$ $\bar{1}_2B_1$ $(2\bar{1}\bar{3})$ $\bar{1}_2C_1] + 2_1$	

133	$(3\bar{1}1)\ \Gamma_2A_12_1$	*1 0 0
	$(2\bar{1}\bar{1})\ (2\bar{1}1)\ \Gamma_2'A_1C_1 \quad (3\bar{1}1)\ \Gamma_2A_1C_1 \quad (3\bar{1}\bar{1})\ (3\bar{1}1)\ \Gamma_2'A_13_1$	2 0 0
	$(1\bar{1}\bar{1})\ (\bar{1}\bar{1}1)\ \Gamma_2'A_1B_1 \quad (2\bar{1}1)\ \Gamma_2A_1B_1 \quad (2\bar{1}\bar{1})\ 2\bar{1}1)\ \Gamma_2'A_1C_1 \quad (3\bar{1}1)\ \Gamma_2A_1C_1$	$\bar{2}$ 0 0
132	$(3\bar{1}1)\ \Gamma_21_12_1$	*1 0 0
	$(3\bar{1}1)\ \Gamma_2B_12_1 \quad (3\bar{1}2)\ \Gamma_22_12_1$	*1 0 1 *
	$[(2\bar{1}\bar{1})\ (2\bar{1}1)\ \Gamma_2'1_1\ (2\bar{1}\bar{2})\ \Gamma_2A_1/\Gamma_21_1\ (3\bar{1}1)\ \Gamma_21_1] + C_1 \quad [(3\bar{1}\bar{1})\ (3\bar{1}1)\ \Gamma_21_1\ (3\bar{1}\bar{2})\ \Gamma_2A_1/\Gamma_21_1] + 3_1$	2 0 0
	$[(1\bar{1}\bar{1})\ (\bar{1}\bar{1}1)\ \Gamma_2'1_1\ (1\bar{1}\bar{2})\ \Gamma_2A_1/\Gamma_21_1\ (2\bar{1}1)\ \Gamma_21_1] + B_1 \quad [(2\bar{1}\bar{1})\ (2\bar{1}1)\ \Gamma_2'1_1\ (2\bar{1}\bar{2})\ \Gamma_2A_1/\Gamma_21_1\ (3\bar{1}1)\ \Gamma_21_1] + C_1$	$\bar{2}$ 0 0
	$[(302)\ (312)\ A_22_1\ (3\bar{1}\bar{1})\ (3\bar{1}1)\ \Gamma_2'B_1\ (3\bar{1}\bar{2})\ \Gamma_2'2_1/\Gamma_2B_1\ (3\bar{1}2)\ \Gamma_2'2_1] + 3_1$	2 0 1 *
	$[(202)\ (212)\ A_22_1\ (2\bar{1}\bar{1})\ (2\bar{1}1)\ \Gamma_2'B_1\ (2\bar{1}\bar{2})\ \Gamma_2'2_1/\Gamma_2B_1\ (2\bar{1}2)\ \Gamma_2'2_1\ (3\bar{1}1)\ \Gamma_2B_1\ (3\bar{1}2)\ \Gamma_22_1] + C_1$	*2 0 1 *
	$[(1\bar{1}\bar{1})\ (\bar{1}\bar{1}1)\ \Gamma_2'B_1\ (1\bar{1}\bar{2})\ \Gamma_2'2_1/\Gamma_2B_1\ (\bar{1}\bar{1}2)\ \Gamma_2'2_1\ (2\bar{1}1)\ \Gamma_2B_1\ (2\bar{1}2)\ \Gamma_22_1] + B_1$	$\bar{2}$ 0 1 *
131	$(3\bar{1}2)\ \Gamma_2C_12_1 \quad (3\bar{1}3)\ \bar{\Gamma}_23_12_1$	*1 0 2
	$(3\bar{1}1)\ \Gamma_2B_12_1 \quad (3\bar{1}2)\ \Gamma_2C_12_1$	*1 0 $\bar{2}$
	$(2\bar{1}3)\ \Gamma_22_1C_1 \quad (3\bar{1}3)\ \Gamma_22_13_1$	2 0 1 *
	$(1\bar{1}3)\ \Gamma_22_1B_1 \quad (2\bar{1}3)\ \Gamma_22_1C_1$	$\bar{2}$ 0 1 *
	$[(302)\ (312)\ A_2C_1\ (303)\ (313)\ A_23_1\ (3\bar{1}\bar{2})\ (3\bar{1}2)\ \Gamma_2'C_1\ (3\bar{1}3)\ (3\bar{1}3)\ \Gamma_2'3_1\ (3\bar{1}\bar{3})\ \Gamma_2C_1] + 3_1$	2 0 2
	$[(202)\ (212)\ A_2C_1\ (203)\ (213)\ A_23_1\ (2\bar{1}\bar{2})\ (2\bar{1}2)\ \Gamma_2'C_1\ (2\bar{1}3)\ (2\bar{1}3)\ \Gamma_2'3_1\ (2\bar{1}\bar{3})\ \Gamma_2C_1\ (3\bar{1}2)\ \Gamma_2C_1\ (3\bar{1}3)\ 1_23_1] + C_1$	*2 0 2
	$[(1\bar{1}\bar{2})\ (\bar{1}\bar{1}2)\ \Gamma_2'C_1\ (1\bar{1}3)\ (\bar{1}\bar{1}3)\ \Gamma_2'3_1\ (1\bar{1}\bar{3})\ \Gamma_2C_1\ (2\bar{1}2)\ \Gamma_2C_1\ (2\bar{1}3)\ \Gamma_23_1] + B_1$	$\bar{2}$ 0 2
	$[(302)\ (312)\ A_2C_1\ (3\bar{1}\bar{1})\ (3\bar{1}1)\ \Gamma_2'B_1\ (3\bar{1}\bar{2})\ (3\bar{1}2)\ \Gamma_2'C_1\ (3\bar{1}\bar{2})\ \Gamma_2B_1\ (3\bar{1}\bar{3})\ \Gamma_2C_1] + 3_1$	2 0 $\bar{2}$
	$[(202)\ (212)\ A_2C_1\ (2\bar{1}\bar{1})\ (2\bar{1}\,1)\ \Gamma_2'B_1\ (2\bar{1}\bar{2})\ (2\bar{1}\bar{2})\ \Gamma_2'C_1\ (2\bar{1}\bar{2})\ \Gamma_2B_1\ (2\bar{1}\bar{3})\ \Gamma_2C_1\ (3\bar{1}1)\ \Gamma_2B_1\ (3\bar{1}2)\ \Gamma_2C_1] + C_1$	*2 0 $\bar{2}$
	$[(1\bar{1}\bar{1})\ (\bar{1}\bar{1}1)\ \Gamma_2'B_1\ (1\bar{1}\bar{2})\ (\bar{1}\bar{1}2)\ \Gamma_2'C_1\ (1\bar{1}\bar{2})\ \Gamma_2B_1\ (1\bar{1}\bar{3})\ \Gamma_2C_1\ (2\bar{1}1)\ \Gamma_2B_1\ (2\bar{1}2)\ \Gamma_2C_1] + B_1$	$\bar{2}$ 0 $\bar{2}$
	II. $\sigma_\beta = 2$	
323	$(0\bar{1}\bar{1})\ (\bar{1}10)\ (0\bar{2}\bar{1})\ (\bar{1}\bar{2}0)\ \bar{B}_2A_3\Gamma_2 \quad (111)\ 1_2A_1A_1 \quad (1\bar{1}\bar{1})\ \bar{B}_2\Gamma_3'\Gamma_2$	0 0 0
	$(0\bar{1}\bar{1})\ (\bar{1}10)\ (0\bar{2}\bar{1})\ (\bar{1}\bar{2}0)\ \bar{B}_2A_3\Gamma_2' \quad (1\bar{1}\bar{1})\ \bar{B}_2\Gamma_3'\Gamma_2'$	0 1 0
	$[(010)\ B_1A_3\ (0\bar{1}\bar{1})\ (0\bar{2}\bar{1})\ \bar{B}_2A_3/\bar{B}_2\Gamma_3'\ (020)\ (021)\ (120)\ (121)\ 2_1A_3] + A_3 \quad [(0\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ (0\bar{2}\bar{1})\ (\bar{2}\bar{1}0)\ \bar{B}_2A_3\ (1\bar{1}\bar{1})\ \bar{B}_2\Gamma_3'] + \bar{\Gamma}_3'$	0 I 0

($\beta\gamma\alpha$) Pattern (continued)

σ-Block	Sequence Set	Product α β γ
322	(111) $1_2 1_1 A_1$ (0$\bar{2}\bar{2}$) $\bar{2}_2 A_3 \bar{1}_2$ (1$\bar{2}\bar{2}$) $\bar{2}_2 1_2 A_1/\bar{2}_2 \bar{1}'_3 1_2$	0 0 0
	(111) $1_2 B_1 A_1$ (112) $1_2 2_1 A_1$ (1$\bar{2}\bar{2}$) $\bar{2}'_2 2_1 A_1$	0 0 1 *
	(0$\bar{2}\bar{2}$) $\bar{2}_2 A_3 \bar{1}'_2$ (1$\bar{2}\bar{2}$) $\bar{2}_2 \bar{1}'_3 \bar{1}'_2$	0 1 0
	[(021) $2_1 1_1$ (0$\bar{2}\bar{2}$) $\bar{2}_2 A_3/\bar{2}_2 \bar{1}'_3$ (121) $2_1 1_1$ (1$\bar{2}\bar{2}$) $\bar{2}_2 A_3/\bar{2}_2 \bar{1}'_3$] + A_3 [(0$\bar{2}\bar{2}$) $\bar{2}_2 A_3$ (1$\bar{2}\bar{2}$) $\bar{2}_2 \bar{1}'_3$] + $\bar{1}'_3$	0 $\bar{1}$ 0
	(0$\bar{1}\bar{2}$) ($\bar{1}\bar{1}$) $\bar{B}_2 B_3 \bar{1}'_2$ (0$\bar{2}\bar{2}$) $2_2 B_3 \bar{1}'_2$ ($\bar{1}\bar{2}$) ($\bar{1}\bar{2}$) $\bar{B}_2 2_1 \bar{1}'_2$	0 1 1 *
	[(002) $A_2 2_1$ (012) $B_2 2_1$ (0$\bar{1}\bar{2}$) $\bar{B}_2 B_3$ (021) (121) $2_1 B_3$] + A_3 [(022) (122) $2_1 2_1$ (0$\bar{2}\bar{2}$) (1$\bar{2}\bar{2}$) $2_2 B_3$ (0$\bar{2}\bar{2}$) $\bar{2}'_2 B_3$] + A_3	0 $\bar{1}$ 1 *
	[(010) $B_1 A_3$ (0$\bar{1}\bar{1}$) (0$\bar{2}\bar{1}$) ($\bar{1}$0) ($\bar{1}\bar{2}$0) $\bar{B}_2 A_3$ (0$\bar{1}\bar{1}$) (0$\bar{1}\bar{2}$) (0$\bar{2}\bar{1}$) $\bar{B}_2 \bar{B}_2$ (0$\bar{1}\bar{2}$) $\bar{B}_2 B_3$] + A_3	0 $\bar{1}$ $\bar{1}$
	[(020) (021) (120) (121) $2_1 A_3$ (0$\bar{2}\bar{2}$) (1$\bar{2}\bar{2}$) $2_2 \bar{B}_2/2_2 2_3$ (0$\bar{2}\bar{2}$) (1$\bar{2}\bar{2}$) $\bar{2}_2 \bar{B}_2/\bar{2}_2 A_3/\bar{2}'_2 2_3$] + A_3 (1$\bar{2}\bar{2}$) $\bar{2}_2 \bar{1}'_3 A_3$ (0$\bar{1}\bar{2}$) ($\bar{1}\bar{1}$) $\bar{B}_2 B_3 \bar{1}'_3$ (0$\bar{2}\bar{2}$) $2_2 B_3 \bar{1}'_3$ ($\bar{1}\bar{2}$) ($\bar{1}\bar{2}$) $\bar{B}_2 2_1 \bar{1}'_3$ (0$\bar{1}\bar{1}$) ($\bar{1}$0) (0$\bar{2}\bar{1}$) ($\bar{2}$0) $\bar{B}_2 A_3 A_3$ (1$\bar{1}\bar{1}$) $\bar{B}_2 \bar{1}'_3 A_3$	
321	(112) $1_2 C_1 A_1$ (113) $1_2 3_1 A_1$ (1$\bar{2}\bar{2}$) $\bar{2}'_2 C_1 A_1$ (1$\bar{2}\bar{3}$) $\bar{2}'_2 3_1 A_1$ ($\bar{1}\bar{1}$2) ($\bar{1}\bar{2}$2) $\bar{B}_2 C_1 \bar{1}_3$ ($\bar{1}\bar{1}$3) ($\bar{1}\bar{2}$3) $\bar{B}_2 3_1 \bar{1}_3$	0 0 2
	[(0$\bar{1}\bar{2}$) ($\bar{1}\bar{1}$) $\bar{B}_2 B_3$ (0$\bar{2}\bar{2}$) $2_2 B_3$ (0$\bar{2}\bar{2}$) $\bar{2}'_2 B_3$ (0$\bar{2}\bar{3}$) $\bar{2}_2 B_3$ ($\bar{1}\bar{1}$2) ($\bar{1}\bar{2}$2) $\bar{B}_2 2_1$] + $\bar{1}_2$ (111) $1_2 B_1 A_1$ (112) $1_2 C_1 A_1$ (1$\bar{2}\bar{2}$) $\bar{2}'_2 C_1 A_1$	0 0 $\bar{2}$
	(0$\bar{2}\bar{3}$) $\bar{2}_2 B_3 \bar{1}'_2$	0 1 1 *
	[(0$\bar{2}\bar{3}$)] + $A_3 \bar{1}'_3$	0 $\bar{1}$ 1 *
	[(0$\bar{2}\bar{3}$) (1$\bar{2}\bar{3}$) $\bar{2}_2 \bar{B}_2/\bar{2}_2 2_3$] + A_3 (0$\bar{2}\bar{3}$) $\bar{2}_2 B_3 \bar{1}'_3$	0 $\bar{1}$ $\bar{1}$
	($\bar{1}\bar{1}$2) ($\bar{1}\bar{2}$2) $\bar{B}_2 C_1 \bar{1}'_2$ ($\bar{1}\bar{1}$3) ($\bar{1}\bar{2}$3) $\bar{B}_2 3_1 \bar{1}'_2$	0 1 2
	[(0$\bar{1}\bar{2}$) ($\bar{1}\bar{1}$) $\bar{B}_2 B_3$ (0$\bar{2}\bar{2}$) $2_2 B_3$ (0$\bar{2}\bar{2}$) $\bar{2}'_2 B_3$ (0$\bar{2}\bar{3}$) $\bar{2}_2 B_3$ ($\bar{1}\bar{1}$2) ($\bar{1}\bar{2}$2) $\bar{B}_2 2_1$] + $\bar{1}'_2$	0 1 $\bar{2}$
	[(002) $A_2 C_1$ (012) $B_2 C_1$ (003) $A_2 3_1$ (013) $B_2 3_1$ (022) $2_1 C_1$ (023) 2_2 3_1 (122) $2_1 C_1$ (123) $2_1 3_1$] + A_3	0 $\bar{1}$ 2
	[($\bar{1}\bar{1}$2) $\bar{1}$22) $\bar{B}_2 C_1$ ($\bar{1}\bar{1}$3) ($\bar{1}\bar{2}$3) $\bar{B}_2 3_1$] + $A_3 \bar{1}'_3$	
	[(002) $A_2 C_1$ (012) $B_2 C_1$ (0$\bar{1}\bar{2}$) $\bar{B}_2 B_3$ (021) $2_1 B_3$ (022) $2_1 C_1$ (0$\bar{2}\bar{2}$) $2_2 B_3$] + A_3	0 $\bar{1}$ 2
	[(121) $2_1 B_3$ (122) $2_1 C_1$ (1$\bar{2}\bar{2}$) $2_2 B_3$ (1$\bar{2}\bar{2}$) $\bar{2}'_2 B_3$ (1$\bar{2}\bar{3}$) $\bar{2}_2 B_3$] + A_3	
	[(0$\bar{1}\bar{2}$) ($\bar{1}\bar{1}$) $\bar{B}_2 B_3$ (0$\bar{2}\bar{2}$) $2_2 B_3$ (0$\bar{2}\bar{2}$) $\bar{2}'_2 B_3$ (0$\bar{2}\bar{3}$) $\bar{2}_2 B_3$ ($\bar{1}\bar{1}$2) ($\bar{1}\bar{2}$2) $\bar{B}_2 2_1$] + $A_3 \bar{1}'_3$	

223	(111) $1_2A_1l_1$ ($\bar{2}\bar{2}0$) ($\bar{2}\bar{2}1$) $\bar{2}_2A_3I_2$	0 0 0
	($\bar{2}\bar{2}0$) ($\bar{2}\bar{2}1$) $\bar{2}_2A_3I'_2$	0 1 0
	(120) (121) $2_1A_3l_1$ $[(\bar{2}\bar{2}0)$ ($\bar{2}\bar{2}1$) $\bar{2}_2A_3] + \bar{I}'_3$	0 Ī 0
	($\bar{2}\bar{2}0$) ($\bar{2}\bar{2}1$) $\bar{2}_2A_3A_3$	0 $\bar{I}\bar{I}$
	(111) $1_2A_2B_1$ (211) $1_2A_1B_1$ ($2\bar{1}\bar{1}$) ($2\bar{2}\bar{1}$) $\bar{B}_2I_3B_1$ ($\bar{2}\bar{2}1$) $\bar{2}'_2A_1B_1$	*1 0 0
	($2\bar{1}\bar{1}$) ($2\bar{2}\bar{1}$) $\bar{B}_2\bar{I}'_22_1$	*1 1 0
	(120) (121) $2_1A_3B_3$ $[(200)$ A_2A_3 (210) B_2A_3 ($2\bar{1}\bar{1}$) ($2\bar{2}\bar{1}$) $\bar{B}_2A_3/\bar{B}_2\bar{I}'_3$ (220) (221) $2_1A_3] + 2_1$	*1 Ī 0
	$[(010)$ B_1A_3 ($0\bar{1}\bar{1}$) ($0\bar{2}\bar{1}$) $\bar{B}_2A_3/\bar{B}_2\bar{I}'_3$ (020) (021) $2_1A_3] + A_3$	$\bar{I}\bar{I}$ 0
	$[(0\bar{1}\bar{1})$ ($\bar{1}\bar{1}0$) ($0\bar{2}\bar{1}$) ($\bar{1}\bar{2}0$) $\bar{B}_2A_3$ ($1\bar{1}\bar{1}$) $\bar{B}_2I'_3$ ($\bar{2}\bar{2}0$) ($\bar{2}\bar{2}1$) $\bar{2}_2A_3] + \bar{B}_2A_3$	
222	(111) $1_2l_1l_1$ ($1\bar{2}\bar{2}$) $\bar{2}_2I_2l_1$ ($\bar{2}\bar{2}1$) $\bar{2}_2l_1I_2$	0 0 0
	(111) $1_2B_1l_1$ (112) $1_22_1l_1$ ($1\bar{2}\bar{2}$) $\bar{2}'_22_1l_1$	0 0 1 *
	(121) $2_1l_2l_2$ ($1\bar{2}\bar{2}$) $\bar{2}_2I'_2l_2$ ($\bar{2}\bar{2}1$) $\bar{2}_2l_1I'_2$	0 1 0
	(121) $2_1l_1l_1$ ($1\bar{2}\bar{2}$) $\bar{2}_2A_3l_1/\bar{2}_2\bar{I}'_3l_1$ $[(\bar{2}\bar{2}1)$ $\bar{2}_2l_1] + \bar{I}'_3$	0 Ī 0
	(122) $2_12_1l_2$ ($\bar{2}\bar{2}1$) $\bar{2}_2B_3I'_2$ ($\bar{2}\bar{2}2$) $\bar{2}_22_1I'_2$	0 1 1 *
	(121) $2_1B_3l_1$ (122) $2_12_1l_1$ ($1\bar{2}\bar{2}$) $2_2B_3l_1$	0 Ī 1 *
	(120) (121) $2_1A_3l_1$ ($1\bar{2}\bar{2}$) $2_2\bar{B}_2l_1/2_22_3l_1$ ($1\bar{2}\bar{2}$) $\bar{2}_2\bar{B}_2l_1/\bar{2}_2A_3l_1/\bar{2}'_22_3l_1$ ($\bar{2}\bar{2}0$) ($\bar{2}\bar{2}1$) $\bar{2}_2A_3A_3$ ($\bar{2}\bar{2}1$) $\bar{2}_2B_3I'_3$ ($\bar{2}\bar{2}2$) $\bar{2}_22_1I'_3$	0 $\bar{I}\bar{I}$
	(111) $1_2l_1B_1$ ($1\bar{2}\bar{2}$) $\bar{2}_2I_2B_1$ (211) $1_2l_12_1$ ($\bar{2}\bar{2}1$) $\bar{2}'_2l_12_1$ ($2\bar{2}\bar{2}$) $\bar{2}_2I_32_1$	*1 0 0
	$[(111)$ 1_2B_1 (112) 1_22_1 ($1\bar{2}\bar{2}$) $\bar{2}'_22_1] + B_1$ $[(211)$ 1_2B_1 (212) 1_12_1 ($\bar{2}\bar{2}1$) $\bar{2}'_2B_1$ ($2\bar{2}\bar{2}$) ($\bar{2}\bar{2}2$) $\bar{2}'_22_1] + 2_1$	*1 0 1 *
	(221) $2_1l_22_1$ ($2\bar{2}\bar{2}$) $\bar{2}_2I'_22_1$	*1 1 0
	$[(121)$ 2_1l_1 ($1\bar{2}\bar{2}$) $\bar{2}_2A_3/\bar{2}_2\bar{I}'_3] + B_3$ $[(221)$ 2_1l_1 ($2\bar{2}\bar{2}$) $\bar{2}_2A_3/\bar{2}_2\bar{I}'_3] + 2_1$	*1 Ī 0
	$[(021)$ (121) 2_1l_1 ($0\bar{2}\bar{2}$) ($1\bar{2}\bar{2}$) $\bar{2}_2A_3/\bar{2}_2\bar{I}'_3] + A_3$ $[(\bar{2}\bar{2}1)$ 2_2l_1 ($\bar{2}\bar{2}1$) $\bar{2}'_2l_1] + \bar{B}_22_3$	$\bar{I}\bar{I}$ 0
	$[(010)$ B_1A_3 ($0\bar{1}\bar{1}$) ($0\bar{2}\bar{1}$) ($\bar{1}\bar{1}0$) ($\bar{1}\bar{2}0$) $\bar{B}_2A_3$ ($0\bar{1}\bar{1}$) ($0\bar{1}\bar{2}$) ($0\bar{2}\bar{1}$) $\bar{B}_2\bar{B}_2$ ($0\bar{1}\bar{2}$) $\bar{B}_22_3] + A_3$ $[(020)$ (021) (120) (121) 2_1A_3 ($0\bar{2}\bar{2}$) ($1\bar{2}\bar{2}$) $2_2\bar{B}_2/$ 2_22_3 ($0\bar{2}\bar{2}$) ($1\bar{2}\bar{2}$) $\bar{2}_2\bar{B}_2/\bar{2}_2A_3/\bar{2}'_22_3] + A_3$ ($\bar{2}\bar{2}0$) ($\bar{2}\bar{2}1$) $\bar{2}_2A_3A_3$ $[(0\bar{2}\bar{2})$ $\bar{2}_2A_3$ ($1\bar{2}\bar{2}$) $\bar{2}_2I'_3$ ($\bar{2}\bar{2}1$) $\bar{2}_2l_1] + \bar{B}_2A_3$	
	(212) $B_22_12_1$ (222) $2_12_12_1$	*1 1 1 *
	$[(121)$ 2_1B_3 (122) 2_12_1 ($1\bar{2}\bar{2}$) 2_2B_3 ($\bar{2}1\bar{2}$) $\bar{B}_22_1$ ($\bar{2}\bar{2}2$) 2_22_1 ($\bar{2}\bar{2}2$) $\bar{2}'_22_1] + B_3$	*1 Ī 1 *

($\beta\gamma\alpha$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
222	$[(202)\ A_1 2_1\ (212)\ B_2 2_1\ (221)\ 2_1 B_3\ (222)\ 2_1 2_1\ (2\bar{1}\bar{2})\ \bar{B}_2 B_3\ (2\bar{2}\bar{2})\ 2_2 B_3\ 2\bar{2}\bar{2})\ \bar{2}'_2 B_3] + 2_1$	
	$[(120)\ (121)\ 2_1 A_3\ (1\bar{2}\bar{2})\ 2_2\bar{B}_2/2_2 2_3\ (1\bar{2}\bar{2})\ \bar{2}_2\bar{B}_2/\bar{2}_2 A_3/\bar{2}'_2 2_3\ (\bar{2}\bar{2}1)\ 2_2 1_1\ (\bar{2}\bar{2}1)\ \bar{2}'_2 1_1] + B_3$	*1 $\bar{1}$ $\bar{1}$
	$[(200)\ A_2 A_3\ (210)\ B_2 A_3\ (2\bar{1}\bar{1})\ (2\bar{2}\bar{1})\ \bar{B}_2 A_3\ (2\bar{1}\bar{1})\ (2\bar{1}\bar{2})\ (2\bar{2}\bar{1})\ \bar{B}_2\bar{B}_2\ (2\bar{1}\bar{2})\ \bar{B}_2 2_3\ (220)\ (221)\ 2_1 A_3] + 2_1$	
	$[(002)\ A_2 2_1\ (012)\ B_2 2_1\ (0\bar{1}\bar{2})\ \bar{B}_2 B_3\ (021)\ (121)\ 2_1 B_3\ (022)\ (122)\ 2_1 2_1\ (0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ 2_2 B_3\ (0\bar{2}\bar{2})\ \bar{2}'_2 B_3] + A_3$	$\bar{1}$ $\bar{1}$ 1 *
	$[(\bar{1}\bar{1}2)\ (\bar{1}\bar{2}2)\ (\bar{2}\bar{1}2)\ \bar{B}_2 2_1\ (0\bar{2}\bar{2})\ 2_2 B_3\ (0\bar{1}\bar{2})\ (\bar{1}\bar{1}1)\ \bar{B}_2 B_3\ (\bar{2}\bar{2}1)\ \bar{2}_2 B_3\ (\bar{2}\bar{2}2)\ 2_2 2_1\ (\bar{2}\bar{2}2)\ \bar{2}_2 2_1/\bar{2}'_2 2_1] + \bar{B}_2$	
	$[(\bar{2}\bar{1}2)\ \bar{B}_2 2_1\ (\bar{2}\bar{2}2)\ 2_2 2_1\ (\bar{2}\bar{2}2)\ \bar{2}'_2 2_1] + 2_3$	
221	$(112)\ 1_1 C_1 1_1\ \ (113)\ 1_1 3_1 1_1\ \ (1\bar{2}\bar{2})\ \bar{2}'_2 C_1 1_1\ \ (1\bar{2}\bar{3})\ \bar{2}'_2 3_1 1_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_2 C_1 \bar{1}_3\ \ (\bar{2}\bar{2}3)\ \bar{2}_2 3_1 \bar{1}_3$	0 0 2
	$(111)\ 1_2 B_1 1_1\ \ (112)\ 1_2 C_1 1_1\ \ (1\bar{2}\bar{2})\ \bar{2}'_2 C_1 1_1\ \ (\bar{2}\bar{2}1)\ \bar{2}_2 B_3 \bar{1}_2\ \ (\bar{2}\bar{2}2)\ \bar{2}_2 2_1 \bar{1}_2$	0 0 $\bar{2}$
	$(122)\ 2_1 C_1 1_2\ \ (123)\ 2_1 3_1 1_2\ \ (\bar{2}\bar{2}2)\ \bar{2}_2 C_1 \bar{1}'_2\ \ (\bar{2}\bar{2}3)\ \bar{2}_2 3_1 \bar{1}'_2$	0 1 2
	$(122)\ 2_1 C_1 1_2\ \ (\bar{2}\bar{2}1)\ \bar{2}_2 B_3 \bar{1}'_2\ \ (\bar{2}\bar{2}2)\ \bar{2}_2 2_1 \bar{1}'_2$	0 1 $\bar{2}$
	$(122)\ 2_1 C_1 1_1\ \ (123)\ 2_1 3_1 1_2\ \ [(\bar{2}\bar{2}2)\ \bar{2}_2 C_1\ \ (\bar{2}\bar{2}3)\ \bar{2}_2 3_1] + \bar{1}'_3 A_3$	0 $\bar{1}$ 2
	$[(121)\ 2_1 B_3\ (122)\ 2_1 C_1\ (1\bar{2}\bar{2})\ 2_2 B_3\ (1\bar{2}\bar{2})\ \bar{2}'_2 B_3\ (1\bar{2}\bar{3})\ \bar{2}_2 B_3] + 1_1\ \ [(\bar{2}\bar{2}1)\ \bar{2}_2 B_3\ (\bar{2}\bar{2}2)\ \bar{2}_2 2_1] + A_3$	0 $\bar{1}$ $\bar{2}$
	$(121)\ 2_1 B_3 1_1\ \ (1\bar{2}\bar{2})\ 2_2 B_3 1_1\ \ (1\bar{2}\bar{2})\ \bar{2}'_2 B_3 1_1\ \ (1\bar{2}\bar{3})\ \bar{2}_2 B_3 1_1$	0 $\bar{1}$ $\bar{2}$
	$(112)\ 1_2 C_1 B_1\ \ (113)\ 1_2 3_1 B_1\ \ (1\bar{2}\bar{2})\ \bar{2}'_2 C_1 B_1\ \ (1\bar{2}\bar{3})\ \bar{2}'_2 3_1 B_1$	*1 0 2
	$(212)\ 1_1 C_1 2_1\ \ (213)\ 1_1 3_1 2_1\ \ (2\bar{2}\bar{2})\ (\bar{2}\bar{2}2)\ \bar{2}'_2 C_1 2_1\ \ (2\bar{2}\bar{3})\ (\bar{2}\bar{2}3)\ \bar{2}'_2 3_1 2_1$	
	$[(111)\ 1_2 B_1\ (112)\ 1_2 C_1\ (1\bar{2}\bar{2})\ \bar{2}'_2 C_1] + B_1\ \ [(211)\ 1_2 B_1\ (212)\ 1_2 C_1\ (\bar{2}\bar{2}1)\ \bar{2}'_2 B_1\ (2\bar{2}\bar{2})\ (\bar{2}\bar{2}2)\ \bar{2}'_2 C_1\ (2\bar{2}\bar{3})\ \bar{2}'_2 3_1] + 2_1$	*1 0 $\bar{2}$
	$(0\bar{2}\bar{3})\ (1\bar{2}\bar{3})\ \bar{2}_2\bar{B}_2 A_3/\bar{2}_2 2_3 A_3$	$\bar{1}$ $\bar{1}$ 0
	$(2\bar{2}\bar{3})\ \bar{2}_2 B_3 2_1$	*1 $\bar{1}$ 1 *
	$(1\bar{2}\bar{3})\ \bar{2}_2\bar{B}_2 B_3/\bar{2}_2 2_3 B_3\ \ (2\bar{2}\bar{3})\ \bar{2}_2 B_2 2_1/\bar{2}_2 2_3 2_1$	*1 $\bar{1}$ $\bar{1}$
	$(0\bar{2}\bar{3})\ \bar{2}_2 B_3\bar{B}_2$	$\bar{1}$ $\bar{1}$ 1 *
	$(212)\ B_2 C_1 2_1\ \ (213)\ B_2 3_1 2_1\ \ (222)\ 2_1 C_1 2_1\ \ (223)\ 2_1 3_1 2_1$	*1 1 2
	$(212)\ B_2 C_1 2_1\ \ (222)\ 2_1 C_1 2_1$	*1 1 $\bar{2}$

	$[(122)\ 2_1C_1\ (123)\ 2_1\mathrm{3}_1\ (\overline{2}\overline{1}2)\ \bar{B}_2C_1\ (\overline{2}\overline{1}3)\ \bar{B}_2\mathrm{3}_1\ (\overline{2}\overline{2}2)\ 2_2C_1\ (\overline{2}\overline{2}3)\ 2_2\mathrm{3}_1\ (\overline{\overline{2}2}2)\ \bar{2}'_2C_1\ (\overline{\overline{2}2}3)\ \bar{2}'_2\mathrm{3}_1] + B_3$	*1 Ī 2
	$[(202)\ A_2C_1\ (212)\ B_2C_1\ (203)\ A_2\mathrm{3}_1\ (213)\ B_2\mathrm{3}_1\ (222)\ 2_1C_1\ (223)\ 2_1\mathrm{3}_1] + 2_1$	
	$[(121)\ 2_1B_3\ (122)\ 2_1C_1\ (1\overline{2}\overline{2})\ 2_2B_3\ (1\overline{2}\overline{\overline{2}})\ \bar{2}'_2B_3\ (1\overline{2}\overline{\overline{3}})\ \bar{2}_2B_3\ (\overline{2}\overline{1}2)\ \bar{B}_2C_1\ (\overline{2}\overline{2}2)\ 2_2C_1\ (\overline{\overline{2}2}2)\ \bar{2}'_2C_1] + B_3$	*1 Ī 2
	$[(202)\ A_2C_1\ (212)\ B_2C_1\ (2\overline{1}\overline{2})\ \bar{B}_2B_3\ (221)\ 2_1B_3\ (222)\ 2_1C_1\ (2\overline{2}\overline{2})\ 2_2B_3\ (2\overline{\overline{2}}\overline{2})\ \bar{2}'_2B_3\ (2\overline{\overline{2}}\overline{\overline{3}})\ \bar{2}'_2B_3] + 2_1$	
	$(2\overline{1}\overline{2})\ \bar{B}_2B_32_1\quad (221)\ 2_1B_32_1\quad (2\overline{2}\overline{2})\ 2_2B_32_1\quad (2\overline{\overline{2}}\overline{2})\ \bar{2}'_2B_32_1\quad (2\overline{\overline{2}}\overline{\overline{3}})\ \bar{2}_2B_32_1$	*1 $\overline{1}$ 2
	$[(002)\ A_2C_1\ (012)\ B_2C_1\ (003)\ A_2\mathrm{3}_1\ (013)\ B_2\mathrm{3}_1\ (022)\ (122)\ 2_1C_1\ (023)\ (123)\ 2_1\mathrm{3}_1] + A_3$	$\overline{1}$ 1 2
	$[(\overline{1}\overline{1}2)\ (\overline{1}\overline{2}2)\ \bar{B}_2C_1\ (\overline{1}\overline{1}3)\ (\overline{1}\overline{2}3)\ \bar{B}_2\mathrm{3}_1\ (\overline{\overline{2}}\overline{2}2)\ \bar{2}_2C_1\ (\overline{\overline{2}}\overline{2}3)\ \bar{2}_2\mathrm{3}_1] + \bar{B}_2A_3\quad [(\overline{2}\overline{1}2)\ \bar{B}_2C_1\ (\overline{2}\overline{2}2)\ 2_2C_1\ (\overline{\overline{2}}\overline{2}2)\ \bar{2}'_2C_1\ (\overline{2}\overline{1}3)\ \bar{B}_2\mathrm{3}_1\ (\overline{2}\overline{2}3)\ 2_2\mathrm{3}_1$ $(\overline{\overline{2}}\overline{2}3)\ \bar{2}'_2\mathrm{3}_1] + \bar{B}_22_3$	
	$[(002)\ A_2C_1\ (012)\ B_2C_1\ (0\overline{1}\overline{2})\ \bar{B}_2B_3\ (021)\ (121)\ 2_1B_3\ (022)\ (122)\ 2_1C_1\ (0\overline{2}\overline{2})\ (1\overline{2}\overline{2})\ 2_2B_3] + A_3\quad [(1\overline{2}\overline{\overline{2}})\ \bar{2}'_2B_3\ (1\overline{2}\overline{\overline{3}})\ \bar{2}_2B_3] + A_3$	$\overline{1}$ 1 2
	$[(0\overline{2}\overline{2})\ 2_2B_3\ (0\overline{2}\overline{\overline{2}})\ \bar{2}'_2B_3\ (0\overline{2}\overline{\overline{3}})\ (\overline{\overline{2}}2\overline{1})\ \bar{2}_2B_3\ (0\overline{1}\overline{2})\ (\overline{1}\overline{1}1)\ \bar{B}_2B_3] + \bar{B}_2A_3\quad [(\overline{1}\overline{1}2)\ (\overline{1}\overline{2}2)\ \bar{B}_22_1\ (\overline{\overline{2}}\overline{2}2)\ \bar{2}_22_1] + \bar{B}_2A_3$	
	$[(\overline{2}\overline{1}2)\ \bar{B}_2C_1\ (\overline{2}\overline{2}2)\ 2_2C_1\ (\overline{\overline{2}}\overline{2}2)\ \bar{2}'_2C_1] + \bar{B}_22_3$	
123	$[(211)\ 1_2A_1\ (2\overline{1}\overline{1})\ (2\overline{2}\overline{1})\ \bar{B}_2\bar{1}_3\ (\overline{\overline{2}}\overline{2}1)\ \bar{2}'_2A_1] + C_1\quad [(311)\ 1_2A_1\ (3\overline{1}\overline{1})\ (3\overline{2}\overline{1})\ \bar{B}_2\bar{1}_3\ (\overline{3}\overline{2}1)\ \bar{2}'_2A_1] + 3_1$	2 0 0
	$(111)\ 1_2A_1B_1\quad [(211)\ 1_2A_1\quad (2\overline{1}\overline{1})\ (2\overline{2}\overline{1})\ \bar{B}_2\bar{1}_3\quad (\overline{\overline{2}}\overline{2}1)\ \bar{2}'_2A_1] + C_1$	$\bar{2}$ 0 0
	$(2\overline{1}\overline{1})\ (2\overline{2}\overline{1})\ \bar{B}_2\bar{1}'_2C_1\quad (3\overline{1}\overline{1})\ (3\overline{2}\overline{1})\ \bar{B}_2\bar{1}'_23_1$	2 1 0
	$(2\overline{1}\overline{1})\ (2\overline{2}\overline{1})\ \bar{B}_2\bar{1}'_2C_1$	$\bar{2}$ 1 0
	$(300)\ A_2A_33_1\quad (310)\ B_2A_33_1\quad (3\overline{1}\overline{1})\ (3\overline{2}\overline{1})\ \bar{B}_2A_33_1/\bar{B}_2\bar{1}'_33_1\quad (320)\ (321)\ 2_1A_33_1$	2 Ī 0
	$(200)\ A_2A_3C_1\quad (210)\ B_2A_3C_1\quad (2\overline{1}\overline{1})\ (2\overline{2}\overline{1})\ \bar{B}_2A_3C_1/\bar{B}_2\bar{1}'_3C_1\quad (220)\ (221)\ 2_1A_3C_1$	*2 Ī 0
	$(120)\ (121)\ 2_1A_3B_3$	$\bar{2}$ Ī 0
	$(120)\ (121)\ 2_1A_3B_3$	$\bar{2}\overline{1}$ 0
122	$[(\overline{3}\overline{2}1)\ \bar{2}_21_1] + \bar{B}_22_3$	$\overline{1}$ 1 0
	$[(\overline{3}\overline{2}\overline{2})\ \bar{2}_22_1] + B_3$	*1 Ī 1 *
	$(\overline{3}\overline{2}1)\ \bar{2}_21_1B_3$	*1 $\overline{1}$ 1
	$[(\overline{3}\overline{2}\overline{2})\ \bar{2}_22_1] + \bar{B}_22_3$	$\overline{1}$ 1 1 *
	$[(211)\ 1_21_1\quad (\overline{2}\overline{2}1)\ \bar{2}'_21_1\quad (2\overline{\overline{2}}\overline{2})\ \bar{2}_2\bar{1}_3] + C_1\quad [(311)\ 1_21_1\quad (\overline{3}\overline{2}1)\ \bar{2}'_21_1\quad (3\overline{2}\overline{\overline{2}})\ \bar{2}_2\bar{1}_3] + 3_1$	2 0 0
	$(111)\ 1_21_2B_1\quad (1\overline{2}\overline{\overline{2}})\ \bar{2}_2\bar{1}_2B_1\quad (211)\ 1_21_1C_1\quad (\overline{\overline{2}}\overline{2}1)\ \bar{2}'_21_1C_1\quad (2\overline{\overline{2}}\overline{\overline{2}})\ \bar{2}_2\bar{1}_3C_1$	$\bar{2}$ 0 0

($\beta\gamma\alpha$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
122	$[(211)\ 1_1B_1\ \ (212)\ 1_12_1\ \ (\overline{2}\overline{2}1)\ \overline{2}'_2B_1\ \ (2\overline{2}\overline{2})\ (\overline{2}\overline{2}2)\ \overline{2}'_22_1] + C_1\ \ [(311)\ 1_2B_1\ \ (312)\ 1_12_1\ \ (\overline{3}21)\ \overline{2}'_2B_1\ \ (3\overline{2}\overline{2})\ (\overline{3}\overline{2}2)\ \overline{2}'_22_1] + 3_1$	2 0 1
	$[(111)\ 1_2B_1\ \ (112)\ 1_22_1\ \ (1\overline{2}\overline{2})\ \overline{2}'_22_1] + B_1\ \ [(211)1_2B_1\ \ (212)\ 1_12_1\ \ (\overline{2}21)\ \overline{2}'_2B_1\ \ (2\overline{2}\overline{2})\ (\overline{2}\overline{2}2)\overline{2}'_22_1] + C_1$	$\bar{2}$ 0 1
	$(221)\ 2_11_2C_1\ \ (2\overline{2}\overline{2})\ \overline{2}_2\overline{1}'_2C_1\ \ (321)\ 2_11_23_1\ \ (3\overline{2}\overline{2})\ \overline{2}_2\overline{1}'_23_1$	2 1 0
	$(221)\ 2_11_2C_1\ \ (2\overline{2}\overline{2})\ \overline{2}_2\overline{1}'_2C_1$	$\bar{2}$ 1 0
	$(221)\ 2_11_1C_1\ \ (2\overline{2}\overline{2})\ \overline{2}_2A_3C_1/\overline{2}_2\overline{1}'_3C_1\ \ (3\bar{2}1)\ 2_11_13_1\ \ (3\overline{2}\overline{2})\ \overline{2}_2A_33_1/\overline{2}_2\overline{1}'_33_1$	2 $\bar{1}$ 0
	$(121)\ 2_11_1B_1\ \ (1\overline{2}\overline{2})\ \overline{2}_2A_3B_1/\overline{2}_2\overline{1}'_3B_1\ \ (221)\ 2_11_1C_1\ \ (2\overline{2}\overline{2})\ \overline{2}_2A_3C_1/\overline{2}_2\overline{1}'_3C_1$	$\bar{2}$ $\bar{1}$ 0
	$[(121)\ 2_11_1\ \ (1\overline{2}\overline{2})\ \overline{2}_2A_3/\overline{2}_2\overline{1}'_3] + B_3$	$\bar{2}$ $\bar{1}$ 0
	$[(120)\ (121)\ 2_1A_3\ \ (1\overline{2}\overline{2})\ 2_2\bar{B}_2/2_22_3\ \ (1\overline{2}\overline{2})\ \overline{2}_2\bar{B}_2/\overline{2}_2A_3/\overline{2}_22_3\ \ (\overline{2}21)\ 2_21_1\ \ (\overline{2}21)\ \overline{2}'_21_1\ \ (\overline{3}21)\ \overline{2}_21_1] + B_3$	
	$(212)\ B_22_1C_1\ \ (222)\ 2_12_1C_1\ \ (312)\ B_22_13_1\ \ (322)\ 2_12_13_1$	2 1 1 *
	$(212)\ B_22_1C_1\ \ (222)\ 2_12_1C_1$	$\bar{2}$ 1 1 *
	$(302)\ A_22_13_1\ \ (312)\ B_22_13_1\ \ (3\overline{1}\overline{2})\ \bar{B}_2B_33_1\ \ (321)\ 2_1B_33_1\ \ (322)\ 2_12_13_1\ \ (3\overline{2}\overline{2})\ 2_2B_33_1\ \ (3\overline{2}\overline{2})\ \overline{2}'_2B_33_1$	2 $\bar{1}$ 1 *
	$[(202)\ A_22_1\ \ (212)\ B_22_1\ \ (2\overline{1}\overline{2})\ \bar{B}_2B_3\ \ (221)\ 2_1B_3\ \ (222)\ 2_12_1\ \ (2\overline{2}\overline{2})\ 2_2B_3\ \ (2\overline{2}\overline{2})\ \overline{2}'_2B_3] + C_1$	$\bar{2}$ $\bar{1}$ 1 *
	$[(121)\ 2_1B_3\ \ (122)\ 2_12_1\ \ (1\overline{2}\overline{2})\ 2_2B_3\ \ (\overline{2}\overline{1}2)\ \bar{B}_22_1\ \ (\overline{2}\overline{2}2)\ 2_22_1\ \ (\overline{2}\overline{2}2)\ \overline{2}'_22_1\ \ (\overline{2}\overline{3}2)\ \overline{2}_22_1] + B_3$	
	$[(300)\ A_2A_2\ \ (310)\ B_2A_3\ \ (3\overline{1}\overline{1})\ (3\bar{2}\overline{1})\ \bar{B}_2A_3\ \ (3\overline{1}\overline{1})\ (3\overline{1}\overline{2})\ (3\bar{2}\overline{1})\ \bar{B}_2\bar{B}_2\ \ (3\overline{1}\overline{2})\ \bar{B}_22_3] + 3_1$	2 $\bar{1}$ $\bar{1}$
	$[(320)\ (321)\ 2_1A_3\ \ (3\overline{2}\overline{2})\ 2_2\bar{B}_2/2_22_3\ \ (3\overline{2}\overline{2})\ \overline{2}_2\bar{B}_2/\overline{2}'_22_3/\overline{2}_2A_3] + 3_1$	
	$[(200)\ A_2A_3\ \ (210)\ B_2A_3\ \ (2\overline{1}\overline{1})\ (2\bar{2}\overline{1})\ \bar{B}_2A_3\ \ (2\overline{1}\overline{1})\ (2\overline{1}\overline{2})\ (2\bar{2}\overline{1})\ \bar{B}_2\bar{B}_2\ \ (2\overline{1}\overline{2})\ \bar{B}_22_3] + C_1$	*2 $\bar{1}$ $\bar{1}$
	$[(220)\ (221)\ 2_1A_3\ \ (2\overline{2}\overline{2})\ 2_2\bar{B}_2/2_22_3\ \ (2\overline{2}\overline{2})\ \overline{2}_2\bar{B}_2/\overline{2}'_22_3/\overline{2}_2A_3] + C_1$	
	$[(120)\ (121)\ 2_1A_3\ \ (1\overline{2}\overline{2})\ 2_2\bar{B}_2/2_22_3\ \ (1\overline{2}\overline{2})\ \overline{2}_2\bar{B}_2/\overline{2}'_22_3/\overline{2}_2A_3] + B_3\ \ (\overline{2}21)\ 2_21_1B_3\ \ (\overline{2}21)\ \overline{2}'_21_1B_3\ \ (\overline{3}21)\ \overline{2}_21_1B_3$	$\bar{2}$ $\bar{1}$ $\bar{1}$
	$[(121)\ 2_1B_3\ \ (122)\ 2_12_1\ \ (1\overline{2}\overline{2})\ 2_2B_3\ \ (\overline{2}\overline{1}2)\ \bar{B}_22_1\ \ (\overline{2}\overline{2}2)\ 2_22_1\ \ (\overline{2}\overline{2}2)\ \overline{2}'_22_1\ \ (\overline{3}\overline{2}2)\ \overline{2}_22_1] + B_3$	$\bar{2}$ $\bar{1}$ 1 *
121	$[(\overline{3}\overline{2}2)\ \overline{2}_2C_1\ \ (\overline{3}\overline{2}3)\ \overline{2}_23_1] + B_3$	*1 $\bar{1}$ 2
	$[(\overline{3}\overline{2}2)\ \overline{2}_2C_1] + B_3$	*1 $\bar{1}$ $\bar{2}$
	$[(\overline{3}\overline{2}2)\ \overline{2}_2C_1\ \ (\overline{3}\overline{2}3)\ \overline{2}_23_1] + \bar{B}_22_3$	$\bar{1}$ $\bar{1}$ 2
	$[(\overline{3}\overline{2}2)\ \overline{2}_2C_1] + B_3$	$\bar{1}$ $\bar{1}$ $\bar{2}$

(312) $1_1C_13_1$ (313) $1_13_13_1$ ($3\bar{2}\bar{2}$) ($\bar{3}\bar{2}2$) $\bar{2}'_2C_13_1$ ($3\bar{2}\bar{3}$) ($\bar{3}\bar{2}3$) $\bar{2}'_23_13_1$	2 0 2
(212) $1_1C_1C_1$ (213) $1_13_1C_1$ ($2\bar{2}\bar{2}$) ($\bar{2}\bar{2}2$) $\bar{2}'_2C_1C_1$ ($2\bar{2}\bar{3}$) ($\bar{2}\bar{2}3$) $\bar{2}'_23_1C_1$	*2 0 2
(112) $1_2C_1B_1$ (113) $1_23_1B_1$ ($1\bar{2}\bar{2}$) $\bar{2}'_2C_1B_1$ ($1\bar{2}\bar{3}$) $\bar{2}'_23_1B_1$	$\bar{2}$ 0 2
(311) $1_2B_13_1$ (312) $1_2C_13_1$ ($\bar{3}\bar{2}1$) $\bar{2}'_2B_13_1$ ($3\bar{2}\bar{2}$) ($\bar{3}\bar{2}2$) $\bar{2}'_2C_13_1$	2 0 $\bar{2}$
(211) $1_2B_1C_1$ (212) $1_2C_1C_1$ ($\bar{2}\bar{2}1$) $\bar{2}'_2B_1C_1$ ($2\bar{2}\bar{2}$) ($\bar{2}\bar{2}2$) $\bar{2}'_2C_1C_1$	*2 0 $\bar{2}$
(111) $1_2B_1B_1$ (112) $1_2C_1B_1$ ($1\bar{2}\bar{2}$) $\bar{2}'_2C_1B_1$	$\bar{2}$ 0 $\bar{2}$
($1\bar{2}\bar{3}$) $\bar{2}_2\bar{B}_2B_3/\bar{2}_22_3B_3$	$\bar{2}$ $\bar{1}$ 0
($2\bar{2}\bar{3}$) $\bar{2}_2B_3C_1$ ($3\bar{2}\bar{3}$) $\bar{2}_2B_33_1$	2 $\bar{1}$ 1 *
($2\bar{2}\bar{3}$) $\bar{2}_2B_3C_1$	$\bar{2}$ $\bar{1}$ 1 *
($2\bar{2}\bar{3}$) $\bar{2}_2\bar{B}_2C_1/\bar{2}_22_3C_1$ ($3\bar{2}\bar{3}$) $\bar{2}_2\bar{B}_23_1/\bar{2}_22_33_1$	2 $\bar{1}$ $\bar{1}$
($1\bar{2}\bar{3}$) $\bar{2}_2\bar{B}_2B_3/\bar{2}_22_3B_3$ ($2\bar{2}\bar{3}$) $\bar{2}_2\bar{B}_2C_1/\bar{2}_22_3C_1$	2 $\bar{1}$ $\bar{1}$
[(212) B_2C_1 (213) B_23_1 (222) 2_1C_1 (223) 2_13_1] + C_1 [(312) B_2C_1 (313) B_23_1 (322) 2_1C_1 (323) 2_13_1] + 3_1	2 1 2
(212) $B_2C_1C_1$ (213) $B_23_1C_1$ (222) $2_1C_1C_1$ (223) $2_13_1C_1$	$\bar{2}$ 1 2
(212) $B_2C_1C_1$ (222) $2_1C_1C_1$ (312) $B_2C_13_1$ (322) $2_1C_13_1$	2 1 $\bar{2}$
(212) $B_2C_1C_1$ (222) $2_1C_1C_1$	$\bar{2}$ 1 $\bar{2}$
(302) $A_2C_13_1$ (312) $B_2C_13_1$ (303) $A_23_13_1$ (313) $B_23_13_1$ (322) $2_1C_13_1$ (323) $2_13_13_1$	2 $\bar{1}$ 2
(202) $A_2C_1C_1$ (212) $B_2C_1C_1$ (203) $A_23_1C_1$ (213) $B_23_1C_1$ (222) $2_1C_1C_1$ (223) $2_13_1C_1$	*2 $\bar{1}$ 2
[(122) 2_1C_1 (123) 2_13_1 ($2\bar{1}\bar{2}$) $\bar{B}_2C_1$ ($2\bar{1}\bar{3}$) $\bar{B}_23_1$ ($2\bar{2}\bar{2}$) 2_2C_1($2\bar{2}\bar{3}$) 2_23_1 ($\bar{2}\bar{2}2$) $\bar{2}'_2C_1$ ($\bar{2}\bar{2}3$) $\bar{2}'_23_1$ ($\bar{3}\bar{2}2$) $\bar{2}_2C_1$ ($\bar{3}\bar{2}3$) $\bar{2}_23_1$] + B_3	$\bar{2}$ $\bar{1}$ 2
[(302) A_2C_1 (312) B_2C_1 ($3\bar{1}\bar{2}$) $\bar{B}_2B_3$ (321) 2_1B_3 (322) 2_1C_1 ($3\bar{2}\bar{2}$) 2_2B_3 ($3\bar{2}\bar{2}$) $\bar{2}'_2B_3$ ($3\bar{2}\bar{3}$) $\bar{2}_2B_3$] + 3_1	2 $\bar{1}$ $\bar{2}$
[(202) A_2C_1 (212) B_2C_1 ($2\bar{1}\bar{2}$) $\bar{B}_2B_3$ (221) 2_1B_3 (222) 2_1C_1 ($2\bar{2}\bar{2}$) 2_2B_3 ($2\bar{2}\bar{2}$) $\bar{2}'_2B_3$ ($2\bar{2}\bar{3}$) $\bar{2}_2B_3$] + C_1	*2 $\bar{1}$ $\bar{2}$
[(121) 2_1B_3 (122) 2_1C_1 ($1\bar{2}\bar{2}$) 2_2B_3 ($1\bar{2}\bar{2}$) $\bar{2}'_2B_3$ ($1\bar{2}\bar{3}$) $\bar{2}_2B_3$] + B_3	$\bar{2}$ $\bar{1}$ $\bar{2}$
[($\bar{2}\bar{1}2$) B_2C_1 ($\bar{2}\bar{2}2$) 2_2C_1 ($\bar{2}\bar{2}2$) $\bar{2}'_2C_1$ ($\bar{3}\bar{2}2$) $\bar{2}_2C_1$] + B_3	
[($3\bar{1}\bar{2}$) $\bar{B}_2B_3$ (321) 2_1B_3 ($3\bar{2}\bar{2}$) 2_2B_3 ($3\bar{2}\bar{2}$) $\bar{2}'_2B_3$ ($3\bar{2}\bar{3}$) $\bar{2}_2B_3$] + 3_1	2 $\bar{1}$ 2
[($2\bar{1}\bar{2}$) $\bar{B}_2B_3$ (221) 2_1B_3 ($2\bar{2}\bar{2}$) 2_2B_3 ($2\bar{2}\bar{2}$) $\bar{2}'_2B_3$ ($2\bar{2}\bar{3}$) $\bar{2}_2B_3$] + C_1	*2 $\bar{1}$ 2
[(122) 2_1C_1 (123) 2_13_1 ($2\bar{1}\bar{2}$) $\bar{B}_2C_1$ ($2\bar{1}\bar{3}$) $\bar{B}_23_1$ ($\bar{2}\bar{2}2$) 2_2C_1 ($\bar{2}\bar{2}3$) 2_23_1] + B_3	$\bar{2}$ $\bar{1}$ 2
[($\bar{2}\bar{2}2$) $\bar{2}'_2C_1$ ($\bar{2}\bar{2}3$) $\bar{2}'_23_1$ ($\bar{3}\bar{2}2$) $\bar{2}_2C_1$ ($\bar{3}\bar{2}3$) $\bar{2}_23_1$] + B_3	
[(121) 2_1B_3 (122) 2_1C_1 ($1\bar{2}\bar{2}$) 2_2B_3 ($1\bar{2}\bar{2}$) $\bar{2}'_2B_3$ ($1\bar{2}\bar{3}$) $\bar{2}_2B_3$] + B_3	$\bar{2}$ $\bar{1}$ 2
[($\bar{2}\bar{1}2$) B_2C_1 ($\bar{2}\bar{2}2$) 2_2C_1 ($\bar{2}\bar{2}2$) $\bar{2}'_2C_1$ ($\bar{3}\bar{2}2$) $\bar{2}_2C_1$] + B_3	

($\alpha\gamma$) Pattern

σ-Block	Set	Substrates and Sequences by Polarity − −	− +	+ −	+ +	Product α β γ
33		(101) A_1A_1	(0$\bar{1}\bar{1}$) ($\bar{1}\bar{1}$0) (1$\bar{1}\bar{1}$) $A_3\bar{1}_2$		($\bar{1}\bar{1}$1) $\bar{1}'_3\bar{1}_2$	0 0 0
		(0$\bar{1}\bar{1}$) ($\bar{1}\bar{1}$0) (1$\bar{1}\bar{1}$) $A_3\bar{1}'_2$		($\bar{1}\bar{1}$1) $\bar{1}'_3\bar{1}'_2$	($\bar{1}$21) $\bar{1}'_3\bar{1}_2$	0 1 0
		(020) (021) (120) (121) (02$\bar{1}$) (12$\bar{1}$) ($\bar{1}$20) ($\bar{1}$21) ($\bar{1}\bar{2}$1) ($\bar{1}$2$\bar{1}$) ($\bar{1}\bar{2}$0) $\bar{1}'_2A_2$	A_2A_2	($\bar{1}\bar{2}$1) $\bar{1}'_3\bar{1}'_2$		0 2 0
32			(101) $A_1\bar{1}_1$		($\bar{1}\bar{1}$1) $\bar{1}_2\bar{1}_1$	0 0 0
			($\bar{1}\bar{1}$1) $\bar{1}'_2\bar{1}_1/\bar{1}'_2\bar{1}_2$		($\bar{1}$21) $\bar{1}_2\bar{1}_1$	0 1 0
		(0$\bar{2}\bar{2}$) (1$\bar{2}\bar{2}$) $A_3\bar{2}'_2$	(021) (121) ($\bar{1}$21) $A_2\bar{1}_1$ ($\bar{1}\bar{2}$1) $\bar{1}'_2\bar{1}_1$			0 2 0
		(101) A_1B_1	(102) $A_1\bar{2}_1$	($\bar{1}\bar{1}$1) $\bar{1}_2B_1$	($\bar{1}\bar{1}$2) $\bar{1}_3\bar{2}_1$	0 0 1
		(101) A_1B_1	(102) $A_1\bar{2}_1$	($\bar{1}\bar{1}$1) $\bar{1}_2B_1$	($\bar{1}\bar{1}$2) $\bar{1}_3\bar{2}_1$	0 0 $\bar{1}$
			($\bar{1}\bar{1}$2) $\bar{1}'_2\bar{2}_1$		($\bar{1}\bar{2}$2) $\bar{1}_3\bar{2}_1$	0 1 1
			($\bar{1}\bar{1}$2) $\bar{1}'_2\bar{2}_1$		($\bar{1}\bar{2}$2) $\bar{1}_3\bar{2}_1$	0 1 $\bar{1}$
	A	(0$\bar{1}\bar{1}$) (1$\bar{1}\bar{1}$) ($\bar{1}\bar{1}$0) $A_3A_3/A_3\bar{B}_2$	(0$\bar{2}\bar{2}$) (1$\bar{2}\bar{2}$) $A_3\bar{2}_2$	($\bar{1}\bar{1}$1) $\bar{1}'_3\bar{B}_2/\bar{1}'_3A_3$		0 $\bar{1}$ $\bar{1}$
		(021) (121) ($\bar{1}$21) A_2B_2 ($\bar{1}\bar{2}$1) $\bar{1}'_2B_2$	(022) (122) ($\bar{1}$22) $A_2\bar{2}_1$ ($\bar{1}\bar{2}$2) $\bar{1}'_2\bar{2}_1$			0 2 1
	A	(021) (121) ($\bar{1}$21) A_2A_2/A_2B_2 ($\bar{1}\bar{2}$1) $\bar{1}'_2A_2/\bar{1}'_2B_2$	(022) (122) ($\bar{1}$22) $A_2\bar{2}_1$ ($\bar{1}\bar{2}$2) $\bar{1}'_2\bar{2}_1$			0 2 $\bar{1}$
	B	(0$\bar{2}\bar{2}$) (1$\bar{2}\bar{2}$) $A_3\bar{2}'_2$		($\bar{1}\bar{2}$1) $\bar{1}'_3\bar{B}_2$		0 $\bar{2}$ $\bar{1}$
31		(102) A_1C_1	(103) $A_1\bar{3}_1$	($\bar{1}\bar{2}$1) $\bar{1}_3C_1$	($\bar{1}\bar{3}$1) $\bar{1}_3\bar{3}_1$	0 0 2
	A	(101) A_1B_1 (102) A_1C_1		($\bar{1}\bar{2}$1) $\bar{1}_3C_1$		0 0 $\bar{2}$
		($\bar{1}\bar{2}$1) $\bar{1}'_2C_1$	($\bar{1}\bar{3}$1) $\bar{1}'_2\bar{3}_1$	($\bar{1}\bar{2}\bar{2}$1) $\bar{1}_3C_1$	($\bar{1}\bar{2}\bar{3}$1) $\bar{1}_3C_1$	0 1 2
	A	($\bar{1}\bar{1}$1) $\bar{1}'_2B_1$ ($\bar{1}\bar{2}$1) $\bar{1}'_2C_1$		($\bar{1}\bar{2}$1) $\bar{1}_3C_1$		0 1 $\bar{2}$
		(022) (122) ($\bar{1}$22) A_2C_1 ($\bar{1}\bar{2}$2) $\bar{1}'_2C_1$	(023) (123) ($\bar{1}$23) $A_2\bar{3}_1$ ($\bar{1}\bar{2}$3) $\bar{1}'_2\bar{3}_1$			0 2 2

	A	(022) (122) ($\bar{1}$22) A_2C_1 ($\bar{1}\bar{2}2$) $\bar{1}'_2C_1$				0 2 $\bar{2}$
		(021) (121) ($\bar{1}$21) A_2B_2 ($\bar{1}\bar{2}1$) $\bar{1}'_2B_2$				
	B	($0\bar{2}\bar{2}$) ($1\bar{2}\bar{2}$) A_3C_2				0 $\bar{2}$ $\bar{2}$
23				(101) 1_1A_1	($1\bar{1}\bar{1}$) $1_1\bar{1}_2$	0 0 0
				($1\bar{1}\bar{1}$) $1_1\bar{1}'_2$	($1\bar{2}\bar{1}$) $1_1\bar{1}_2$	0 1 0
		($\bar{2}\bar{2}$0) ($\bar{2}\bar{2}$1) ($\bar{2}\bar{2}\bar{1}$) $\bar{2}'_2A_2$		(120) (121) ($12\bar{1}$) 1_1A_2 ($1\bar{2}\bar{1}$) $1_1\bar{1}'_2$		0 2 0
		(101) B_1A_1		(201) 2_1A_1	($2\bar{1}\bar{1}$) $2_1\bar{1}_2$	1 0 0
	A	(101) B_1A_1	($1\bar{1}\bar{1}$) ($\bar{2}\bar{1}$0) $B_3\bar{1}_2$	(201) 2_1A_1	($2\bar{1}\bar{1}$) $2_1\bar{1}_2$	$\bar{1}$ 0 0
		($1\bar{1}\bar{1}$) ($\bar{2}\bar{1}$0) $B_3\bar{1}'_2$		($2\bar{1}\bar{1}$) $2_1\bar{1}'_2$	($2\bar{2}\bar{1}$) $2_1\bar{1}_2$	1 1 0
		($1\bar{1}\bar{1}$) ($\bar{2}\bar{1}$0) $B_3\bar{1}'_2$		($2\bar{1}\bar{1}$) $2_1\bar{1}'_2$	($2\bar{2}\bar{1}$) $2_1\bar{1}_2$	$\bar{1}$ 1 0
	A	(0$\bar{1}\bar{1}$) ($\bar{1}$10) ($1\bar{1}\bar{1}$) A_3A_3	($1\bar{1}\bar{1}$) ($\bar{2}\bar{1}$0) $B_3\bar{1}'_3$	($1\bar{1}\bar{1}$) 1_1A_3 ($\bar{1}\bar{1}$1) $\bar{1}'_3A_3$	($2\bar{1}\bar{1}$) $2_1\bar{1}'_3$	$\bar{1}$ $\bar{1}$ 0
		($\bar{1}$10) ($\bar{1}\bar{1}$1) ($\bar{2}\bar{1}$0) ($\bar{2}\bar{1}$1) $\bar{B}_2A_3$		($\bar{2}\bar{2}$0) $\bar{2}_2A_3$		
		(120) (121) ($12\bar{1}$) B_2A_2		(220) (221) ($22\bar{1}$) 2_1A_2 ($2\bar{2}\bar{1}$) $1_1\bar{1}'_2$		1 2 0
	A	(020) (021) ($02\bar{1}$) A_2A_2		(220) (221) ($22\bar{1}$) 2_1A_2		$\bar{1}$ 2 0
		(120) (121) ($12\bar{1}$) B_2A_2		($2\bar{2}\bar{1}$) $2_1\bar{1}'_2$		
	B				($2\bar{2}\bar{1}$) $2_1\bar{1}'_3$	$\bar{1}$ $\bar{2}$ 0
22					(101) 1_1l_1	0 0 0
					(111) 1_2l_2	0 1 0
			($\bar{2}\bar{2}\bar{1}$) $\bar{2}'_2l_1$	($1\bar{2}\bar{2}$) $1_1\bar{2}'_2$		0 2 0
				(101) 1_1B_1	(102) 1_12_1	0 0 1
				(101) 1_1B_1	(102) 1_12_1	0 0 $\bar{1}$
					(112) 1_22_1	0 1 1
					(112) 1_22_1	0 1 $\bar{1}$
	A	(0$\bar{1}\bar{1}$) ($1\bar{1}\bar{1}$) ($\bar{1}$10) A_3A_3		($1\bar{1}\bar{1}$) 1_1A_3 ($\bar{2}\bar{2}$0) $\bar{2}_2A_3$	($1\bar{2}\bar{2}$) $1_1\bar{2}_2$	0 $\bar{1}$ $\bar{1}$
		($\bar{1}$10) ($\bar{1}\bar{1}$1) ($\bar{2}\bar{1}$0) $\bar{B}_2A_3$		($1\bar{1}\bar{1}$) ($1\bar{1}\bar{2}$) $1_1\bar{B}_2$		
		($\bar{2}\bar{2}$1) $\bar{2}'_2B_2$	($\bar{2}\bar{2}\bar{2}$) $\bar{2}'_22_1$	(121) 1_1B_2		0 2 1

(αγ) Pattern (continued)

σ-Block	Set	Substrates and Sequences by Polarity − −	− +	+ −	+ +	Product α β γ
22	A	$(\bar{2}\bar{2}0)\ \bar{2}'_2A_2\ (\bar{2}\bar{2}1)\ \bar{2}'_2B_2$	$(\bar{2}\bar{2}2)\ \bar{2}'_22_1$	$(120)\ 1_1A_2\ (121)\ 1_1B_2$		0 2 Ī
	B			$(12\bar{1})\ 1_1\bar{B}_2\ (1\bar{2}\bar{2})\ 1_12'_2$	$(1\bar{2}\bar{2})\ 1_12_2$	0 $\bar{2}$ 1
			$(101)\ B_11_1$		$(201)\ 2_11_1$	1 0 0
			$(\bar{1}01)\ B_11_1$		$(\bar{2}01)\ 2_11_1$	Ī 0 0
					$(211)\ 2_11_2$	1 1 0
					$(\bar{2}11)\ 2_11_2$	Ī 1 0
	A		$(\bar{1}\bar{1}1)\ (\bar{2}\bar{1}1)\ \bar{B}_21_1$		$(\bar{2}\bar{2}1)\ \bar{2}_21_1$	1 $\bar{1}$ 0
			$(121)\ B_21_1$	$(2\bar{2}\bar{2})\ 2_12'_2$		1 2 0
	A		$(021)\ A_21_1\ (121)\ B_21_1$	$(2\bar{2}\bar{2})\ 2_12'_2$		Ī 2 0
	B		$(\bar{1}21)\ \bar{B}_21_1\ (\bar{2}\bar{2}1)\ \bar{2}'_21_1$		$(\bar{2}21)\ 2_21_1$	Ī 2 0
		$(101)\ B_1B_1$	$(102)\ B_12_1$	$(201)\ 2_1B_1$	$(202)\ 2_12_1$	1 0 1
		$(\bar{1}01)\ B_1B_1$	$(\bar{1}02)\ B_12_1$	$(\bar{2}01)\ 2_1B_1$	$(\bar{2}02)\ 2_12_1$	1 0 Ī
		$(101)\ B_1B_1$	$(102)\ B_12_1$	$(201)\ 2_1B_1$	$(202)\ 2_12_1$	Ī 0 1
		$(\bar{1}01)\ B_1B_1$	$(\bar{1}02)\ B_12_1$	$(\bar{2}01)\ 2_1B_1$	$(\bar{2}02)\ 2_12_1$	Ī 0 Ī
	A	$(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2$		$(2\bar{1}\bar{1})\ (2\bar{1}\bar{2})\ 2_1\bar{B}_2$	$(2\bar{2}\bar{2})\ 2_1\bar{2}_2$	1 $\bar{1}$ 1
	A	$(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2$		$(2\bar{1}\bar{1})\ (2\bar{1}\bar{2})\ 2_1\bar{B}_2$	$(2\bar{2}\bar{2})\ 2_1\bar{2}_2$	Ī $\bar{1}$ 1
	B	$(\bar{1}\bar{1}1)\ (\bar{2}\bar{1}1)\ \bar{B}_2B_3$	$(\bar{1}\bar{1}2)\ (\bar{2}\bar{1}2)\ \bar{B}_22_1$	$(1\bar{1}\bar{2})\ 1_1B_3$	$(\bar{2}\bar{1}2)\ 2_32_1\ (\bar{2}\bar{2}2)\ \bar{2}_32_1$	$\bar{1}$ 1 1
	B	$(\bar{1}\bar{1}1)\ (\bar{2}\bar{1}1)\ \bar{B}_2B_3$	$(\bar{1}\bar{1}2)\ (\bar{2}\bar{1}2)\ \bar{B}_22_1$	$(1\bar{1}\bar{2})\ 1_1B_3$	$(\bar{2}\bar{1}2)\ 2_32_1\ (\bar{2}\bar{2}2)\ \bar{2}_32_1$	$\bar{1}$ 1 Ī
		$(121)\ B_2B_2$	$(122)\ B_22_1$	$(221)\ 2_1B_2$		1 2 1
	A	$(120)\ B_2A_2\ (121)\ B_2B_2$	$(122)\ B_22_1$	$(220)\ 2_1A_2\ (221)\ 2_1B_2$		1 2 Ī
	B			$(2\bar{2}\bar{1})\ 2_1\bar{B}_2\ (2\bar{2}\bar{2})\ 2_1\bar{2}'_2$	$(2\bar{2}\bar{2})\ 2_12_2$	1 $\bar{2}$ 1
	C	$(021)\ A_2B_2\ (121)\ B_2B_2$	$(122)\ B_22_1$	$(221)\ 2_1B_2$		Ī 2 1

	D	(020) A_2A_2 (021) A_2B_2	(022) $A_2\bar{2}_1$ (122) $B_2\bar{2}_1$	(220) $\bar{2}_1A_2$ (221) $\bar{2}_1B_2$		$\bar{1}$ 2 $\bar{1}$
		(120) B_2A_2 (121) B_2B_2				
	E			(2$\bar{2}$1) $\bar{2}_1\bar{B}_2$ (2$\bar{2}\bar{2}$) $\bar{2}_1\bar{2}'_2$	(2$\bar{2}\bar{2}$) $\bar{2}_1\bar{2}_2$	$\bar{1}$ $\bar{2}$ $\bar{1}$
	F		($\bar{1}$22) $\bar{B}_2\bar{2}_1$ ($\bar{2}\bar{2}$2) $\bar{2}'_2\bar{2}_1$		($\bar{2}\bar{2}$2) $\bar{2}_3\bar{2}_1$	$\bar{1}$ $\bar{2}$ 1
	F		($\bar{1}$22) $\bar{B}_2\bar{2}_1$ ($\bar{2}\bar{2}$2) $\bar{2}'_2\bar{2}_1$		($\bar{2}\bar{2}$2) $\bar{2}_3\bar{2}_1$	$\bar{1}$ $\bar{2}$ $\bar{1}$
21				(102) $\bar{1}_1C_1$	(103) $\bar{1}_1\bar{3}_1$	0 0 2
	A			(101) $\bar{1}_1B_1$ (102) $\bar{1}_1C_1$		0 0 $\bar{2}$
				(112) $\bar{1}_2C_1$	(113) $\bar{1}_2\bar{3}_1$	0 1 2
	A			(112) $\bar{1}_2C_1$		0 1 $\bar{2}$
	B	($\bar{1}\bar{1}$1) ($\bar{2}\bar{1}$1) $\bar{B}_2B_3$		(1$\bar{1}$2) $\bar{1}_1B_3$		0 $\bar{1}$ $\bar{2}$
		($\bar{2}\bar{2}$2) $\bar{2}'_2C_1$	($\bar{2}\bar{2}$3) $\bar{2}'_2\bar{3}_1$			0 2 2
	A	($\bar{2}\bar{2}$2) $\bar{2}'_2C_1$ ($\bar{2}\bar{2}$1) $\bar{2}'_2B_2$		(121) $\bar{1}_2B_2$		0 2 $\bar{2}$
	B			(1$\bar{2}\bar{2}$) $\bar{1}_1C_2$	(1$\bar{2}\bar{3}$) $\bar{1}_1\bar{3}_2$	0 $\bar{2}$ $\bar{2}$
		(102) B_1C_1	(103) $B_1\bar{3}_1$	(202) $\bar{2}_1C_1$	(203) $\bar{2}_1\bar{3}_1$	1 0 2
	A	(101) B_1B_1 (102) B_1C_1		(201) $\bar{2}_1B_1$ (202) $\bar{2}_1C_1$		1 0 $\bar{2}$
		(102) B_1C_1	(103) $B_1\bar{3}_1$	(202) $\bar{2}_1C_1$	(203) $\bar{2}_1\bar{3}_1$	$\bar{1}$ 0 2
	A	(101) B_1B_1 (102) B_1C_1		(201) $\bar{2}_1B_1$ (202) $\bar{2}_1C_1$		$\bar{1}$ 0 $\bar{2}$
	A	($\bar{1}$12) ($\bar{2}$12) $\bar{B}_2C_1$	($\bar{1}$13) ($\bar{2}$13) $\bar{B}_2\bar{3}_1$	($\bar{2}$12) $\bar{2}_3C_1$ ($\bar{2}\bar{2}$2) $\bar{2}_3C_1$	($\bar{2}$13) $\bar{2}_3\bar{3}_1$ ($\bar{2}\bar{2}$3) $\bar{2}_3\bar{3}_1$	$\bar{1}$ $\bar{1}$ 2
	B	($\bar{1}\bar{1}$1) ($\bar{2}\bar{1}$1) $\bar{B}_2B_3$ ($\bar{1}$12) ($\bar{2}$12) $\bar{B}_2C_1$		($\bar{2}\bar{2}$1) $\bar{2}_2B_3$(1$\bar{1}$2) $\bar{1}_1B_3$		$\bar{1}$ $\bar{1}$ $\bar{2}$
				($\bar{2}$12) $\bar{2}_3C_1$ ($\bar{2}\bar{2}$2) $\bar{2}_3C_1$		
		(122) B_2C_1	(123) $B_2\bar{3}_1$			1 2 2
	A	(121) B_2B_2 (122) B_2C_1		(221) $\bar{2}_1B_2$		1 2 $\bar{2}$
	B	(022) A_2C_1 (122) B_2C_1	(023) $A_2\bar{3}_1$ (123) $B_2\bar{3}_1$			$\bar{1}$ 2 2
	C	(022) A_2C_1 (122) B_2C_1	(221) $\bar{2}_1B_2$			$\bar{1}$ 2 $\bar{2}$
		(021) A_2B_2 (121) B_2B_2				

($\alpha\gamma$) Pattern (continued)

σ-Block	Set	Substrates and Sequences by Polarity − −	− +	+ −	+ +	Product α β γ
21	D			($2\bar{2}\bar{2}$) 2_1C_2	($2\bar{2}\bar{3}$) 2_13_2	1 $\bar{2}$ $\bar{2}$
	D			($2\bar{2}\bar{2}$) 2_1C_2	($2\bar{2}\bar{3}$) 2_13_2	$\bar{1}$ $\bar{2}$ $\bar{2}$
	E	($\bar{1}\bar{2}2$) $\bar{B}_2C_1$ ($\bar{2}\bar{2}2$) $\bar{2}'_2C_1$	($\bar{1}\bar{2}3$) $\bar{B}_23_1$ ($\bar{2}\bar{2}3$) $\bar{2}'_23_1$	($\bar{2}\bar{2}2$) 2_3C_1	($\bar{2}\bar{2}3$) 2_33_1	$\bar{1}$ 2 2
	F	($\bar{1}\bar{2}2$) $\bar{B}_2C_1$ ($\bar{2}\bar{2}2$) $\bar{2}'_2C_1$		($\bar{2}\bar{2}2$) 2_3C_1		$\bar{1}$ 2 $\bar{2}$
13		(201) C_1A_1	($2\bar{1}\bar{1}$) $C_1\bar{I}_3$	(301) 3_1A_1	($3\bar{1}\bar{1}$) $3_1\bar{I}_3$	2 0 0
	A	(101) B_1A_1 (201) C_1A_1	($2\bar{1}\bar{1}$) $C_1\bar{I}_2$ ($1\bar{1}\bar{1}$) ($\bar{2}\bar{1}0$) $B_3\bar{I}_2$			$\bar{2}$ 0 0
		($2\bar{1}\bar{1}$) $C_1\bar{I}'_2$	($2\bar{2}\bar{1}$) $C_1\bar{I}_3$	($3\bar{1}\bar{1}$) $3_1\bar{I}'_2$	($3\bar{2}\bar{1}$) $3_1\bar{I}_3$	2 1 0
	A	($2\bar{1}\bar{1}$) $C_1\bar{I}'_2$ ($1\bar{1}\bar{1}$) ($\bar{2}\bar{1}0$) $B_3\bar{I}'_2$	($2\bar{2}\bar{1}$) $C_1\bar{I}_2$			$\bar{2}$ 1 0
		(220) (221) (22$\bar{1}$) C_1A_2 ($2\bar{2}\bar{1}$) $C_1\bar{I}'_2$		(320) (321) (32$\bar{1}$) 3_1A_2 ($3\bar{2}\bar{1}$) $3_1\bar{I}'_2$		2 2 0
	A	(120) (121) (12$\bar{1}$) B_2A_2				$\bar{2}$ 2 0
		(220) (221) (22$\bar{1}$) C_1A_2 ($2\bar{2}\bar{1}$) $C_1\bar{I}'_2$				
	B	($\bar{2}\bar{2}0$) ($\bar{2}\bar{2}1$) C_2A_3		($\bar{3}\bar{2}0$) ($\bar{3}\bar{2}1$) 3_2A_3		$\bar{2}$ $\bar{2}$ 0
12			(201) C_1I_1		(301) 3_1I_1	2 0 0
	A		(101) B_1I_1 (201) C_1I_1			$\bar{2}$ 0 0
			(211) C_1I_2		(311) 3_1I_2	2 1 0
	A		(211) C_1I_2			$\bar{2}$ 1 0
		($2\bar{2}\bar{2}$) $C_1\bar{2}'_2$		($3\bar{2}\bar{2}$) $3_1\bar{2}'_2$		2 2 0
	A	($2\bar{2}\bar{2}$) $C_1\bar{2}'_2$	(121) B_2I_1			$\bar{2}$ 2 0
	B		($\bar{2}\bar{2}1$) C_2I_1		($\bar{3}\bar{2}1$) 3_2I_1	$\bar{2}$ $\bar{2}$ 0
		(201) C_1B_1	(202) C_12_1	(301) 3_1B_1	(302) 3_12_1	2 0 1
		(201) C_1B_1	(202) C_12_1	(301) 3_1B_1	(302) 3_12_1	2 0 $\bar{1}$
	A	(101) B_1B_1 (201) C_1B_1	(102) B_12_1 (202) C_12_1			$\bar{2}$ 0 1
	A	(101) B_1B_1 (201) C_1B_1	(102) B_12_1 (202) C_12_1			$\bar{2}$ 0 $\bar{1}$

	A	(2$\bar{1}\bar{1}$) (2$\bar{1}\bar{2}$) $C_1\bar{B}_2$	(2$\bar{1}\bar{2}$) C_12_3 (2$\bar{2}\bar{2}$) $C_1\bar{2}_3$	(3$\bar{1}\bar{1}$) (3$\bar{1}\bar{2}$) $3_1\bar{B}_2$	(3$\bar{1}\bar{2}$) 3_12_3 (3$\bar{2}\bar{2}$) $3_1\bar{2}_3$	2 $\bar{1}$ $\bar{1}$
	B	(2$\bar{1}\bar{1}$) (2$\bar{1}\bar{2}$) $C_1\bar{B}_2$(1$\bar{1}\bar{1}$) ($\bar{2}$10) $B_3\bar{B}_2$				$\bar{2}$ $\bar{1}$ $\bar{1}$
		(221) C_1B_2		(321) 3_1B_2		2 2 1
	A	(220) C_1A_2 (221) C_1B_2		(320) 3_1A_2 (321) 3_1B_2		2 2 $\bar{1}$
	B	(2$\bar{2}\bar{1}$) $C_1\bar{B}_2$ (2$\bar{2}\bar{2}$) $C_1\bar{2}'_2$	(2$\bar{2}\bar{2}$) C_12_3	(3$\bar{2}\bar{1}$) $3_1\bar{B}_2$ (3$\bar{2}\bar{2}$) $3_1\bar{2}'_2$	(3$\bar{2}\bar{2}$) 3_12_3	2 $\bar{2}$ $\bar{1}$
	C	(121) B_2B_2 (221) C_1B_2	(122) B_22_1			$\bar{2}$ 2 1
	D	(120) B_2A_2 (121) B_2B_2	(122) B_22_1			$\bar{2}$ 2 $\bar{1}$
		(220) C_1A_2 (221) C_1B_2				
	E	(2$\bar{2}\bar{1}$) $C_1\bar{B}_2$ (2$\bar{2}\bar{2}$) $C_1\bar{2}'_2$	(2$\bar{2}\bar{2}$) C_12_2			$\bar{2}$ $\bar{2}$ $\bar{1}$
	F		($\bar{2}\bar{2}\bar{2}$) C_22_1		($\bar{3}\bar{2}\bar{2}$) 3_22_1	$\bar{2}$ $\bar{2}$ 1
	F		($\bar{2}\bar{2}\bar{2}$) C_22_1		($\bar{3}\bar{2}\bar{2}$) 3_22_1	$\bar{2}$ $\bar{2}$ $\bar{1}$
11		(202) C_1C_1	(203) C_13_1	(302) 3_1C_1	(303) 3_13_1	2 0 2
	A	(201) C_1B_1 (202) C_1C_1		(301) 3_1B_1 (302) 3_1C_1		2 0 $\bar{2}$
	B	(102) B_1C_1 (202) C_1C_1	(103) B_13_1 (203) C_13_1			$\bar{2}$ 0 2
	C	(101) B_1B_1 (102) B_1C_1 (201) C_1B_1				$\bar{2}$ 0 $\bar{2}$
		(202) C_1C_1				
	A	(221) C_1B_2		(321) 3_1B_2		2 2 $\bar{2}$
	B	(2$\bar{2}\bar{2}$) C_1C_2	(2$\bar{2}\bar{3}$) C_13_2	(3$\bar{2}\bar{2}$) 3_1C_2	(3$\bar{2}\bar{3}$) 3_13_2	2 $\bar{2}$ $\bar{2}$
	C	(122) B_2C_1	(123) B_23_1			$\bar{2}$ 2 2
	D	(122) B_2C_1 (221) C_1B_2 (121) B_2B_2				$\bar{2}$ 2 $\bar{2}$
	E	(2$\bar{2}\bar{2}$) C_1C_2	(2$\bar{2}\bar{3}$) C_13_2			$\bar{2}$ $\bar{2}$ $\bar{2}$
	F	($\bar{2}\bar{2}\bar{2}$) C_2C_1	($\bar{2}\bar{2}\bar{3}$) C_23_1	($\bar{3}\bar{2}\bar{2}$) 3_2C_1	($\bar{3}\bar{2}\bar{3}$) 3_13_1	$\bar{2}$ $\bar{2}$ 2
	G	($\bar{2}\bar{2}\bar{2}$) C_2C_1		($\bar{3}\bar{2}\bar{2}$) 3_2C_1		$\bar{2}$ $\bar{2}$ $\bar{2}$

($\alpha\gamma\alpha$) Pattern

σ-Block	Sequence Sets	Product α β γ
23	(101)$B_1A_1A_1$ (201) $2_1A_1A_1$ (2$\bar{1}\bar{1}$) $2_1I_2A_1$ [SET 23–100A]$_5$+$A_2\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$ [SET 23–110A]$_{12}$+I_2A_2	0 0 0
	(2$\bar{2}\bar{1}$) $2_1I'_3I_2$ [SET 23–110A]$_{12}$+I'_2	0 1 0
	(2$\bar{2}\bar{1}$) $2_1I'_3I'_2$ [SET 33–020]$_{13}$ [SET 23–020]$_7$ [SET 23–120]$_7$+A_2 [SET 23–120A]$_{10}$+$A_2A_2A_3\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$	0 2 0
22	[(101) B_1l_1 (201) 2_1l_1]+$A_1A_3\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$ [(1$\bar{1}\bar{1}$) (2$\bar{1}\bar{1}$) $\bar{B}_2l_1$ (2$\bar{2}\bar{1}$) $\bar{2}_1l_1$]+I_2A_2	0 0 0
	(211) $2_1l_2\bar{I}_2/2_1l_2\bar{I}_3/2_1l_2\bar{I}'_3$ (1$\bar{1}\bar{1}$) (2$\bar{1}\bar{1}$) $\bar{B}_2l_1I'_2$ (2$\bar{2}\bar{1}$) $\bar{2}_2l_1I'_2$ (1$\bar{2}\bar{1}$) $\bar{B}_2l_1I_2$ (2$\bar{2}\bar{1}$) $\bar{2}'_2l_1I_2$ (2$\bar{2}\bar{1}$) $2_2l_1I_2$	0 1 0
	[SET 32–020]$_6$+A_2 (121) $B_2l_1A_2$ (1$\bar{2}\bar{1}$) $\bar{B}_2l_1I'_2$ (1$\bar{2}\bar{2}$) $1_1\bar{2}'_2A_2$ (2$\bar{2}\bar{1}$) $2_2l_1I'_2$ (2$\bar{2}\bar{1}$) $\bar{2}'_2l_1A_2/\bar{2}'_2l_1I'_2$	0 2 0
	(2$\bar{2}\bar{2}$) $2_1\bar{2}'_2A_2$ [(021) A_2l_1 (121) B_2l_1 (2$\bar{2}\bar{2}$) $2_1\bar{2}'_2$]+$A_2A_2A_3\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$	
	[SET 22–101]$_4$+A_1 [SET 22–101]$_4$+$A_3\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$	0 0 1
	[SET 22–101]$_4$+A_1 [SET 22–101]$_4$+$A_3\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$ [SET 22–111B]$_{10}$+I_2A_2	0 0 $\bar{1}$
	[SET 22–111B]$_{10}$+I'_2 (1$\bar{2}\bar{2}$) $\bar{B}_2l_1I_2$ (2$\bar{2}\bar{2}$) $2_2l_1I_2$ (2$\bar{2}\bar{2}$) $\bar{2}'_2l_1I_2$	0 1 $\bar{1}$
	[SET 32–011A]$_{10}$ [SET 23–110A]$_{12}$ [SET 22–011A]$_{11}$ [SET 22–110A]$_3$ [SET 22–111A]$_5$+A_3 [SET 22–111A]$_5$+$A_3\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$	0 $\bar{1}$ $\bar{1}$
	[SET 22–111B]$_7$+I'_3	
	[SET 32–021]$_8$+A_2 (121) $B_2B_2A_2/1_1B_2A_2$ (122) $B_2l_1A_2$ (221) $2_1B_2A_2$ (2$\bar{2}\bar{1}$) $\bar{2}'_2B_2A_2$ (2$\bar{2}\bar{2}$) $\bar{2}'_2l_1A_2$	0 2 1
	[SET 22–121C]$_4$+$A_2A_2A_3\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$	
	[SET 32–021A]$_{12}$ [SET 22–021A]$_5$ [SET 22–121A]$_5$+A_2 (1$\bar{2}\bar{2}$) $\bar{B}_2l_1I'_2$ (2$\bar{2}\bar{2}$) $2_2l_1I'_2$ (2$\bar{2}\bar{2}$) $\bar{2}'_2l_1I'_2$	0 2 $\bar{1}$
	[SET 22–121D]$_8$+$A_2A_2A_3\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$	
	[(2$\bar{2}\bar{1}$) $2_1\bar{B}_2$ (2$\bar{2}\bar{2}$) $2_1\bar{2}'_2$ (2$\bar{2}\bar{2}$) 2_12_2]+$\bar{I}_2\bar{I}_3\bar{I}'_3$ (1$\bar{2}\bar{2}$) $\bar{B}_2l_1\bar{I}'_3$ (2$\bar{2}\bar{2}$) $\bar{2}'_2\bar{2}_1I'_3$ (2$\bar{2}\bar{2}$) $2_2l_1I'_3$	0 $\bar{2}$ $\bar{1}$
21	[SET 21–102]$_4$+$A_1A_3\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$ [SET 21–112A]$_8$+I_3	0 0 2
	[SET 21–102A]$_4$+$A_1A_3\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$ [SET 21–112B]$_8$+I_2A_2	0 0 $\bar{2}$
	[SET 21–122E]$_6$+I_3	0 1 2
	[SET 21–112B]$_8$+I'_2 (1$\bar{2}\bar{2}$) $\bar{B}_2C_1I_2$ (2$\bar{2}\bar{2}$) $\bar{2}'_2C_1I_2$ (2$\bar{2}\bar{2}$) $2_3C_1I_2$	0 1 $\bar{2}$
	[SET 31–022]$_8$+A_2 (122) $B_2C_1A_2$ (123) $B_2\beta_1A_2$ (2$\bar{2}\bar{2}$) $\bar{2}'_2C_1A_2$ (2$\bar{2}\bar{3}$) $\bar{2}'_2\beta_1A_2$ [SET 21–122B]$_4$+$A_2A_2A_3\bar{I}_2\bar{I}_3\bar{I}'_2\bar{I}'_3$	0 2 2

	$[\text{SET 31–022A}]_4\,[\text{SET 21–022A}]_3\,[\text{SET 21–122A}]_3 + \text{A}_2$	0 2 $\bar{2}$
	$[\text{SET 21–122C}]_3 + \text{A}_2 A_2 A_3 \bar{1}_2 \bar{1}_3 \bar{1}'_2 \bar{1}'_3$ $(\bar{1}\bar{2}2)\ \bar{\text{B}}_2\text{C}_1\bar{1}'_2$ $(\bar{2}\bar{2}2)\ \bar{2}'_2\text{C}_1\bar{1}'_2$ $(\bar{2}\bar{2}2)\ 2_3\text{C}_1\bar{1}'_2$	
	$(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ \text{A}_3\text{C}_2\,\text{A}_3$ $(1\bar{2}\bar{2})\ 1_1\text{C}_2\text{A}_3$ $(1\bar{2}\bar{3})\ 1_1 3_2\text{A}_3$ $[(2\bar{2}\bar{2})\ 2_1\text{C}_2$ $(2\bar{2}\bar{3})\ 2_1 3_2] + \text{A}_3 A_3 \bar{1}_2 \bar{1}_3 \bar{1}'_2 \bar{1}'_3$	0 $\bar{2}$ $\bar{2}$
13	$(101)\ \text{B}_1\text{A}_1 1_1$ $(201)\ 2_1\text{A}_1 1_1$ $(2\bar{1}\bar{1})\ 2_1\bar{1}_2 1_1$	0 0 0
	$(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ \text{B}_3\bar{1}'_2 1_2$ $(2\bar{1}\bar{1})\ 2_1\bar{1}'_2 1_2$ $(2\bar{2}\bar{1})\ 2_1\bar{1}_2 1_2$	0 1 0
	$[\text{SET 23–120}]_7 + 1_1$ $(\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ \text{C}_2\text{A}_3\bar{2}'_2$ $(\bar{3}\bar{2}0)\ (\bar{3}\bar{2}1)\ 3_2\text{A}_3\,\bar{2}'_2$	0 2 0
	$(101)\ \text{B}_1\text{A}_1\text{B}_1$ $(201)\ 2_1\text{A}_1\text{B}_1$ $(2\bar{1}\bar{1})\ 2_1\bar{1}_2\text{B}_1$ $[\text{SET 13–200}]_4 + 2_1$ $[\text{SET 13–200A}]_5 + B_3$	1 0 0
	$[\text{SET 23–100}]_3 + \text{B}_1 A_3$ $[\text{SET 23–100A}]_5 + \bar{B}_2$ $[\text{SET 13–200}]_4 + 2_1$ $[\text{SET 13–200A}]_5 + \bar{B}_2 B_3 2_2 2_3$	$\bar{1}$ 0 0
	$[\text{SET 13–210}]_4 + 2_1$ $[\text{SET 13–210A}]_3 + 2_2 2_3$	1 1 0
	$[\text{SET 13–210}]_4 + 2_1$ $[\text{SET 13–210A}]_3 + \bar{B}_2 B_3 2_2 2_3$	$\bar{1}$ 1 0
	$[\text{SET 23–110A}]_{12} + \bar{\text{B}}_2\text{A}_3$	$\bar{1}\bar{1}$ 0
	$[\text{SET 23–120}]_7 + \text{B}_2$ $[\text{SET 13–220}]_8 + 2_1$ $[\text{SET 13–220A}]_7 + B_3$	1 2 0
	$[\text{SET 33–020}]_{13}\,[\text{SET 23–020}]_7 + \text{A}_2 A_3$ $[\text{SET 23–120}]_7 + \text{B}_2$ $[\text{SET 23–120A}]_{10} + A_3$	$\bar{1}$ 2 0
	$(2\bar{2}\bar{1})\ 2_1\bar{1}'_3\bar{\text{B}}_2$ $[\text{SET 13–220}]_8 + 2_1$ $[\text{SET 13–220A}]_7 + \bar{B}_2 B_3 2_2 2_3$	
	$(\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ \text{C}_2\text{A}_3\bar{2}'_2$ $(\bar{3}\bar{2}0)\ (\bar{3}\bar{2}1)\ 3_2\text{A}_3\bar{2}'_2$	$\bar{1}$ 2 0
12	$(101)\ \text{B}_1 1_1 1_1$ $(201)\ 2_1 1_1 1_1$	0 0 0
	$(211)\ 2_1 1_2 1_2$	0 1 0
	$(\bar{2}\bar{2}1)\ \text{C}_2 1_1 \bar{2}'_2$ $(\bar{3}\bar{2}1)\ 3_2 1_1 \bar{2}'_2$ $(121)\ \text{B}_2 1_1 1_1$ $(2\bar{2}\bar{2})\ 2_1\bar{2}'_2 1_1$	0 2 0
	$(101)\ \text{B}_1\text{B}_1 1_1$ $(102)\ \text{B}_1 2_1 1_1$ $(201)2_1\text{B}_1 1_1$ $(202)\ 2_1 2_1 1_1$	0 0 1
	$(101)\ \text{B}_1\text{B}_1 1_1$ $(102)\ \text{B}_1 2_1 1_1$ $(201)\ 2_1\text{B}_1 1_1$ $(202)\ 2_1 2_1 1_1$	0 0 $\bar{1}$
	$[\text{SET 22–111A}]_5 + 1_1$ $[\text{SET 22–111B}]_7 + \bar{1}'_3$	0 $\bar{1}\bar{1}$
	$(121)\ \text{B}_2\text{B}_2 1_1$ $(122)\ \text{B}_2 2_1 1_1$ $(\bar{2}\bar{2}2)\ \text{C}_2 2_1 \bar{2}'_2$ $(221)\ 2_1\text{B}_2 1_1$ $(\bar{3}\bar{2}2)\ 3_2 2_1 \bar{2}'_2$	0 2 1
	$(121)\ \text{B}_2\text{B}_2 1_1$ $(122)\ \text{B}_2 2_1 1_1$ $(\bar{2}\bar{2}2)\ \text{C}_2 2_1 \bar{2}'_2$ $(221)\ 2_1\text{B}_2 1_1$ $(\bar{3}\bar{2}2)\ 3_2 2_1 \bar{2}'_2$	0 2 $\bar{1}$
	$(\bar{1}\bar{2}2)\ \bar{\text{B}}_2 2_1 \bar{1}'_3$ $(\bar{2}\bar{2}2)\ \bar{2}'_2 2_1 \bar{1}'_3$ $(2\bar{2}\bar{1})\ 2_1\bar{\text{B}}_2 1_1$ $(2\bar{2}\bar{2})\ 2_1\bar{2}'_2 1_1$ $(2\bar{2}\bar{2})\ 2_1 2_2 1_1$ $(\bar{2}\bar{2}2)\ 2_3 2_1 \bar{1}'_3$	0 $\bar{2}$ $\bar{1}$
	$(101)\ \text{B}_1 1_1 \text{B}_1/\text{B}_1 1_1 B_3$ $(201)\ 2_1 1_1 \text{B}_1/\text{C}_1 1_1 2_1/\text{C}_1 1_1 B_3$ $(301)\ 3_1 1_1 2_1$	1 0 0
	$(101)\ \text{B}_1 1_1 \text{B}_1/\text{B}_1 1_1 A_3/\text{B}_1 1_1 \bar{B}_2$ $(201)2_1 1_1 \text{B}_1/2_1 1_1 A_3/2_1 1_1 \bar{B}_2/\text{C}_1 1_1 2_1$ $(301)\ 3_1 1_1 2_1$ $[\text{SET 12–200A}]_2 + \bar{B}_2 B_3 2_2 2_3$	$\bar{1}$ 0 0

($\alpha\gamma\alpha$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
12	(211) $C_1l_2\mathfrak{2}_1$ (311) $3_1l_2\mathfrak{2}_1$	1 1 0
	(211) $C_1l_2\mathfrak{2}_1/C_1l_2\mathfrak{2}_2/C_1l_2\mathfrak{2}_3$ (311) $3_1l_2\mathfrak{2}_1$	$\bar{1}$ 1 0
	[SET 32–011A]$_{10}$ [SET 22–011A]$_{11}$ [SET 22–110A]$_3$ [SET 22–111A]$_5 + A_3$ ($\bar{2}\bar{2}1$) $C_2l_1\bar{\mathfrak{2}}_2$ ($\bar{3}\bar{2}1$) $3_2l_1\bar{\mathfrak{2}}_2$	$\bar{1}\,\bar{1}$ 0
	($2\bar{2}\bar{2}$) $C_1\bar{\mathfrak{2}}'_2B_3/C_1\bar{\mathfrak{2}}'_2\mathfrak{2}_1/2_1\bar{\mathfrak{2}}'_2B_2$ (121) $B_2l_1B_2/B_2l_1B_3$ ($3\bar{2}\bar{2}$) $3_1\mathfrak{2}'_2\mathfrak{2}_1$	1 2 0
	[SET 32–020]$_6$ [SET 22–020]$_2 + A_2A_3$ (021) $A_2l_1A_3$ (121) $B_2l_1B_2/B_2l_1A_3/B_2l_1\bar{B}_2/B_2l_1B_3/B_2l_12_2/B_2l_12_3$	$\bar{1}$ 2 0
	($2\bar{2}\bar{2}$) $C_1\bar{\mathfrak{2}}'_2\bar{B}_2/C_1\bar{\mathfrak{2}}'_2B_3/C_1\bar{\mathfrak{2}}'_22_2/C_1\bar{\mathfrak{2}}'_22_3/2_1\bar{\mathfrak{2}}'_2B_2/2_1\bar{\mathfrak{2}}'_2A_3$	
	($\bar{1}\bar{2}1$) $\bar{B}_2l_1\bar{B}_2$ ($\bar{2}\bar{2}1$) $\bar{\mathfrak{2}}'_2l_1\bar{B}_2/C_2l_1\bar{\mathfrak{2}}'_2$ ($\bar{2}\bar{2}1$) $2_2l_1\bar{B}_2$ ($\bar{3}\bar{2}1$) $3_2l_1\bar{\mathfrak{2}}'_2$	$\bar{1}\,\bar{2}$ 0
	[SET 22–101]$_4 + B_1$ [SET 12–201]$_4 + 2_1$ [SET 12–201A]$_4 + B_3$	1 0 1
	[SET 22–101]$_4 + B_1$ [SET 12–201]$_4 + 2_1$ [SET 12–201A]$_4 + B_3$	1 0 $\bar{1}$
	[SET 22–101]$_4 + B_1A_3\bar{B}_2$ [SET 12–201]$_4 + 2_1$ [SET 12–201A]$_4 + \bar{B}_2B_32_22_3$	$\bar{1}$ 0 1
	[SET 22–101]$_4 + B_1A_3\bar{B}_2$ [SET 12–201]$_4 + 2_1$ [SET 12–201A]$_4 + \bar{B}_2B_32_22_3$	$\bar{1}$ 0 $\bar{1}$
	[SET 22–111A]$_5 + B_3$ [SET 12–211A]$_8 + 2_1$ [SET 12–211B]$_4 + B_3$	1 $\bar{1}\,\bar{1}$
	[SET 22–111A]$_5 + B_3A_3\bar{B}_2$ [SET 12–211A]$_8 + 2_1$ [SET 12–211B]$_4 + \bar{B}_2B_32_22_3$	$\bar{1}$ $\bar{1}\,\bar{1}$
	[SET 22–111B]$_7 + \bar{B}_2$ ($\bar{2}\bar{2}2$) $C_2\mathfrak{2}_1\bar{\mathfrak{2}}_2$ ($\bar{3}\bar{2}2$) $3_2\mathfrak{2}_1\bar{\mathfrak{2}}_2$	$\bar{1}\,\bar{1}$ 1
	[SET 22–111B]$_7 + \bar{B}_2$ ($\bar{2}\bar{2}2$) $C_2\mathfrak{2}_1\bar{\mathfrak{2}}_2$ ($\bar{3}\bar{2}2$) $3_2\mathfrak{2}_1\bar{\mathfrak{2}}_2$	$\bar{1}\,\bar{1}$ $\bar{1}$
	(121) $B_2B_2B_2/B_2B_2B_3$ (122) $B_2\mathfrak{2}_1B_2/B_2\mathfrak{2}_1B_3$ (221) $C_1B_2\mathfrak{2}_1/C_1B_2B_3/\mathfrak{2}_1B_2B_2$ (321) $3_1B_2\mathfrak{2}_1$	1 2 1
	[SET 22–121A]$_5 + B_2$ [SET 12–221A]$_4 + 2_1$ [SET 12–221D]$_5 + B_3$	1 2 $\bar{1}$
	[SET 12–221B]$_6 + 2_1$ [SET 12–221E]$_3 + B_3$	1 $\bar{2}\,\bar{1}$
	[SET 32–021]$_8$ [SET 22–021]$_3 + A_2A_3$ [SET 22–121]$_3 + B_2$ [SET 22–121C]$_4 + A_3$	$\bar{1}$ 2 1
	[SET 12–221C]$_3 + \bar{B}_2B_32_22_3$ (221) $C_1B_2\mathfrak{2}_1$ (321) $3_1B_2\mathfrak{2}_1$	
	[SET 32–021]$_8$ [SET 22–021]$_3 + A_2A_3$ [SET 22–121]$_3 + B_2$ [SET 22–121C]$_4 + A_3$	$\bar{1}$ 2 $\bar{1}$
	[SET 12–221D]$_3 + \bar{B}_2B_32_22_3$ (221) $C_1B_2\mathfrak{2}_1$ (321) $3_1B_2\mathfrak{2}_1$	
	[SET 12–221B]$_6 + 2_1$ [SET 12–221E]$_3 + \bar{B}_2B_32_22_3$	$\bar{1}$ $\bar{2}\,\bar{1}$

	$(\bar{2}\bar{2}2)\ C_2 2_1 \bar{2}_2'$ $(\bar{3}\bar{2}2)\ 3_2 2_1 \bar{2}_2'$	$\bar{1}\ 2\ 1$
	$(\bar{1}\bar{2}2)\ \bar{B}_2 2_1 \bar{B}_2$ $(\bar{2}\bar{2}2)\ C_2 2_1 \bar{2}_2'/\bar{2}_2' 2_1 \bar{B}_2$ $(\bar{2}\bar{2}2)\ 2_3 2_1 \bar{B}_2$ $(\bar{3}\bar{2}2)\ 3_2 2_1 \bar{2}_2'$	$\bar{1}\ 2\ \bar{1}$
11	$(102)\ B_1 C_1 1_1$ $(103)\ B_1 3_1 1_1$ $(202)\ 2_1 C_1 1_1$ $(203)\ 2_1 3_1 1_1$	$0\ 0\ 2$
	$(101)\ B_1 B_1 1_1$ $(102)\ B_1 C_1 1_1$ $(201)\ 2_1 B_1 1_1$ $(202)\ 2_1 C_1 1_1$	$0\ 0\ \bar{2}$
	$(\bar{2}\bar{2}2)\ C_2 C_1 \bar{2}_2'$ $(\bar{2}\bar{2}3)\ C_2 3_1 \bar{2}_2'$ $(\bar{3}\bar{2}2)\ 3_2 C_1 \bar{2}_2'$ $(\bar{3}\bar{2}3)\ 3_2 3_1 \bar{2}_2'$ $(122)\ B_2 C_1 1_1$ $(123)\ B_2 3_1 1_1$	$0\ 2\ 2$
	$(\bar{2}\bar{2}2)\ C_2 C_1\ \bar{2}_2'$ $(121)\ B_2 B_2 1_1$ $(122)\ B_2 C_1 1_1$ $(\bar{3}\bar{2}2)\ 3_2 C_1\ \bar{2}_2'$ $(221)\ 2_1 B_2 1_1$	$0\ 2\ \bar{2}$
	$[\text{SET}]\ 21\text{–}102]_4 + B_1$ $[\text{SET}\ 11\text{–}202]_4 + 2_1$ $[\text{SET}\ 11\text{–}202\text{B}]_4 + B_3$	$1\ 0\ 2$
	$[\text{SET}\ 21\text{–}102\text{A}]_4 + B_1$ $[\text{SET}\ 11\text{–}202\text{A}]_4 + 2_1$ $[\text{SET}\ 11\text{–}202\text{C}]_4 + B_3$	$1\ 0\ \bar{2}$
	$[\text{SET}\ 21\text{–}102]_4 + B_1 A_3$ $[\text{SET}\ 21\text{–}102]_4 + A_3 \bar{B}_2$ $[\text{SET}\ 11\text{–}202]_4 + 2_1$ $[\text{SET}\ 11\text{–}202\text{B}]_4 + \bar{B}_2 B_3 2_2 2_3$	$\bar{1}\ 0\ 2$
	$[\text{SET}\ 21\text{–}102\text{A}]_4 + B_1 A_3$ $[\text{SET}\ 21\text{–}102\text{A}]_4 + A_3 \bar{B}_2$ $[\text{SET}\ 11\text{–}202\text{A}]_4 + 2_1$ $[\text{SET}\ 11\text{–}202\text{C}]_4 + \bar{B}_2 B_3 2_2 2_3$	$\bar{1}\ 0\ \bar{2}$
	$[\text{SET}\ 21\text{–}112\text{A}]_8 + \bar{B}_2$ $(\bar{2}\bar{2}2)\ C_2 C_1 2_3$ $(\bar{2}\bar{2}3)\ C_2 3_1 2_3$ $(\bar{3}\bar{2}2)\ 3_2 C_1 2_3$ $(\bar{3}\bar{2}3)\ 3_2 3_1 2_3$	$\bar{1}\ \bar{1}\ 2$
	$[\text{SET}\ 21\text{–}112\text{B}]_6 + \bar{B}_2$ $(\bar{2}\bar{2}2)\ C_2 C_1 2_2$ $(\bar{3}\bar{2}2)\ 3_2 C_1 2_2$	$\bar{1}\ \bar{1}\ \bar{2}$
	$(122)\ B_2 C_1 B_2 / B_2 C_1 B_3$ $(123)\ B_2 3_1 B_2 / B_2 3_1 B_3$	$1\ 2\ 2$
	$(122)\ B_2 C_1 B_2 / B_2 C_1 B_3$ $(221)\ C_1 B_2 2_1$ $(123)\ B_2 3_1 B_2 / B_2 3_1 B_3$ $(321)\ 3_1 B_2 2_1$	$1\ 2\ \bar{2}$
	$[\text{SET}\ 31\text{–}022]_8\ [\text{SET}\ 21\text{–}022]_2 + A_2 A_3$ $(022)\ A_2 C_1 A_3$ $(122)\ B_2 C_1 B_2 / B_2 C_1 A_3$ $(023)\ A_2 3_1 A_3$ $(123)\ B_2 3_1 B_2 / B_2 3_1 A_3$	$\bar{1}\ 2\ 2$
	$[(122)\ B_2 C_1$ $(123)\ B_2 3_1] + \bar{B}_2 B_3 2_2 2_3$	
	$[\text{SET}\ 31\text{–}022\text{A}]_4\ [\text{SET}\ 21\text{–}022\text{A}]_3 + A_2 A_3$ $[\text{SET}\ 21\text{–}122\text{A}]_3 + B_2$	$\bar{1}\ 2\ \bar{2}$
	$[\text{SET}\ 21\text{–}122\text{C}]_5 + A_3$ $(221)\ C_1 B_2 2_1$ $(321)\ 3_1 B_2 2_1$ $[\text{SET}\ 11\text{–}222\text{D}]_3 + \bar{B}_2 B_3 2_2 2_3$	
	$(2\bar{2}\bar{2})\ C_1 C_2 2_1 / C_1 C_2 B_3$ $(2\bar{2}\bar{3})\ C_1 3_2 2_1 / C_1 3_2 B_3$ $(3\bar{2}\bar{2})\ 3_1 C_2 2_1$ $(3\bar{2}\bar{3})\ 3_1 3_2 2_1$	$1\ \bar{2}\ \bar{2}$
	$(2\bar{2}\bar{2})\ C_1 C_2 2_1$ $(2\bar{2}\bar{3})\ C_1 3_2 2_1$ $(3\bar{2}\bar{2})\ 3_1 C_2 2_1$ $(3\bar{2}\bar{3})\ 3_1 3_2 2_1$ $[(2\bar{2}\bar{2})\ C_1 C_2$ $(2\bar{2}\bar{3})\ C_1 3_2] + \bar{B}_2 B_3 2_2 2_3$	$\bar{1}\ \bar{2}\ \bar{2}$
	$[\text{SET}\ 21\text{–}122\text{E}]_6 + \bar{B}_2$ $[\text{SET}\ 11\text{–}222\text{F}]_4 + \bar{2}_2'$	$\bar{1}\ 2\ 2$
	$(\bar{1}\bar{2}2)\ \bar{B}_2 C_1 \bar{B}_2$ $(\bar{2}\bar{2}2)\ \bar{2}_2' C_1 \bar{B}_2 / C_2 C_1 \bar{2}_2'$ $(\bar{2}\bar{2}2)\ 2_3 C_1 \bar{B}_2$ $(\bar{3}\bar{2}2)\ 3_2 C_1 \bar{2}_2'$	$\bar{1}\ 2\ \bar{2}$

($\alpha\gamma\beta$) Pattern

σ-Block	Sequence Sets	Product α β γ
I. $\sigma_\beta = 3$		
333	(0$\bar{1}\bar{1}$) ($\bar{1}$10) (1$\bar{1}\bar{1}$) $A_3\bar{1}'_2A_1$ ($\bar{1}\bar{1}$1) $\bar{1}_3\bar{1}'_2A_1$ ($\bar{1}\bar{2}$1) $\bar{1}'_3\bar{1}_2A_1$	0 0 0
332	($\bar{1}\bar{1}$1) $\bar{1}'_21_2A_1$ ($\bar{1}\bar{2}$1) $\bar{1}_21_2A_1$ $[\text{SET 32–011A}]_{10} + \bar{1}_2$	0 0 0
	$[\text{SET 32–011A}]_{10} + \bar{1}'_2$	0 0 1
	$[\text{SET 32–011A}]_{10} + A_3\bar{1}'_3$ [(101) A_1B_1 (102) A_12_1 ($\bar{1}\bar{1}$1) $\bar{1}_2B_1$ ($\bar{1}\bar{1}$2) $\bar{1}_32_1/\bar{1}'_22_1$ ($\bar{1}\bar{2}$2) $\bar{1}_32_1$] $+ A_3$	0 0 $\bar{1}$
331	(102) $A_1C_1A_2$ (103) $A_13_1A_2$ ($\bar{1}\bar{1}$2) $\bar{1}_3C_1A_2/\bar{1}'_2C_1A_2$	0 0 2
	($\bar{1}\bar{1}$3) $\bar{1}_33_1A_2/\bar{1}'_23_1A_2$ ($\bar{1}\bar{2}$2) $\bar{1}_3C_1A_2$ ($\bar{1}\bar{2}$3) $\bar{1}_33_1A_2$	
233	(1$\bar{1}\bar{1}$) $1_1\bar{1}'_2A_1$ (1$\bar{2}\bar{1}$) $1_1\bar{1}_2A_1$ $[\text{SET 23–110A}]_{12} + \bar{1}_2$	0 0 0
	$[\text{SET 23–110A}]_{12} + \bar{1}'_2$	1 0 0
	$[\text{SET 23–110A}]_{12} + \bar{1}'_3$ $[\text{SET 23–110A}]_{12}[\text{SET 23–110A}]_5[\text{SET 23–110}]_4 + A_3$	$\bar{1}$ 0 0
232	$[\text{SET 22–011A}]_{11} + \bar{1}_2$ (111) $1_21_2A_1$ ($\bar{1}\bar{1}$1) ($\bar{2}\bar{1}$1) $\bar{B}_21_1\bar{1}_2$ ($\bar{2}\bar{2}$1) $\bar{2}_21_1\bar{1}_2$	0 0 0
	$[\text{SET 22–011A}]_{11} + \bar{1}'_2$ $[\text{SET 22–111B}]_7 + \bar{1}_2$	0 0 1
	$[\text{SET 22–011A}]_{11} + A_3\bar{1}'_3$ $[\text{SET 22–111B}]_7 + \bar{1}_2$ [(101) 1_1B_1 (102) 1_12_1 (112) 1_22_1] $+ A_3$	0 0 $\bar{1}$
	$[\text{SET 22–111A}]_5 + \bar{1}_2$ ($\bar{1}\bar{1}$1) ($\bar{2}\bar{1}$1) $\bar{B}_21_1\bar{1}'_2$ ($\bar{2}\bar{2}$1) $\bar{2}_21_1\bar{1}'_2$	1 0 0
	$[\text{SET 22–111A}]_5 + \bar{1}_2$ [($\bar{1}\bar{1}$1) ($\bar{2}\bar{1}$1) $\bar{B}_21_1$ ($\bar{2}\bar{2}$1) $\bar{2}_21_1$] $+ \bar{1}'_3$	$\bar{1}$ 0 0
	[(101) B_11_1 (201) 2_11_1 (211) 2_11_2 ($\bar{1}\bar{1}$1) ($\bar{2}\bar{1}$1) $\bar{B}_21_1$ ($\bar{2}\bar{2}$1) $\bar{2}_21_1$] $+ A_3$	
	$[\text{SET 22–111A}]_5[\text{SET 22–111B}]_7 + \bar{1}'_2$	1 0 1
	$[\text{SET 22–111A}]_5 + A_3\bar{1}'_3$ $[\text{SET 22–111B}]_7 + \bar{1}'_2$	1 0 $\bar{1}$
	$[\text{SET 22–111A}]_5 + \bar{1}'_2$ $[\text{SET 22–111B}]_7 + A_3\bar{1}'_3$	$\bar{1}$ 0 1
	$[\text{SET 22–111A}]_5[\text{SET 22–111B}]_7 + A_3\bar{1}'_3$ $[\text{SET 22–101}]_4$ [(212) 2_12_1] $+ A_3$	$\bar{1}$ 0 $\bar{1}$
231	($\bar{1}\bar{1}$1) ($\bar{2}\bar{1}$1) $\bar{B}_2B_3\bar{1}_2$ (1$\bar{1}\bar{2}$) $1_1B_3\bar{1}_2$	0 0 1*
	(102) $1_1C_1A_2$ (103) $1_13_1A_2$ (112) $1_2C_1A_2$ (113) $1_23_1A_2$ ($\bar{1}\bar{1}$1) ($\bar{2}\bar{1}$1) $\bar{B}_2B_3\bar{1}'_2$	0 0 2

	$(1\bar{1}\bar{2})\ 1_1B_3\bar{1}'_2$ $[\text{SET 22–112A}]_8 + A_2\bar{1}_2$	
	$[(\bar{1}\bar{1}1)\ (\bar{2}\bar{1}1)\ \bar{B}_2B_3\ \ (1\bar{1}\bar{2})\ 1_1B_3] + \bar{1}'_3$ $[\text{SET 22–112B}]_8 + \bar{1}_2$	0 0 $\bar{2}$
	$[\text{SET 22–112A}]_8 + \bar{1}'_2$	1 0 2
	$[\text{SET 22–112B}]_8 + \bar{1}'_2$	1 0 $\bar{2}$
	$[(102)\ B_1C_1\ \ (103)\ B_13_1\ \ (202)\ (212)\ 2_1C_1\ \ (203)\ (213)\ 2_13_1] + A_2$ $[\text{SET 22–112A}]_8 + A_3\bar{1}'_3$	$\bar{1}$ 0 2
	$[(101)\ B_1B_1\ \ (102)\ B_1C_1\ \ (201)\ 2_1B_1\ \ (202)\ (212)\ 2_1C_1] + A_3$ $[\text{SET 22–112A}]_8 + A_3\bar{1}'_3$	$\bar{1}$ 0 $\bar{2}$
133	$(201)\ C_1A_1A_2\ \ (2\bar{1}\bar{1})\ C_1\bar{1}_3A_2/C_1\bar{1}'_2A_2\ \ (2\bar{2}\bar{1})\ C_1\bar{1}_3A_2\ \ (301)\ 3_1A_1A_2\ \ (3\bar{1}\bar{1})\ 3_1\bar{1}_3A_2/3_1\bar{1}'_2A_2\ \ (3\bar{2}\bar{1})\ 3_1\bar{1}_3A_2$	2 0 0
132	$(201)\ C_1l_1A_2\ \ (211)\ C_1l_2A_2\ \ (301)\ 3_1l_1A_2\ \ (311)\ 3_1l_2A_2$ $[\text{SET 12–211A}]_8 + A_2\bar{1}_2$	2 0 0
	$(2\bar{1}\bar{1})\ (2\bar{1}\bar{2})\ C_1\bar{B}_2\bar{1}_2\ \ (1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2\bar{1}_2$	$\bar{2}$ 0 0
	$[\text{SET 12–211A}]_8 + \bar{1}'_2$	2 0 1
	$[\text{SET 12–211A}]_8 + A_3\bar{1}'_3$ $[(201)C_1B_1\ \ (202)\ (212)\ C_12_1\ \ (301)\ 3_1B_1\ \ (302)\ (312)\ 3_12_1] + A_2$	2 0 $\bar{1}$
	$(2\bar{1}\bar{1})\ (2\bar{1}\bar{2})\ C_1\bar{B}_2\bar{1}'_2\ \ (1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2\bar{1}'_2$	$\bar{2}$ 0 1
	$[(101)\ B_1B_1\ \ (201)\ C_1B_1\ \ (102)\ B_12_1\ \ (202)\ C_12_1] + A_3\ \ [(2\bar{1}\bar{1})\ (2\bar{1}\bar{2})\ C_1\bar{B}_2\ \ (1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{B}_2] + A_3\bar{1}'_3$	$\bar{2}$ 0 $\bar{1}$
131	$(202)\ (212)\ C_1C_1A_2\ \ (203)\ (213)\ C_13_1A_2\ \ (302)\ (312)\ 3_1C_1A_2\ \ (303)\ (313)\ 3_13_1A_2$	2 0 2
	$(201)\ C_1B_1A_2\ \ (202)\ (212)\ C_1C_1A_2\ \ (301)\ 3_1B_1A_2\ \ (302)\ (312)\ 3_1C_1A_2$	2 0 $\bar{2}$
	$(102)\ B_1C_1A_2\ \ (202)\ (212)\ C_1C_1A_2\ \ (103)\ B_13_1A_2\ \ (203)\ (213)\ C_13_1A_2$	$\bar{2}$ 0 2
II. $\sigma_\beta = 2$		
323	$(0\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ (1\bar{1}\bar{1})\ A_3\bar{1}'_2l_1\ \ (\bar{1}\bar{1}1)\ \bar{1}'_3\ \bar{1}'_2\ 1_1\ \ (\bar{1}\bar{2}1)\ \bar{1}'_3\bar{1}_2l_1$	0 0 0
	$[\text{SET 33–020}]_{13} + 2_1\ \ (0\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ (1\bar{1}\bar{1})\ A_3\bar{1}'_2B_1\ \ (\bar{1}\bar{1}1)\ \bar{1}'_3\bar{1}'_2B_1\ \ (\bar{1}\bar{2}1)\ \bar{1}'_3\bar{1}_2B_1$	0 1 0
	$[\text{SET 33–020}]_{13} + 2_1\ \ (0\bar{1}\bar{1})\ (\bar{1}\bar{1}0)\ (1\bar{1}\bar{1})\ A_3\bar{1}'_2B_1\ \ (\bar{1}\bar{1}1)\ \bar{1}'_3\bar{1}'_2B_1\ \ (\bar{1}\bar{2}1)\ \bar{1}'_3\bar{1}_2B_1$	0 $\bar{1}$ 0
322	$(\bar{1}\bar{1}1)\ \bar{1}'_2l_2l_1\ \ (\bar{1}\bar{2}1)\ \bar{1}_2l_2l_1$	0 0 0
	$(\bar{1}\bar{1}1)\ \bar{1}'_2l_2B_1\ \ (\bar{1}\bar{2}1)\ \bar{1}_2l_2B_1\ \ (0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}'_2l_1\ \ (021)\ (121)\ (\bar{1}21)\ A_2l_12_1\ \ (\bar{1}\bar{2}1)\ \bar{1}'_2l_12_1$	0 1 0
	$(\bar{1}\bar{1}1)\ \bar{1}'_2\ 1_2B_1\ \ (\bar{1}\bar{2}1)\ \bar{1}_2l_2B_1\ \ (0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}'_21_1\ \ (021)\ (121)\ (\bar{1}21)\ A_2l_12_1\ \ (\bar{1}\bar{2}1)\ \bar{1}'_2l_12_1$	0 $\bar{1}$ 0
	$(\bar{1}\bar{1}2)\ \bar{1}'_22_1l_2\ \ (\bar{1}\bar{2}2)\ \bar{1}_32_1l_2$	0 0 1
	$(\bar{1}\bar{1}2)\ \bar{1}'_22_1l_1\ \ (\bar{1}\bar{2}2)\ \bar{1}_32_1l_1$	0 0 $\bar{1}$

($\alpha\gamma\beta$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
322	$[\text{SET 32-021}]_8 + 2_1$	0 1 1
	$[\text{SET 32-021A}]_{12} + 2_1$ $[(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}'_2$ $(\bar{1}\bar{1}2)\ \bar{1}'_2 2_1$, $(\bar{1}\bar{2}1)\ \bar{1}'_3\bar{B}_2$ $(\bar{1}\bar{2}2)\ \bar{1}_3 2_1] + B_3$	0 1 $\bar{1}$
	$[\text{SET 32-021}]_8 + 2_1$	0 $\bar{1}$ 1
	$[\text{SET 32-021A}]_{12} + 2_1$ $[(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}'_2$ $(\bar{1}\bar{1}2)\ \bar{1}'_2 2_1$ $(\bar{1}\bar{2}1)\ \bar{1}'_3\bar{B}_2$ $(\bar{1}\bar{2}2)\ \bar{1}_3 2_1] + B_3$	0 $\bar{1}$ $\bar{1}$
	$[\text{SET 32-011A}]_{10} + \bar{B}_2 A_3$ $[(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3\bar{2}'_2$ $(\bar{1}\bar{2}1)\ \bar{1}'_3\bar{B}_2] + \bar{B}_2 2_3$	0 $\bar{1}\bar{1}$
	$[(101)\ A_1B_1$ $(102)\ A_1 2_1$ $(\bar{1}\bar{1}1)\ \bar{1}_2B_1$ $(\bar{1}\bar{1}2)\ \bar{1}_3 2_1/\bar{1}'_2 2_1$ $(\bar{1}\bar{2}2)\ \bar{1}_3 2_1] + A_3$	
321	$(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3C_2\bar{2}_2$	0 $\bar{1}\bar{1}$
	$(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3C_2\bar{2}'_2$ $(\bar{1}\bar{1}2)\ \bar{1}'_2C_1 1_1$ $(\bar{1}\bar{1}3)\ \bar{1}'_2 3_1 1_1$ $(\bar{1}\bar{2}2)\ \bar{1}_3C_1 1_1$ $(\bar{1}\bar{2}3)\ \bar{1}_3 3_1 1_1$	0 0 2
	$[\text{SET 31-022}]_8 + 2_1$ $(\bar{1}\bar{1}2)\ \bar{1}'_2C_1B_2$ $(\bar{1}\bar{1}3)\ \bar{1}'_2 3_1B_2$ $(\bar{1}\bar{2}2)\ \bar{1}_3C_1B_2$ $(\bar{1}\bar{2}3)\ \bar{1}_2 3_1B_2$	0 1 2
	$[\text{SET 31-022A}]_8 + 2_1$	0 1 $\bar{2}$
	$[\text{SET 31-022}]_8 + 2_1$ $(102)\ A_1C_1A_2$ $(103)\ A_1 3_1A_2$ $(\bar{1}\bar{1}2)\ \bar{1}_3C_1A_2/\bar{1}'_2C_1B_2$ $(\bar{1}\bar{1}3)\ \bar{1}_3 3_1A_2/\bar{1}'_2 3_1B_2$ $(\bar{1}\bar{2}2)\ \bar{1}_3C_1B_2$ $(\bar{1}\bar{2}3)\ \bar{1}_3 3_1B_2$	0 $\bar{1}$ 2
	$[\text{SET 31-022Al}]_8 + 2_1$	0 $\bar{1}$ $\bar{2}$
	$(0\bar{2}\bar{2})\ (1\bar{2}\bar{2})\ A_3C_2\bar{2}'_2$	0 $\bar{1}\bar{2}$
223	$(1\bar{1}\bar{1})\ 1_1\bar{1}'_2 1_1$ $(1\bar{2}\bar{1})\ 1_1\bar{1}_2 1_1$	0 0 0
	$[\text{SET 23-020}]_7 + 2_1$ $(1\bar{1}\bar{1})\ 1_1\bar{1}'_2B_1$ $(1\bar{2}\bar{1})\ 1_1\bar{1}_2B_1$	0 1 0
	$[\text{SET 23-020}]_7 + 2_1$ $(1\bar{1}\bar{1})\ 1_1\bar{1}'_2B_1$ $(1\bar{2}\bar{1})\ 1_2\bar{1}_2B_1$	0 $\bar{1}$ 0
	$(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{1}'_2 1_2$ $(2\bar{1}\bar{1})\ 2_1\bar{1}'_2 1_2$ $(2\bar{2}\bar{1})\ 2_1\bar{1}_2 1_2$	1 0 0
	$(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{1}'_2 1_1$ $(2\bar{1}\bar{1})\ 2_1\bar{1}'_2 1_1$ $(2\bar{2}\bar{1})\ 2_1\bar{1}_2 1_1$	$\bar{1}$ 0 0
	$[\text{SET 23-120}]_7 + 2_1$	1 1 0
	$[\text{SET 23-120}]_7 + 2_1$	1 $\bar{1}$ 0
	$[\text{SET 23-120A}]_{10} + 2_1$ $[(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{1}'_2$ $(2\bar{1}\bar{1})\ 2_1\bar{1}'_2$ $(2\bar{2}\bar{1})\ 2_1\bar{1}_2/2_1\bar{1}'_3] + B_3$	$\bar{1}$ 1 0
	$[\text{SET 23-120A}]_{10} + 2_1$ $[(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{1}'_2$ $(2\bar{1}\bar{1})\ 2_1\bar{1}'_2$ $(2\bar{2}\bar{1})\ 2_1\bar{1}_2/2_1\bar{1}'_3] + B_3$	$\bar{1}$ $\bar{1}$ 0
	$[\text{SET 23-110A}]_{12}$ $[(2\bar{2}\bar{1})\ 2_1\bar{1}'_3] + \bar{B}_2 2_3$ $[\text{SET 23-100A}]_5\,[\text{SET 23-110}]_4 + A_3$	$\bar{1}\bar{1}$ 0

222	(111) $1_2 1_2 1_1$	0 0 0
	(111) $1_2 1_2 B_1$ (121) $1_1 1_1 2_1$ ($\bar{2}\bar{2}1$) $\bar{2}'_2 1_1 2_1$ (1$\bar{2}\bar{2}$) $1_1 \bar{2}'_2 2_1$	0 1 0
	(111) $1_2 1_2 B_1$ (121) $1_1 1_1 2_1$ ($\bar{2}\bar{2}1$) $\bar{2}'_2 1_1 2_1$ (1$\bar{2}\bar{2}$) $1_1 \bar{2}'_2 2_1$	0 $\bar{1}$ 0
	(112) $1_2 2_1 1_1$	0 0 1
	(112) $1_2 2_1 1_1$	0 0 $\bar{1}$
	(121) $1_1 B_2 2_1$ (122) $1_1 2_1 2_1$ ($\bar{2}\bar{2}1$) $\bar{2}'_2 B_2 2_1$ ($\bar{2}\bar{2}2$) $\bar{2}'_2 2_1 2_1$	0 1 1
	[(112) $1_2 2_1 (1\bar{2}\bar{1})$ $1_1 \bar{B}_2$ (1$\bar{2}\bar{2}$) $1_1 2_2$ (1$\bar{2}\bar{2}$) $1_1 \bar{2}'_2$] + B_3 [(120) $1_1 A_2$ (121) $1_1 B_2$ ($\bar{2}\bar{2}0$) $\bar{2}'_2 A_2$ ($\bar{2}\bar{2}1$) $\bar{2}'_2 B_2$ ($\bar{2}\bar{2}2$) $\bar{2}'_2 B_2$] + 2_1	0 1 $\bar{1}$
	(121) $1_1 B_2 2_1$ (122) $1_1 2_1 2_1$ ($\bar{2}\bar{2}1$) $\bar{2}'_2 B_2 2_1$ ($\bar{2}\bar{2}2$) $\bar{2}'_2 2_1 2_1$	0 $\bar{1}$ 1
	[(112) $1_2 2_1$ (1$\bar{2}\bar{1}$) $1_1 \bar{B}_2$ (1$\bar{2}\bar{2}$) $1_1 2_2$ (1$\bar{2}\bar{2}$) $1_1 \bar{2}'_2$] + B_3 [(120) $1_1 A_2$ (121) $1_1 B_2$ ($\bar{2}\bar{2}0$) $\bar{2}'_2 A_2$ ($\bar{2}\bar{2}1$) $\bar{2}'_2 B_2$ ($\bar{2}\bar{2}2$) $\bar{2}'_2 B_2$] + 2_1	0 $\bar{1}$ $\bar{1}$
	[(101) $1_1 B_1$ (102) $1_1 2_1$ (112) $1_2 2_1$] + A_3 [SET 22-011A]$_{11}$ + $\bar{B}_2 A_3$ [(1$\bar{2}\bar{1}$) $1_1 \bar{B}_2$ (1$\bar{2}\bar{2}$) $1_1 2_2$ (1$\bar{2}\bar{2}$) $1_1 \bar{2}'_2$] + $\bar{B}_2 2_3$	0 $\bar{1}$ $\sqcap$1
	(211) $2_1 1_2 1_2$	1 0 0
	(211) $2_1 1_2 1_2$	$\bar{1}$ 0 0
	(121) $B_2 1_1 2_1$ (221) $2_1 1_1 2_1$ ($2\bar{2}\bar{2}$) $2_1 \bar{2}'_2 2_1$	1 1 0
	(121) $B_2 1_1 2_1$ (221) $2_1 1_1 2_1$ ($2\bar{2}\bar{2}$) $2_2 \bar{2}'_2 2_1$	1 $\bar{1}$ 0
	[(021) $A_2 1_1$ (121) $B_2 1_1$ (221) $2_1 1_1$ ($2\bar{2}\bar{2}$) $2_1 \bar{2}'_2$] + 2_1 [($\bar{1}\bar{2}1$) $\bar{B}_2 1_1$ (211) $2_1 1_2$ ($\bar{2}\bar{2}1$) $2_2 1_1$ ($\bar{2}\bar{2}1$) $\bar{2}'_2 1_1$] + B_3	$\bar{1}$ 1 0
	[(021) $A_2 1_1$ (121) $B_2 1_1$ (221) $2_1 1_1$ ($2\bar{2}\bar{2}$) $2_1 \bar{2}'_2$] + 2_1 [($\bar{1}\bar{2}1$) $\bar{B}_2 1_1$ (211) $2_1 1_2$ ($\bar{2}\bar{2}1$) $2_2 1_1$ ($\bar{2}\bar{2}1$) $\bar{2}'_2 1_1$] + B_3	$\bar{1}$ $\bar{1}$ 0
	[(101) $B_1 1_1$ (201) $2_1 1_1$ (211) $2_1 1_2$] + A_3 [($\bar{1}\bar{1}1$) ($\bar{2}1$1) $\bar{B}_2 1_1$ ($\bar{2}\bar{2}1$) $\bar{2}_2 1_1$] + $\bar{B}_2 A_3$ [($\bar{1}\bar{2}1$) $\bar{B}_2 1_1$ ($\bar{2}\bar{2}1$) $2_2 1_1$ ($\bar{2}\bar{2}1$) $\bar{2}'_2 1_1$] + $\bar{B}_2 2_3$	$\bar{1}$ $\sqcap$1 0
	(212) $2_1 2_1 1_1$	1 0 1
	(212) $2_1 2_1 1_1$	1 0 $\bar{1}$
	(212) $2_1 2_1 1_1$	$\bar{1}$ 0 1
	(212) $2_1 2_1 1_1$	$\bar{1}$ 0 $\bar{1}$
	(121) $B_2 B_2 2_1$ (122) $B_2 2_1 2_1$ (221) $2_1 B_2 2_1$ (222) $2_1 2_1 2_1$	1 1 1
	(120) $B_2 A_2 2_1$ (121) $B_2 B_2 2_1$ (122) $B_2 2_1 2_1$ (220) $2_1 A_2 2_1$ (221) $2_1 B_2 2_1$ (222) $2_1 2_1 2_1$	1 1 $\bar{1}$
	(121) $B_2 B_2 2_1$ (122) $B_2 2_1 2_1$ (221) $2_1 B_2 2_1$ (222) $2_1 2_1 2_1$	1 $\bar{1}$ 1
	(120) $B_2 A_2 2_1$ (121) $B_2 B_2 2_1$ (122) $B_2 2_1 2_1$ (220) $2_1 A_2 2_1$ (221) $2_1 B_2 2_1$ (222) $2_1 2_1 2_1$	1 $\bar{1}$ $\bar{1}$

($\alpha\gamma\beta$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
222	$[(2\bar{2}\bar{1})\ 2_1\bar{B}_2\ \ (2\bar{2}\bar{2})\ 2_12_2\ \ (2\bar{2}\bar{2})\ 2_1\bar{2}_2'] + 2_3$	1 $\bar{1}$
	(021) $A_2B_22_1$ (121) $B_2B_22_1$ (122) $B_22_12_1$ (221) $2_1B_22_1$ (222) $2_12_12_1$	$\bar{1}$ 1 1
	[SET 22–121D]$_8 + 2_1$ (222) $2_12_12_1$ [SET 22–121E]$_3$ [SET 22–121F]$_3$ $[(212)\ 2_12_1] + B_3$	$\bar{1}$ 1 $\bar{1}$
	(021) $A_2B_22_1$ (121) $B_2B_22_1$ (122) $B_22_12_1$ (221) $2_1B_22_1$ (222) $2_12_12_1$	$\bar{1}$ $\bar{1}$ 1
	[SET 22–121D]$_8 + 2_1$ (222) $2_12_12_1$ [SET 22–121E]$_3$ [SET 22–121F]$_3$ $[(212)\ 2_12_1] + B_3$	$\bar{1}$ $\bar{1}$ $\bar{1}$
	[SET 22–101]$_4$ $[(212)\ 2_12_1] + A_3$ [SET 22–111A]$_5 + \bar{B}_2A_3$ [SET 22–121E]$_3 + \bar{B}_22_3$	$\bar{1}$ $\bar{1}$
	$[(\bar{1}\bar{2}2)\ \bar{B}_22_1\ \ (\bar{2}\bar{2}2)\ 2_32_1\ \ (\bar{2}\bar{2}2)\ \bar{2}_2'2_1] + 2_3$	$\bar{1}$ 1
	[SET 22–101]$_4$ $[(212)\ 2_12_1] + A_3$ [SET 22–111B]$_7 + \bar{B}_2A_3$ [SET 22–121F]$_3 + \bar{B}_22_3$	$\bar{1}$ $\bar{1}$
221	$(1\bar{2}\bar{2})\ 1_1C_2\bar{2}_2\ \ (1\bar{2}\bar{3})\ 1_13_2\bar{2}_2$	0 $\bar{1}$
	(112) $1_2C_11_1$ (113) $1_23_11_1$ $(1\bar{2}\bar{2})\ 1_1C_2\bar{2}_2'$ $(1\bar{2}\bar{3})\ 1_13_2\bar{2}_2'$	0 0 2
	(112) $1_2C_11_1$	0 0 $\bar{2}$
	(112) $1_2C_1B_2$ (113) $1_23_1B_2$ (122) $1_1C_12_1$ (123) $1_13_12_1$ $(\bar{2}\bar{2}2)\ \bar{2}_2'C_12_1$ $(\bar{2}\bar{2}3)\ \bar{2}_2'3_12_1$	0 1 2
	(121) $1_1B_22_1$ (122) $1_1C_12_1$ $(\bar{2}\bar{2}1)\ \bar{2}_2'B_22_1$ $(\bar{2}\bar{2}2)\ \bar{2}_2'C_12_1$	0 1 $\bar{2}$
	$[(102)\ 1_1C_1\ (103)\ 1_13_1] + A_2$ $[(112)\ 1_2C_1\ (113)\ 1_23_1] + B_2$ $[(122)\ 1_1C_1\ (123)1_13_1\ (\bar{2}\bar{2}2)\ \bar{2}_2'C_1\ (\bar{2}\bar{2}3)\ \bar{2}_2'3_1] + 2_1$	0 $\bar{1}$ 2
	(121) $1_1B_22_1$ (122) $1_1C_12_1$ $(\bar{2}\bar{2}1)\ \bar{2}_2'B_22_1$ $(\bar{2}\bar{2}2)\ \bar{2}_2'C_12_1$	0 $\bar{1}$ $\bar{2}$
	$(\bar{1}\bar{1}1)\ (\bar{2}\bar{1}1)\ \bar{B}_2B_3\bar{B}_2\ \ (1\bar{1}2)\ 1_1B_3\bar{B}_2\ \ (1\bar{2}\bar{2})\ 1_1C_2\bar{2}_2'\ \ (1\bar{2}\bar{3})\ 1_13_2\bar{2}_2'$	0 $\bar{1}$
	(212) $2_1C_11_1$ (213) $2_13_11_1$ $(2\bar{2}\bar{2})\ 2_1C_2\bar{2}_2'$ $(2\bar{2}\bar{3})\ 2_13_2\bar{2}_2'$	1 0 2
	(212) $2_1C_11_1$	1 0 $\bar{2}$
	(212) $2_1C_11_1$ (213) $2_13_11_1$ $(2\bar{2}\bar{2})\ 2_1C_2\bar{2}_2'$ $(2\bar{2}\bar{3})\ 2_13_2\bar{2}_2'$	$\bar{1}$ 0 2
	(212) $2_1C_11_1$	$\bar{1}$ 0 $\bar{2}$
	$(2\bar{2}\bar{2})\ 2_1C_2\bar{2}_2\ \ (2\bar{2}\bar{3})\ 2_13_2\bar{2}_2$	1 $\bar{1}$
	$(2\bar{2}\bar{2})\ 2_1C_2\bar{2}_2\ \ (2\bar{2}\bar{3})\ 2_13_2\bar{2}_2$	$\bar{1}$ $\bar{1}$
	(122) $B_2C_12_1$ (123) $B_23_12_1$ (222) $2_1C_12_1$ (223) $2_13_12_1$	1 1 2

	$(121)\ B_2B_2\mathbf{2}_1\quad(122)\ B_2C_1\mathbf{2}_1\quad(221)\ \mathbf{2}_1B_2\mathbf{2}_1\quad(222)\ \mathbf{2}_1C_1\mathbf{2}_1$	1 1 2
	$(122)\ B_2C_1\mathbf{2}_1\quad(123)\ B_2\mathbf{3}_1\mathbf{2}_1\quad(222)\ \mathbf{2}_1C_1\mathbf{2}_1\quad(223)\ \mathbf{2}_1\mathbf{3}_1\mathbf{2}_1$	1 $\bar{1}$ 2
	$(121)\ B_2B_2\mathbf{2}_1\quad(122)\ B_2C_1\mathbf{2}_1\quad(221)\ \mathbf{2}_1B_2\mathbf{2}_1\quad(222)\ \mathbf{2}_1C_1\mathbf{2}_1$	1 $\bar{1}$ 2
	$[\text{SET 21–122B}]_4\quad[(222)\ \mathbf{2}_1C_1\ (223)\ \mathbf{2}_1\mathbf{3}_1]+2_1\quad[\text{SET 21–122E}]_6+B_3\quad[(212)\ \mathbf{2}_1C_1\ (213)\ \mathbf{2}_1\mathbf{3}_1]+B_2$	$\bar{1}$ 1 2
	$[(022)\ A_2C_1\ (122)\ B_1C_1\ (221)\ \mathbf{2}_1B_2\ (222)\ \mathbf{2}_1C_1]+2_1\quad[(\bar{1}\bar{2}2)\ \bar{B}_2C_1\ (\bar{2}\bar{2}2)\ 2_3C_1\ (\bar{2}\bar{2}2)\ \bar{2}'_2C_1]+B_3$	$\bar{1}$ 1 2
	$[\text{SET 21–122B}]_4\,[(222)\ \mathbf{2}_1C_1\ (223)\ \mathbf{2}_1\mathbf{3}_1]+2_1\quad[\text{SET 21–122E}]_6+B_3\quad[(212)\ \mathbf{2}_1C_1\ (213)\ \mathbf{2}_1\mathbf{3}_1]+B_2$	$\bar{1}$ $\bar{1}$ 2
	$[(102)\ B_1C_1\ (103)\ B_1\mathbf{3}_1\ (202)\ \mathbf{2}_1C_1\ (203)\ \mathbf{2}_1\mathbf{3}_1]+A_2$	
	$[(022)\ A_2C_1\ (122)\ B_2C_1\ (221)\ \mathbf{2}_1B_2\ (222)\ \mathbf{2}_1C_1]+2_1\quad[(\bar{1}\bar{2}2)\ \bar{B}_2C_1\ (\bar{2}\bar{2}2)\ 2_3C_1\ (\bar{2}\bar{2}2)\ \bar{2}'_2C_1]+B_3$	$\bar{1}$ $\bar{1}$ 2
	$(2\bar{2}\bar{2})\ \mathbf{2}_1C_2\bar{2}'_2\quad(2\bar{2}\bar{3})\mathbf{2}_1\mathbf{3}_2\bar{2}'_2$	1 $\bar{1}$ $\bar{2}$
	$(2\bar{2}\bar{2})\ \mathbf{2}_1C_2\bar{2}'_2\quad(2\bar{2}\bar{3})\ \mathbf{2}_1\mathbf{3}_2\bar{2}'_2$	$\bar{1}$ $\bar{1}$ $\bar{2}$
	$[\text{SET 21–102}]_4\,[(212)\ \mathbf{2}_1C_1\ (213)\ \mathbf{2}_1\mathbf{3}_1]+A_3\quad[\text{SET 21–112A}]_8+\bar{B}_2A_3\quad[\text{SET 21–122E}]_6+\bar{B}_2\mathbf{2}_3$	$\bar{1}$ $\bar{1}$ 2
	$[\text{SET 21–102A}]_4\,[(212)\ \mathbf{2}_1C_1\ (213)\ \mathbf{2}_1\mathbf{3}_1]+A_3\quad[\text{SET 21–112B}]_8+\bar{B}_2A_3\quad[\text{SET 21–122F}]_3+B_2\mathbf{2}_3$	$\bar{1}$ $\bar{1}$ 2
123	$(\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ C_2A_3\bar{2}_2\quad(\bar{3}\bar{2}0)\ (\bar{3}\bar{2}1)\ 3_2A_3\bar{2}_2$	$\bar{1}$ $\bar{1}$ 0
	$[(2\bar{1}\bar{1})\ C_1\bar{1}'_2\ (2\bar{2}\bar{1})\ C_1\bar{1}_3\ (3\bar{1}\bar{1})\ 3_1\bar{1}'_2\ (3\bar{2}\bar{1})\ 3_1\bar{1}_3]+1_1\quad[(\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ C_2A_3\ (\bar{3}\bar{2}0)\ (\bar{3}\bar{2}1)\ 3_2A_3]+\bar{2}'_2$	2 0 0
	$(1\bar{1}\bar{1})\ (\bar{2}\bar{1}0)\ B_3\bar{1}'_2\mathbf{1}_1\quad(2\bar{1}\bar{1})\ C_1\bar{1}'_2\mathbf{1}_1\quad(2\bar{2}\bar{1})\ C_1\bar{1}_2\mathbf{1}_1$	2 0 0
	$[\text{SET 13–210}]_4+B_2\quad[\text{SET 13–220}]_8+2_1$	2 1 0
	$[\text{SET 13–200}]_4+A_2\quad[\text{SET 13–210}]_4+B_2\quad[\text{SET 13–220}]_8+2_1$	2 $\bar{1}$ 0
	$(120)\ (121)\ (12\bar{1})\ B_2A_2\mathbf{2}_1\quad(220)\ (221)\ (22\bar{1})\ C_1A_2\mathbf{2}_1\quad(2\bar{2}\bar{1})\ C_1\bar{1}'_2\mathbf{2}_1$	2 1 0
	$(120)\ (121)\ (12\bar{1})\ B_2A_2\mathbf{2}_1\quad(220)\ (221)\ (22\bar{1})\ C_1A_2\mathbf{2}_1\quad(2\bar{2}\bar{1})\ C_1\bar{1}'_2\mathbf{2}_1$	2 $\bar{1}$ 0
	$(\bar{2}\bar{2}0)\ (\bar{2}\bar{2}1)\ C_2A_3\bar{2}'_2\quad(\bar{3}\bar{2}0)\ (\bar{3}\bar{2}1)\ 3_2A_3\bar{2}'_2$	$\bar{2}$ $\bar{1}$ 0
122	$(\bar{2}\bar{2}1)\ C_2\mathbf{1}_1\bar{2}_2\quad(\bar{3}\bar{2}1)\ 3_2\mathbf{1}_1\bar{2}_2$	$\bar{1}$ $\bar{1}$ 0
	$(\bar{2}\bar{2}2)\ C_2\mathbf{2}_1\bar{2}_2\quad(\bar{3}\bar{2}2)\ 3_2\mathbf{2}_1\bar{2}_2$	$\bar{1}$ $\bar{1}$ 1
	$(\bar{2}\bar{2}2)\ C_2\mathbf{2}_1\bar{2}_2\quad(\bar{3}\bar{2}2)\ 3_2\mathbf{2}_1\bar{2}_2$	$\bar{1}$ $\bar{1}$ $\bar{1}$
	$(211)\ C_1\mathbf{1}_2\mathbf{1}_1\quad(311)\ 3_1\mathbf{1}_2\mathbf{1}_1\quad(\bar{2}\bar{2}1)\ C_2\mathbf{1}_1\bar{2}'_2\quad(\bar{3}\bar{2}1)\ 3_2\mathbf{1}_1\bar{2}'_2$	2 0 0
	$(211)\ C_1\mathbf{1}_2\mathbf{1}_1$	2 0 0

($\alpha\gamma\beta$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
122	(211) $C_1 1_2 B_2$ (311) $3_1 1_2 B_2$ (221) $C_1 1_1 2_1$ (321) $3_1 1_1 2_1$ (2$\bar{2}\bar{2}$) $C_1 \bar{2}'_2 2_1$ (3$\bar{2}\bar{2}$) $3_1 \bar{2}'_2 2_1$	2 1 0
	(201) $C_1 1_1 A_2$ (301) $3_1 1_1 A_2$ (211) $C_1 1_2 B_2$ (311) $3_1 I_2 B_2$ (221) $C_1 1_1 2_1$ (321) $3_1 1_1 2_1$ (2$\bar{2}\bar{2}$) $C_1 \bar{2}'_2 2_1$ (3$\bar{2}\bar{2}$) $3_1 \bar{2}'_2 2_1$	2 $\bar{1}$ 0
	(121) $B_2 1_1 2_1$ (221) $C_1 1_1 2_1$ (2$\bar{2}\bar{2}$) $C_1 \bar{2}'_2 2_1$	$\bar{2}$ 1 0
	(121) $B_2 1_1 2_1$ (221) $C_1 1_1 2_1$ (2$\bar{2}\bar{2}$) $C_1 \bar{2}'_2 2_1$	$\bar{2}$ $\bar{1}$ 0
	(2$\bar{2}\bar{1}$) $C_2 1_1 \bar{2}'_2$ (3$\bar{2}\bar{1}$) $3_2 1_1 \bar{2}'_2$	$\overline{2\,1}$ 0
	(2$\bar{2}\bar{2}$) $C_2 2_1 \bar{2}'_2$ (3$\bar{2}\bar{2}$) $3_2 2_1 \bar{2}'_2$	2 0 1
	(2$\bar{2}\bar{2}$) $C_2 2_1 \bar{2}'_2$ (3$\bar{2}\bar{2}$) $3_2 2_1 \bar{2}'_2$	2 0 $\bar{1}$
	(221) $C_1 B_2 2_1$ (222) $C_1 2_1 2_1$ (321) $3_1 B_2 2_1$ (322) $3_1 2_1 2_1$	2 1 1
	[SET 12–221A]$_4$ [(222) $C_1 2_1$ (322) $3_1 2_1$] + 2_1 [SET 12–221B]$_6$ + B_3 [(212) $C_1 2_1$ (312) $3_1 2_1$] + B_2	2 1 $\bar{1}$
	(221) $C_1 B_2 2_1$ (222) $C_1 2_1 2_1$ (321) $3_1 B_2 2_1$ (322) $3_1 2_1 2_1$	2 $\bar{1}$ 1
	[SET 12–221A]$_4$ [(222) $C_1 2_1$ (322) $3_1 2_1$] + 2_1 [SET 12–221B]$_6$ + B_3 [(212) $C_1 2_1$ (312) $3_1 2_1$] + B_2	2 $\bar{1}$ $\bar{1}$
	[SET 12–201]$_4$ [(212) $C_1 2_1$ (312) $3_1 2_1$] + A_3 [SET 12–211A]$_8$ + $\bar{B}_2 A_3$ [SET 12–221B]$_6$ + $\bar{B}_2 2_3$	2 $\overline{1\,1}$
	(121) $B_2 B_2 2_1$ (122) $B_2 2_1 2_1$ (221) $C_1 B_2 2_1$ (222) $C_1 2_1 2_1$	$\bar{2}$ 1 1
	[SET 12–221D]$_5$ + 2_1 (222) $C_1 2_1 2_1$ [SET 21–221E]$_3$ [(212) $C_1 2_1$] + B_3	$\bar{2}$ 1 $\bar{1}$
	(121) $B_2 B_2 2_1$ (122) $B_2 2_1 2_1$ (221) $C_1 B_2 2_1$ (222) $C_1 2_1 2_1$	$\bar{2}$ $\bar{1}$ 1
	[SET 12–221D]$_5$ + 2_1 (222) $C_1 2_1 2_1$ [SET 12–221E]$_3$ [(212)$C_1 2_1$] + B_3	$\bar{2}$ $\bar{1}$ $\bar{1}$
	[SET 12–201]$_4$ [(212) $C_1 2_1$] + A_3 [SET 12–211B]$_4$ + $\bar{B}_2 A_3$ [SET 12–221E]$_3$ + $\bar{B}_2 2_3$	$\bar{2}$ $\overline{1\,1}$
	(2$\bar{2}\bar{2}$) $C_2 2_1 \bar{2}'_2$ (3$\bar{2}\bar{2}$) $3_2 2_1 \bar{2}'_2$	$\overline{2\,1}$ 1
	(2$\bar{2}\bar{2}$) $C_2 2_1 \bar{2}'_2$ (3$\bar{2}\bar{2}$) $3_2 2_1 \bar{2}'_2$	$\overline{2\,1}$ $\bar{1}$
121	(2$\bar{2}\bar{2}$) $C_2 C_1 \bar{2}_2$ (2$\bar{2}\bar{3}$) $C_2 3_1 \bar{2}_2$ (3$\bar{2}\bar{2}$) $3_2 C_1 \bar{2}_2$ (3$\bar{2}\bar{3}$) $3_2 3_1 \bar{2}_2$	$\overline{1\,1}$ 2
	(2$\bar{2}\bar{2}$) $C_2 C_1 \bar{2}_2$ (3$\bar{2}\bar{2}$) $3_2 C_1 \bar{2}_2$	$\overline{1\,1}$ $\bar{2}$
	(2$\bar{2}\bar{2}$) $C_1 C_2 \bar{2}_2$ (2$\bar{2}\bar{3}$) $C_1 3_2 \bar{2}_2$ (3$\bar{2}\bar{2}$) $3_1 C_2 \bar{2}_2$ (3$\bar{2}\bar{3}$) $3_1 3_2 \bar{2}_2$	2 $\overline{1\,1}$
	(2$\bar{2}\bar{2}$) $C_1 C_2 \bar{2}_2$ (2$\bar{2}\bar{3}$) $C_1 3_2 \bar{2}_2$	$\bar{2}$ $\overline{1\,1}$

$[(2\bar{2}\bar{2})\ C_1C_2\ (\bar{2}\bar{2}2)\ C_2C_1\ (2\bar{2}\bar{3})\ C_13_2\ (\bar{2}\bar{2}3)\ C_23_1\ (3\bar{2}\bar{2})\ 3_1C_2\ (\bar{3}\bar{2}2)\ 3_2C_1\ (3\bar{2}\bar{3})\ 3_13_2\ (\bar{3}\bar{2}3)\ 3_23_1] + \bar{2}'_2$	2 0 2
$(\bar{2}\bar{2}\bar{2})\ C_2C_1\bar{2}'_2\quad(\bar{3}\bar{2}\bar{2})\ 3_2C_1\bar{2}'_2$	2 0 $\bar{2}$
$(2\bar{2}\bar{2})\ C_1C_2\bar{2}'_2\quad(2\bar{2}\bar{3})\ C_13_2\bar{2}'_2$	$\bar{2}$ 0 2
$(222)\ C_1C_12_1\quad(223)\ C_13_12_1\quad(322)\ 3_1C_12_1\quad(323)\ 3_13_12_1$	2 1 2
$(221)\ C_1B_22_1\quad(222)\ C_1C_12_1\quad(321)\ 3_1B_22_1\quad(322)\ 3_1C_12_1$	2 1 $\bar{2}$
$[\text{SET 11–202}]_4 + A_2\quad[(212)\ C_1C_1\ (213)\ C_13_1\ (312)\ 3_1C_1\ (313)\ 3_13_1] + B_2\quad[(222)\ C_1C_1\ (223)\ C_13_1\ (322)\ 3_1C_1\ (323)\ 3_13_1] + 2_1$	2 $\bar{1}$ 2
$[\text{SET 11–202A}]_4 + A_2\quad[(221)\ C_1B_2\ (222)\ C_1C_1\ (321)\ 3_1B_2\ (322)\ 3_1C_1] + 2_1$	2 $\bar{1}$ $\bar{2}$
$(2\bar{2}\bar{2})\ C_1C_2\bar{2}'_2\quad(2\bar{2}\bar{3})\ C_13_2\bar{2}'_2\quad(3\bar{2}\bar{2})\ 3_1C_2\bar{2}'_2\quad(3\bar{2}\bar{3})\ 3_13_2\bar{2}'_2$	2 $\bar{1}$ $\bar{2}$
$[\text{SET 11–202B}]_4 + A_2\quad[(122)\ B_2C_1\ (123)\ B_23_1\ (222)\ C_1C_1\ (223)\ C_13_1] + 2_1$	$\bar{2}$ 1 2
$[(121)\ B_2B_2\ (122)\ B_2C_1\ (221)\ C_1B_2\ (222)\ C_1C_1] + 2_1$	$\bar{2}$ 1 $\bar{2}$
$[\text{SET 11–202B}]_4 + A_2\quad[(122)\ B_2C_1\ (123)\ B_23_1\ (222)\ C_1C_1\ (223)\ C_13_1] + 2_1$	$\bar{2}$ $\bar{1}$ 2
$[(121)\ B_2B_2\ (122)\ B_2C_1\ (221)\ C_1B_2\ (222)\ C_1C_1] + 2_1$	$\bar{2}$ $\bar{1}$ $\bar{2}$
$(2\bar{2}\bar{2})\ C_1C_2\bar{2}'_2\quad(2\bar{2}\bar{3})\ C_13_2\bar{2}'_2$	2 $\bar{1}$ $\bar{2}$
$(\bar{2}\bar{2}\bar{2})\ C_2C_1\bar{2}'_2\quad(\bar{2}\bar{2}\bar{3})\ C_23_1\bar{2}'_2\quad(\bar{3}\bar{2}\bar{2})\ 3_2C_1\bar{2}'_2\quad(\bar{3}\bar{2}\bar{3})\ 3_23_1\bar{2}'_2$	$\bar{2}$ $\bar{1}$ 2
$(\bar{2}\bar{2}\bar{2})\ C_2C_1\bar{2}'_2\quad(\bar{3}\bar{2}\bar{2})\ 3_2C_1\bar{2}'_2$	$\bar{2}$ $\bar{1}$ $\bar{2}$

σ-Block	Sequence Sets	Product α β γ
32	$[\text{SET 32-001}]_4 + \text{A}_1 A_3 \bar{I}_2 \bar{I}_3 \bar{I}'_2 \bar{I}'_3$ $[\text{SET 32-011A}]_{10} + \bar{\text{I}}_2 A_2$	0 0 0
	$[\text{SET 32-011}]_4 + \bar{I}_2 \bar{I}_3 \bar{I}'_3$ $[\text{SET 32-011A}]_{10} + \bar{\text{I}}'_2$ $[\text{SET 32-021B}]_3 + \bar{\text{I}}_2$	0 1 0
	$[\text{SET 33-020}]_{13}$ $[\text{SET 32-020}]_6$ $[\text{SET 32-021}]_8 + \text{A}_2$	0 2 0
	$[\text{SET 32-021A}]_{12} + \text{A}_2 A_2 A_3 \bar{I}_2 \bar{I}'_2 \bar{I}_3 \bar{I}'_3$ $[\text{SET 32-021B}]_3 + \bar{\text{I}}'_2$	
22	$[(101)\ 1_1\text{B}_1\ (102)\ 1_1 2_1] + \text{A}_1 A_3 \bar{I}_2 \bar{I}_3 \bar{I}'_2 \bar{I}'_3$ $[\text{SET 22-011A}]_{11} + \bar{\text{I}}_2 A_2$	0 0 0
	$(112)\ 1_2 2_1 \bar{I}_2 / 1_2 2_1 \bar{I}_3 / 1_2 2_1 \bar{I}'_3$ $(1\bar{2}\bar{1})\ 1_1 \bar{\text{B}}_2 \bar{\text{I}}_2$ $(1\bar{2}\bar{\bar{2}})\ 1_1 \bar{2}'_2 \bar{\text{I}}_2$ $(1\bar{2}\bar{2})\ 1_1 2_2 \bar{\text{I}}_2$ $[\text{SET 22-011A}]_{11} + \bar{\text{I}}'_2$	0 1 0
	$[\text{SET 23-020}]_7$ $[\text{SET 22-020}]_2$ $[\text{SET 22-021}]_3 + \text{A}_2$	0 2 0
	$[\text{SET 22-021A}]_5 + \text{A}_2 A_2 A_3 \bar{I}_2 \bar{I}_3 \bar{I}'_2 \bar{I}'_3$ $[\text{SET 22-021B}]_3 + \bar{\text{I}}'_2$	
	$[\text{SET 22-101}]_4 + \text{A}_1 A_3 \bar{I}_2 \bar{I}_3 \bar{I}'_2 \bar{I}'_3$	1 0 0
	$[\text{SET 22-101}]_4 + \text{A}_1 A_3 \bar{I}_2 \bar{I}_3 \bar{I}'_2 \bar{I}'_3$ $[\text{SET 22-111A}]_5 + \bar{\text{I}}_2 A_2$	$\bar{1}$ 0 0
	$(2\bar{2}\bar{1})\ 2_1 \bar{\text{B}}_2 \bar{\text{I}}_2$ $(2\bar{2}\bar{\bar{2}})\ 2_1 \bar{2}'_2 \bar{\text{I}}_2$ $(2\bar{2}\bar{2})\ 2_1 2_2 \bar{\text{I}}_2$	1 1 0
	$(1\bar{1}\bar{1})$ $(\bar{2}\bar{1}0)\ \text{B}_3 \bar{\text{B}}_2 \bar{\text{I}}'_2$ $(2\bar{1}\bar{1})$ $(2\bar{1}\bar{2})\ 2_1 \bar{\text{B}}_2 \bar{\text{I}}'_2$ $(2\bar{2}\bar{1})\ 2_1 \bar{\text{B}}_2 \bar{\text{I}}_2$ $(2\bar{2}\bar{\bar{2}})\ 2_1 \bar{2}_2 \bar{\text{I}}'_2 / 2_1 \bar{2}'_2 \bar{\text{I}}_2$ $(2\bar{2}\bar{2})\ 2_1 2_2 \bar{\text{I}}_2$	$\bar{1}$ 1 0
	$[\text{SET 32-011A}]_{10}$ $[\text{SET 23-110A}]_{12}$ $[\text{SET 22-011A}]_{11}$ $[\text{SET 22-110A}]_3$ $[\text{SET 22-111B}]_7 + \text{A}_3$ $[\text{SET 22-111A}]_5 + \bar{\text{I}}'_3$	$\bar{1}\bar{1}$ 0
	$[\text{SET 22-111B}]_7 + A_3 \bar{I}_2 \bar{I}_3 \bar{I}'_2 \bar{I}'_3$	
	$[\text{SET 23-120}]_7$ $[\text{SET 22-120}]_2$ $[\text{SET 22-121}]_3 + \text{A}_2$ $[\text{SET 22-121 B}]_3 + \bar{\text{I}}'_2$ $[\text{SET 22-121A}]_5 + \text{A}_2 A_2 A_3 \bar{I}_2 \bar{I}_3 \bar{I}'_2 \bar{I}'_3$	1 2 0
	$[\text{SET 23-120A}]_{10}$ $[\text{SET 22-120A}]_3$ $[\text{SET 22-121C}]_4 + \text{A}_2$	$\bar{1}$ 2 0
	$[\text{SET 22-121D}]_8 + \text{A}_2 A_2 A_3 \bar{I}_2 \bar{I}_3 \bar{I}'_2 \bar{I}'_3$ $[\text{SET 22-121E}]_3 + \bar{\text{I}}'_2$	
	$[\text{SET 22-121F}]_3 + \bar{I}_2 \bar{I}_3 \bar{I}'_3$	$\bar{1}\bar{2}$ 0
12	$[\text{SET 12-201}]_4 + \text{A}_1 A_3 \bar{I}_2 \bar{I}_3 \bar{I}'_2 \bar{I}'_3$ $[\text{SET 12-211A}]_8 + \bar{\text{I}}_3$	2 0 0
	$[\text{SET 12-201}]_4 + \text{A}_1 A_3 \bar{I}_2 \bar{I}_3 \bar{I}'_2 \bar{I}'_3$ $[\text{SET 12-211B}]_4 + \bar{\text{I}}_2 A_2$	$\bar{2}$ 0 0
	$(2\bar{2}\bar{1})\ \text{C}_1 \bar{\text{B}}_2 \bar{\text{I}}_2$ $(2\bar{2}\bar{\bar{2}})\ \text{C}_1 \bar{2}'_2 \bar{\text{I}}_2$ $(2\bar{2}\bar{2})\ \text{C}_1 2_3 \bar{\text{I}}_2$ $(3\bar{2}\bar{1})\ 3_1 \bar{\text{B}}_2 \bar{\text{I}}_2$ $(3\bar{2}\bar{\bar{2}})\ 3_1 \bar{2}'_2 \bar{\text{I}}_2$ $(3\bar{2}\bar{2})\ 3_1 2_3 \bar{\text{I}}_2$	2 1 0

	$(2\bar{1}\bar{1})$ $(2\bar{1}\bar{2})$ $C_1\bar{B}_2\bar{1}'_2$ $(1\bar{1}\bar{1})$ $(\bar{2}\bar{1}0)$ $B_3\bar{B}_2\bar{1}'_2$ $(2\bar{2}\bar{1})$ $C_1\bar{B}_2\bar{1}_2$ $(2\bar{2}\bar{2})$ $C_1\bar{2}'_2\bar{1}_2$ $(2\bar{2}\bar{2})$ $C_1\bar{2}_2\bar{1}_2$	2 1 0
	$[\text{SET 13–220}]_8$ $[\text{SET 12–220}]_2$ $[\text{SET 12–221}]_2 + A_2$	2 2 0
	$[\text{SET 12–221A}]_4 + A_2A_2A_3\bar{1}_2\bar{1}_3\bar{1}'_2\bar{1}'_3$ $[\text{SET 12–221C}]_6 + \bar{1}'_2$	
	(120) $(12\bar{1})$ $B_2A_2A_2$ (121) $B_2A_2A_2/B_2B_2A_2/B_2\bar{1}_1A_2$ (221) $C_1B_2A_2$ $(2\bar{2}\bar{2})$ $C_1\bar{2}'_2A_2/C_1\bar{2}'_2\bar{1}'_2$	2 2 0
	$[\text{SET 12–221D}]_5 + A_2A_2A_3\bar{1}_2\bar{1}_3\bar{1}'_2\bar{1}'_3$ $(2\bar{2}\bar{1})$ $C_1\bar{B}_2\bar{1}'_2$ (122) $B_2\bar{2}_1A_2$ $(2\bar{2}\bar{2})$ $C_1\bar{2}_2\bar{1}'_2$	
	$[\text{SET 13–220B}]_4$ $[\text{SET 12–220B}]_2$ $[\text{SET 12–221F}]_2 + A_3$ $[\text{SET 12–221F}]_2 + A_3\bar{1}_2\bar{1}_3\bar{1}'_2\bar{1}'_3$	$\bar{2}$ 2 0
31	(101) $A_1B_1\bar{1}_1$ (102) $A_1\bar{2}_1\bar{1}_1$ $(\bar{1}\bar{1}1)$ $\bar{1}_2B_1\bar{1}_1$ $(\bar{1}\bar{1}2)$ $\bar{1}_3\bar{2}_1\bar{1}_1$	0 0 0
	$(\bar{1}\bar{1}2)$ $\bar{1}'_2\bar{2}_1\bar{1}_2/\bar{1}'_2\bar{2}_1\bar{1}_2/\bar{1}'_2\bar{2}_1\bar{1}_3/\bar{1}'_2\bar{2}_1\bar{1}'_3$ $(\bar{1}\bar{2}2)$ $\bar{1}_3\bar{2}_1\bar{1}_2/\bar{1}_3\bar{2}_1\bar{1}_2/\bar{1}_3\bar{2}_1\bar{1}_3/\bar{1}_3\bar{2}_1\bar{1}'_3$	0 1 0
	(021) (121) $(\bar{1}21)$ $A_2B_2\bar{1}_1$ $(\bar{1}\bar{2}1)$ $\bar{1}'_2B_2\bar{1}_1$ $(0\bar{2}\bar{2})$ $(1\bar{2}\bar{2})$ $A_3C_2\bar{2}'_2$ (022) (122) $(\bar{1}22)$ $A_2\bar{2}_1\bar{1}_1$ $(\bar{1}\bar{2}2)$ $\bar{1}'_2\bar{2}_1\bar{1}_1$	0 2 0
	(101) $A_1B_1B_1/A_1B_1B_3$ (102) $A_1C_1B_3/A_1C_1\bar{2}_1/A_1\bar{2}_1B_1$ (103) $A_1\bar{3}_1\bar{2}_1$ $(\bar{1}\bar{1}1)$ $\bar{1}_2B_1B_1$ $(\bar{1}\bar{1}2)$ $\bar{1}_3\bar{2}_1B_1/\bar{1}_3C_1\bar{2}_1/\bar{1}_3C_1B_3/\bar{1}_3\bar{3}_1\bar{2}_1$	0 0 1
	$[\text{SET 32–001}]_4 + B_1A_3\bar{B}_2$ $[\text{SET 31–002}]_4 + \bar{2}_1$ $[\text{SET 31–002A}]_3 + \bar{B}_2B_3\bar{2}_2\bar{2}_3$	0 0 $\bar{1}$
	$(\bar{1}\bar{1}2)$ $\bar{1}'_2C_1\bar{2}_1$ $(\bar{1}\bar{1}3)$ $\bar{1}'_2\bar{3}_1\bar{2}_1$ $(\bar{1}\bar{2}2)$ $\bar{1}_3C_1\bar{2}_1$ $(\bar{1}\bar{2}3)$ $\bar{1}_3\bar{3}_1\bar{2}_1$	0 1 1
	$(\bar{1}\bar{1}1)$ $\bar{1}'_2B_1\bar{2}_2/\bar{1}'_2B_1\bar{2}_3$ $(\bar{1}\bar{1}2)$ $\bar{1}'_2C_1\bar{2}_1/\bar{1}'_2C_1\bar{2}_2/\bar{1}'_2C_1\bar{2}_3/\bar{1}_3C_1\bar{2}_2/\bar{1}_3C_1\bar{2}_3$ $(\bar{1}\bar{1}3)$ $\bar{1}'_2\bar{3}_1\bar{2}_1$ $(\bar{1}\bar{2}2)$ $\bar{1}_3C_1\bar{2}_1$ $(\bar{1}\bar{2}3)$ $\bar{1}_3\bar{3}_1\bar{2}_1$	0 1 $\bar{1}$
	$[\text{SET 32–011A}]_{10} + A_3\bar{B}_2$ $(0\bar{2}\bar{2})$ $(1\bar{2}\bar{2})$ $A_3C_2\bar{2}_2$	0 $\bar{1}$ $\bar{1}$
	$[\text{SET 32–021}]_8 + B_2$ $[\text{SET 31–022}]_8 + 2_1$ $[\text{SET 31–022A}]_8 + B_3$	0 2 1
	$[\text{SET 33–020}]_{13}$ $[\text{SET 32–020}]_6 + A_2$ $[\text{SET 32–021}]_8 + B_2$ $[\text{SET 32–021A}]_{12} + A_3$ $[\text{SET 31–022}]_8 + 2_1$ $[\text{SET 31–022A}]_8 + \bar{B}_2B_3\bar{2}_2\bar{2}_3$	0 2 $\bar{1}$
	$(0\bar{2}\bar{2})$ $(1\bar{2}\bar{2})$ $A_3\bar{2}'_2\bar{B}_2/A_3C_2\bar{2}'_2$ $(\bar{1}\bar{2}1)$ $\bar{1}'_3\bar{B}_2\bar{B}_2$	0 $\bar{2}$ $\bar{1}$
21	(101) $1_1B_1\bar{1}_1$ (102) $1_1B_1\bar{2}_1$	0 0 0
	(112) $1_2\bar{2}_1\bar{1}_2$	0 1 0
	$(\bar{2}\bar{2}1)$ $\bar{2}'_2B_2\bar{1}_1$ $(\bar{2}\bar{2}2)$ $\bar{2}'_2\bar{2}_1\bar{1}_1$ (121) $1_1B_2\bar{1}_1$ $(1\bar{2}\bar{2})$ $1_1C_2\bar{2}'_2$ $(1\bar{2}\bar{3})$ $1_1\bar{3}_2\bar{2}'_2$	0 2 0
	(101) $1_1B_1B_1/1_1B_1B_3$ (102) $1_1\bar{2}_1B_1/1_1C_1\bar{2}_1/1_1C_1B_3$ (103) $1_1\bar{3}_1\bar{2}_1$	0 0 1
	$[(101)\ 1_1B_1\ (102)\ 1_1\bar{2}_1] + B_1A_3\bar{B}_2$ (102) $1_1C_1\bar{2}_1$ (103) $1_1\bar{3}_1\bar{2}_1$ $[(101)1_1B_1$ (102) $1_1C_1] + \bar{B}_2B_3\bar{2}_2\bar{2}_3$	0 0 $\bar{1}$
	(112) $1_2C_1\bar{2}_1$ (113) $1_2\bar{3}_1\bar{2}_1$	0 1 1
	(112) $1_2C_1\bar{2}_1/1_2C_1\bar{2}_2/1_2C_1\bar{2}_3$ (113) $1_2\bar{3}_1\bar{2}_1$	0 1 $\bar{1}$

($\alpha\gamma\gamma$) Pattern (continued)

σ-Block	Sequence Sets	Product α β γ
21	$[\text{SET 23–110A}]_{12}\,[\text{SET 22–110A}]_3\,[\text{SET 22–111B}]_7 + \text{A}_3$ $[\text{SET 22–011A}]_{11} + \text{A}_3\bar{\text{B}}_2$ $(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{\text{B}}_2\text{B}_3\bar{\text{B}}_2$ $(1\bar{1}2)$ $1_1\text{B}_3\bar{\text{B}}_2$ $(1\bar{2}\bar{2})$ $1_1\text{C}_2\bar{2}_2$ $(1\bar{2}\bar{3})$ $1_1 3_2 \bar{2}_2$	0 $\bar{1}$ $\bar{1}$
	$(\bar{2}\bar{2}1)$ $\bar{2}'_2\text{B}_2\text{B}_2/\bar{2}'_2\text{B}_2B_3$ $(\bar{2}\bar{2}2)$ $\bar{2}'_2\text{C}_1 2_1/\bar{2}'_2\text{C}_1B_3/\bar{2}'_2 2_1\text{B}_2$ (121) $1_1\text{B}_2\text{B}_2/1_1\text{B}_2B_3$ $(\bar{2}\bar{2}3)$ $\bar{2}'_2 3_1 2_1$	0 2 1
	$[\text{SET 23–020}]_7\,[\text{SET 22–020}]_2 + \text{A}_2A_3$ $(\bar{2}\bar{2}1)$ $\bar{2}'_2\text{B}_2\text{B}_2$ $(\bar{2}\bar{2}2)$ $\bar{2}'_2 2_1\text{B}_2/\bar{2}'_2\text{C}_1 2_1$ $(\bar{2}\bar{2}3)$ $\bar{2}'_2 3_1\text{B}_2$ (121) $1_1\text{B}_2\text{B}_2$	0 2 $\bar{1}$
	$[\text{SET 22–021A}]_5 + A_3$ $[\text{SET 21–022A}]_3 + \bar{B}_2B_3 2_2 2_3$	
	$(1\bar{2}\bar{1})$ $1_1\bar{\text{B}}_2\bar{\text{B}}_2$ $(1\bar{2}\bar{2})$ $1_1\bar{2}'_2\bar{\text{B}}_2/1_1\text{C}_2\bar{2}'_2$ $(1\bar{2}2)$ $1_1 2_2\bar{\text{B}}_2$ $(1\bar{2}\bar{3})$ $1_1 3_2\bar{2}'_2$	0 $\bar{2}$ $\bar{1}$
	(101) $\text{B}_1\text{B}_1 1_1$ (102) $\text{B}_1 2_1 1_1$ (201) $2_1\text{B}_1 1_1$ (202) $2_1 2_1 1_1$	1 0 0
	(101) $\text{B}_1\text{B}_1 1_1$ (102) $\text{B}_1 2_1 1_1$ (201) $2_1\text{B}_1 1_1$ (202) $2_1 2_1 1_1$	$\bar{1}$ 0 0
	$(\bar{1}\bar{1}1)$ $(\bar{2}\bar{1}1)$ $\bar{\text{B}}_2\text{B}_3 1_1$ $(\bar{1}\bar{1}2)$ $(\bar{2}\bar{1}2)$ $\bar{\text{B}}_2 2_1 1_1$ $(1\bar{1}2)$ $1_1\text{B}_3 1_1$ $(\bar{2}\bar{1}2)$ $2_3 2_1 1_1$ $(\bar{2}\bar{2}2)$ $\bar{2}_3 2_1 1_1$	$\bar{1}$ $\bar{1}$ 0
	(121) $\text{B}_2\text{B}_2 1_1$ (122) $\text{B}_2 2_1 1_1$ (221) $2_1\text{B}_2 1_1$ $(2\bar{2}\bar{2})$ $2_1\text{C}_2\bar{2}'_2$ $(2\bar{2}\bar{3})$ $2_1 3_2\bar{2}'_2$	1 2 0
	(021) $\text{A}_2\text{B}_2 1_1$ (121) $\text{B}_2\text{B}_2 1_1$ (122) $\text{B}_2 2_1 1_1$ (221) $2_1\text{B}_2 1_1$ $(2\bar{2}\bar{2})$ $2_1\text{C}_2\bar{2}'_2$ $(2\bar{2}\bar{3})$ $2_1 3_2\bar{2}'_2$	$\bar{1}$ 2 0
	$(\bar{1}\bar{2}2)$ $\bar{\text{B}}_2 2_1 1_1$ $(\bar{2}\bar{2}2)$ $\bar{2}'_2 2_1 1_1$ $(\bar{2}\bar{2}2)$ $2_3 2_1 1_1$	$\bar{1}$ 2 0
	$[\text{SET 22–101}]_4 + \text{B}_1$ $[\text{SET 21–102}]_4 + 2_1$ $[\text{SET 21–102A}]_4 + B_3$	1 0 1
	$[\text{SET 22–101}]_4 + \text{B}_1A_3\bar{B}_2$ $[\text{SET 21–102}]_4 + 2_1$ $[\text{SET 21–102A}]_4 + \bar{B}_2B_3 2_2 2_3$	1 0 $\bar{1}$
	$[\text{SET 22–101}]_4 + \text{B}_1$ $[\textit{SET} \text{ 21–102}]_4 + 2_1$ $[\text{SET 21–102A}]_4 + B_3$	$\bar{1}$ 0 1
	$[\text{SET 22–101}]_4 + \text{B}_1A_3\bar{B}_2$ $[\text{SET 21–102}]_4 + 2_1$ $[\text{SET 21–102A}]_4 + \bar{B}_2B_3 2_2 2_3$	$\bar{1}$ 0 $\bar{1}$
	$(1\bar{1}1)$ $(\bar{2}10)$ $\text{B}_3\bar{\text{B}}_2\bar{\text{B}}_2$ $(2\bar{1}1)$ $(2\bar{1}2)$ $2_1\bar{\text{B}}_2\bar{\text{B}}_2$ $(2\bar{2}\bar{2})$ $2_1\bar{2}_2\bar{\text{B}}_2/2_1\text{C}_2\bar{2}_2$ $(2\bar{2}\bar{3})$ $2_1 3_2\bar{2}_2$	1 $\bar{1}$ $\bar{1}$
	$(1\bar{1}1)$ $(\bar{2}10)$ $\text{B}_3\bar{\text{B}}_2\bar{\text{B}}_2$ $(2\bar{1}1)$ $(2\bar{1}2)$ $2_1\bar{\text{B}}_2\bar{\text{B}}_2$ $(2\bar{2}\bar{2})$ $2_1\bar{2}_2\bar{\text{B}}_2/2_1\text{C}_2\bar{2}_2$ $(2\bar{2}\bar{3})$ $2_1 3_2\bar{2}_2$	$\bar{1}$ $\bar{1}$ $\bar{1}$
	$[\text{SET 22–111B}]_7\,[\text{SET 21–012B}]_3 + \text{B}_3$ $[\text{SET 21–112A}]_8 + 2_1$ $[\text{SET 21–112B}]_8 + B_3$	$\bar{1}$ $\bar{1}$ 1
	$[\text{SET 22–111B}]_7\,[\text{SET 21–012B}]_3 + \text{B}_3$ $[\text{SET 21–112A}]_8 + 2_1$ $[\text{SET 21–112B}]_8 + \bar{B}_2B_3 2_2 2_3$ $[\text{SET 22–111B}]_7 + A_3\bar{B}_2$	$\bar{1}$ $\bar{1}$ $\bar{1}$
	(121) $\text{B}_2\text{B}_2\text{B}_2/\text{B}_2\text{B}_2B_3$ (122) $\text{B}_2\text{C}_1 2_1/\text{B}_2\text{C}_1B_3/\text{B}_2 2_1\text{B}_2$ (123) $\text{B}_2 3_1 2_1$ (221) $2_1\text{B}_2\text{B}_2/2_1\text{B}_2B_3$	1 2 1
	$[\text{SET 23–120}]_7\,[\text{SET 22–120}]_2 + \text{A}_2A_3$ (121) $\text{B}_2\text{B}_2\text{B}_2$ (122) $\text{B}_2\text{C}_1 2_1/\text{B}_2 2_1\text{B}_2$ (123) $\text{B}_2 3_1 2_1$ (221) $2_1\text{B}_2\text{B}_2$	1 2 $\bar{1}$
	$[\text{SET 22–121A}]_5 + A_3$ $[\text{SET 21–122A}]_3 + \bar{B}_2B_3 2_2 2_3$ $[\text{SET 21–122F}]_3 + 2_2 2_3$	

	$(2\bar{2}\bar{1})\ 2_1\bar{B}_2\bar{B}_2$ $(2\bar{2}\bar{2})\ 2_1\bar{2}'_2\bar{B}_2/2_1C_2\bar{2}_2$ $(2\bar{2}\bar{2})\ 2_12_2\bar{B}_2$ $(2\bar{2}\bar{3})\ 2_13_2\bar{2}'_2$	$1\ \bar{2}\ \bar{1}$
	$[\text{SET 22–121C}]_4+\text{B}_2$ $[\text{SET 21–122B}]_4+2_1$ $[\text{SET 21–122C}]_5+B_3$	$\bar{1}\ 2\ 1$
	$[\text{SET 23–120A}]_{10}\,[\text{SET 22–120A}]_3+\text{A}_2A_3$ $[\text{SET 22–121C}]_4+\text{B}_2$ $[\text{SET 22–121D}]_8+A_3$ $[\text{SET 21–122B}]_4+2_1$ $[\text{SET 21–122C}]_5+\bar{B}_2B_32_22_3$	$\bar{1}\ 2\ \bar{1}$
	$(2\bar{2}\bar{1})\ 2_1\bar{B}_2\bar{B}_2$ $(2\bar{2}\bar{2})\ 2_1\bar{2}'_2\bar{B}_2/2_1C_2\bar{2}'_2$ $(2\bar{2}\bar{2})\ 2_12_2\bar{B}_2$ $(2\bar{2}\bar{3})\ 2_13_2\bar{2}'_2$	$\bar{1}\ \bar{2}\ \bar{1}$
	$(\bar{1}\bar{2}2)\ \bar{B}_2C_12_1$ $(\bar{2}\bar{2}2)\ \bar{2}'_2C_12_1$ $(\bar{1}\bar{2}3)\ \bar{B}_23_12_1$ $(\bar{2}\bar{2}3)\bar{2}'_23_12_1$ $(\bar{2}\bar{2}2)\ 2_3C_12_1$ $(\bar{2}\bar{2}3)\ 2_33_12_1$	$\bar{1}\ \bar{2}\ 1$
	$(\bar{1}\bar{2}2)\ \bar{B}_2C_12_1$ $(\bar{2}\bar{2}2)\ \bar{2}'_2C_12_1$ $(\bar{2}\bar{2}2)\ 2_3C_12$	$\bar{1}\ \bar{2}\ \bar{1}$
11	$(201)\ C_1B_11_1$ $(202)\ C_12_11_1$ $(301)\ 3_1B_11_1$ $(302)\ 3_12_11_1$	$2\ 0\ 0$
	$(101)\ B_1B_11_1$ $(201)\ C_1B_11_1$ $(102)\ B_12_11_1$ $(202)\ C_12_11_1$	$\bar{2}\ 0\ 0$
	$(221)\ C_1B_21_1$ $(2\bar{2}\bar{2})\ C_1C_2\bar{2}'_2$ $(2\bar{2}\bar{3})\ C_13_2\bar{2}'_2$ $(321)\ 3_1B_21_1$ $(3\bar{2}\bar{2})\ 3_1C_2\bar{2}'_2$ $(3\bar{2}\bar{3})\ 3_13_2\bar{2}'_2$	$2\ 2\ 0$
	$(121)\ B_2B_21_1$ $(221)\ C_1B_21_1$ $(2\bar{2}\bar{2})\ C_1C_2\bar{2}'_2$ $(122)\ B_22_11_1$ $(2\bar{2}\bar{3})\ C_13_2\bar{2}'_2$	$\bar{2}\ 2\ 0$
	$(\bar{2}\bar{2}2)\ C_22_11_1$ $(\bar{3}\bar{2}2)\ 3_22_11_1$	$\bar{2}\ \bar{2}\ 0$
	$[\text{SET 12–201}]_4+\text{B}_1$ $[\text{SET 11–202}]_4+2_1$ $[\text{SET 11–202A}]_4+B_3$	$2\ 0\ 1$
	$[\text{SET 12–201}]_4+\text{B}_1A_3\bar{B}_2$ $[\text{SET 11–202}]_4+2_1$ $[\text{SET 11–202A}]_4+\bar{B}_2B_32_22_3$	$2\ 0\ \bar{1}$
	$[\text{SET 12–201A}]_4+\text{B}_1$ $[\text{SET 11–202B}]+2_1$ $[\text{SET 11–202C}]_4+B_3$	$\bar{2}\ 0\ 1$
	$[\text{SET 12–201A}]_4+\text{B}_1A_3\bar{B}_2$ $[\text{SET 11–202B}]_4+2_1$ $[\text{SET 11–202C}]_4+\bar{B}_2B_32_22_3$	$\bar{2}\ 0\ \bar{1}$
	$[\text{SET 12–211A}]_8+\bar{\text{B}}_2$ $(2\bar{2}\bar{2})\ C_1C_2\bar{2}_3$ $(2\bar{2}\bar{3})C_13_2\bar{2}_3$ $(3\bar{2}\bar{2})\ 3_1C_2\bar{2}_3$ $(3\bar{2}\bar{3})\ 3_13_2\bar{2}_3$	$2\ \bar{1}\ \bar{1}$
	$(2\bar{1}\bar{1})$ $(2\bar{1}\bar{2})\ C_1\bar{B}_2\bar{B}_2$ $(1\bar{1}\bar{1})$ $(2\bar{1}0)\ B_3\bar{B}_2\bar{B}_2$ $(2\bar{2}\bar{2})\ C_1C_2\bar{2}_2$ $(2\bar{2}\bar{3})\ C_13_2\bar{2}_2$	$\bar{2}\ \bar{1}\ \bar{1}$
	$(221)\ C_1B_2B_2/C_1B_2B_3$ $(321)\ 3_1B_2B_2/3_1B_2B_3$	$2\ 2\ 1$
	$[\text{SET 13–220}]_8\,[\text{SET 12–220}]_2+\text{A}_2A_3$ $[(221)\ C_1B_2\ (321)\ 3_1B_2]+B_2\bar{B}_2B_32_22_3$ $(220)\ C_1A_2A_3$ $(221)\ C_1B_2A_3$ $(320)\ 3_1A_2A_3$ $(321)\ 3_1B_2A_3$	$2\ 2\ \bar{1}$
	$[\text{SET 12–221B}]_6+\bar{\text{B}}_2$ $[\text{SET 11–222B}]_4+\bar{2}'_2$	$2\ \bar{2}\ \bar{1}$
	$(121)\ B_2B_2B_2/B_2B_2B_3$ $(122)\ B_2C_12_1/B_22_1B_2/B_2C_1B_3$ $(221)\ C_1B_2B_2/C_1B_2B_3$ $(123)\ B_23_12_1$	$\bar{2}\ 2\ 1$
	$[\text{SET 13–220A}]_3\,[\text{SET 12–220A}]_2+\text{A}_2A_3$ $(121)\ B_2B_2B_2$ $(122)\ B_2C_12_1/B_22_1B_2$ $(123)\ B_23_12_1$ $(221)\ C_1B_2B_2$ $[\text{SET 12–221D}]_5+A_3$ $[\text{SET 11–222D}]_3+\bar{B}_2B_32_22_3$	$\bar{2}\ 2\ \bar{1}$
	$(2\bar{2}\bar{1})\ C_1\bar{B}_2\bar{B}_2$ $(2\bar{2}\bar{2})\ C_1\bar{2}'_2B_2/C_1C_2\bar{2}'_2$ $(2\bar{2}\bar{2})\ C_12_2\bar{B}_2$ $(2\bar{2}\bar{3})\ C_13_2\bar{2}'_2$	$\bar{2}\ 2\ \bar{1}$
	$(\bar{2}\bar{2}2)\ C_2C_12_1/C_2C_1B_3$ $(\bar{2}\bar{2}3)\ C_23_12_1$ $(\bar{3}\bar{2}2)\ 3_2C_12_1/3_2C_1B_3$ $(\bar{3}\bar{2}3)\ 3_23_12_1$	$\bar{2}\ \bar{2}\ 1$
	$[(\bar{2}\bar{2}2)\ C_22_1\ (\bar{3}\bar{2}2)\ 3_22_1]+A_3\bar{B}_2$ $[\text{SET 11–222F}]_4+2_1$ $[(\bar{2}\bar{2}2)\ C_2C_1\ (\bar{3}\bar{2}2)\ 3_2C_1]+\bar{B}_2B_32_22_3$	$\bar{2}\ \bar{2}\ \bar{1}$

19. References

[1] A few publications have begun to appear which devote themselves to the theoretical problems of synthesis design and are listed chronologically as Refs. [2–17].

[2] Corey, E. J.: Pure Appl. Chem., *14*, 19 (1967).

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[4] Corey, E. J., Wipke, T.: Science *166*, 178 (1969).

[5] Ireland, R.E.: Organic synthesis. Prentice-Hall 1969.

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[11] Corey, E. J., Wipke, W. T., Cramer, R. D., Howe, W. J.: J. Am. Chem. Soc. *94*, 421 (1972), and adjacent papers.

[12] Powers, G. J., Jones, R. L.: AlChE.J. *19*, 1204 (1973).

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[14] Wipke, W. T.: in: Computer representation and manipulation of chemical information. (W. T. Wipke, S. R. Heller, R. J. Feldmann and E. Hyde, ed.) New York: Wiley and Sons 1974.

[15] Blair, J., Gasteiger, J., Gillespie, C., Gillespie, P. D., Ugi, I.: in Ref. [14] (1974).

[16] Hendrickson, J. B.: J. Am. Chem. Soc. *97*, 5763 (1975).

[17] Hendrickson, J. B.: J. Am. Chem. Soc. *97*, 5784 (1975).

[18] Stereochemistry may be considered another category, including number of asymmetric centers, interrelation on skeleton, and thermodynamic preference or stability. The view taken here is that this category is of secondary importance to the development of a general synthesis system, and can largely be incorporated among considerations of skeleton.

[19] The points are not always defined in the same way. In some discussions they are treated as single, "main" intermediates [4,7,11,14], in others as generalized intermediates [9] or as particular sets of components variously defined [6,15,16]. The consequences of and insights from the different definitions constitute an interesting study in itself.

[20] The term *tree* is a graph theory usage for a graph with no cycles rooted on one point, but many starting compounds may be capable of more than one route to the target, so that this graph is not truly a tree, but contains cycles. This is apparent in the representation of Fig. 2, especially if the bottom part is labeled as elemental carbon (or "coal, air and water"), the simplest starting material with routes to all intermediates. On the other hand a synthesis tree is a directed graph (lines are vectors) and has no directed cycles, which are infinitely redundant.

[21] Power's analysis of DNA synthesis [13] begins with the starting materials and successfully employs an efficiency criterion (*i.e.*, yield, time, cost) to compare and evaluate routes. This is, however, a limited case with only four starting materials and intensely tested reaction conditions.

[22] Simon, H. A.: The architecture of complexity. Proc. Am. Phil. Soc. *106*, 467 (1962).

[23] A survey of actual completed syntheses [24] shows commonly twice as many refunctionalization steps as construction steps, which is far from the ideal proposed. In fact there are very few self-consistent syntheses in the survey. This implies that some refunctionalization will have to be accepted, and flexibility of the criteria in actual use to accommodate this is discussed below. However, the initial focus on self-consistent sequences represents an important force toward economy of steps.

[24] Anand, N., Bindra, J. S., Ranganathan, S.: Art in organic synthesis, Holden-Day (1970); the title of this book is indicative of the present state of systematics in synthesis design.

[25] The three examples are summarized in Ref. [24]. 1, p. 181; 2, p. 4; 3, p. 130. The variety of steroid syntheses is clearly shown by their very different bondsets; others may be found in Refs. [24] and [26].

[26] Klhrem, A. A., Titov, Yu. A.: Total steroid synthesis. New York: Plenum Press 1970.

[27] Markezich, R. L., Willy, W. E., McCarry, B. E., Johnson, W. S.: J. Am. Chem. Soc. *95*, 4414 (1973) and succeeding communications.

[28] The term *synthon* [2] is used here specifically to define a particular skeleton followed through successive steps of a synthesis as part of a growing larger molecule, ultimately part of the target molecule. It begins as the starting material with an initial functionality, and the functionality on the synthon skeleton then changes through the synthesis to the functionality it bears in the target. Thus a synthon has one defined skeleton and varying functionality dependent on the point in the synthetic sequence at which it is discussed.

[29] The product functionality may be either exactly that of the target or may differ from it in a way which is still deemed acceptable to refunctionalize after the self-consistent construction sequence is complete. In many syntheses a target secondary alcohol existed as a ketone at an earlier stage, etc.

[30] The availability of starting materials may be regarded as *primary* if the substance is commercially accessible, or *secondary* if it is referenced in the literature with a reliable preparation, adding a step or two (but of known difficulty) to the sequence. These availability factors, as well as cost, can be relatively easily quantitatively assessed on a common basis and applied as relative merit judgments to the sequences derived from various starting materials.[13]

[31] Syntheses in Ref. [24] which seemed out of line with present considerations (peptides, nucleotides) or were relatively simple conceptually (usually molecules of theoretical interest, not natural products) were not included in the survey. About 90 syntheses were examined.

[32] Woodward, R. B., Bader, F. E., Bickel, H., Frey, A. J., Kierstead, R. W.: Tetrahedron *2*, 1 (1958).

[33] Boeckelheide, V., Phillips, J. B.: J. Am. Chem. Soc. *85*, 1545 (1963).

[34] Barton, D. H. R., Deflorin, A. M., Edwards, O. E.: J. Chem. Soc. *1956*, 530.

[35] An initial survey is offered in Ref. [16] and a full treatment is in preparation.

[36] Hendrickson, J. B., Bogard, T. L., Fisch, M. E., Grossert, S., Yoshimura, N.: J. Am. Chem. Soc. *96*, 7781 (1974).

[37] The number of construction sites per synthon is $2\lambda/k$. If the average synthesis has an average synthon size of 4 carbons, then the number of synthons, $k = n_0/4$ and the number of constructions per synthon will average $(2 + 8(\Delta r - 1)/n_0)$. If no cyclizations occur in the bondset, $\Delta r = r_0 - r = 0$ and there are 1.2—1.6 sites per synthon for targets of $n_0 = 10$—20 carbons. At the other extreme, if $\Delta r = 3$ rings created, there are 3.6—2.8 sites per synthon for targets of 10—20 carbons, respectively.

[38] The non-linear isobutane part-skeleton of three construction sites  each three carbons from the other has been omitted. The possible overlap of reactive strands is very small. Also omitted are three-construction sites linked in a ring in the synthon, which are cyclic forms of the patterns in Fig. 3. These are somewhat more restrictive than their linear counterparts in Fig. 3 but not significantly different.

[39] If the branches bear functionality in a real case it is ignored here since it is not functionality required to activate (and define) the particular half-reaction. Certain partial synthons exhibit branched (non-linear) arrangement of functionality, *e.g.* malonate and acetoacetate carbanions in alkylation or α,β-unsaturated ketones in α-alkylation. In these cases, one of the two functionalized strands out from the α-carbon may be deemed extraneous to the definition, as discussed in Ref. [17].

[40] The construction span is usually the functional span shown in Table 1 but not always since the construction span must include the constructed link and hence at least the α-carbon on both sides even though in some cases there is no product functionality on one synthon ($f_\alpha = 0$ in product, as in alkylation), *e.g.*, acetylene alkylation (Table 1).

[41] The masterlist in Table 3 is a slightly altered presentation of Table 8 in Ref. [17]. It incorporates also the variants on certain half-reactions discussed in the appendix of Ref. [17]. These variants incorporate the net change of certain construction + refunctionalization

combinations which commonly occur in practice, *e.g.*, the creation of certain carbanions by reduction, as R—X + Mg → R—MgX, as a preliminary to the A_1 reaction (combined *f*-list: 1 → 0 → 0, for refunctionalization followed directly by construction).

[42] Certain limitations on excess functionality are defined in the Appendix, Ref. [17], and so a few such half-reactions are not in the materlist, and cannot appear in the general sequence lists. These omitted *f*-lists are few, as discussed previously [17].

[43] External overlap is regarded as redundant and not listed if a half-reaction of lower half-span on the main synthon can achieve the same conversion. Thus internal $\bar{1}_2$ and $\bar{2}_2$ are equivalent to secondary external $\bar{1}_3$ and $\bar{2}_3$ as B_1 is normally the same as primary external B_2 or B_3, but $\bar{1} \rightarrow \bar{2}$ can only happen with primary external B_3, not internal B_1, when the $\bar{2}$ product refers to a double bond formed across the prior construction link (B_3 product $\bar{2}\bar{1}0$). These cases may be confirmed from the masterlist (Table 3).

[44] One exception was made on chemical judgment: RH half-reactions of the *A* and *B* series ($A_1A_2A_3B_1B_2B_3$) with $f = 1$ on an adjacent carbon to the construction site were disallowed on grounds of facile β-elimination pre-empting construction.

[45] The problem of definition of Z is only serious with single Z attachments ($f = 1,2$ or 3). These might be subdivided as electron-withdrawing (NO_2, $-SO_2R$, $-PR_3^+$, $-SR_2^+$, etc.) for use in half-reactions $B_1, B_3, \bar{1}_2$, etc., as leaving groups (—X, $-OSO_2R$, etc.) for 1_1 and $\bar{1}'_3$, or as electron-donating to double bonds (—OH, —OR, —OCOR, $-NR_2$, etc.) for $\bar{1}'_2$ or $\bar{2}'_2$. There are problems, however, in that the categories overlap for certain groups and differently for different half-reaction contexts.

[46] Corey, E. J., Vlattas, I., Andersen, N. H., Harding, K.: J. Am. Chem. Soc. *90*, 3247 (1968).

[47] Bentley, P. H.: Chem. Soc. Rev. *2*, 29 (1973).

[48] Synthon size must be understood as only the carbons of the synthon skeleton which are carried intact into the target skeleton. Thus ethyl proprionate, enol ethers of pyruvates, acrylic acid and α-methoxypropionic acid should all appear in the same group as three-carbon synthons.

[49] Fused bicyclics are rare among available starting materials and, along with the few others too complex for this simple, linear format, could be exempted into a separate named list. Even unsystematically presented however, these complex molecules will be so few as to present little search problem. However, a derivative system could simply arrange them, grouped into common skeletons, by using a predefined skeletal numbering system as an *f*-list order, *e.g.*, a ten-digit *f*-list for naphthalene skeletons, etc.

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Rearrangements and Interconversions of Carbenes and Nitrenes

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Contents

I. Introduction

The chemistry of short-lived intermediates is difficult to study because usually the species cannot be directly observed under the reaction conditions. Much of the knowledge is therefore obtained by deduction from product studies. In the present review we are dealing mainly with intramolecular gas-phase reactions, and the carbenes and nitrenes in question are most frequently generated from diazo-compounds and azides (or in heterocyclic systems valence isomers thereof, triazoloazines and tetrazoloazines). It is known that diazo-compounds and azides yield carbenes and nitrenes, respectively, by low-temperature photolysis [1,2]. However, the cycloheptatrienylidenes and azepinylidenes invoked in many reaction mechanisms have not yet been observed by any spectroscopic means, and their existence is deduced exclusively from their chemistry.

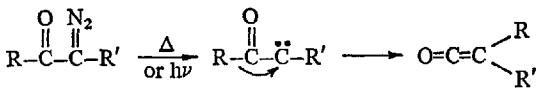
When discussing the interconversion of reactive intermediates it is of interest to have some idea of their relative stabilities. For this purpose, we are making extensive use of thermochemical estimates. These estimates will not be precise of course, for only two of the most crucial heats of formation are known with reasonable accuracy: those of CH_2 and NH. Nevertheless, when comparing closely related carbenes and nitrenes, the errors committed in the estimates will be nearly identical for the different species, and the *differences* in heats of formation — that is, the relative stabilities — will be at least qualitatively correct. Entropy differences are usually disregarded in this context, since they would contribute only ca. 2—3 kcal/mol to the free energies, and thus are within the uncertainties in the heat of formation estimates.

In this review, pyrolysis is always, when nothing else is expressly stated, carried out in a gas-phase flow-system as described, for example, in Ref.[57].

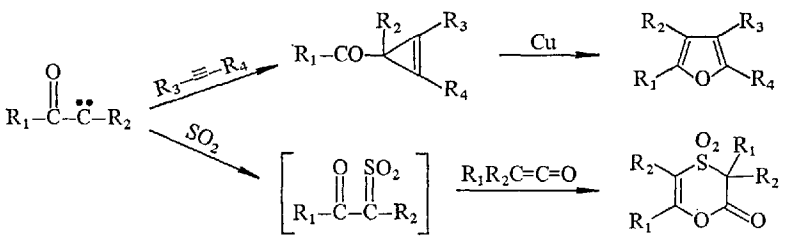
II. Wolff-Type Rearrangements

1. Oxocarbenes

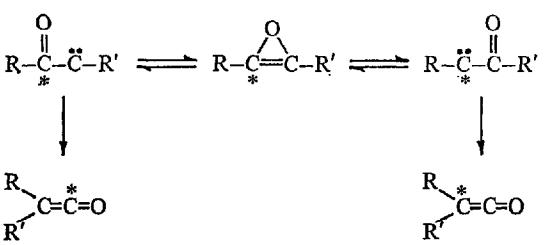
The Wolff-rearrangement of oxocarbenes derived from diazoketones is probably the most widely known carbene rearrangement [1].



There is much evidence that this is indeed a reaction of the carbene, at least for the photolytic reaction and for the thermal reaction in the gas-phase [1,7], although in solution one cannot always be sure that rearrangement is not concerted with decomposition of the diazoketone (*vide infra*). The rearrangement is suppressed by photosensitized decomposition, which should give a triplet carbene and/or triplet diazoketone, thereby supporting the view that it is a singlet species which undergoes rearrangement [3]. Thermally or catalytically produced oxocarbenes have been intercepted in solution by cycloaddition [4] and perhaps by SO_2: [5]

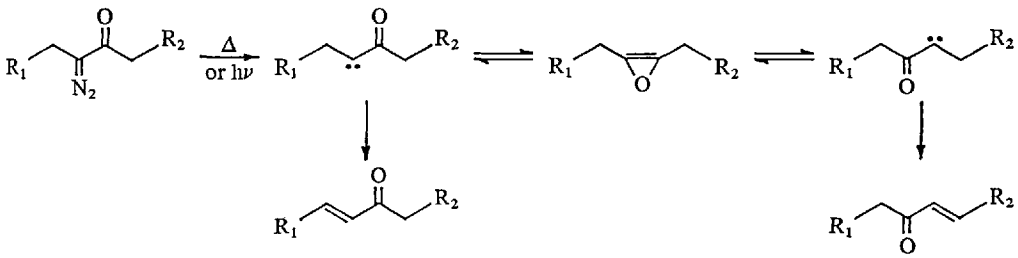


In the context of the present review, the possibility of carbene-carbene interconversion in the Wolff-rearrangement is of particular importance. Radioactive labeling has demonstrated that such interconversion takes place, presumably *via* an oxirene [6].



The oxirene participation is up to 100% in gas-phase photolysis, and less in solution. Oxirenes can also be involved in thermolysis [7], usually to a smaller extent than in photolysis, their significance increasing with the temperature. Matlin and

Sammes [7] have taken advantage of the low-energy 1,2-hydrogen shift in carbenes [8] in order to demonstrate oxirene participation:



Oxirene is formally a 4π antiaromatic system, and furthermore contains considerable ring strain. The ring strain in cyclopropene is ca. 53 kcal/mol [9]. Oxirenes are therefore expected to be short-lived high-energy intermediates. There has been much discussion among the theoreticians whether oxirene is more or less stable than the isomeric oxocarbene. The conflicting results of calculations are indicated in Fig. 1.

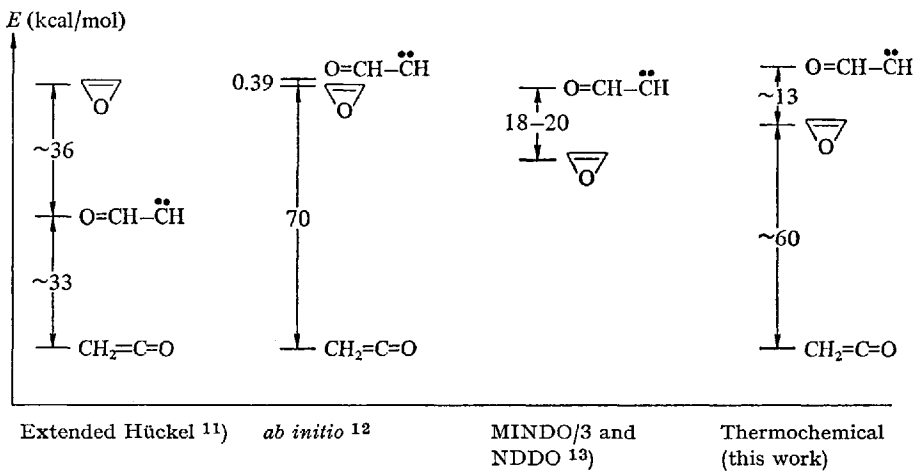


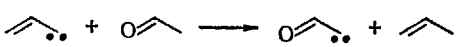
Fig. 1. Calculated heats of formation of oxirene, formylcarbene and ketene (CH_2=C=O = −11.4 kcal/mol [21])

The results are typical of the methods: Extended Hückel overestimates ring strain and favors unbound structures [10]. The semiempirical NDO methods usually underestimate ring strain and thus make small rings too stable [10]. The *ab initio* results, which should be the best, are intermediate between the semiempirical ones. The *ab initio* geometries were not optimized, however, and therefore the absolute energies will not be correct.

A more reliable ordering of the energies can be obtained thermochemically. Even though the required heats of formation of oxirene and formylcarbene are not known, they can be estimated with sufficient precision using thermochemical

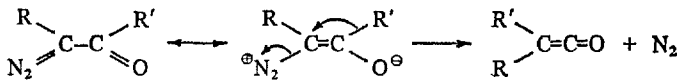
group increments [14], isodesmic reactions and a calculated negative resonance energy in oxirene of ca. 5.5 kcal/mol [15] (Table 1). The results are shown graphically in Fig. 1. Although the error in these estimates is several kcal/mol due to the lack of precise data for more closely related compounds, the values are probably more correct than those obtained by MO-methods. The thermochemical results are in qualitative agreement with the MINDO/3 and NDDO calculatations [13] and show that the oxocarbenes should indeed rearrange exothermically to oxirenes, and the oxirenes to ketenes. There is nothing to prevent an oxocarbene from

Table 1. Estimated heats of formation related to the Wolff-rearrangement

Species [1]	ΔH_f^0 (kcal/mol)	Source
 (T)	99.3	 92[16] 41.4[17] 34.1 kcal/mol[16–18]
	~97.3	Method of Bergman[19]
	~98.3±1	Average
 (S)	60±5	 98 −40[14] 5[14]
		ΔH_f^0 () ≅ 98 − 40 − 5 + singlet–triplet splitting + R.E. (allyl) − R.E. (acetonyl)[17, 20] ≈ 60±5 kcal/mol.
	~46.8	ΔH_f^0 () = ΔH_f^0 () + ΔH_f^0 (▽) − ΔH_f^0 (▽) + R.E. () ≅ −12.6[14] + 66.6[14] −12.74[14] + ~5.5[15]
CH_2=C=O	−11.4	Ref.[21]
HN  (T)	~108	ΔH_f^0 () + $\Delta\Delta H_f^0$ (imine − alkene)[14] ≃ 98 + 10
	~91	ΔH_f^0 () = ΔH_f^0 () + ΔH_f^0 (▽) − ΔH_f^0 (▽) + R.E. () = 30.40[22] + 66.6 −12.74 ~6.7[15]
	89±1	Ref.[23]
 (T)	105±2	Ref.[24]
	113±1	89±1 + $\Delta\Delta H_f^0$ ()
 (T)	~115	Ref.[24]

[1] T = triplet; S = singlet.

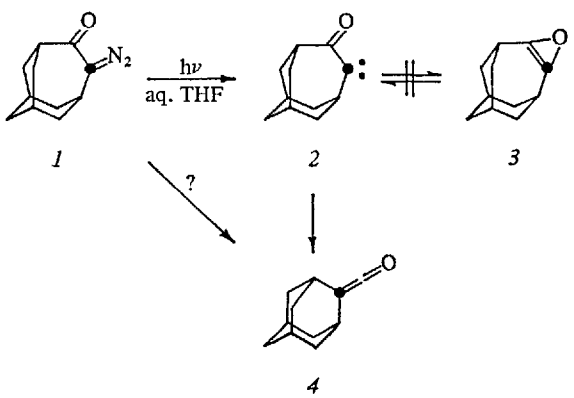
rearranging *directly* to a ketene, and this is apparently what happens in many thermal systems in solution. Furthermore, in solution there is a higher probability that the diazoketone exists in the sterically less demanding *syn*-conformation, which may undergo concerted reaction [25].



Even when oxirenes are intermediates, their lifetimes may be very short. Photolysis of diazoacetaldehyde in an argon matric at 8 K with concomitant IR-observation showed fomation of ketene, but no absorption due to oxirene could be detected [26].

It would be interesting to repeat this experiment with labeled diazoacetaldehyde, in order to determine whether or not oxirene is involved in this case.

If one increases the strain of the oxirene ring system sufficiently (by ca. 12—14 kcal/mol) its formation from an oxocarbene will no longer be thermochemically favorable. Such a situation appears to be realized in the homoadamantane derivative *1*, which did not react by way of the oxirene *3* [27]. The rearrangement of *2* to the adamantane *4* will release ca. 10 kcal/mol of strain [28]. It must be emphasized,



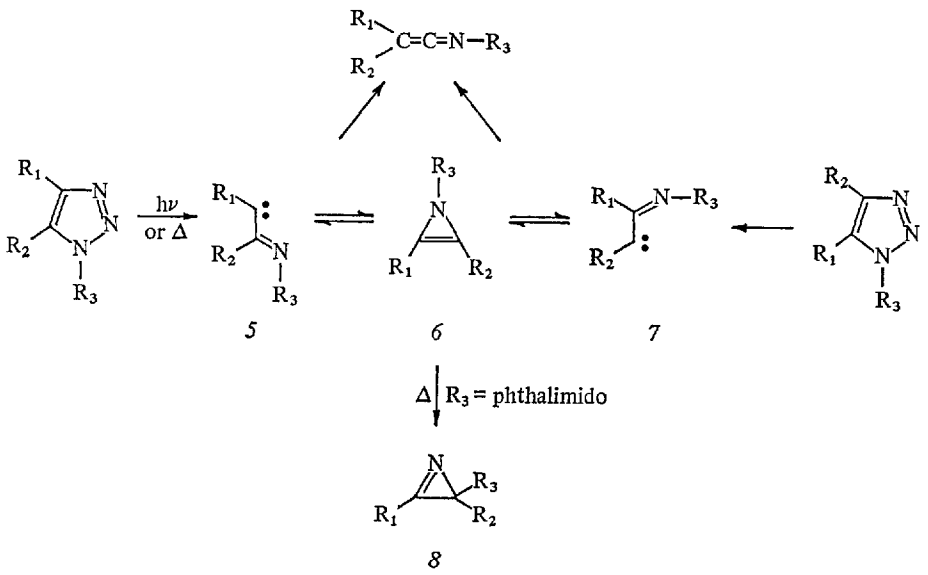
1 *2* *3* *4*

however, that these 10 kcal/mol of strain would also be liberated in a concerted reaction *1* → *4*, and the necessary *syn*-conformation of *1* could favor such a process [7,25].

2. Iminocarbenes

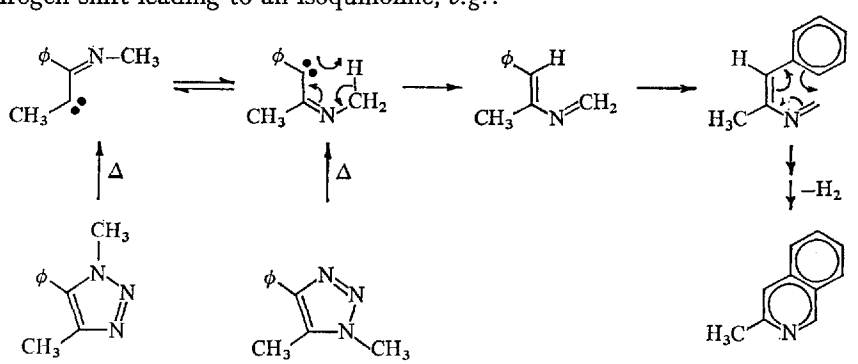
Iminocarbenes can be generated by thermolysis or photolysis of triazoles. Like the oxocarbenes they ondergo a Wolff-type rearrangement [29,30] and also carbene-carbene interconversion *via* a symmetrical intermediate, most likely the

antiaromatic 1*H*-azirine (*6*) [30,31]. The thermochemistry (Table 1) indicates that the reaction *5* → *6* (Scheme 1) is exothermic,

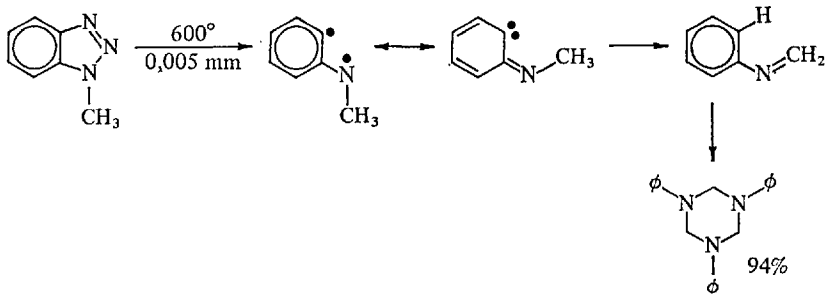


Scheme 1

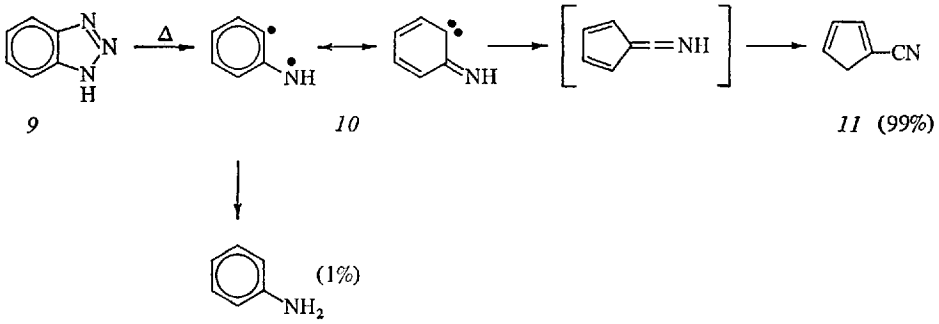
and evidence for its occurrence was provided by the isolation of the stable 2*H*-azirine (*8*), formed by rearrangement of *6*, when R_3 = phthalimido (Scheme 1) [31]. When R_3 was alkyl, the interconverting iminocarbenes *5* and *7* underwent a 1,4-hydrogen shift leading to an isoquinoline, *e.g.*:



The first such 1,4-shift was observed in the gas-phase pyrolysis of 1-methylbenzotriazole, where the N-phenylformimine was isolated in the form of its trimer [32]. Since the trimer collected in the cold-trap at —196 °C — and not in the warmer air-cooled part of the apparatus — trimerization must have taken place in the trap after condensation.



In annelated triazoles the Wolff-rearrangement leads to ring contraction. Thus gas-phase pyrolysis of benzotriazole (*9*) in a stream of argon gives a 99% yield of 1-cyanocyclopentadiene (*11*) and 1% of aniline, the latter being formed, presumably, *via* H-abstraction by the intermediate 1,3-diradicals 10 [33]. The diradical has been directly observed by ESR [34].



9 *10* *11* (99%)

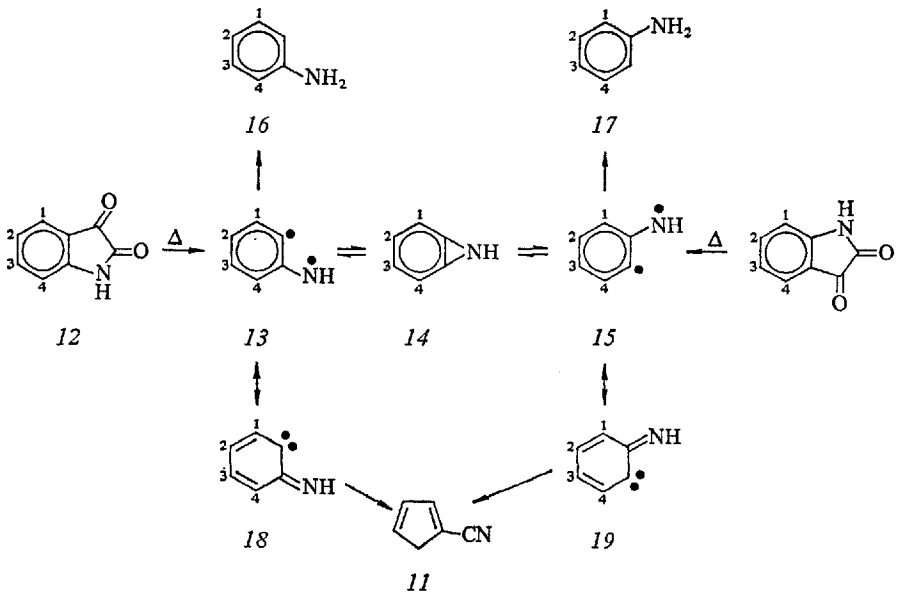
Several substituted benzotriazoles, [33] pyridotriazoles, [33] and isatins [35] react analogously. In the case of isatin (*12*) it was shown by substitution that a symmetrical intermediate, the 1*H*-benzazirine (*14*) is involved [35] (Scheme 2).

Table 2. Pyrolysis of isatins [35] [1]

		Relative yield	
Isatin *12*	*T* °C	*16*	*17*
2-CH_3	600	100	0
2-CH_3	900	94	6
2-CH_3	1100	94	6
4-CH_3	900	95	5
1- or 3-CH_3 (mixture)	900	95	5

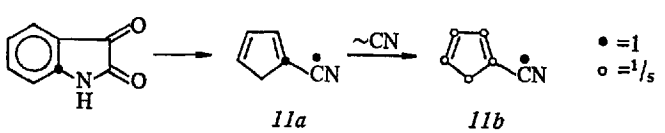
[1] Pressure: 0.005—0.10 mm throughout.

Thus each mono-methylisatin *12* gave the expected aniline *16* plus a 5—6% relative yield of the isomeric aniline *17* (Scheme 2, Table 2). Since only the two anilines expected from interconversion *via 14* were formed, methyl-migrations can be discounted. The formation of 5—6% of *17* from *12* implies a 10—12% intermediacy of 1*H*-benzazirine (*14*) in the aniline forming rection.



Scheme 2

Assuming that the strain-energy in 1*H*-benzazirine is the same as in benzocyclopropene, its heat of formation can be estimated (Table 1). These data indicate that the cyclization *13* → *14* is still exothermic by 1—2 kcal/mol. It may well be that the involvement of *14* increases if the rates of the product forming reactions are decreased. The above experiments allow no conclusion as to the level of importance of *14* in the ring contraction to *11*, for the two iminocarbenes *18* and *19* will yield the *same* cyanocyclopentadiene, *11*. In order to clarify this point we prepared ^{13}C-labeled isatin and pyrolyzed it at 715°/0.15 mm [81]. The cyanocyclopentadiene obtained was equally labeled on all ring-carbon atoms, but the CN-group was five times as much labeled as any other carbon atom.

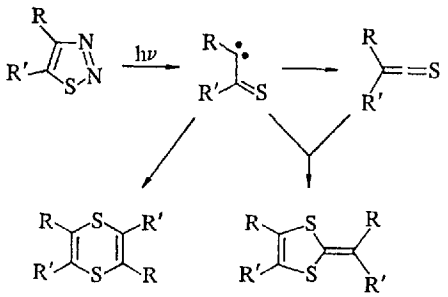


This result demonstrates *quantitative intermediacy of 1H-benzazirine in the ring contraction reaction*. The first formed product will be *11a*, which is equally labeled

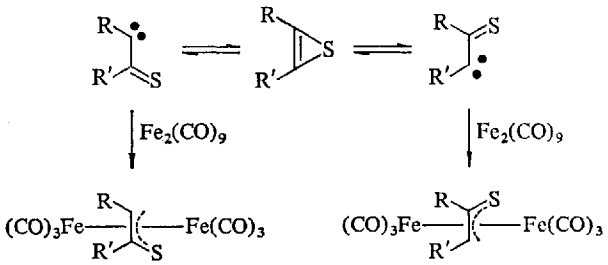
on CN and C—1. Subsequent sigmatropic CN-migrations [33] will randomize the C—1 label over the five ring carbon atoms, resulting in the 5:1 ratio observed (*11b*).

3. Thioxo- and Selenoxocarbenes

The decomposition of 1,2,3-thiadiazoles gives thioxocarbenes which undergo a Wolff-type rearrangement [36].

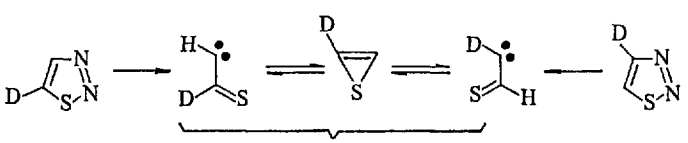


When the thiadiazole was decomposed in the presence of diironnonacarbonyl it was possible to isolate a complex of the intermediate thioxocarbene[37], and to show by substituent labeling that a carbene-carbene isomerization had occurred, presumably *via* the thiirene:



The corresponding selenadiazoles behave analogously [37].

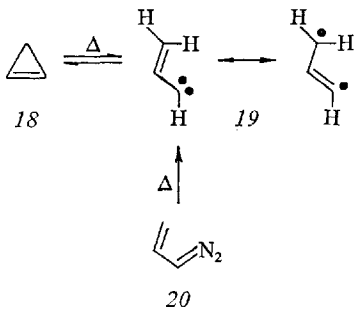
The formation of thioketene has been confirmed by direct observation during matrix photolysis of 1,2,3-thiadiazole [36d]. In addition, ethynyl mercaptan was observed in this work. The simultaneous formation of two deuterated ethynyl mercaptans in the photolysis of 4- or 5-deuterio-1,2,3-thiadiazole implies the involvement of a symmetrical intermediate, thiirene [36d]:



HC≡C–SD + DC≡C–SH + HDC=S

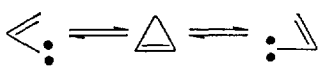
4. Vinylcarbenes

The strain energy of cyclopropene is about 53 kcal/mol. The energy of a normal C—C bond is about 83 kcal/mol. If all the cyclopropene strain were concentrated in one C—C bond, then only ca. 30 kcal/mol extra energy would be required to break the bond. Indeed, cyclopropenes thermally open to vinylcarbenes with activation energies of 30—40 kcal/mol [19,38–40]. (Table 3). The carbene-diradical resonance hybride *19* can also be formed from appropriately substituted vinyldiazoalkanes (*20*) [41,42].



18 *19* *20*

Inasmuch as the cyclopropene ring opening is reversible [19], it constitutes a carbene-carbene interconversion:



19 *18* *19*

In comparison with oxo- and iminocarbenes, cyclization has now become the predominant reaction; a Wolff-type rearrangement to allene [38] is not very well known for simple vinylcarbenes, even though it is thermochemically favorable:

ΔH_f^0: 66.6 ~98 46 kcal/mol

It does take place in cyclic systems where the cyclopropene is more highly strained (Scheme 3).

The heat of formation of triplet vinylcarbene is estimated as 97—99.3 kcal/mol (Table 1). With an activation energy of ca. 35.2 kcal/mol, the transition state for cyclopropene ring opening lies at $\Delta H \sim 100.3$ kcal/mol, *i.e.* only 1—4 kcal/mol above the triplet carbene. Substituted vinylcarbenes give stable ESR signals, the Curie law dependence of which indicate that either the ground states are triplets, or the triplets are within 4 kcal/mol of a ground state singlet [42a]. If the triplet is

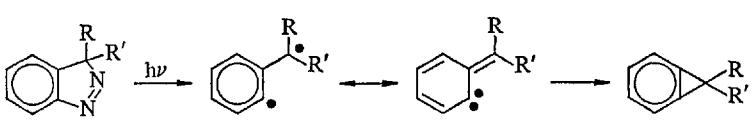
Table 3. Activation parameters for thermal isomerization of cyclopropenes

Starting material	E_a(kcal/mol)	log A	$\Delta S^{\ddagger}$ (e.u.)	Phase	Ref.
	35.2 ± 1.3	12.13		gas	38)
	34.7 ± 1.2	11.4		gas	38)
	37.60 ± 1.2	13.5 ± 0.5		gas	39)
	36.60 ± 0.85	13.0 ± 0.4		gas	39)
	39.00 ± 1.35	13.4 ± 0.6		gas	39)
	39.97 ± 2.00	12.5 ± 0.8		gas	39)
	32.6 [1])	11.8 [1])		gas	19)
	29.8 ± 1.1		− 17.8	benzene	40)

[1]) Parameters are for optical isomerization.

indeed the ground-state, and if the singlet-triplet splitting is a few kcal/mol[a]), the ring closure *19* → *18* will have virtually no activation energy. Bergman [19]) estimated that the transition state for ring closure of 1,3-diethylvinylcarbene can be no more than 6 kcal/mol above the triplet carbene. If the singlet-triplet splitting is 6 kcal/mol, the activation energy will be zero.

Benzocyclopropenes can be prepared by photolysis of 3*H*-indazoles (*21*) [41]):

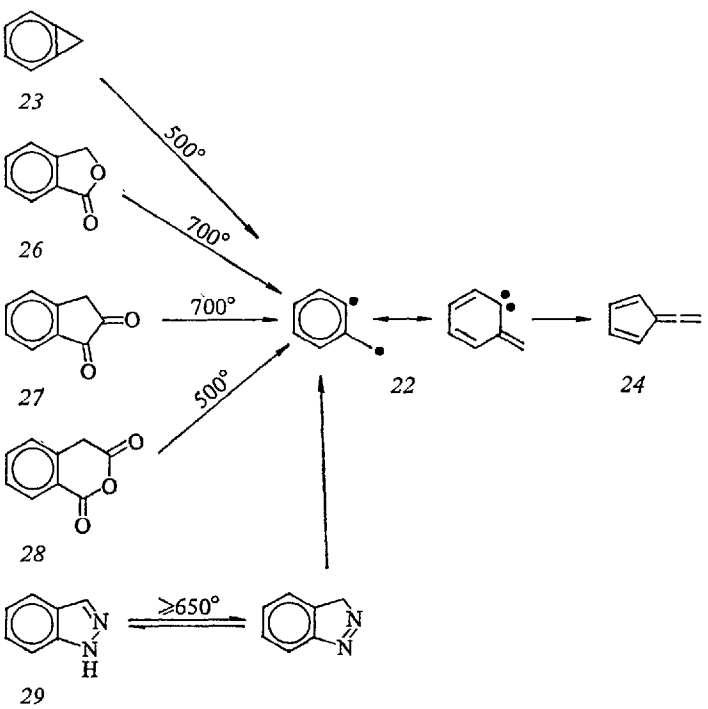


21 *22* *23*

[a]) For CH_2 the singlet-triplet splitting is 8–9 kcal/mol [43]).

The intermediate diradical-methylenecyclohexadienylidene *22* shows a triplet ESR spectrum at 77 K and rearranges to the benzocyclopropene *23* on warming to room temperature [41].

The reaction is reversible, for the gas-phase thermolysis of benzocyclopropene under mild conditions yields the Wolff-type rearrangement product of *22*, namely fulvenallene (*24*) [44]. Several other precursors of carbene *22* are known [44–48] (Scheme 3, Table 4).

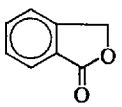
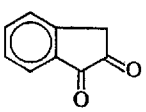
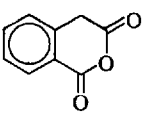


Scheme 3

Those precursors which require high temperature also give some ethynylcyclopentadiene (*25*), but this is most probably due to a secondary isomerization, independently established [44,46] (Table 4):

24 *25*

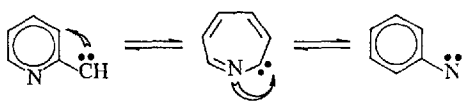
Table 4. Formation of fulvenallene and ethynylcyclopentadiene

Starting material	T °C	P mm	 *24*	 *25*	 *23*	Ref.
 *23*	515	0.01	14.2	$\leqslant$ 0.75	85	44)
	590	0.1	81	$<$ 2	15	
	800	0.01	74	16	0	
 *26*	760	0.01	70	12	—	44,45)
	850	0.01	71	16	—	
	1000	0.01	9.6	25	—	
 *27*	700	~0.05	2	—	1	46)
	750	~0.05	7	—	3	
	850	~0.05	55	—	8	
	900	~0.05	63	2—5	4	
	950	~0.05	68	2—5	3	
	1000	~0.05	72	5—10	0.5	
 *28*	520	$2,N_2$	20	—	—	47)
	570	$2,N_2$	71	—	—	
mixture (1:2.6) of *24* and *25* repyrolyzed twice	1000	0.01	24	76		44)
Mixture (1:2.6) of *24* and *25* repyrolyzed four times	1000	0.01	20	80		

III. Aromatic Carbene-Carbene Interconversions

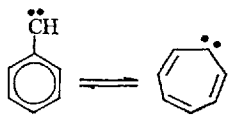
1. Introduction

The observation [49] that 2-pyridylcarbene and phenylnitrene interconvert in the gas-phase *via* an intermediate which has an arrangement of atoms as in 2-azepinylidene [Eq. (1)] led to the prediction that



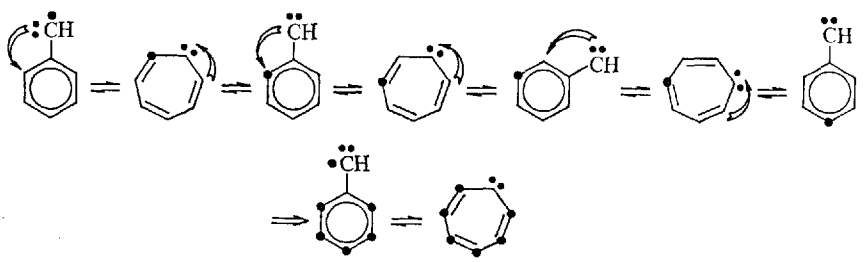
(1)

phenylcarbene and cycloheptatrienylidene should similarly interconvert [Eq. (2)].



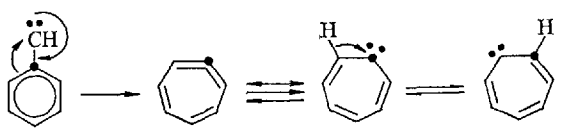
(2)

The reversibility of this process should lead to carbon scrambling in phenylcarbene [Eq. (3)].



(3)

Written as above [Eqs. (1), (2)] the ring expansion of an arylcarbene is nothing else than a Wolff-rearrangement of a vinylcarbene. The Wolff-rearrangement could lead initially to an allene [Eq. (4)] and since strained allenes can be converted to carbenes [50] it is *a priori* difficult to describe the species which we shall call cycloheptatrienylidene: a carbene or an allene or both?



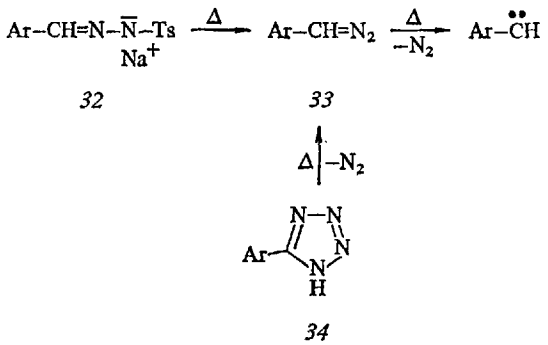
30 *31* (4)

We might further expect a Wolff-type *H*-migration interconverting the cycloheptatrienylidenes *30* and *31* [Eq. (4)]. The sum of Eq. (3) and Eq. (4) would be complete carbon scrambling, which has, in fact, been observed [51].

In the next section we shall consider some simple carbene expansions. The complete carbon scrambling is discussed in Section III.8 in connection with ring contraction.

2. The Ring Expansion

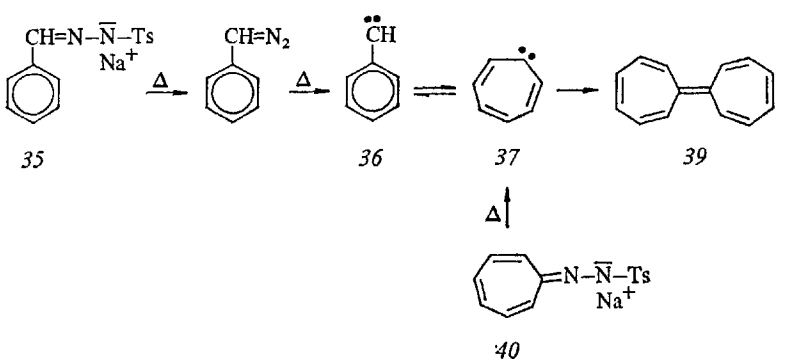
Acrylcarbenes can be generated in the gas-phase by pyrolysis of aldehyde tosylhydrazone salts, aryldiazomethanes [52–54], or 5-aryltetrazoles [55–57]. The immediate carbene precursor is in each case



32 33 34 (5)

the diazomethane (*33*), which can be isolated by mild pyrolysis of *32* [58] or *34* [57] [Eq. (5)].

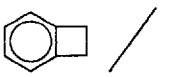
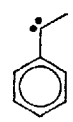
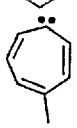
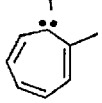
Evidence for the interconversion of phenylcarbene and cycloheptatrienylidene was obtained by gas-phase pyrolysis of the corresponding tosylhydrazone sodium salts, *35* and *40*, which both yielded the dimer of cycloheptatrienylidene, heptafulvalene (*39*) [Eq. (6)]. [59,60,54]



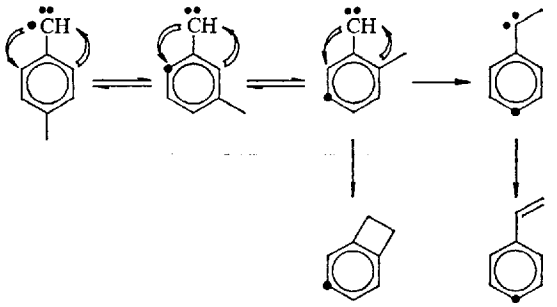
35 36 37 39 40 (6)

Heptafulvalene (*39*) is also formed by thermal or photolytic decomposition of *40* in solution [61a], but not from *35* in solution. The existence of *37* in solution is established by its nucleophilic addition to alkenes [61b,f], when generated by decomposition of the salt *40*. Evidence for the reversibility of *36* ⇄ *37* was obtained by gas-phase generation of the tolylcarbenes, which interconvert according to Eq. (3), all yielding benzocyclobutene and styrene [Eq. (7) and Table 5] [53,57].

Table 5. Rearrangement products of tolylcarbenes and methylcycloheptatrienylidenes

Carbene	Precursor [1]	T °C	P_{mm}	Rel. yield 	Ref.
	Tosylhydrazone	250	10^{-2}	6.0	57)
	Tosylhydrazone	250	1	1.45	52)
	Tosylhydrazone	350	1	2.3—3.0	52)
	Tetrazole [6]	420	10^{-2}	4.0	57)
	Diazo	420	0.5	2.8	53)
	Tetrazole [6]	610	$4 \cdot 10^{-2}$	1.65	57)
	Tetrazole [6]	800	$4 \cdot 10^{-2}$	0.37	57)
	Diazo	700 [2]	Low	3.0	62)
	Diazo	150 [3]	760	0.45	52)
	Diazo	30, hν	2	1.4	63)
	Diazo	420	0.5	~0.8 (1.1)	53) (1b)
	Diazo	700 [2]	Low	0.80	62)
	Diazo	30, hν	2	0.7	63)
	Tosylhydrazone	250 [4]	40	0:0	63)
	Tosylhydrazone	250 [4]	0.4	0:0	57)
	Tosylhydrazone	320 [4]	0.3—0.4	0:0	57)
	Tetrazole [6]	320 [5]	10^{-2}	0:0	57)
	Tetrazole [6]	420 [5]	10^{-2}	0.75	57)
	Tosylhydrazone	400 [4]	0.3	0.9	57)
	Tetrazole [6]	420 [5]	0.1—0.2	0.93	57)
	Diazo	420	0.5	0.8 (1.1)	53) (1b)
	Tetrazole[6,7]	420	1	0.9	57)
	Tetrazole [6,7]	420	10	0.9	57)
	Tetrazole [6]	610	$3 \cdot 10^{-2}$	0.8	57)
	Tetrazole [6]	800	$5 \cdot 10^{-2}$ —$6 \cdot 10^{-2}$	0.33	57)
	Diazo	700 [2]	Low	0.83	62)
	Diazo	30, hν	2	0.5	63)
	Diazo	420	0.5	0:1	53)
	Tosylhydrazone	720	10^{-3}—10^{-2}	0:1	57)
	Tosylhydrazone	450	6	~1	63)
	Tosylhydrazone	350	3	~0:1	63)

[1]) Refer to Eq. (5).
[2]) "Flash vacuum pyrolysis". The contact times are shorter here than under our conditions, resulting in a lower effective temperature.
[3]) "Violent", presumably explosive reaction.
[4]) Dimethylheptafulvalene and dimethylstilbene are formed.
[5]) Dimethylheptafulvalene not detectable.
[6]) Tetrazoles always give benzonitriles in a side-reaction.
[7]) p-Tolyldiazomethane isolated from the pyrolysate.

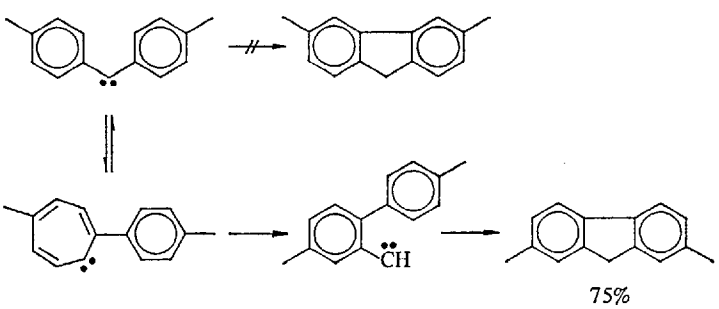


(7)

The reaction mechanism shown in Eq. (7) was confirmed by ^{13}C-labeling of p-tolylcarbene[62].

p-Tolylcarbene generated from the tosylhydrazone yields dimethylheptafulvalene in the temperature interval 250—400 °C (Table 5). Above 400 °C the rearrangement in Eq. (7), leading to benzocyclobutene and styrene takes place. From this it appears that the multiple rearrangement in Eq. (7) has a higher activation energy than the simple rearrangement in Eq. (6). It is hard to find a convincing explanation for this, but it is perhaps significant that p-tolylcarbene formed from the tetrazole *34 via* p-tolyldiazomethane, which is isolable, *does not give any detectable dimethylheptafulvalene* (Table 5). Therefore, *the yield of heptafulvalene cannot be used to measure either the equilibrium constant or extent of carbene-carbene rearrangements.*

The formation of fluorenes from diarylcarbenes [64] has been shown to proceed by carbene-carbene rearrangements [60,63]. Thus, di-p-tolylcarbene gave only 2,7-dimethylfluorene (75%), and not 3,6-dimethylfluorene [60] [Eq. (8)]. Similar results were obtained with p-tolyl phenyl carbene [63], p-methoxyphenyl phenyl carbene [63], p-biphenylylcarbene [63], and p-nitrophenyl phenyl carbene [65]. In addition to the fluorene, Jones *et al.*[63] isolated triphenylheptafulvene and diphenyl-

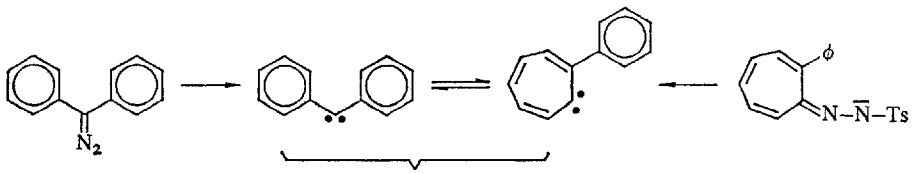


(8)

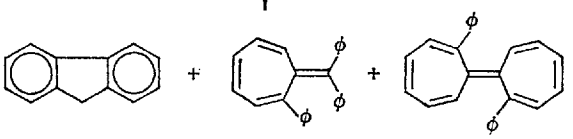
75%

heptafulvalene (30—35%) from both diphenyldiazomethane and 2-phenyltropone tosylhydrazone [Eq. (9)].

There is, however, one report in the literature of a diarylcarbene yielding a fluorene which cannot involve carbene-carbene rearrangement [Eq. (10)] [66].

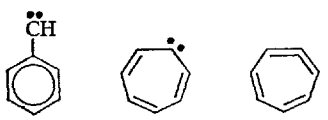


(9)



(10)

3. Quantum-Chemical and Thermochemical Calculations



36 *37* *38*

Semiempirical INDO calculations [67] of the species *36*—*38* indicate the relative energies $36 > 37 > 38$; the allene *38* can be destabilized by benzannelation in positions which decrease the number of Kekulé structures [67]. However, the calculated energy differences are small, and the reverse result is obtained with the CNDO/2, Extended Hückel, and MINDO/2 methods [56,57,68]:

$$36 < 37 .$$

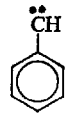
A comparison of the results is shown in Table 6.

The safest conclusion is perhaps that none of the semiempirical methods at the present level of sophistication are capable of producing reliable energies for large carbenes and related species. Again, a thermochemical estimate is both cheaper and more useful. The procedure has been outlined elsewhere [24]. The results are included in Table 6.

Unfortunately, no thermochemical data for strained allenes are known, and an estimate for *38* cannot be made with reasonable accuracy. It is conceivable, however, that *38* is comparable in stability to *36* and *37*, and that a resonance *37* ⟷ *38* would stabilize the cycloheptatrienylidene *37*.

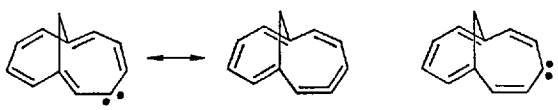
In this connection it is interesting to note that carbene *41* appears to react as an allene, undergoing 1,2-dimerization, but the isomeric carbene *42* undergoes

Table 6. Quantum-chemical and thermochemical estimates of the total energies of phenylcarbene and its isomers

Species	Energy Method Spin state	$-E_{tot}$ (eV) CNDO/2 [1] S[56]	EH [1] S[56]	INDO [67] S	ΔH_f^0 (kcal/mol) MINDO/2 [1] S[68]	Thermochem.[24] T
 *36*		1466.472	598.209	1417.539	107	102
 *37*		1465.970	597.497	1417.877	120	115
 *38*				1418.475		
ΔH_f^0 (*37*) $-\Delta H_f^0$ (*36*) (kcal/mol)		11.5	16.4	−7.79	13	13

[1] Geometries were not optimized for CNDO/2, Extended Hückel (EH), and MINDO/2 calculations.

1,1-dimerization and 1,1-addition to olefins [70]. The chemistry of the cycloheptatrienylidenes so far discovered is that of a carbene rather than an allene.

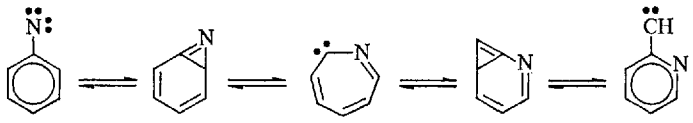


41 *42*

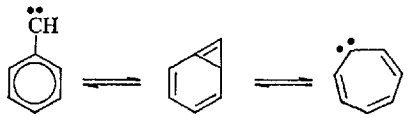
4. A Bicyclic Intermediate?

Although the ring expansions [Eqs. (1)—(4)] have been represented above as one-step reactions, it is conceivable that a bicyclic intermediate is involved. This would form by a simple vinylcarbene-cyclopropene cyclization [Eqs. (11)—(12)].

Furthermore, the bicyclic intermediates, *e.g.* *44* ⇄ *46*, could interconvert directly [71,63], thus bypassing carbenes *45* and *37*. It is therefore important to know the relative energies of the carbenes and the bicyclic intermediates. The heat of formation of *48* can be estimated by various thermochemical schemes [24], yielding values between 115 and 128 kcal/mol. The lower value is obtained by adding the strain energy of benzocyclopropene (70 ± 1 kcal/mol [23]) to the strain free value obtained



43 44 45 46 47 (11)



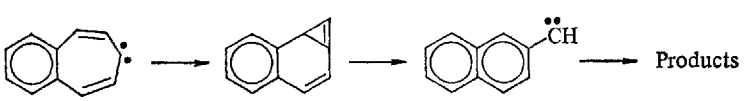
36 48 37 (12)

by group additivity [14] (45.0 kcal/mol). Even if *48* contained no strain whatsoever apart from normal cyclopropene strain, its ΔH_f^0 would be ~110 kcal/mol [24]. The unambiguous result is therefore that the reaction *36* → *48* is endothermic, and most probably, the reaction *37* → *48* is also endothermic. Inclusion of entropy would further raise the relative free energy of *48*.

5. Stabilizing and Destabilizing the Bicyclic Intermediates

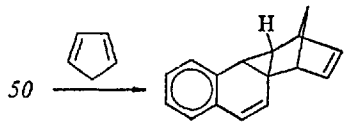
In order to obtain reliable heats of formation of the condensed cyclopropenes, we have used a combined Force Field-SCF-MO procedure [72] which reproduces experimental heats of formation and geometries of strained hydrocarbons and hydrocarbon radicals remarkably well. The method is at the limit of its applicability with the highly strained cyclopropenes which concern us here, and the calculated heats of formation of benzocyclopropene and naphthocyclopropene are 7—8 kcal/mol too low (Table 7). Therefore, we have added an empirical correction of 7—8 kcal/mol to the calculated values (Table 7). The heat of formation of *48* obtained in this way is lower than the thermochemical estimate, but Eq. (12) is still endothermic. To the extent that the singlet-triplet splitting in phenylcarbene is greater than zero, [Ep. (12)] will be correspondingly less endothermic. The transient formation of bicycloheptatriene *48* in the ring expansion of phenylcarbene — with an activation energy of about 10 kcal/mol — now seems perfectly possible. Since the ring expansion has been observed only in the gas-phase, and not in solution, it is evident that an activation energy is required.

The reaction in [Eq. (13)] has been observed both in the gas-phase and in solution [63]. When carbene *49* was generated from the



49 50 51 (13)

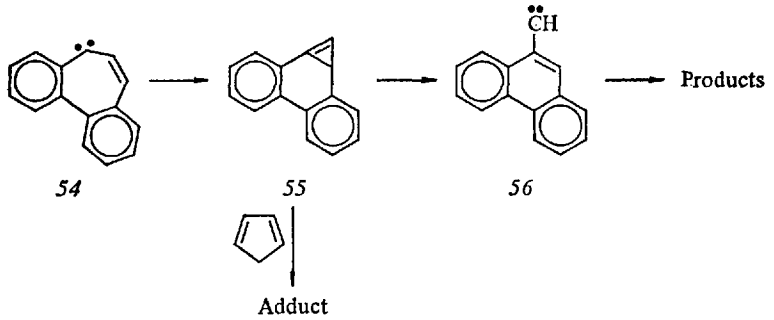
corresponding tosylhydrazone salt, products derived from 2-naphthylcarbene *51* were isolated [63]. In solution, it was possible to trap the intermediate *50* in 16% yield using cyclopentadiene [74] [Eq. (14)].



(14)

Table 7 shows that the carbene cyclization *51* → *50* has now become exothermic by 2—3 kcal/mol. The reason for this is that when *51* closes to *50*, only the *difference* in resonance energy between naphthalene and benzene is lost, *i.e.* 10—15 kcal/mol. Thus benzannelation will stabilize the bicyclic intermediate relative to the parent carbenes.

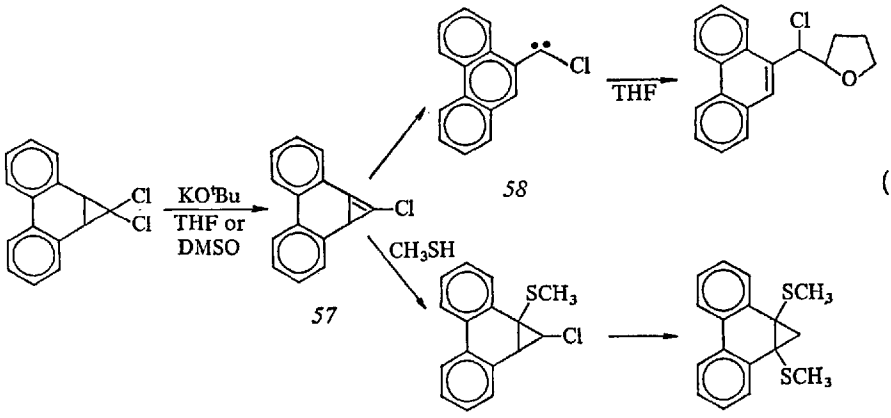
This effect is even more pronounced in the phenanthryl series where, starting from the tosylhydrazone salt of *54*, the cyclopropene *55* was trapped in up to 73% yield using cyclopentadiene [74] [Eq. (15)].



(15)

Table 7 shows that the bicyclic intermediate *55* is now several kcal/mol more stable than carbene *56*.

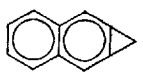
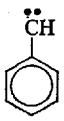
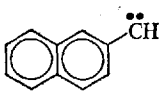
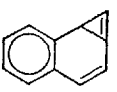
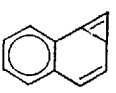
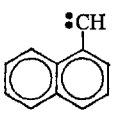
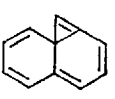
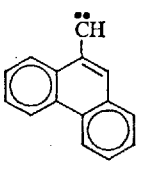
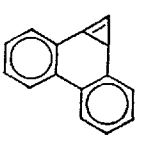
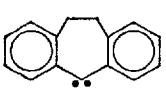
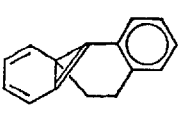
The cyclopropene *57* has also been generated in solution by the reaction shown in [Eq. (16)], and it was trapped with methanethiol [75].



(16)

In the absence of trapping agents, products derived from insertion of the phenanthrylcarbene *58* into the solvent were isolated. Hence, the energy barrier separating *57* and *58* cannot be very high.

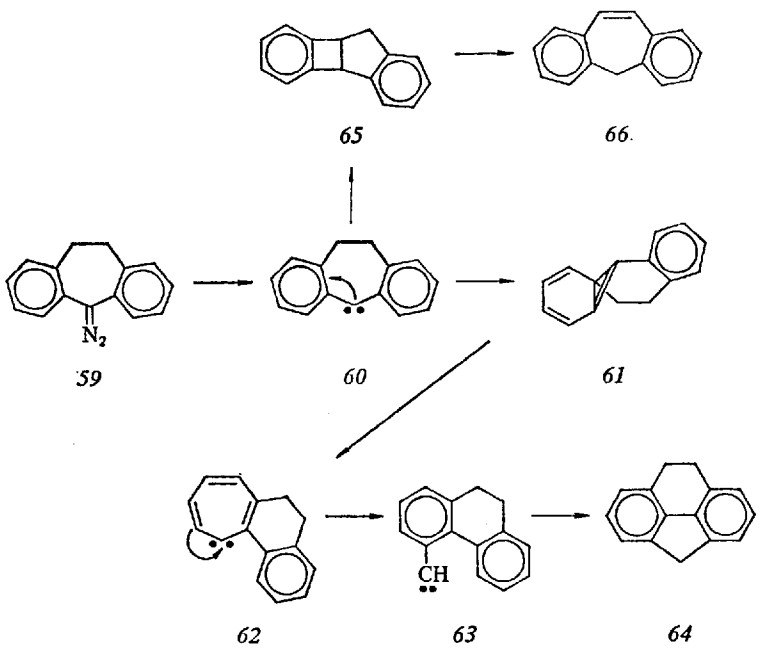
Table 7. Force field — SCF and thermochemical calculations [73]

Carbene (triplet)	ΔH_f^0 (kcal/mol) (thermochem.)	Bicyclic	ΔH_f^0 (kcal/mol) [1] exptl.	FF	$FF_{corr.}$	Th.	$\Delta\Delta H_f^0$ [3]
			89±1	81	89		
			104	97	105		
 *36*	102	 *48*		104	112	115–128 [24]	10
 *51*	118	 *50*		107	115	116 [2]	−2–3
				115	123		+5
 *52*	118	 *53*		142	150		+32
 *56*	132	 *55*		120	128	124 [2]	−4–8
 *60*	129 ± 1	 *61*		144	152		+23

[1] FF = force field — SCF calculation; Th. = thermochemical estimate.
[2] By using ΔH_f^0 (*48*) = 112, and group increments.
[3] ΔH_f^0 (bicyclic) − ΔH_f^0 (triplet carbene).

Above the intermediates were stabilized by decreasing the loss of resonance energy with respect to the carbenes. It is also possible to destabilize the intermediates by increasing their strain. Pyrolysis and photolysis of 5-diazo-10,11-

dihydro-5*H*-dibenzo[a,d]cycloheptene (*59*) is known to yield carbene *60*, which undergoes intermolecular abstraction and insertion in solution [76]. If it were to undergo carbene-carbene rearrangement in the same way as diphenylcarbene gives fluorene [Eq. (8)], it would lead to 8,9-dihydro-4*H*-cyclopenta[d.e.f]-phenantrene (*64*) by the sequence shown in Scheme 4. Indeed, gas-phase pyrolysis of *59* gave up to 25% of *64*, the remaining 75% being 4b,9a-dihydro-9*H*-benzocyclobut[a]-indene (*65*) and dibenzocycloheptene (*66*) [73,77].



Scheme 4

65 is the product of a transannular insertion of carbene *60*, and it rearranges itself thermally to dibenzocycloheptene, *66*. A similar rearrangement of cyclobut-[a]indene is known [78]. The results of pyrolyses at different temperatures are given in Table 8. Assuming that the Arrhenius equation is applicable, and that the A-factors for the reactions *60* → *64* and *60* → *65* have a similar temperature dependence, these data permit the calculation of the difference in activation energy for the two processes of *60*, (Ea_{64}—Ea_{65}). This will probably not be strictly correct under the low-pressure conditions of the experiments (ca. 0.01 mm) [79]. Nevertheless, a plot of the logarithm of the ratio of yields (*65* + *66*)/(*64*) *vs.* 1/T gives a straight line from which

$$Ea_{64} - Ea_{65} \simeq 5 \text{ kcal/mol}$$

Table 8. Pyrolysis products of 5-diazo-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (*59*) [1]

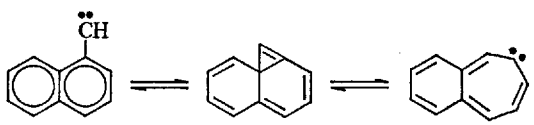
Starting material	*T* °C	Rel. yields (%) *65*	*66*	*64*
59	300	53	43	4
59	385	20.6	73.0	6.3
59	490	1.8	87.5	10.7
59	580	0	84.5	15.5
59	685	0	80	20
59	750	0	78.5	21.5
59	815	0	74	26
65	385	80	20	—
65	580	0	100	—

[1]) *59* was sublimed into the furnace at ca. 40 °C; average pressure outside furnace 0.01 mm. Total yields were 77—100%.

is calculated. In other words, the carbene-carbene rearrangement appears to have an Ea only about 5 kcal/mol higher than the one for the transannular insertion.

If the highly strained cyclopropene *61* is an intermediate or transition state in the ring expansion, calculations of the heats of formation of *60* and *61* (Table 7) predict that the reaction must be endothermic by at least 22 kcal/mol (counting from the triplet ground state [76] of *60*). Ea_{65} must then be at least 17 kcal/mol. Since the singlet-triplet splittings in diarylcarbenes are believed to be very low [80], *i.e.* less than ca. 5 kcal/mol, the activation energies for the singlet carbenes *60* can be correspondingly lowered.

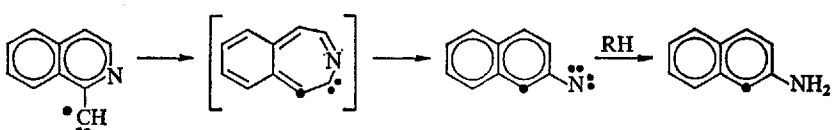
The worst destabilization of a bicycloheptatriene intermediate is obtained by complete loss of resonance.



52 *53*

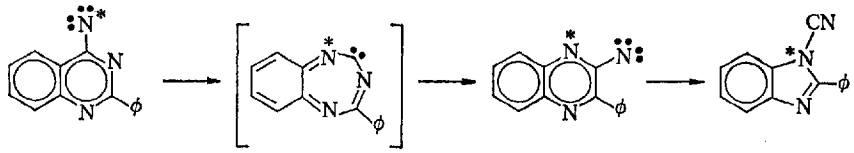
ΔH_f^0 ~118 ~150 kcal/mol (17)

The hypothetical reaction *52* → *53* would be endothermic by ca. 32 kcal/mol (cf. Table 7). Nevertheless, such reactions are known, *e.g.* the gas-phase isomerization of 1-isoquionolylcarbene (*67*) to 2-naphthylnitrene (*68*), which has been verified by ^{13}C-labeling [81], [Eq. (18)],



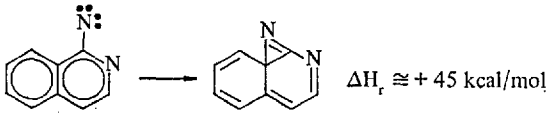
67 *68* (18)

and the clean isomerization of 4-(2-phenylquinazolyl)nitrene (*69*) to 2-(3-phenylquinoxalyl)nitrene (*71*) and then to 1-cyano-2-phenylbenzimidazole (*72*), evidenced by ^{15}N-labeling [81] [Eq. (19) and Section IV.5].



69 *70* *71* *72* (19)

The model reaction in [Eq. (20)] is endothermic by ca. 45 kcal/mol

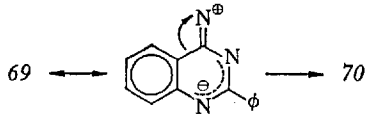


73 *74* (20)

ΔH_f^0 ~128 ~173 kcal/mol

since each ring-nitrogen in *74* increases ΔH_f^0 by ca. 12 kcal/mol [14], but the nitrene-N in *73* decreases its ΔH_f^0 by ca. 2 kcal/mol in comparison with [Eq. (17)] (cf. Section V.7). Nevertheless, the reaction sequence of [Eq. (19)] takes place in solution at 180° [81]. It is even observable, though very slow in refluxing benzene. It competes strongly with intermolecular H-abstraction and dimerization of the solvent radicals. In toluene some bibenzyl is formed. In both toluene and cyclohexane a dimer, probably of the rearranged nitrene *71*, is formed (see Tables 15 and 16). Nitrene dimerization promoted by hydrogen abstraction has been reported previously [82]. It is inconceivable that a nitrene-carbene rearrangement could take place efficiently in solution if it involved an activation energy anywhere near 45 kcal/mol. Alternatively, no intermediate of the kind *53* or *74* can be involved at all; instead the ring expansion has become a one-step process.

It is not surprising that the concerted Wolff-type expansion is particularly favorable in *69*. It is in effect a migration of a phenyl-group, as made clear in the limiting resonance form *75*. Phenyl-migrations are wellknown in Wolff- and Curtius rearrangements [83], in radicals [84], and in cations [85].



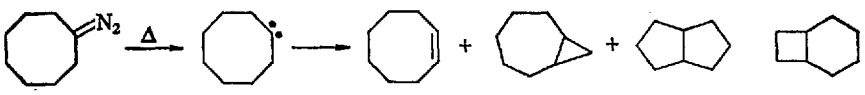
69 *70*

75

Conclusion: the ring expansion of arylcarbenes and arylnitrenes can involve discrete bicycloheptatriene intermediates though not necessarily so. Whether they do or not depends on the stabilities of these intermediates. Bicycloheptatriene instability is no obstacle to ring expansion. The ring expansion of acenaphthylcarbene [86] may be cited as a further example.

6. Digression into Transannular Reactions

The observation that the carbene-carbene rearrangement *60* → *64* (Scheme 4) does take place, and that in so doing the carbene must move out of the molecular plane, approaching the geometry of *61*, implied that the transannular reaction *60* → *65* had a sizeable activation energy. This was not to be expected *a priori*, for it is known that alicyclic carbenes undergo such transannelations in competition with 1,2-H shifts [1], [*e.g.* Eq. (21)] and the latter are calculated to have almost zero activation energies by semiempirical MO-procedures [8].

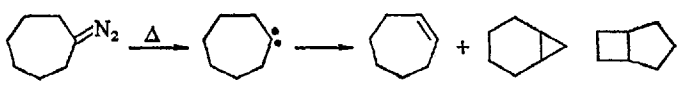


	45%	9%	46%	0%
ΔH_f^0~	−6.2	−3.8	−22.3	−6.1

kcal/mol

(21)

However, no 1,4-transannular reaction is known for cycloheptylidene [1], even though it is thermodynamically feasible [Eq. (22)].



	21%	79%	0%
ΔH_f^0~	−1.8	0.4	1

kcal/mol

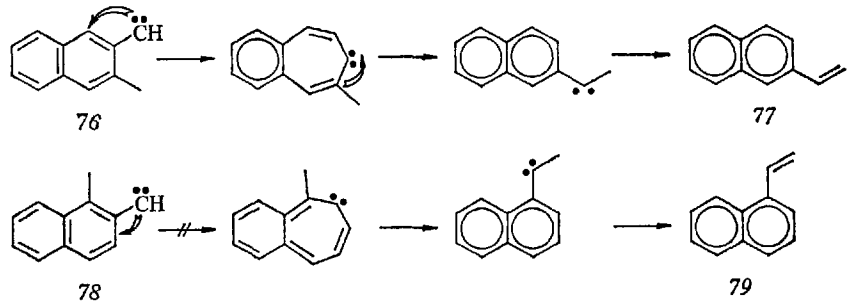
(22)

Since thermochemistry does not control the rearrangements of alicyclic carbenes, it is probable that conformations do. It is also probable that several of these reactions have sizeable activation energies, and that even 1,2-hydrogen shifts in cyclic carbenes have activation energies. There seems to be a general reluctance to form four-membered rings in this type of reaction [1].

7. The Synergic Nucleophilic and Electrophilic Properties of Carbenes

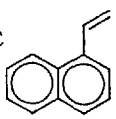
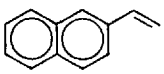
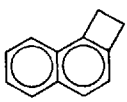
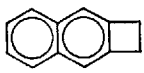
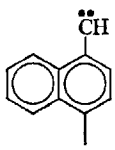
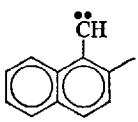
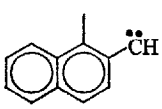
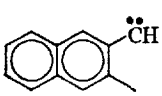
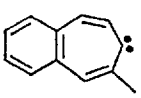
It is known that most carbenes, including arylcarbenes, undergo intermolecular electrophilic addition to double bonds [87]. Then we might expect that if arylcarbenes cyclize intramolecularly to bicycloheptatrienes [*e.g.* Eqs. (12), (13)], this should be an electrophilic addition, and the carbene should add preferentially to the double bond of highest bond order [63]. Gas-phase experiments with substituted naphthylcarbenes indicated that such was the case [63].

Thus, the 2-naphthylcarbene *76* added only to the 1,2-double bond of naphthalene, leading to 2-vinylnaphthalene (*77*). Carbene *78* did not add to the weaker 2,3-double bond, which would have led to 1-vinylnaphthalene, *79* (Scheme 5 and Table 9). However, other carbenes do not react in this way, and it will be shown



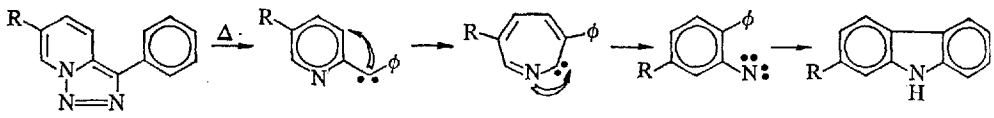
Scheme 5

Table 9. Pyrolysis of methylnaphthaldehyde tosylhydrazone sodium salts at 5 mm [63]

Carbene	T °C	Yield (%)			
					
	350	0		0	
	350		0	17.5	
	350	0		16	
	350		55		2.2
	300		53		4.2
	250		70.5		5.6
	200		48.5		5.9
	350		24		2.5

below that the selectivities observed in carbene ring expansions do not follow bond orders. In fact, the carbenes do not react simply as either electrophiles or nucleophiles, but as both.

2-Pyridyl phenyl carbene rearranges in the gas-phase to 2-biphenylylnitrene. The latter cyclizes to carbazole in 100% yield [49] [Eq. (23)].

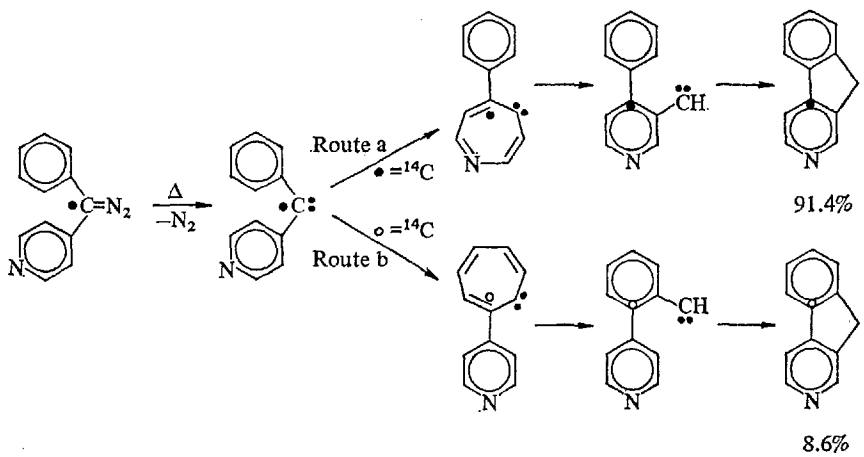


R = H or CH_3

(23)

Substituent labeling (R = CH_3 or H) confirms the skeletal rearrangement. The results demonstrate a 100% regiospecific pyridine ring expansion.

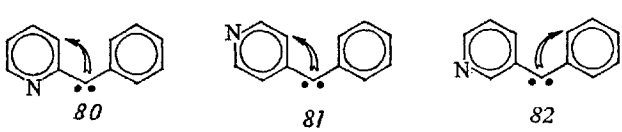
4-Pyridyl phenyl carbene rearranges analogously to 2-azafluorene. Here, carbon labeling is necessary in order to distinguish the rings undergoing expansion. ^{14}C-labeling followed by degradation of the 2-azafluorene-^{14}C to 4-aminonicotinic acid and CO_2 established that 91.4% of the label was situated in the pyridine ring; 8,6% in the benzene ring [77] [Eq. (24)].



(24)

3-Pyridyl phenyl carbene yields a ca. 56:44 mixture of 1- and 3-azafluorene [77]. ^{13}C-labeling of the carbene followed by a complete analysis of the ^{13}C-NMR spectra of azafluorenes proved that the 1-azafluorene was 100% labeled in the benzene ring, and the 3-azafluorene was at least 84% labeled in the benzene ring. Thus, this carbene undergoes at least 93% expansion of the benzene ring [Eq. (25)].

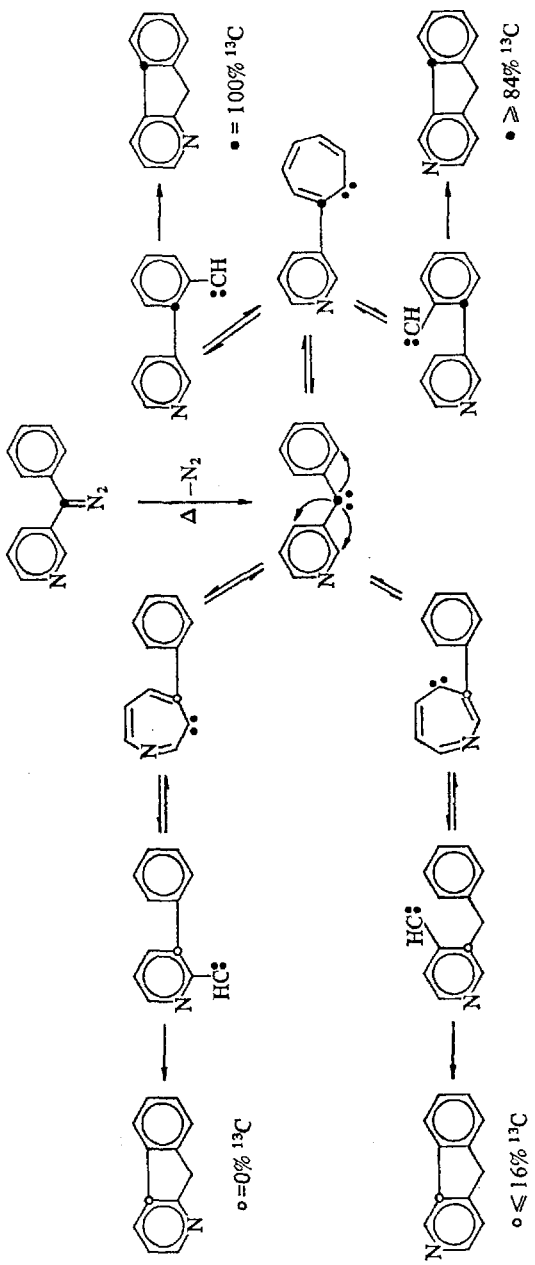
The direction of ring expansion is summarised in formulae *80*—*82*.



80 *81* *82*

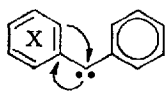
Bond order cannot be the determining factor, because the bond orders of pyridine and benzene are — to the best of our knowledge — identical [88]. Furthermore, carbenes *81* and *82* show opposite selectivities, even though they both have the opportunity of adding to a 3,4-pyridine bond. The same goes for the pair *80*, *82*.

(25)



The carbene does not react as an electrophile, because in that case *80* and *81* should definitely attack the benzene ring. Neither does it react as a pure nucleophile, as in that case all three carbenes should preferentially attack the pyridine ring.

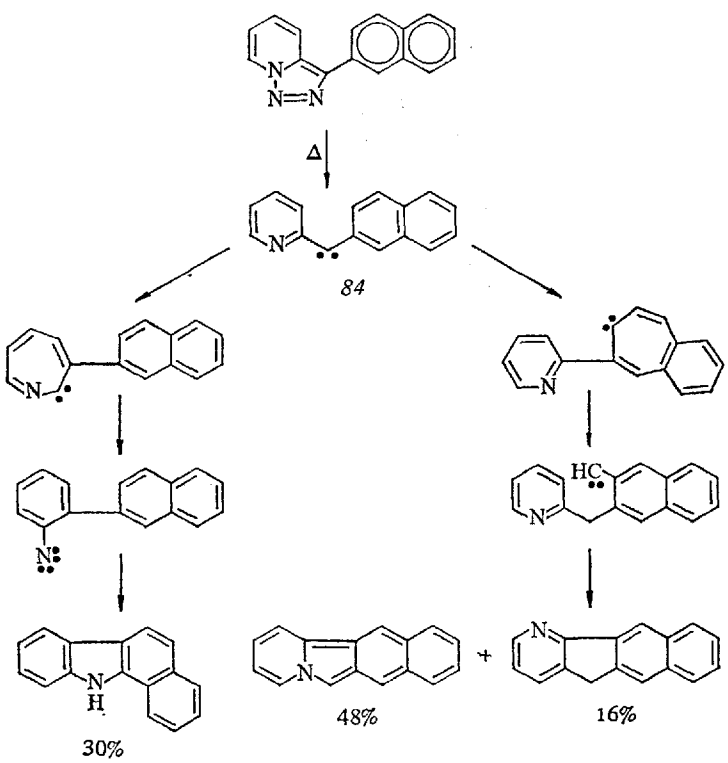
The selectivities of these and other carbenes can be understood in terms of a simultaneous electrophilic and nucleophilic attack, symbolized in formula *83*.



83

The carbene lone-pair goes into the lowest vacant molecular orbital (LUMO) of the most electrophilic ring. The vacant carbene p-orbital undergoes an electrophilic substitution onto the *o*-position of the ring. The electrons come from the HOMO of that ting. Ring expansion will then be favored by a low-lying LUMO, a high-lying HOMO, and a high electron density in the *ortho*-position.

The two interactions are synergic. The donor property of the carbene makes it more electrophilic. The ring becomes more electron-rich by the donation, and electrophilic substitution then becomes faster. In *80* and *81* the carbene is situated in the electrophilic 2- and 4-positions of pyridine. The electron density in position 3



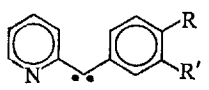
Scheme 6

is low, but electrophilic substitution is known to occur. In *82* the carbene is not in an electrophilic position. The coefficients of the LUMO is low in position 3, and the coefficients of the HOMO are low in positions 2 and 4. The donor-acceptor properties of the carbene are maximally hindered with respect to the pyridine ring, and in fact reaction occurs with the benzene ring.

2-Pyridyl 2-naphthyl carbene (*84*) undergoes espansion of both the pyridine and the naphthalene rings [56] (Scheme 6).

The LUMO energy in naphthalene is lower than in benzene, and the carbene can now act as a nucleophile with respect to both rings. The naphthylcarbenes always prefer to attack the 1-position in naphthalene [63], which has the highest electron density and the lowest localization energy for electrophilic substitution.

The carbenes *85 a–f* all expand exclusively into the pyridine ring.

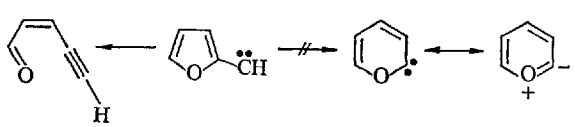


85 a–f

	R	R′
a	H	H
b	OCH_3	H
c	Cl	H
d	NO_2	H
e	CN	H
f	H	NO_2

It was expected that the nitro and cyano groups in *85 d* and *e* would have lowered the benzene LUMO sufficiently that reaction could occur there. However, these LUMOS are localized essentially on the substituent groups, and the LUMO coefficient in the carbene position is low, judging from the electron densities in nitro- and cyanobenzene radical anions [89a]. Furthermore, these groups deactivate all ring positions towards electrophilic substitution. An example from the nitrene field, which shows that a p-cyano group may decelerate ring expansion, will be discussed in Section IV.1.

The reports that 2-furfurylidene and 2- and 3-thenylidene do not undergo ring expansion, but ring open instead [90] are understandable in terms of the donor-acceptor properties: furane and thiophene are

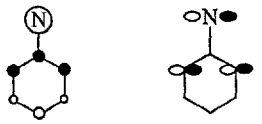


too electron rich, the LUMO energies are too high, and the carbene-LUMO interactions are strongly disfavoured.

Quantum-chemical (Extended Hückel, CNDO/2, and INDO) calculations fully corroborate the contention tht arylcarbenes and -nitrenes can function as nucleophiles during ring expansion. The argument is independent of the question of formation of bicyclic intermediates. Calculations of the phenylnitrene energy surface show that the nitrene loses electron density, and C-1 gains electron density until the transition state for ring expansion is reached [57].

The Extended Hückel and CNDO/2 procedures give conflicting predictions of the most stable ground state conformations of phenylcarbene and phenylnitrene.

However, on bending the carbene or nitrene 10° out of the molecular plane – as required for rearrangement — both methods give identical answers: the carbene or nitrene lone-pair conjugates with the ring. The HOMO and LUMO orbitals in phenylnitrene are shown below. The more electrophilic the ring, the more pronounced



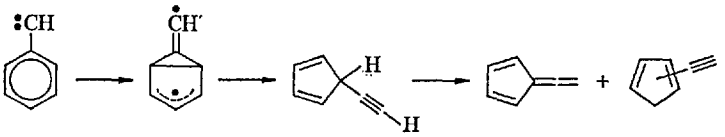
(π) Homo (p) Lumo

the stabilization of (π) HOMO will be.

A molecular model shows that, irrespective of the ground state conformation, an attempt to perform a ring expansion in phenylcarbene by means of an overlap between the vacant carbene p-orbital and a ring-p-orbital in an out-of-plane movement of the carbene, will *ipso facto* lead to interaction between the carbene lone-pair and the ring. The success or failure of the reaction depends on whether this interaction is attractive or repulsive, that is, on the ring-LUMO.

8. The Ring Contraction

Flow pyrolysis of phenylcarbene progenitors at temperatures above ca. 580 °C results in two new products: fulvenallene and ethynylcyclopentadiene (the latter is a mixture of two isomers [54]). The mechanism in [Eq. (26)] was first postulated to account for this fact [54,60].

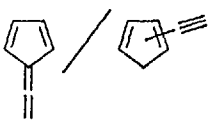


36 *86* *24* *25* (26)

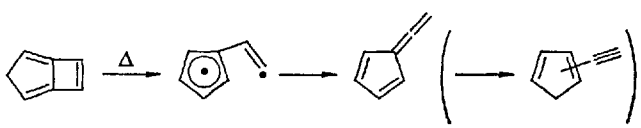
This mechanism would lead initially to *86*, which should undergo facile 1,5-hydrogen shifts to give *25* as the primary product. The direct formation of *24* would constitute a "forbidden" 1,3-shift. However, *25* does not appear to be a primary product. Fulvenallene (*24*) predominates at low temperatures and elevated pressures (Table 10). Thermochemical estimates [24] indicate that [Eq. (26)] is exothermic by ca. 20 kcal/mol, and that *24* and *25* have almost identical heats of formation. Experiments [44,46] show that *24* rearranges to *25* at elevated temperatures (cf. Table 4). Thus the predominance of *24* at low temperatures cannot be due to a rearrangement of *25*.

If *24* is the primary product, it will be chemically activated by the exothermicity of the reaction, *i.e.* ca. 20 kcal/mol; but not only by this. The reaction in [Eq. (26)] also has a considerable activation energy, since it occurs only above ca. 580 °C. The sum of the activation energy and the exothermicity is probably at least 40 kcal/mol [24], all of which will be present in fulvenallene (*24*) as chemical activation,

Table 10. Ring contraction in phenylcarbene

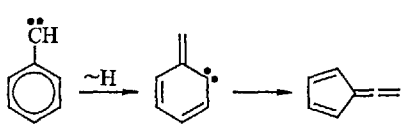
Precursor	T °C	P mm, carrier	Ratio 	Combined yield, %	Ref.
Phenyldiazo-methane	800	~0.05	2.5	14	54)
	900	~0.05	2.1	44	54)
	1000	~0.05	1.3	44	54)
Benzaldehyde tosylhydrazone sodium salt	590	0.1	2.9	2.5	44)
	655	0.1	2.0	8	44)
	800	0.01	1.5	14	44)
	850	0.01	0.8	—	44)
	675	1.5, N_2	3.3	16	92)
	590	5–7, N_2	4.0 ± 0.3	13	92)
5-Phenyltetrazole	800	0.02–0.05	1.3	2.7	57)

and hence accelerate its isomerization to *25*. If the pressure is increased, initially "hot" *24* will be collisionally deactivated, and isomerization to *25* will lose importance. This is precisely what is observed (Table 10). There is a limit to the amount of deactivation which we can achieve under our conditions: too high pressures result in lower pumping speeds, longer residence times in the furnace, and *collisional activation*. The ratio *24*/*25* then decreases again. If the pumping speed is increased, the ratio increases again. These results demonstrate conclusively that chemical activation is involved, and that at least 80% of the primary ring contraction product is fulvenallene, *24*. The same chemical activation effect is observed in the reaction in [Eq. (27)] which also yields fulvenallene [91].



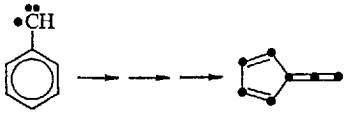
(27)

The products *24* and *25* are also formed in the Wolff-rearrangement of methylenecyclohexadienylidene (Section II.4, Scheme 3), and it was shown that *24* was the exclusive low-temperature product. Since chemical activation is unimportant here, the Wolff-rearrangement must have a much lower activation energy than the ring contraction in phenylcarbene. The proposal, first made by Wiersum [93], that phenylcarbene undergoes a H-shift to methylenecyclohexadienylidene [Eq. (28)] before ring contraction then seems reasonable.



(28)

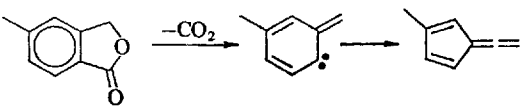
Since ring contraction has a higher activation energy than ring expansion (600° *vs.* 200°), carbon labeling of phenylcarbene should result in limited carbon scrambling according to [Eq. (3)] (p. 88). However, Crow and Paddon-Row [51] observed complete carbon scrambling, implying that H-shifts must take place somewhere along the reaction coordinate before ring contraction, *e.g.* by means of [Eq. (4)] (p. 88)



The tolycarbenes did not give any methylfulvenallenes, and did not undergo ^{13}C-scrambling in the rearrangement to benzocyclobutene and styrene [Eq. (7)]. Hence, the relative rate constants can be derived [51]:

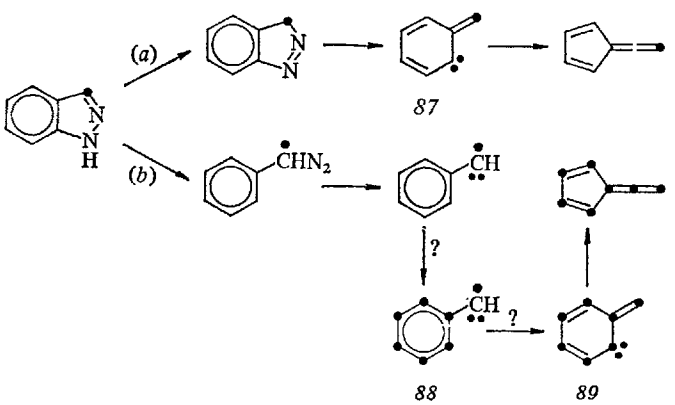
$$k_{\text{ring expansion}} > k_{\text{H-shift}} > k_{\text{ring contraction}} .$$

When the Wolff-intermediates are generated directly (pyrolysis of methylphthalides) ring contraction to methylfulvenallenes does take place [94] [Eq. (29)].



(29)

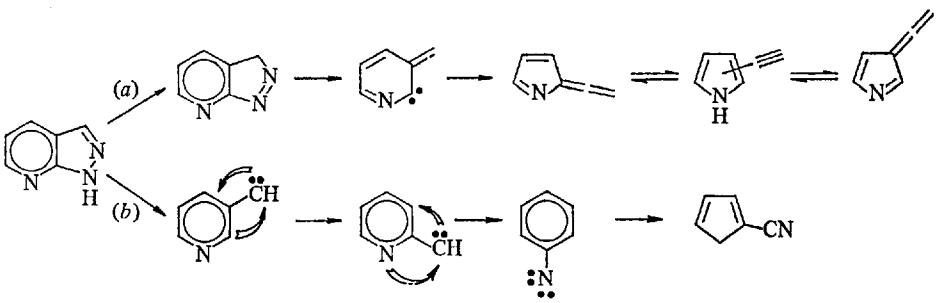
Crow and Paddon-Row [51] also discovered that pyrolysis of ^{13}C-labeled indazole led to fulvenallene containing excess label in the extremity, and being uniformly labeled in all remaining positions. Most probably, there are two reaction pathways [Eq. (30)], one (a) leading directly to methylenecyclohexadienylidene (*87*) which undergoes direct Wolff-rearrangement; the other (b) leading to phenylcarbene, which undergoes carbon scrambling. *If the carbon scrambling is uniform, it must be completed before the rearrangement to methylenecyclohexadienylidene (88 → 89).*



(30)

Evidence for two such reaction pathways was obtained by pyrolysis of pyrazolo-[3,4-*b*]pyridine [95]. Here, the arylcarbene route (b) leads to the pyridylcarbene-

phenylnitrene rearrangement (cf. Section V.3, p. 231) and cyanocyclopentadiene. The methylenecyclohexydienylidene route (a) leads to ethynylpyrroles and azafulvenallenes:



In both systems studied the arylcarbene route (b) increases in importance with increasing temperature.

IV. Nitrene-Nitrene Rearrangements

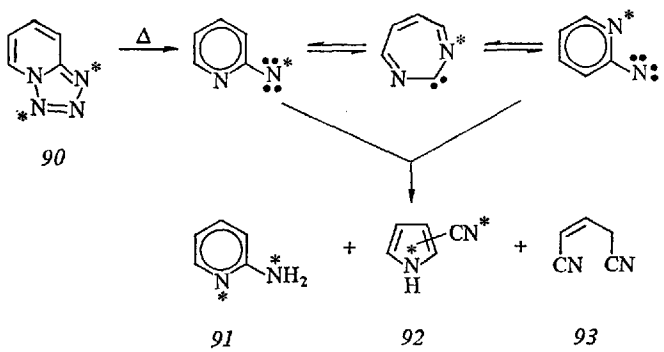
The reactions discussed in this chapter give ample evidence that hetarylnitrenes interconvert *via* intermediates which have an arrangement of atoms as in a seven-membered ring carbene. Such intermediates have never been directly observed, and only in one case can we exclude the existence of "bicyclic intermediates". For the sake of brevity, the ring expansions will be presented as one-step reactions.

1. Pyridylnitrenes

Gas-phase pyrolysis of tetrazolo[1,5-*a*]pyridine produces nitrenes under quite mild conditions ($\geqslant 365$ °C). The nitrenes undergo three intramolecular reactions with the relative rates:

$$k_{\text{ring expansion}} > k_{\text{ring contraction}} > k_{\text{ring opening}} .$$

A minor intermolecular H-abstraction yields 2-aminopyridine. The evidence comes from ^{15}N-labeling, which shows that the nitrogen atoms have interconverted before formation of cyanopyrrole and aminopyridine [96] [Eq. (31)]. The ^{15}N-contents in *91* and *92* were assayed before and after



(31)

conversion to 2-pyridone and pyrrole carboxylic acid, respectively, with the results shown in Table 11.

The product yields at different temperatures are shown in Table 12. The formation of 3-cyanopyrrole is probably mechanistically insignificant, for control experiments show that 2- and 3-cyanopyrrole interconvert at elevated temperatures [33]. If 2-cyanopyrrole is the primary product of ring contraction, it will be chemically activated by >54 kcal/mol due to the exothermicity of the reaction. This will suffice to interchange it with 3-cyanopyrrole.

The pyrolysis of methyltetrazolopyridines (Table 13) proves that all products must be formed after interconversion of the nitrenes according to [Eq. (31)].

As shown below, pyrimidyl- and pyrazinylnitrenes give rise to N-cyanoimidazoles. For this reason, it was thought for a long time that 2-pyridylnitrenes con-

Table 11. Pyrolysis of tetrazolo[1,5-*a*]pyridine-1(3)-^{15}N (*90*) [1]

Product	% ^{15}N [2]	Yield %
Tetrazolo[1,5-*a*]pyridine (*90*)	8.37	
2-Aminopyridine (*91*)	4.18	2
2-Pyridone [3]	2.1	
2-Cyanopyrrole	4.22	68
3-Cyanopyrrole	4.17	17
Pyrrole-2(3)-carboxylic acids [4]	2.15 ± 0.15	

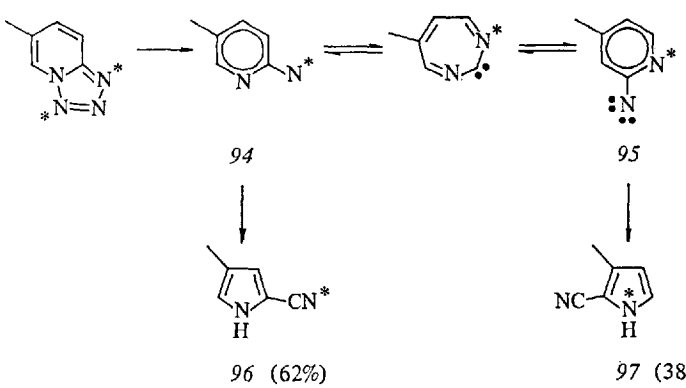
[1] Pyrolysis at 600°, 0.1 mm. Products were separated by GC.
[2] By mass spectrometry (AEI MS 902).
[3] From diazotization of 2-aminopyridine.
[4] From hydrolysis of the mixture of 2- and 3-cyanopyrrole.

Table 12. Pyrolysis of tetrazolo[1,5-*a*]pyridine (*124*) [1] and pyrido[2,3-*a*][1,2,4]-oxadiazol-2-one (*125*) [2]

Starting material	*124*					*125*	
Temperature, °C	380	500	600	700	800	600	790
2-Aminopyridine	15	4	2	1	0.7	0	0
Glutacononitrile	0.3	3	4	4	5	1	3
2-Cyanopyrrole	26	65	68	68	55	3	1
3-Cyanopyrrole	5	15	17	17	27	3	3

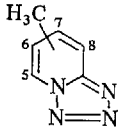
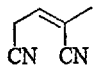
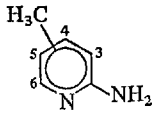
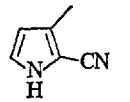
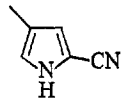
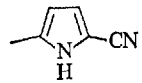
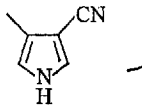
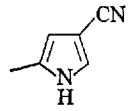
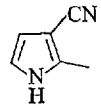
[1] Yields in %, by GC. Pyrolysis of 1.00 g tetrazole at 0.10 mm in 40 min; sublimed in at 100° [92].
[2] Relative yields; pyrolysis of 600 mg oxadiazolone at 0.02 mm in 30 min [100].

tract initially to N-cyanopyrroles. These are unstable and presumably rearrange to 2- and/or 3-cyanopyrroles. To our knowledge, only two N-cyanopyrroles are known: 1-cyano-2,3,4,5-tetrabromopyrrole [92] and N-cyanocarbazole [97]. Both are thermally unstable. A labeling experiment [92] of 5-methyl-2-pyridylnitrene *94* shows, however, that this hypothesis is wrong [Eq. (32)].



(32)

Table 13. Pyrolysis products of x-methyl-tetrazolo[1,5-*a*]pyridines [1]

	T °C/P_{mm}									
8-CH_3	500/0.1	5	—	6	—	—	50			[4]
	380/0.05	2	—	10 [2]	—	—	45			
7-CH_3	350/0.05	1.6	3	4.4 [3]	17	28	—	[4]	[4]	[4]
6-CH_3	380/0.05	6	3	4 [3]	17	28	—	[4]	[4]	[4]
	365/1 N_2	[4]	[4]	[4]	28	44	—	~2	~2	~2
5-CH_3	380/0.05	1.3	—	10 [2]	—	—	45			[4]
	800/0.30	1	—	1	—	—	30	[4]	[4]	[4]

[1] Total yields (by GC peak areas) are given and account for $\geq 90\%$ of isolated material. Yields of 3-cyanopyrroles increase with the temperature and were not usually measured. Cyanopyrroles were identified by NMR and comparison with spectra of authentic specimens [103].

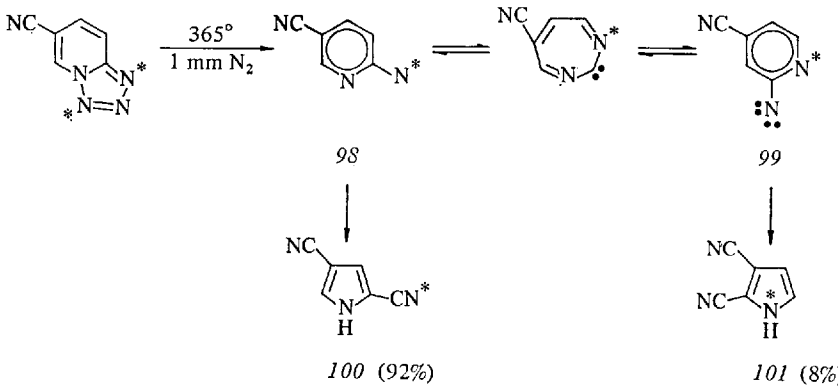
[2] 1:5 mixture of 3- and 6-methyl-2-aminopyridine.

[3] 1:1 mixture of 4- and 5-methyl-2-aminopyridine.

[4] Present, but not measured.

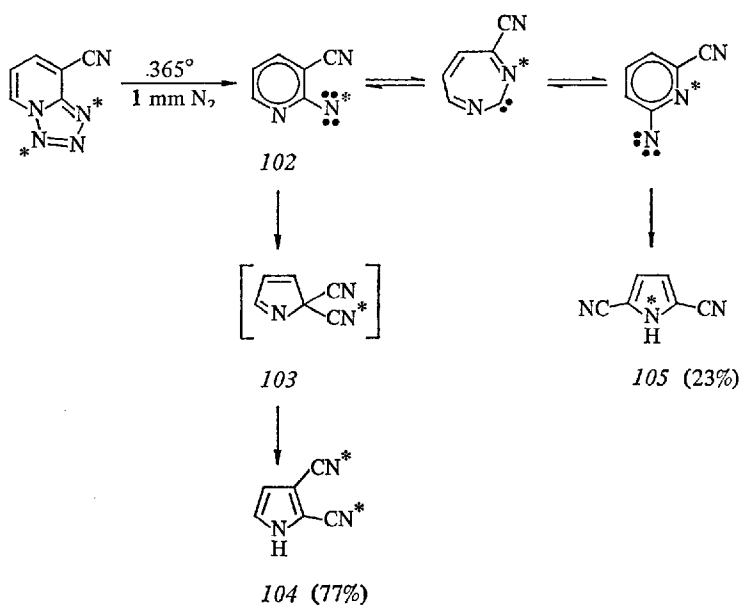
Separation and hydrolysis of the products *96* and *97* demonstrated that *96* was labeled only on the cyano-group; *97* only in the ring. Accordingly, *nitrenes 94 and 95 contract directly to 96 and 97, and not to N-cyanopyrroles.*

An analogous labeling experiment [98] of 5-cyano-2-pyridylnitrene (*98*) showed that only 8% of the dinitriles formed contained ^{15}N in the pyrrole ring. This is the same as the relative yield of *101*, so most likely it is *101* which is ring-labeled [Eq. (33)].



(33)

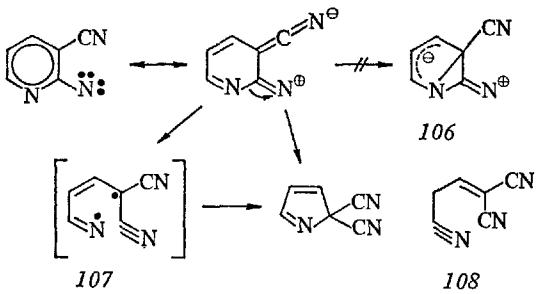
The comparison of *94* and *98* indicates that the CN-group in *98* either accelerates ring contraction or decelerates ring expansion, or both. Both effects are plausible. If *99* were formed to a large extent, ring expansion back to *98* should be difficult because the CN-group in *99* reduces the electron-density in the 3-position. Since *99* is not formed to a large extent, *98* expands at most 16%, and this could be because the cyano-group deactivates all ring positions in *98* towards electrophilic attack (cf. Section III.7).



(34)

Labeled 3-cyano-2-pyridylnitrene (*102*) yielded dinitriles *104* and *105* [99]. The reluctance towards ring expansion is seen in the formation of *104* as the major product [Eq. (34)]. This must take place *via* the 2*H*-pyrrole *103*.

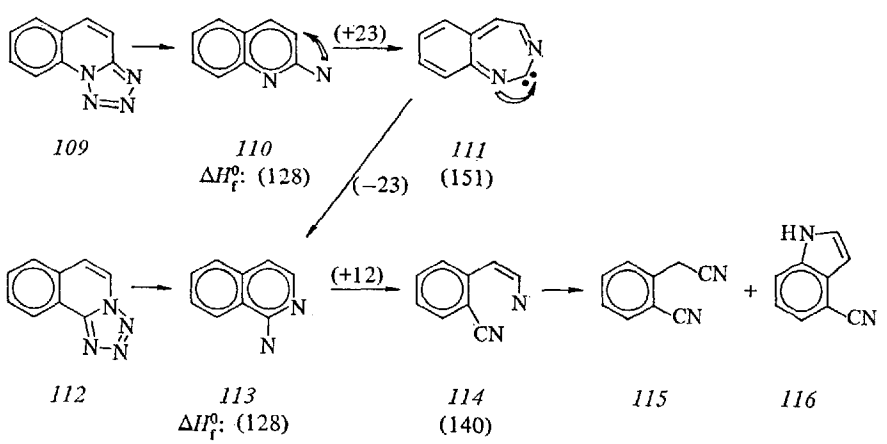
It is possible that electronegative groups accelerate ring contraction by making the nitrene-nitrogens more electron deficient [Eq. (35)]. The reaction may be either concerted or proceed *via* diradical *107*, although the latter is open to question, since no cyanoglutaconononitrile (*108*) was isolated in these reactions. An electrocyclic reaction leading to *106* [100] would not be expected to be favored particularly by the CN-group, which is in a position where it cannot delocalize the negative charge.



(35)

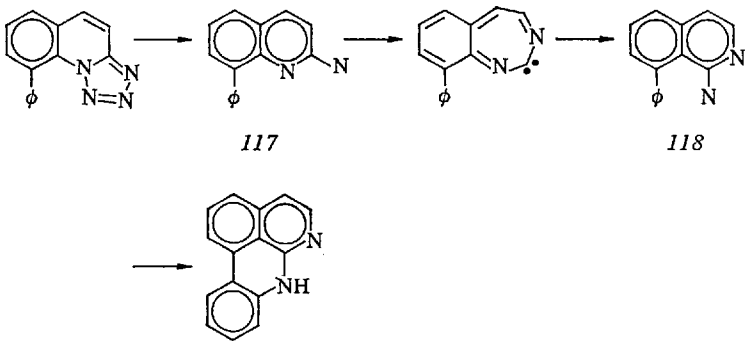
2. Quinolyl- and Isoquinolylnitrenes

The balance between ring opening (to glutaconononitriles) and ring contraction (to cyanopyrroles) is shifted in the quinolyl- and isoquinolylnitrenes. Both give products derived from isoquinolylnitrene [Eq. (36)] namely *115* and *116* [97,100].



(36)

The contention that this is indeed the rearrangement taking place is supported by generation of 8-phenyl-2-quinolylnitrene (*117*), where the sole product (*119*) results from trapping of the isoquinolylnitrene (*118*) [101,102] [Eq. (37)].



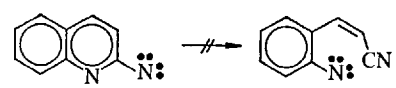
117 *118*

119 (73%)

(37)

Further proof comes from ^{14}C and ^{15}N labeling experiments of 2-quinolylnitrene by Brown and Smith [100].

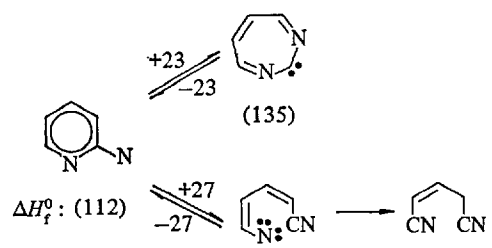
A satisfactory reason for this selective nitrene-nitrene rearrangement is found in thermochemistry. Approximate heats of formation can be estimated as indicated in Table 14. The values are given in parentheses in [Eq. (36)]. The reason why isoquinolylnitrene (*113*) ring opens instead of expanding is simply that the former process is thermodynamically less costly. The analogous ring opening in quinolylnitrene [Eq. (38)] is not observed.



ΔH_f^0: (128) (147–156)

(38)

The thermochemical estimates for the 2-pyridylcarbene system are given in [Eq. (39)].



(135)

ΔH_f^0: (112)

(139)

(39)

In agreement with observations, ring opening is more endothermic than ring expansion. However, in this comparison entropy differences may be larger than usual, and these would tend to decrease the free energy difference between ring opening and ring expansion.

It must be noted that the thermochemical estimates for seven membered ring carbens [24] are very unreliable, and we do not attach much importance to them.

It is much safer to compare *differences* in heats of formation of seven-membered rings. Therefore, the *trends* of the comparison of [Eqs. (36) and (39)] will be correct, irrespective of the accuracy of the absolute values.

Table 14. Estimation of heats of formation of nitrenes and related species

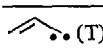
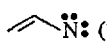
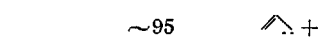
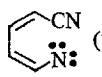
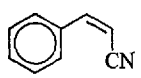
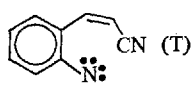
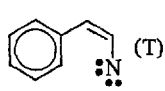
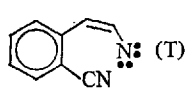
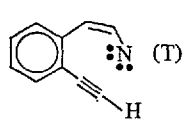
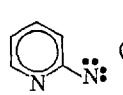
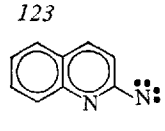
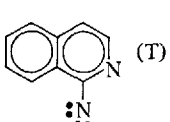
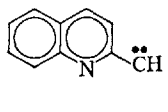
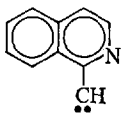
Compound	ΔH_f^0 (kcal/mol)	Source
 (T)	~97	(Table 1)
 (T)	~95	 97 90 [2] 92 kcal/mol
 (T) *120*	~139	From and group increments [14], allowing 10 kcal/mol extra resonance [R.E.() − R.E.()[17]]
	67–76	By group increments [14]
 (T)	147–156	From ΔH_f^0 (⌀ − N) (100 kcal/mol [24]) and group increments
121 idem	144	From ΔH_f^0 (*120*) + $\Delta\Delta H_f^0$ (⌀ − N −) ≃ 139 + 100 − 95
 (T) *122*	107	From group increments, allowing 9 kcal/mol extra reeonance (cf. Ref. [17])
 (T) *114*	139	From ΔH_f^0 (*122*) + $\Delta\Delta H_f^0$ (⌀ − CN − ⌀H) [14] = 107 + 32
 (T)	165	From ΔH_f^0 (*114*) + 26 kcal/mol [14]
 (T) *123*	~112	From ΔH_f^0 (⌀ − N) = 100 [24] and group increments [14]
 &  (T) *110* *113*	128	From ΔH_f^0 (*123*) and group increments) [14]

Table 14. (continued

Compound	ΔH_f^0 (kcal/mol)	Source
 & 	~130	From ΔH_f^0 (2-pyridylcarbene) [24] + group increments [14]
197 *200*		

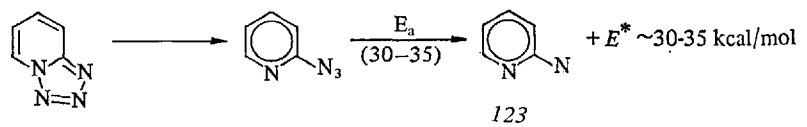
[1]) This requires that R.E. (⟨⟩) = R.E. (⟨⟩N:). The following comparison indicates that this is correct: ΔH_f^0 (ø — NH) — ΔH_f^0 (ø — CH_2) = 10 kcal/mol [104]; ΔH_f^0 (ø — NH_2) — ΔH_f^0 (ø — CH_3) = 9 kcal/mol [14].

[2]) See Table 26.

3. The Oxadiazolone Problem

There remains the astounding observation [100] that pyridylnitrenes generated from pyridooxadiazolone (*125*) give much more glutacononitrile and 3-cyanopyrrole than does *124* (Table 12). The first explanation which comes to mind is that the nitrene from *125* is more highly chemically activated than the one from tetrazolopyridine, *124*.

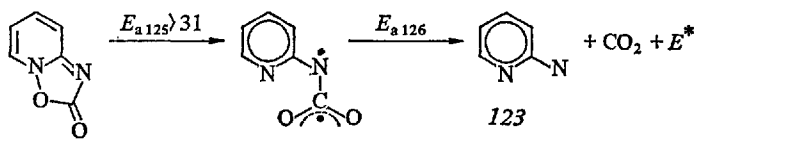
This explanation is, however, untenable. The estimated thermochemical values are indicated in [Eqs. (40) and (41)]. The activation energy for decomposition of 2-azidopyridine cannot be much lower than those of other aromatic azides (~35 kcal/mol [105]). The nitrene in [Eq. (40)] will then be chemically activated by at least 30 kcal/mol initially [24]. In order that the nitrene in [Eq. (41)] be more highly activated, Ea_{126} for the process *126* → *123* must be more than 17 kcal/mol. This is quite surprising since it is an exothermic reaction. The heat of formation of *125* is unknown and difficult to estimate. A reasonable value is —25 kcal/mol. If the reaction *125* → *123* were concerted, an activation energy higher than 73 kcal/mol



124 (112) *123* (112)

ΔH_f^0 (105)

(40)



125 *126* *123*

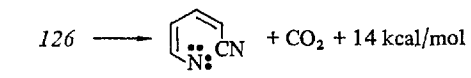
ΔH_f^0 (≪0) (~31) (112) (–94)

(41)

E^* ⟩30 ⟹ E_{a126}⟩17 kcal/mol

would be required. It may be excluded that such a process is efficient at 600° in a flow system.

A clue to the solution comes from the lack of formation of 2-aminopyridine in the pyrolysis of pyridooxadiazolone *125* [100]. Perhaps no nitrenes are formed. The radical nitrogen in the hypothetical intermediate *126* would be electrophilic, and ring opening leading to glutaconononitrile could then be a concerted process [Eq. (42)].

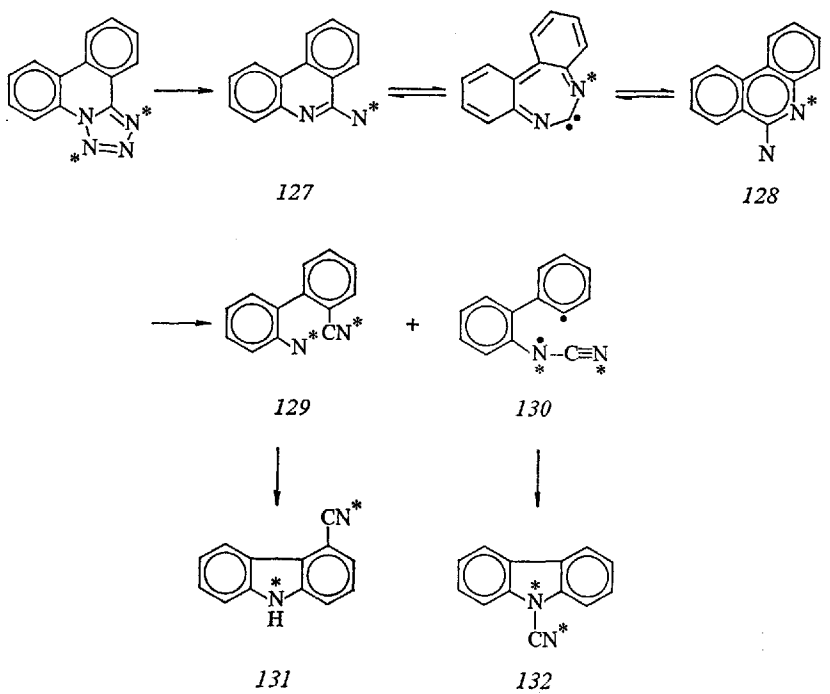


(42)

The reaction should be restudied at higher pressures to determine the importance of chemical activation, and 2-aminopyridine should be resought.

4. 9-Phenanthridylnitrene

We had not expected to find ring expansion in this system. Nevertheless, the ^{15}N-labeling showed that the products *131* and *132* both had undergone nitrogen scrambling, at least to the extent of 70% and probably more [Eq. (43)] [97,101]

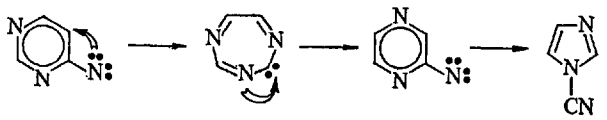


(43)

This is the only system where an "N-cyanopyrrole" (*132*) has been found. The nitrenes have no other alternative but to form *132* or to ring open to *129* with subsequent closure to *131*. The formation of *132* occurs only above 500 °C, in contrast to other hetarylnitrene ring contractions.
The radical pathway *via 130* then seems reasonable, but this cannot be the normal route ro ring contraction, *e.g.* in pyrazinylnitrenes, which yield N-cyanoimidazoles already in solution, or pyridylnitrenes, which contract at 365 °C.

5. 4-Pyrimidyl- and Pyrazinylnitrenes

From the reluctance of 3- and 5-cyano-2-pyridylnitrenes to expand (Section IV.1) one might naïvely expect that 4-pyrimidylnitrene (*133*) should not expand but contract. Quite on the contrary, *133* rearranges almost exclusively to pyrazinylnitrene, *134*.



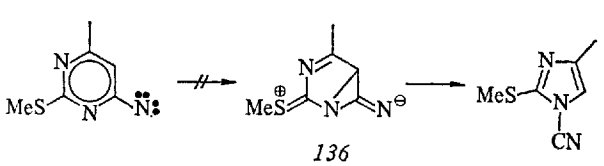
(44)

133 *134* *135*

Derivatives of *133* and *134* yield N-cyanoimidazoles (*135*) both in the gas-phase and in solution (Table 15) [101,106–107]. The activation energies for ring contraction must then be quite low in this case. That nitrenes are involved is demonstrated by the formation of amines in hydrogen rich solvents. Labeling experiments (Table 16) show that at least the major product forming path involves the rearrangement in [Eq. (44)]. So the activation energy for ring expansion in *133* must also be very low; so low that the reaction competes favorably with intermolecular reaction with the solvent.

The gas-phase pyrolysis of 5,7-dimethyltetrazolo[1,5-*c*]pyrimidine also gave a very low yield of a product believed to be 4(5)-cyano-2,5(4)-dimethylimidazole (Table 16). Hydrolysis gave the *unlabeled* acid (Table 16). This indicates that 4-pyrimidylnitrenes *can* undergo direct contraction, albeit in low yield.

We once believed [106] in a "prefulvene" intermediate in the ring contraction. The methylthio-group in *136* was expected to stabilize such an intermediate, and this would explain the facility of ring contraction [Ea. (45)].

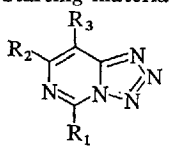
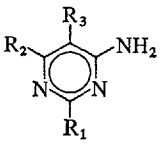
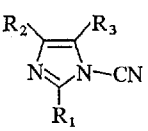
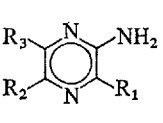


(45)

136

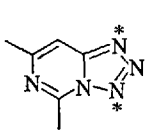
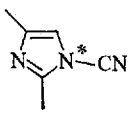
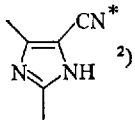
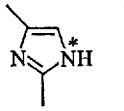
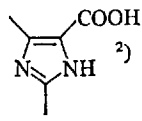
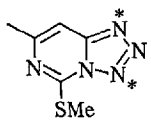
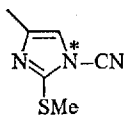
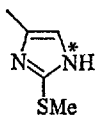
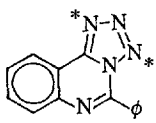
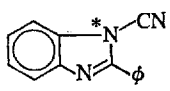
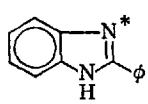
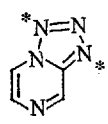
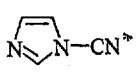
Now that labeling has shown that at least the majority of the ring contraction is not direct, the mechanism in [Eq. (45)] can be discounted.

Table 15. Pyrolysis of tetrazolo[1,5-*c*]pyrimidines and tetrazolo[1,5-*a*]pyrazines

Starting material				Products, %		
						
R_1	R_2	R_3	Conditions			Dimer [3]
Me	Me	H	340 °C/0.03 mm	95	0	0
Me	Me	Me	320 °C/0.01—0.02	100	0	0
MeO	MeO	H	340 °C/0.10 mm	12 [1]	0	0
MeS	Me	H	380 °C/0.01—0.02	88	0	0
			GC. at 300 °C	100	0	0
			125 °C/$CDCl_3$/70 h	89 [2]	0	0
			125 °C/C_6H_{12}/72 h	trace	10	0
ø	—C_4H_4—		380 °C/0.001 mm	99	0	0
			180 °C/C_6H_6/72 h [4]	59	0	10
			180 °C/Toluene/72 h	52	0	45 [5]
			180 °C/C_6H_{12}/72 h	10	0	57
			180 °C/DEA/72 h [6]	0	0	0
						
R_1	R_2	R_3	Conditions			Dimer [3]
H	H	H	380 °C/0.1 mm	65	0	0
			GC. at 300 °C	100 [7]	0	0
			180 °C/C_6H_6/6 h	40	0	0
			125 °C/C_6H_{12}/96 h [8]	trace	10	0
ø	—C_4H_4—		380 °C/0.001 mm	92 [9]	0	0
			180 °C/C_6H_6/72 h	88	0	12
			165 °C/mesitylene/240 h	60	0	25

[1] The starting material exists exclusively in the azido-form. Pyrolysis resulted in extensive tarring.
[2] On the basis of 55% recovery of starting material.
[3] See text.
[4] Same products form slowly (30 days) in refluxing benzene (90°).
[5] Bibenzyl isolated.
[6] DEA = diethylamine; products of reaction with DEA formed.
[7] Based on 50% recovery of starting material.
[8] 25% recovery of starting material.
[9] 8% indoloquinoxaline (*143*) formed.

Table 16. ^{15}N-contents in pyrolysis and degradation products of 4-pyrimidyl- and pyrazinylnitrenes [1]

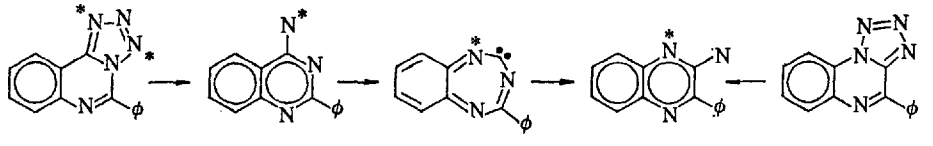
Starting material (labeling, %)	Conditions	Pyrolysis products		Hydrolysis products	
	375°/0.001mm		 [2]		 [2]
(49.8)		(24.8)	(24.1)	(24)	(0)
	400°/0.01mm				
(92)		(46)		(≥37)	
	450°/0.001mm				
(92)		(45)		(45)	
idem (92)	ϕH/180°/72h	(45)		(35)	
	375°/0.001mm				
(50)		(25)		(0)	

[1] ^{15}N-contents (by mass spectrometry) indicated in parentheses. The starting materials were labeled on only *one* N.

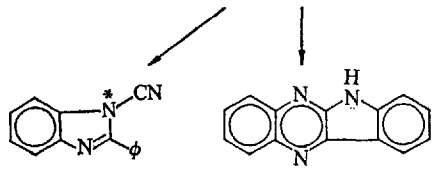
[2] See text.

2-Phenyl-4-quinazolylnitrene (*138*) rearranges to 3-phenyl-2-quinoxalylnitrene (*140*) both in the gas-phase and in solution. The labeling was performed in both media. The rearrangement is complete in the gas-phase, and at least 78% in solution (Table 16). In the gas-phase, only the quinoxaline *141* gave indolo[2,3-*b*]-quinoxaline (*143*) (8%).

Neither *137* nor *141* formed appreciable amounts of *143* in solution. The ring contraction *140* → *142* must therefore be very fast. For the analogous formation of carbazole from 2-biphenylylnitrene [Eq. (47)]

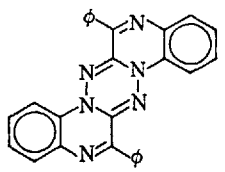


137 138 139 140 141

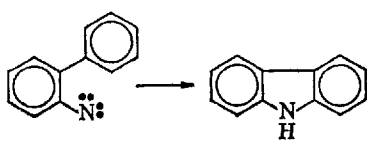


142 143

(46)



144

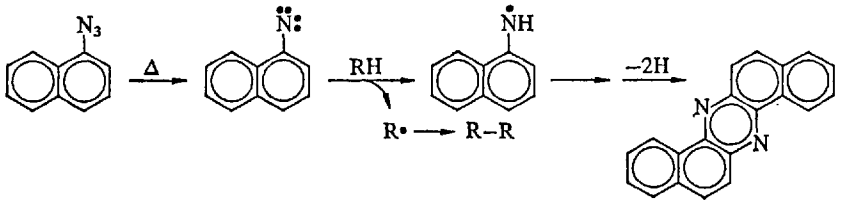


(47)

a rate constant in cyclohexane solution of $2.18 \cdot 10^3$ s^{-1} was measured at 300 K. The activation enthalpy was measured by flash photolysis as 11.46 ± 0.76 kcal/mol [109].

The nitrene-nitrogen in *140* is in movement *away* from the phenyl group at the moment of its birth, due to the requirement of an out-of-plane movement of nitrenes during ring expansion and its reverse [57] (Section III.4). This may suffice to deter nitrene *140* from giving any indoloquinoxaline (*143*), when the nitrene is generated from *137*. An analogous effect is observed in the tolycarbenes [57]. It should be noted, however, that the results do not exclude a direct ring contraction, *139* → *142*.

From the effect of solvent (Table 15) it is evident that the reactions discussed are nitrene reactions: hydrogen-rich solvents suppress ring contraction and give rise to solvent dimer (bibenzyl) and/or a yellow nitrene dimer. The structure of the dimer is not known, but one possibility is shown in *144*. A similar (colorless) dimer was obtained from 9-phenanthridylnitrene at 500 ° [97]. The two dimers formed from *137* and *141* in cyclohexane have nearly identical IR spectra. How could a hydrogen-rich solvent promote dimeriztion? There is evidence from aryl azide decomposition in solution that amino radicals are formed first, and these dimerize and dehydrogenate as shown for 1-naphthylnitrene in [Eq. (48)] [82].

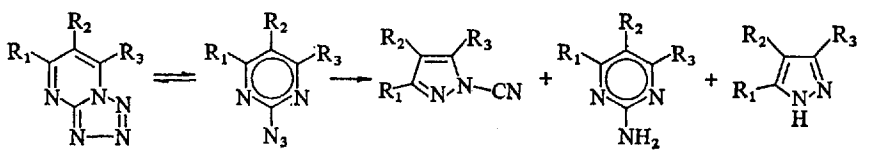


(48)

As mentioned in Section III.5. the facile reaction *138* → *140* → *142* definitely rules out a bicyclic intermediate in this process [see Eqs. (17)—(20)].

6. 2-Pyrimidyl- and 3- Pyridazinylnitrenes

In contrast to 4-pyrimidyl- and pyrazinylnitrenes (Section IV.5) 2-pyrimidylnitrenes give rather low yields of ring contraction — 1-cyanopyrazoles — and quite high yields of 2-aminopyrimidines [Eq. (49) and Table 17)] [106,107].

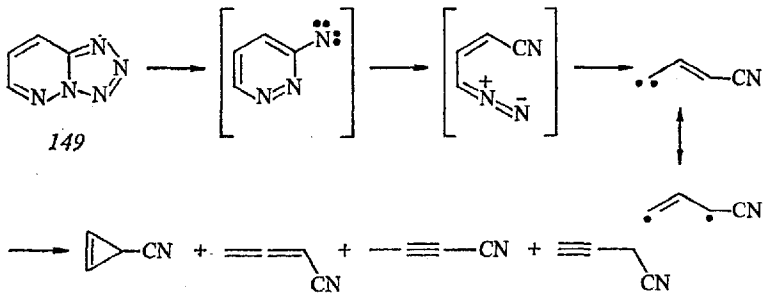


145 *146* *147* *148* (49)

Table 17. Pyrolysis of tetrazolo[1,5-*a*]pyrimidines (*145*) [106,107]

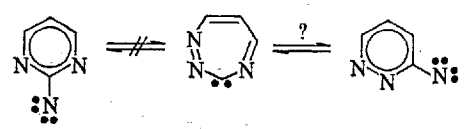
Starting material *145*	R_1	R_2	R_3	Conditions	Products, % *146*	*147*	*148*
a	H	H	H	400 °C/0.1 mm	14.3	17.5	1
				600 °C/0.1 mm	33	7	8
b	Me	H	Me	320 °C/0.05—0.1 mm	15	58	—
				400 °C/0.05 mm	21	34	—
				190 °C/$CDCl_3$	0	64	—
c	MeO	H	Me	380 °C/0.02 mm	trace	40	—
				600 °C/0.1 mm	6	43	—
d	MeS	H	Me	380 °C/0.1 mm	0	17	—
				GC. at 270°	0	100	—
e	Cl	H	Me	380 °C/0.01 mm	2	15	—
				190 °C/$CDCl_3$	0	13	—
f	$-C_4H_4-$		∅	380 °C/0.01 mm	62.5	—	—

Tetrazolo[1,5-*b*]pyridazine (*149*) gives no cyanopyrazole, no aminopyridazine and no aminopyrimidine, but gives instead a mixture of fragmentation products [106] [Eq. (50)].



149 (50)

These products were formed even at temperatures as low as 305°, with 33% conversion of the starting material. It seems very certain, therefore, even though labeling has not been performed, that 3-pyridazinylnitrene and 2-pyrimidinylnitrene do not interconvert [Eq. (51)].



(51)

7. The Ring Expansion - Ring Contraction Dichotomy

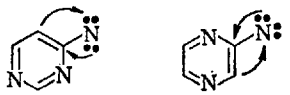
Calculations of different nitrene stabilities are indicated in Table 18. Unfortunately, the CNDO/2 method for pyrazinylnitrene did not converge, so the Extended Hückel result, that pyrazinylnitrene is much more stable than 4-pyrimidylnitrene, stands unconfirmed. However, the chemistry (Section IV.5) certainly agrees with the calculation.

Table 18. Total and binding energies in hetarylnitrenes and isomeric species [1]

	$-E_{tot}$(CNDO/2)	$-E_{tot}$(EH)	$-E_{binding}$(CNDO/2)
2-Pyridylnitrene	1674.036	615.877	162.965
2,7-Diazepinylidene	1670.660	613.355	159.590
Pyrazinylnitrene	—[2]	628.843	—
4-Pyrimidylnitrene	1776.318	623.580	148.975
2,4,7-Triazepinylidene	1772.331	621.495	144.998

[1] In eV. Geometries were not optimized (Ref.[101]).
[2] Did not converge.

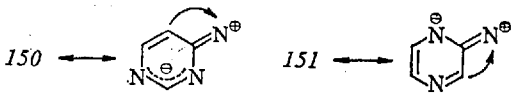
The fact that 4-pyrimidylnitrenes expand, while pyrazinylnitrenes do not, can also be understood in terms of the donor-acceptor requirement in the ring expansion (see Section III.7).



150 *151*

The π-LUMO and p-HOMO interactions are symbolised in *150* and *151*. *150* is a nitrene situated in the very electrophilic 4-pyrimidyl position. The 2-pyrazinyl position appears less electron-deficient as judged from the rates of nucleophilic substitution of the corresponding chlorides [110]. Furthermore, nitrene *150* has to undergo electrophilic substitution onto the relatively electron-rich 5-position in pyrimidine. Pyrazinylnitrene *151* has only an electron-poor α-position to attack. On this basis, expansion of *150* should be faster than that of *151*. The selectivities observed here are the same as in the pyridylcarbenes (Section III.7).

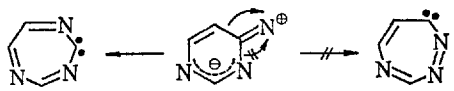
An equivalent argument can be given in terms of the Wolff-type rearrangement. The *ortho, para* relationship of the nitrogen atoms in *150* will make the nitrene-N more positive than in *151* (cf. mesomers *152—153*).



150 *151*

152 *153*

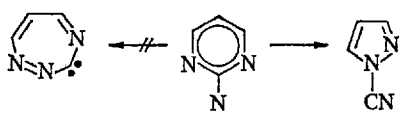
A Wolff-type ring expansion will then be faster in *152* than in *153*. The Wolff-rearrangement produces triazepinylidene *154* rather than *155*, where a weaker N=N bond would be formed [Eq. (52)].



(52)

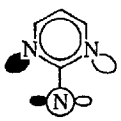
154 *152* *155*

For the same reason, 2-pyrimidylnitrene does not expand; and it contracts only with difficulty. Both processes form a high-energy N=N bond (pyridazine is 19.5 kcal/mol more endothermic than pyrimidine; pyrazole 12.7 kcal/mol more than imidazole [14]).



156

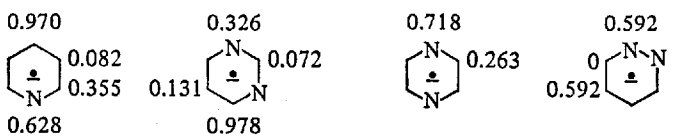
In addition to this, nitrene *156* may enjoy special stabilization by overlap between the empty nitrene p-orbital and the pyrimidine HOMO, which is the assymmetric combination of the two ring-nitrogen lone-pairs [57]. At the same time, the filled nitrene π-orbital will overlap with the LUMO of the ring (*157*).



157

This synergic interaction will stabilize the nitrene in the plane of the ring, thereby preventing rearrangement. Since the singlet nitrene is thus unreactive, reaction occurs mainly after intersystem crossing to the triplet nitrene, and this gives rise to the amines formed.

The ease of ring expansion in the nitrenoazines correlates very nicely with the electron densities in the parent azine radical anions. Since the extra electron in these radicals goes into what was formerly the LUMO of the heterocycle, the electron densities, or splitting parameters, may in the first approximation be used as a guide to the LUMO-coefficients in the azines. The splitting parameters [89b] a_H resp. a_N (in mT) are shown below.

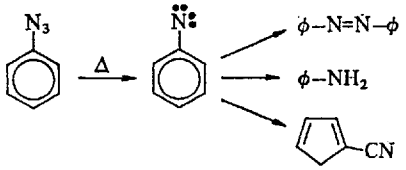


The larger the splitting (the larger the LUMO coefficient), the stronger the π-LUMO interaction in the corresponding nitrenoazine, and the faster is nitrene ring expansion: 4-pyrimidyl > 2-pyridyl > 2-pyrazinyl > 2-pyrimidyl > 3-pyridazinyl.

V. Carbene-Nitrene Rearrangements

1. Phenylnitrene

Phenylnitrene and its substituted derivatives undergo three principal reactions in the gas-phase [Eq. (53)]: (1) dimerization to azobenzene (which can also derive from reaction between phenylnitrene and phenyl azide [109,111]), (2) H-abstraction giving aniline; and (3) ring contraction to 1-cyano-cyclopentadiene [112]. Yields of these and other products are given in Table 19.

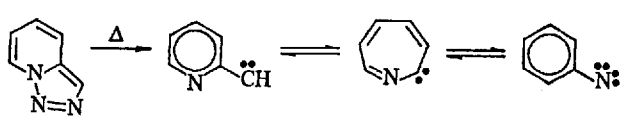


(53)

The data in Table 19 require that the activation energy for ring contraction be very high; even at 800 °C and low pressure the yield is very low. Carrier gases only decrease the yield further, perhaps by collisional deactivation of any "hot" nitrenes that might be present. The best results are obtained by rapid sample introduction (distill in temperature ca. 45 °C at an initial pressure of 10^{-3}—10^{-2} mm), producing an apparent explosion. The apparatus fills with a bluish smoke, the pressure rises to ca. 1 mm, and the temperature of the sample flask rises above 100 °C. Phenyl azide would explode at this temperature at atmospheric presure, as was confirmed by experiment. It may then reasonably be assumed that a high-pressure, high-temperature shock-wave forms in the furnace, thereby providing the necessary energy of activation. Hedaya and co-workers later reported yields of up to 50% of cyanocyclopentadiene [113]. The difference is ascribed to different apparatus design. Substituted phenyl azides behave analogously [114].

2. Interconversion of 2-Pyridylcarbene and Phenylnitrene

At first it was a great surprise that gas-phase generation of 2-pyridylcarbene (*47*) resulted in the same products as obtined from phenylnitrene: 77% azobenzene and 4% aniline at 500°/0.04 mm [Eq. (54)] [49].



158 *47* *45* *43*

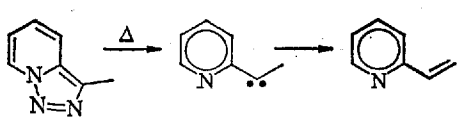
(54)

A 1—3% yield of 1,2-di(2-pyridyl)ethylene was also obtained, indicating that the desired carbene *47* had been formed. Further evidence was obtained by pyrolysis of 3-methyl-*vic*-triazolo[1,5-*a*]pyridine, where the sole reaction product was 2-vinylpyridine (100% at 500°/0.15 mm or 800°/0.20 mm) [Eq. (55)].

Table 19. Pyrolysis of phenyl azide [1]

T °C	P mm	1-Cyanocyclo-pentadiene	Benzo-nitrile	Aniline	Azo benzene	Conditions of intro-duction
300	0.05			0.5	82	20° [2]
400	0.05			5	52.5	20°
450	1.3, air				75	20°
450	1.3, Ar				66	45°
450	1, self-pressure	10	5	5		40° [3,4]
600	1, self-pressure	18	2	2		40° [3]
450	1.3, air	1	5	13	25	45°
700	1.3, air	0.5	2.5	22		20° [5]
750	0.1	0.5	1.6	2		0—20° [6]
800	0.04	1.5	2.5	3		0° [7]
450	1.3, air				46	lg $\varnothing N_3$ in 10 ml $\varnothing H$ [8].
500	0.1				40	lg $\varnothing N_3$ in 7 g $\varnothing NH_2$ [9]

[1] Product yields in %.
[2] 20% azide recovered; yields are corrected for this.
[3] "Violent pyrolysis". See text.
[4] 3% benzene, traces of biphenyl, azobenzene, and diphenylamine isolated; HCN detected by IR.
[5] 23% hydrazobenzene and 0.7% biphenyl isolated.
[6] 0.5% pyridine isolated.
[7] 3% biphenyl, 2.5% diphenylamine, traces of pyridine and azobenzene isolated.
[8] Low yields of aniline, biphenyl, and diphenylamine isolated.
[9] 11% diphenylamine isolated.



(55)

Pyrolysis of *158* at 800°/0.1 mm gave benzene (2.8%), α-picoline (1.1%), benzonitrile (3,7%), and a low yield of 1-cyanocyclopentadiene, identified by its gas-chromatographic retention time, uv and mass spectra.

Pyrolysis of 6-methyl-*vic*-triazolo[1,5-*a*]pyridine (*159*) at 300 °C gave m,m'-azotoluene (80%) and m-toluidine (4%). Pyrolysis at 800 °C/0.10 mm gave the same products as those obtained from m-tolyl azide (Table 20). Innumerable products are formed under these reaction conditions, and only some of them have been identified. However, the gas chromatograms of the product mixtures from

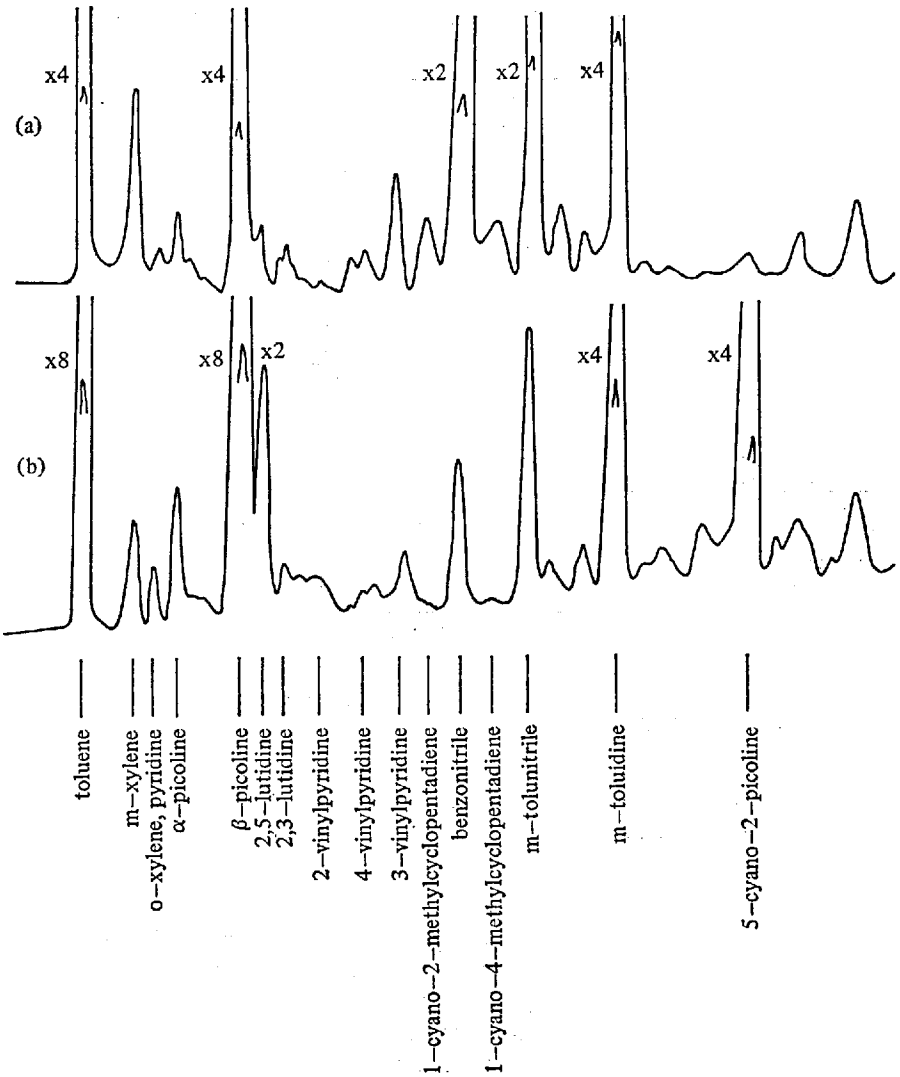
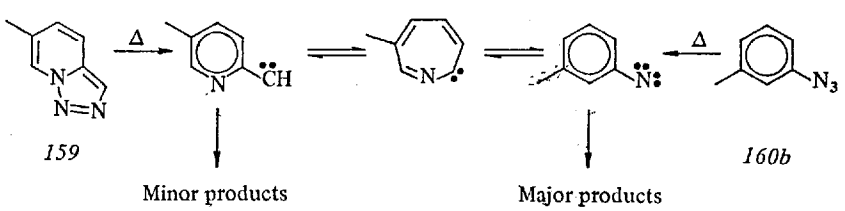


Fig. 2. Gas chromatograms of the pyrolysates from (a) *m*-tolyl azide, (b) 6-methyl-*vic*-triazolo-[1,5-*a*]pyridine

159 and *160b* were almost identical (Fig. 2), and there can be little doubt that the two compounds give rise to a common intermediate.



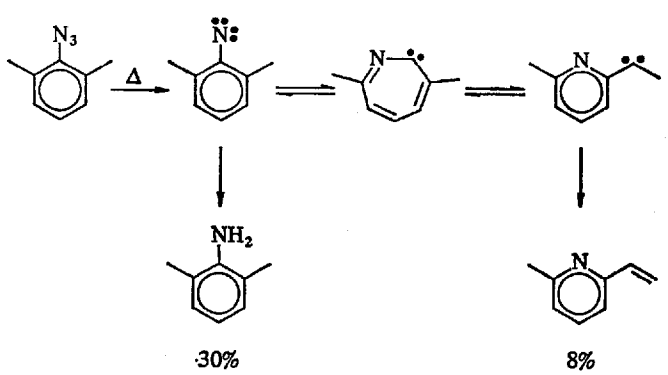
(56)

Table 20. Pyrolysis products of 6-methyl-*vic*-triazolo[1,5-*a*]pyridine (*159*) and *m*-tolyl azide (*160b*) [1]

Starting material Product	*159* 800 °C/0.1 mm	*160b* 450 °C/1.0 mm	Excess ^{15}N-content [2]
Toluene	10.2	3.7	—
m-Xylene	0.34	0.18	—
Pyridine	0.11	—	0
α-Picoline	0.38	0.26	0
β-Picoline	15.3	2.1	0
γ-Picoline	—	—	—
2,5-Lutidine	4.1	0.05	—
2,3-Lutidine	—	0.05	—
4-Vinylpyridine	Trace [3]	Trace [3]	—
3-Vinylpyridine	Trace [3]	0.1	0
2-Vinylpyridine	—	Trace	0
1-Cyano-2-methylcyclopentadiene	Trace [3]	0.2	0
1-Cyano-4-methylcyclopentadiene	Trace [3]	0.4	0
Benzonitrile	0.6	1.0	0
m-Tolunitrile	1.1	0.6	0
m-Toluidine	4.3	2.3	0
2-Cyano-5-methylpyridine	2.0	Trace [4]	—
	500 °C/0.04 mm	400 °C/0.1 mm	
m,m'-Azotoluene	80	Isolated	0
m-Toluidine	~4	Isolated	—
1,2-Di(5-methyl-2-pyridyl)ethylene	~1	0	—

[1] Yields by GC. in %; products identified by R_t, UV, IR, MS, except when stated otherwise.
[2] By pyrolysis of *m*-tolyl azide-3-^{15}N (8.40% ^{15}N).
[3] Identified by R_t, UV, and mass spectra only.
[4] Identified by R_t only.

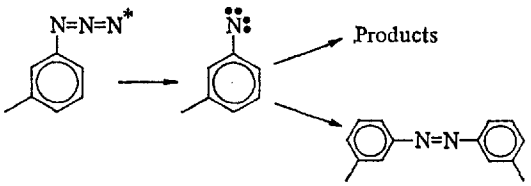
The reason why nitrene products (*e.g.* azobenzenes) predominate in these reactions could be thermodynamic (nitrenes being more stable than carbenes) or kinetic (product formation being faster from nitrenes). In order to check this we generated a sterically hindered nitrene, where intermolecular product formation should be slowed down, and where the corresponding pyridylcarbene would have an activation free [8] escape route. The reaction is shown in [Eq. (57)].



(57)

The maximum yield of 2-vinyl-6-methylpyridine was 8%, and the nitrene product, 2,6-xylidine still predominated (30%) [115]. From this it appears that *the carbene-nitrene equilibrium lies to the side of the nitrene.*

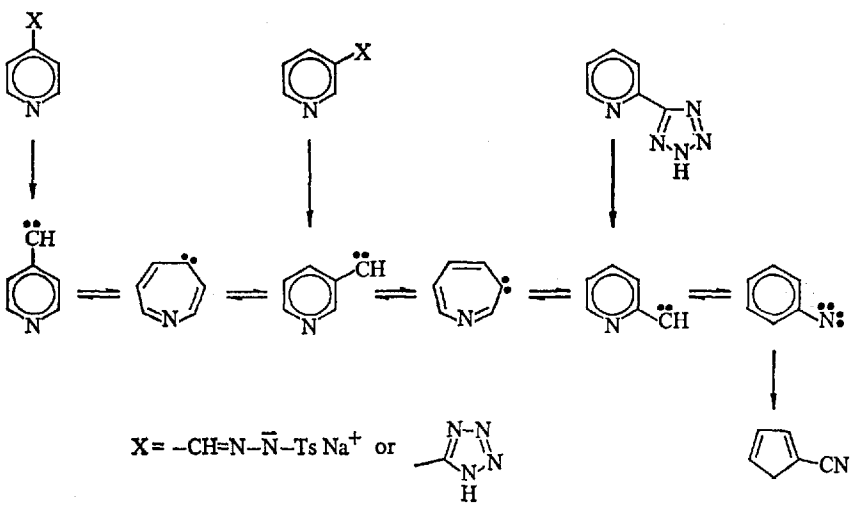
In order to be sure that we are dealing with nitrene reactions, m-tolyl azide-3-^{15}N was pyrolysed under the conditions shown in Table 20. All the nitrogen containing products isolated had lost all of the ^{15}N (the lutidines and 4-vinylpyridine were not isolated). The same was true for m,m'-azotoluene, formed by pyrolysis at 400°/0.1 mm [Eq. (58)].



(58)

3. Chemical Activation in Phenylnitrene Ring Contraction

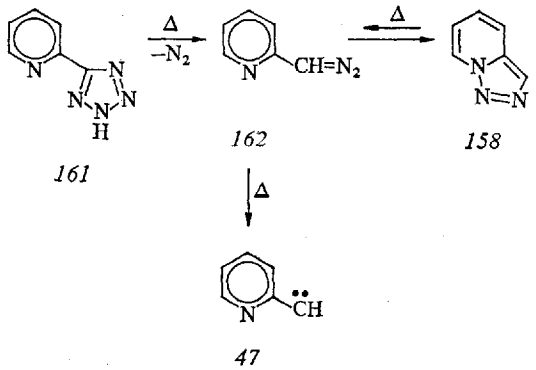
Another surprising result was the observation [55,56] that good yields (20—70%) of cyanocyclopentadiene could be obtained by pyrolysis of 2-, 3-, and 4-(5-tetrazolyl) pyridines as well as of 3- and 4-pyridyldiazomethanes, the latter generated from the tosylhydrazone salts [55].



(59)

5-Aryltetrazoles pyrolyse by way of aryldiazomethanes [Eq. (5), Section III.2] and in the present case *vic*-triazolo[1,5-*a*]pyridine (*158*) was isolable from pyrolysis

of 2-(5-tetrazolyl)pyridine (*161*) [56]. Solution thermolysis of *158* permitted the trapping of 2-pyridyldiazomethane,



(60)

162 [24]. We should then expect that the diazomethane *162* is the immediate carbene precursor, irrespective of the starting material [Eq. (60)]. A difference in product yields cannot, therefore, be due to different reaction mechanisms, but must be ascribed to energetic reasons.

An energy surface based on thermochemical estimates and kinetic experiments [24] is shown in Fig. 3. As before, absolute energies may be inaccurate, but there can be no doubt that 2-pyridylcarbene generated from *161* will initially be more highly activated chemically than the same carbene from *158* (that is, by the difference between the ΔH_f^0 of the carbene and the crest of the energy barrier for

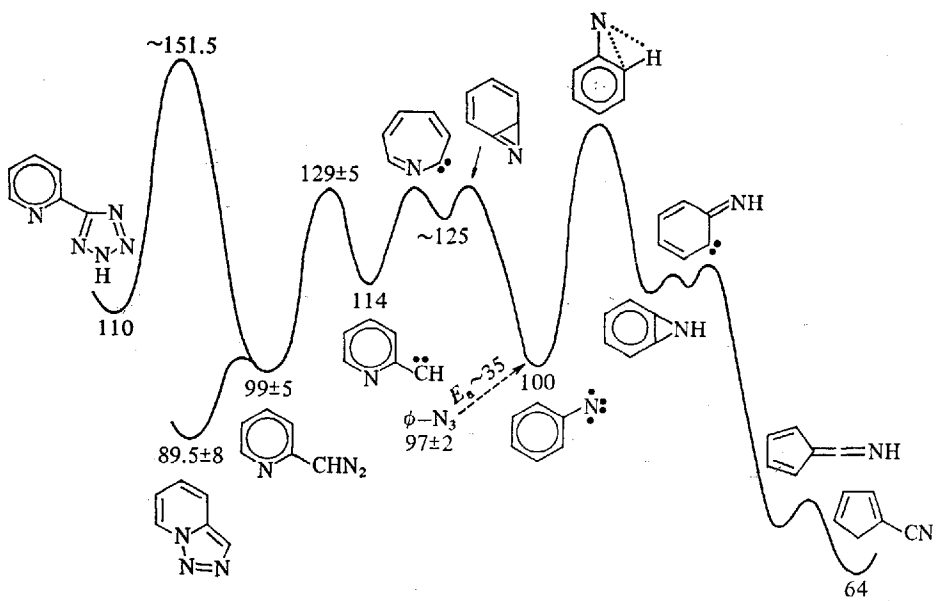
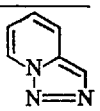
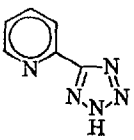
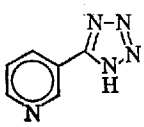
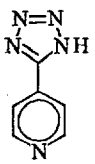
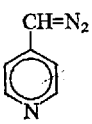


Fig. 3. The C_6H_5N energy profile (values in kcal/mol) [24]

Table 21. Pyrolysis of pyridylcarbene precursors

Starting material	Oven [1]	T °C	P mm [2]	Products, yield %		
					ø—N—N—ø	
	A	500	0.05	33	0	
	A	550	0.001	42.5	0	
	A	550	0.05	33	0	
	A	570—80	0.001	39	0	
	A	570—80	0.05	31	0	
	A	600	0.001	42	0	
	A	650	0.00001	70	0	
	A	650	0.001	48	0	
	A	700	0.001	45	0	
	A	770	0.001	41	0	
	A	800	0.001	32	0	
	A	880	0.001	12	0	
	B	400	0.001	~1	17	15
	B	400	0.1	—	18	
	B	400	1	0—3	77	9
	B	400	10	—	41	3
	B	610	0.001	27	4	
	B	610	0.1	36	7	
	B	610	1	27—30	20—30	
	C	400	0.01	0	24	
	B	400	1	2	12	
	B	515	0.001	13	0	
	B	515	0.1	18	0	
	B	515	1	17	3	
	B	515	10	12	4	
	A	610	0.001	30	0	
	B	400	1	6	12	
	A	560	0.001	51	0	
	B	560	0.001	18	2	
	B	560	0.1	14	3	
	B	560	1	40	7	
	B	560	10	18	4	
	B	350	0.001	6	0.5	
	B	400	0.001	11	6	
	B	400	0.1	10	10	
	B	400	1	3	10	
	B	560	0.001	14	3	
	B	560	0.1	6	5	
	B	560	1	3	8	

[1]) Oven A: 53 × 3 cm quartz tube; flow system.
Oven B: 30 × 2 cm quartz tube; flow system.
Oven C: 53 × 3.5 cm quartz tube; static; 100 mg pyrolyzed for 6 min.
[2]) N_2 carrier gas is used at pressures $\geq$ 1 mm.

decomposition of the starting materials). If the pressure is low enough, and the rearrangements faster than the collision rate, the resulting phenylnitrene will also be chemically activated. If the pressure is raised, the pyridyldiazomethane and subsequent intermediates will be collisionally deactivated, the activation energy for ring contraction will no longer be available; cyanocyclopentadiene will tend to disappear, and azobenzene will form instead. The data in Table 21 support this contention; low temperatures, short pyrolysis tubes, and relatively high pressures favor the production of azobenzene [99]. The effect is not very large because of the short lifetimes of the reactive intermediates, with the consequential low collision numbers, and the use of a low molecular weight bath gas, nitrogen [79].

Further evidence for chemical activation was found in a comparison of the tolyl azides with 6-(5-tetrazolyl)-2-picoline (*163*).

Whereas m- and p-tolyl azides (*160b* and *c*) give rise to the expected cyanocyclopentadienes *164* and *165* (which interconvert thermally [114]) o-tolyl azide (*160a*) could not be forced to undergo the violent decomposition, and only minute C≡N absorptions were visible in the IR spectra of the crude pyrolysates, obtained even from pyrolyses at 900 °C. The main product was *o,o'*-azotoluene (37% at 450 °C/0.1—0.2 mm). The failure of the nitrene from *160a* to contract may be ascribed to collisions with the methyl group, deactivating the nitrene (cf. Ref.[57]).

Pyrolysis of *163* also produces o-tolylnitrene, but now the cyanocyclopentadienes *164—165* were also obtained (Table 22) [99]. If the ring contraction is at all a nitrene reaction, the nitrene from *163* must be "hotter" than the one from *160a*. [The methylcyanocyclopentadienes *164—165* rearrange thermally to benzonitrile [114]. The use of a higher pyrolysis presssure results in a lower yield of benzonitrile, and a higher yield of the primary nitrile, *165*; at the same time, more o-toluidine is formed (Table 22)].

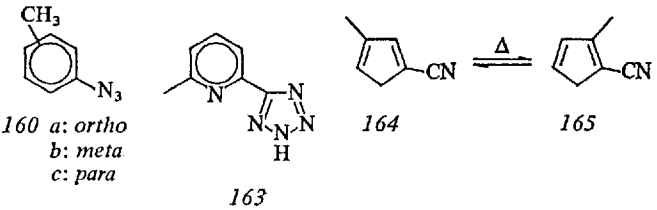
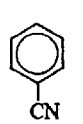
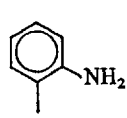
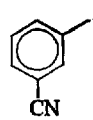


Table 22. Pyrolysis of 6-methyl-2-(5-tetrazolyl)pyridine (*163*) [1]

T °C	*P* mm						
610	0.001	4.9	2.3	2.9	17.8	2.9	2.6
400 [2]	1, N_2	—	4.7	—	Trace	21.9	—

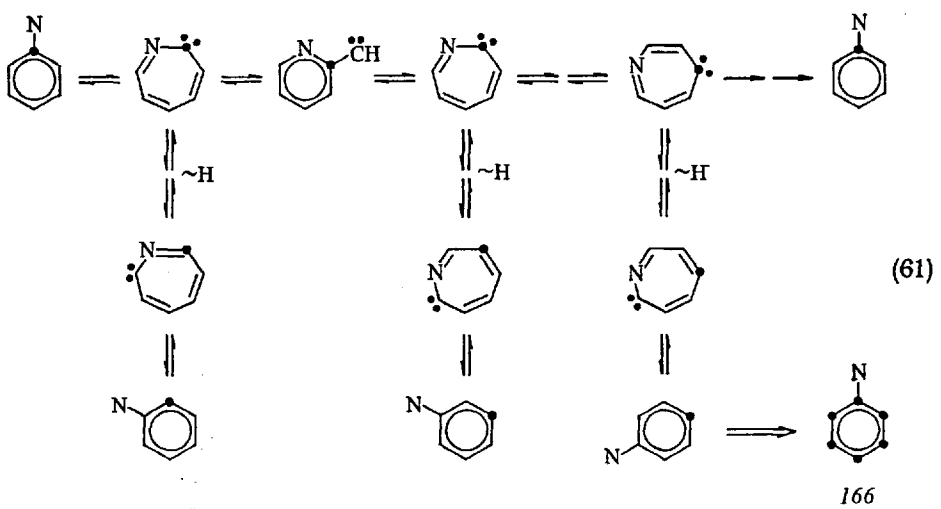
[1] Yields in % based on relative peak areas by GC., *without* correlation factors.
[2] *o,o'*-Dimethylazobenzene formed.

4. Labeling Experiments

On the basis of ^{14}C and ^{13}C labeling experiments it was reported [116,117] that phenylnitrene undergoes essentially complete carbon scrambling prior to ring contraction. Like in the case of phenylcarbene (Section III.8) simple ring expansions/contractions do not suffice to randomize all carbon atoms; hydrogen shifts are needed. Two possible mechanisms, incorporating the original postulates [116, 117] are given in Eqs. (61) and (62). The first involves hydrogen shifts in the azepinylidenes; the second is a ring-walk of the nitrene.

Some evidence for interconversion of all the azepinylidenes [Eq. (61)] is found in the formation of some products otherwise difficult to explain: the formation of 2-, 3-, and 4-vinylpyridine and 2,3-lutidine from *159* (see Table 20). The three vinylpyridines were formed from both m- and p-tolyl azides as wel.

If carbon-scrambled phenylnitrene *166* is formed [Eqs. (61) – (62)] it must be possible to deactive some of these nitrenes and obtain scrambled aniline and azobenzene. Crow reported that aniline was *not* scrambled [117]. To check the point, we



(61)

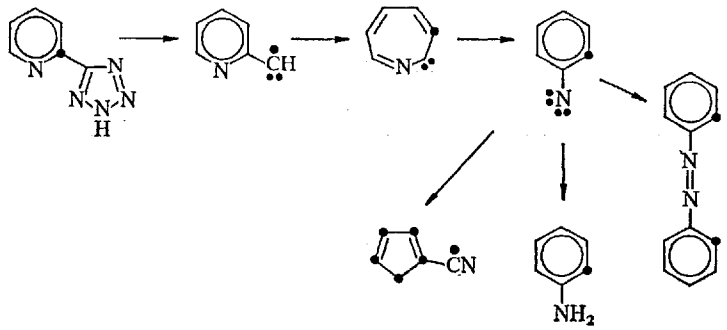
166

(62) (62)

166

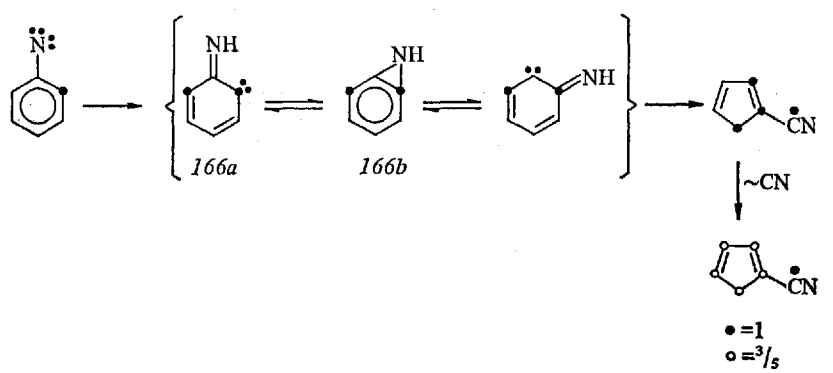
generated 2-pyridylcarbene-^{13}C under conditons which gave both cyanocyclopentadiene, aniline, and azobenzene (610 °C/1 mm N_2), and conditions which gave azobenzene only (400 °C/1 mm N_2). In both cases, *aniline and azobenzene were specifically labeled in the* ortho-*positions only* [Eq. (63)]. [81]

Since no evidence for scrambled nitrenes could be found (namely scrambled aniline and azobenzene), *the scrambling process must take place in an intermediate*



(63)

other than phenylnitrene, and it must occur after the highest activation barrier towards ring contraction has been passed, i.e. in a new intermediate on the down-hill right-hand side of Fig. 3. A closer scrutiny of the cyanocyclopentadiene now revealed that *the scrambling was in fact not complete:* the CN-group carried more label than the ring-carbons, and the ratio CN/C_{ring} was 1.7. This result is in precise agreement with our previous postulate[24] that phenylnitrene isomerizes to iminocyclohexadienylidene, and it is the latter which undergoes a Wolff-type ring contraction (see p. 182). Since the iminocyclohexadienylidenes interconvert *via* 1*H*-benzazirine (cf. Scheme 2), and the cyano-group in the final product undergoes sigmatropic shifts [33], the observed labeling ratio obtains:

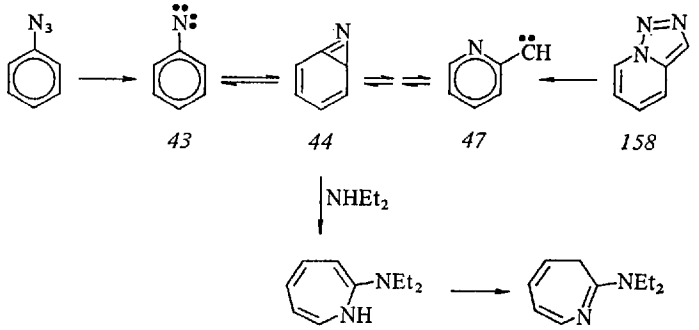


(63a)

The first formed intermediate in Eq. (63a) may be either the iminocarbene *166a* (a H-abstraction reaction) or the benzazirine *166b* (a C—H insertion reaction). The latter is the more attractive pathway in view of the precedence for a direct intramolecular insertion of a singlet arylnitrene into an aliphatic C—H bond [108a]. Furthermore, both theoretical and experimental evidence indicates that the transition state for H-abstraction is linear, whereas for insertion it is triangular [108b]. Phenylnitrene can only adopt the angular transition state. Accordingly, the results are explained without recourse to [Eqs. (61)—(62)]. The final proof that *phenylnitrene does not undergo carbon randomization* was obtained by generation of ^{13}C-labeled 4-pyridylcarbene [cf. Eq. (59)] which resulted in cyanocyclopentadiene, which was *unlabeled* on the CN-group [81]. The now complete C_6H_5N energy surface is shown in Fig. 3. The same type of mechanism was advanced for phenylcarbene [Eq. (28)].

5. Arylnitrenes in Solution

The chemistry of aromatic azides in solution is somewhat outside our domain, and only brief mention can be made here of this rich field. Aryl azides yield azepines by thermolysis or photolysis in nucleophilic solvents [71,82,105,118].
Pyridines are observed in some of these reactions, and the substituent pattern is that expected from nitrene-carbene interconversion [119]. Small yields of azepine have been recorded in the photolysis of *158* [120]. The bicyclic intermediate *44* [Eq. (64)] has been postulated frequently over the last twenty years. A wavelength dependence of the formation of azepines has been observed [122]; the yield of azepine increases with the energy of the light and with the concentration of the trapping agent (diethylamine). At the same time, the yields of competitive processes of the nitrene (carbazole formation from 2-biphenylylnitrene; p-cyanophenylhydrazine from p-cyanophenylnitrene) decrease. The rate of the azepine-forming



(64)

reaction ($3 \cdot 10^4$—$8 \cdot 10^8$ $1 \cdot mol^{-1}s^{-1}$) is believed to be too low for that of a reaction of the singlet nitrene itself [122]. By an analogy with phenylcarbene and bicyclo-[4.1.0]heptatriene (Section III. 4.—5.) one may estimate that the reaction, triplet phenylnitrene →*44* is endothermic by at least 24 kcal/mol. Since the singlet-triplet splitting in nitrenes is unknown, it is impossible to say how high *44* lies above the singlet nitrene. In any case, the 24 kcal/mol are available in both thermal and photochemical decomposition of the azides, and it is quite possible that *44* could form, especially by short wavelength photolysis. It is also possible that *44* could form directly from an excited singlet state of the azide.

On the other hand, the energy of 2-azepinylidene may be lower than that of *44* (cf. Section III.5). Experiment must resolve the question of the nature of the intermediate(s) in the azepine forming reactions.

6. Other Carbene-Nitrene Rearrangements

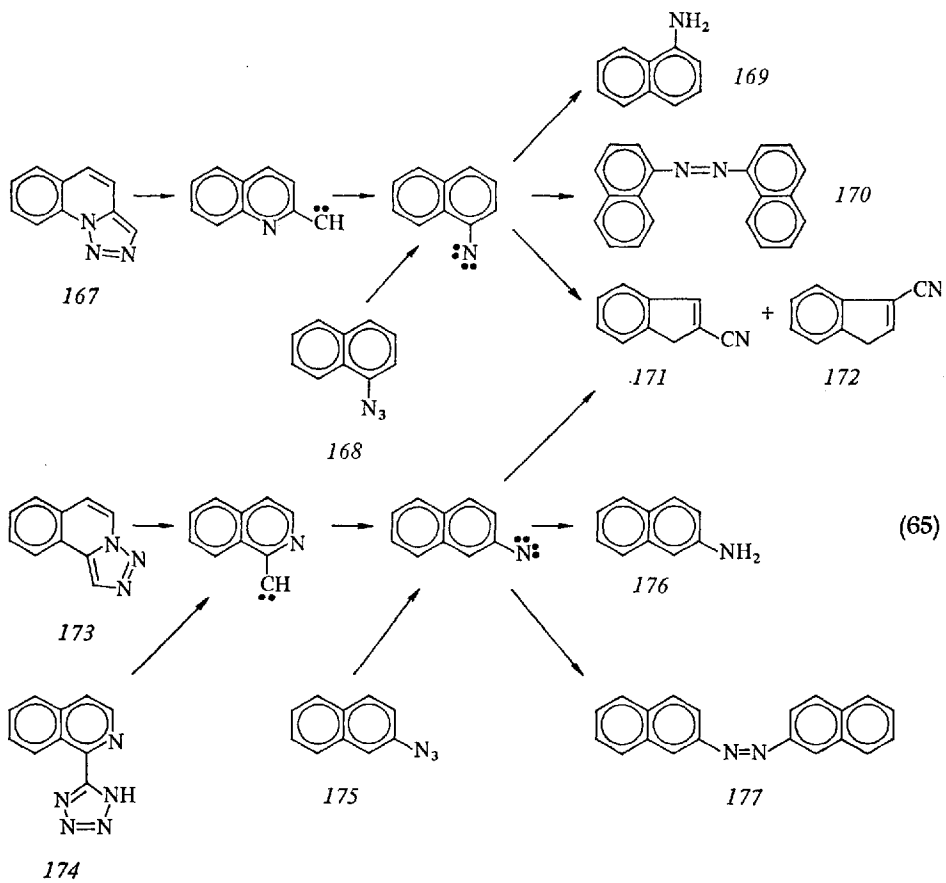
The rearrangement of hetarylcarbenes to arylnitrenes is a general reaction. Further examples are given in [Eqs. (65)—(69)]. Product yields are reported in Tables 23—25.

In the quinolyl- and isoquinolyl series good yields of ring contraction products (*171*, *172*) can be obtained from both triazoles, tetrazoles, and azides (*168*, *175*). In the pyridine series best yields were obtained from tetrazoles (Section V. 2.—3.).

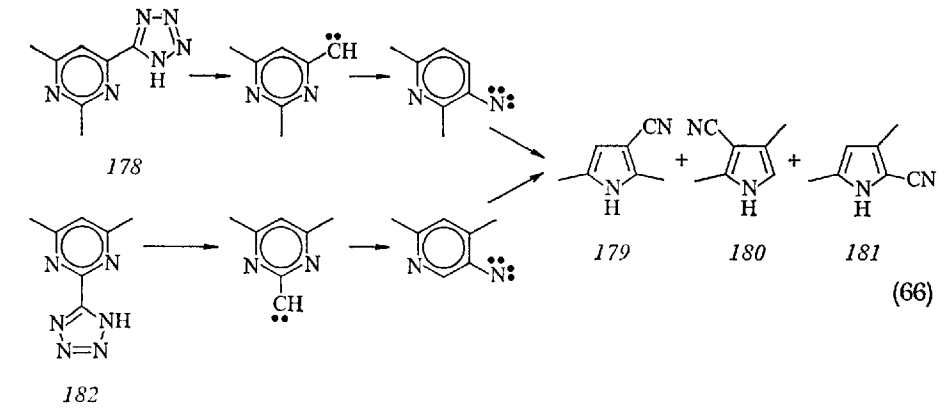
The effect of annelation seems to be a lowering of the activation energy for ring contraction in the nitrenes; azides *168* and *175* contract more easily than phenyl azide (cf. Table 19). The fact that *167* and *173* do give ring contraction products reaffirms the statement that triazoles do not pyrolyze by a mechanism fundamentally different from that of the tetrazoles (p. 232).

The effect of annelation is again seen in a comparison of [Eqs. (67) and (68)]. *183* (R = ø) gives *184* as the main product [123], whereas *187* gives *188* and very little, if any, ring contraction product [56b]. The same increase in the rate of ring contraction as opposed to intramolecular cyclization to carbazole derivatives was also observed in 3-phenyl-2-quinoxalylnitrene [(*140*, Eq. (46)].

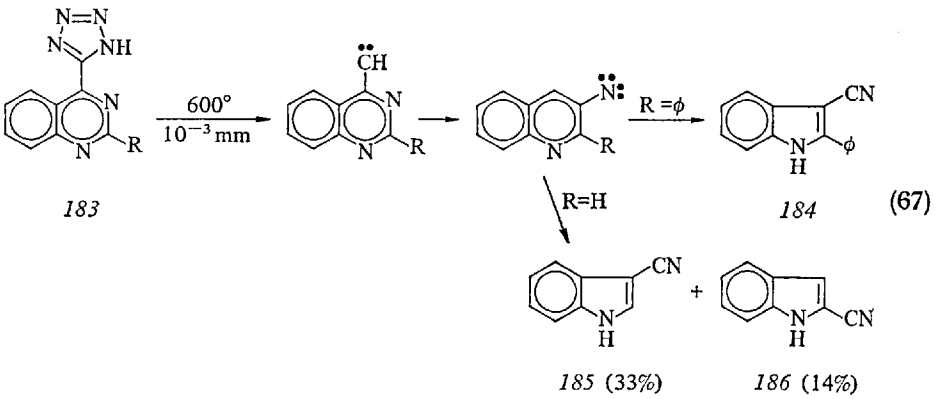
The fact that more than one ring contraction product is formed in each case (*171—172, 179—181, 185—186, 194—195*) implicates chemical activation: the ring contraction is exothermic, and the five-ring nitriles interconvert themselves at



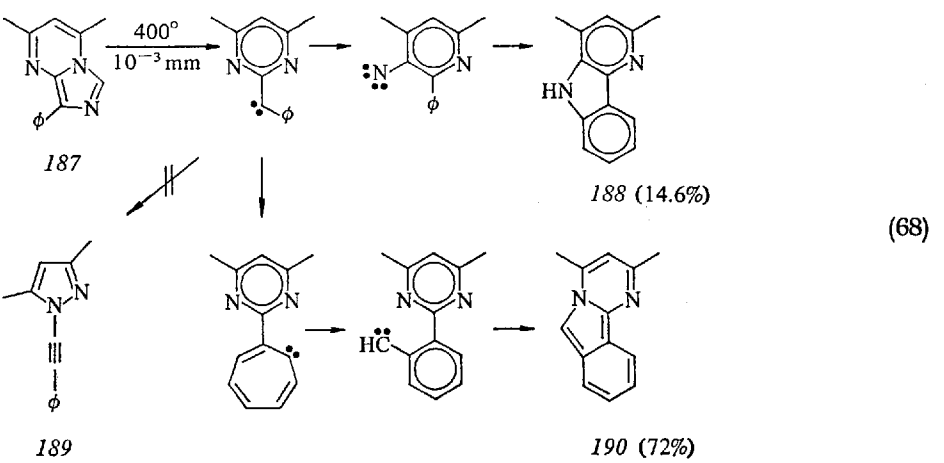
b) The crude pyrolysate of *187* showed a medium C≡N band at 2200 cm^{-1}. No nitrile has been isolated, and it can at most account for 10% of the products. The possible presence of an acetylene (*189*) has been excluded by the failure to obtain its product of reaction with water [77].


178
179
180
181
182

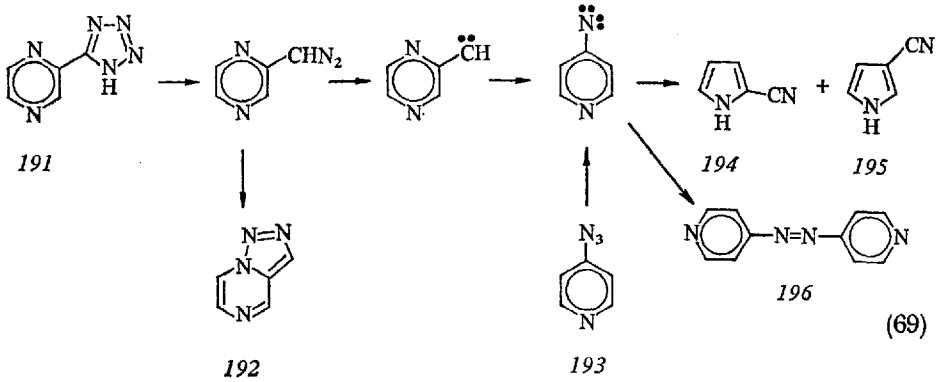
(66)


600°
10^{-3} mm
R =ϕ
R=H
183
184
185 (33%)
186 (14%)

(67)


400°
10^{-3} mm
187
188 (14.6%)
189
190 (72%)

(68)



191 192 193 194 195 196 (69)

Table 23. Products of quinolyl- and isoquinolylcarbenes, and naphthylnitrenes [56,92,123]

Starting material	T °C/P mm	Oven [1]	Products, yield % (cf. Eq. 65)					
			171	*172*	*169*	*176*	*170*	*177*
167	340/10^{-3}	A	~3:1 [5]					
	450/10^{-3}	B	4	3.2	37.6		6	
	510/10^{-3}	A	28	12	6		5	
	400/1, N_2 [6]	B	0.8	3.2	17		33	
173	340/10^{-3}	A	~20:1 [5]					
	500/10^{-3}	A	14	24		7.7		8
	400/1, N_2	B	0.8	3.2		41		33
174	480/10^{-3}	A	16	32		28		
	400/1, N_2	B	3.4	20.6		7.5		6.4
168	500/0.03	B	0	$\leqslant$ 0.01	24		48	
	480/10^{-3}	A	4.6	5.4	12.6		2.4	
	800/0.1 [2]	B	0.7	0.1	1.9			
	1000/0.05 [3]	B	0.25	Trace	0			
175	500/10^{-3}	A	10.6	11		7.8		14
171	1000/0.25 [4]	B	21	16				
172	800/0.02	B	39	61				
	1000/0.25 [4]	B	21	16				

[1] For ovens A and B, see Table 21, footnote [1].
[2] Also formed: 0.15% indene, 29% naphthalene, 0.3% 4(7)-cyanoindene, and 1.3% 1-cyanonaphthalene.
[3] Also formed: 3% indene, 25% naphthalene (80% of all product), 0.25% 4(7)-cyanoindene, 0.25% 5(6)-cyanoindene, and 0.5% 1-cyanonaphthalene.
[4] Also formed: 4-, 5-, 6-, and 7-cyanoindenes; see Ref. [33].
[5] Ratio of 2- to 3-cyanoindene by GC; product yield was very low.
[6] Under the same conditions, 2-(5-tetrazolyl)quinoline gave 2-cyanoindene (2.7%), 3-cyanoindene (10.3%), 1-naphthylamine (20%), and 1,1'-azonaphthalene (13%).

elevated temperatures [33] (Tables 23–25). Increased pressure removes chemical activation, so that *179* becomes the main product from *178*; and *181* becomes the main product from *182* (Table 24). Further, unidentified dimethylcyanopyrroles,

Table 24. Products of pyrimidylcarbenes [124]

Starting material	T °C/P mm	Products, relative peak areas by GC.			
		179	*180*	*181*	Other dimethylcyanopyrroles
178	400/10^{-3}	63	29	7	— [1]
	400/10^{-2}	68	26	6	— [1]
	400/1, N_2	98	1.5	<0.5	—
	600/10^{-3}	70	23	7	—
	600/10^{-1}	79	19	2	—
182	400/10^{-3}	34	22.5	42.5	—
	400/10^{-1}	27	15	58	—
	400/1, N_2	21	10	69	—
	600/10^{-3}	28	22	36	14
	600/10^{-1}	25	22.5	44	8
179	800/10^{-3}	49	32	14	5
181	800/10^{-3}	21.5	22	50	6

[1]) Ca. 15% unidentified product formed as well.

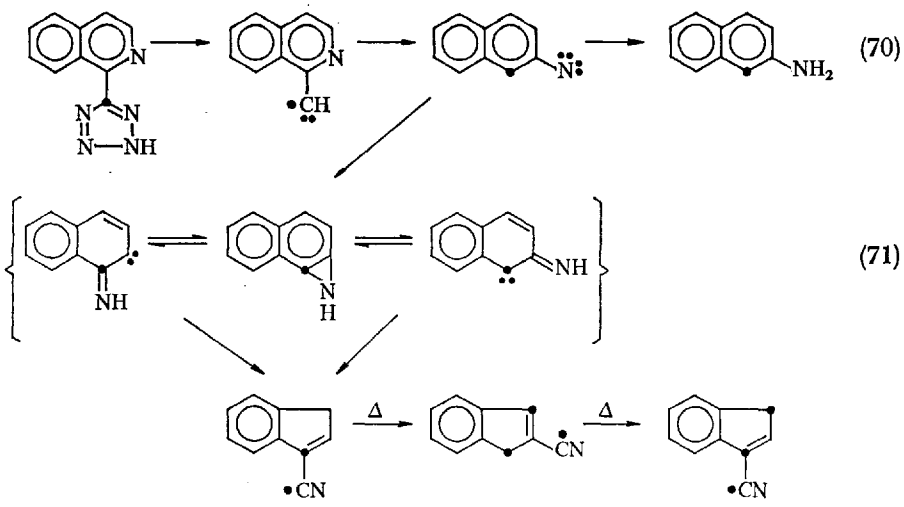
Table 25. Products of pyrazinylcarbene and 4-pyridylnitrene

Starting material	T °C/P mm	Relative yields by NMR/GC				Total yield, %
		194	*195*	*192*	196	
191	450/10^{-3} [1])	~1	~1	~1	~1	≤30
193	400/1 [2])	2	1			≤10
	400/0.05				54	54
194	800/0.01	2	1			98
195	800/0.01	1	2			98

[1]) Unstable products are formed; no acetylenes could be detected by IR or NMR.
[2]) "Violent pyrolysis". Other products formed: 2% pyridine and 17% 4-cyanopyridine.

which must arise through both CN- and CH_3-migrations disappear when the pressure is increased. The primary products, *179* and *181*, respectively, indicate that ring contraction in the nitrenes occurs predominantly to the side which is unsubstituted [124].

The rearrangement of 1-isoquinolylcarbene was corroborated by ^{13}C-labeling [81] [Eq. (70)]. 2-Naphthylamine was labeled only in the 1-position. 3-Cyanoindene was the main product when the reaction was carried out at 400°/1 mm N_2 (cf. Table 23), and it was labeled predominately in the 3-position and on CN, with a very small amount of label in the 1-position. 2-Cyanoindene was equally labeled on C-1 and C-3, and these two positions are interconverted by hydrogen shifts. Since 2- and 3-cyanoindene interconvert at elevated temperatures [33], this explains the formation of label in the 1-position of 3-cyanoindene, which was found to increase with the temperature. The results are therefore entirely consistent with *ring contraction* via *iminocarbenes and naphthazirine* [Eq. (71)] (cf. also p. 236).



(70)

(71)

7. The Stability of Nitrenes

The observation that hetarylcarbenes always rearrange to nitrenes, when possible, suggests that nitrenes are thermodynamically more stable than carbenes (cf. Section V.2). That this is so can be seen by comparing the heats of formation of CH_2 and NH (triplet ground states) with those of some "normal" molecules (Table 26). Normal nitrogen containing compounds have heats of formation

Table 26. Heats of formation of isosteric molecules (kcal/mol)

CH_2 92 ± 1 [1]	CH_3·34 [1]	CH 142 [3]	CH_4 −17.9 [1]	CH_3–CH_3 −20.2 [5] ⌀H 19.8 [5]
:NH 90 [2]	NH_2·45 [4]	N 113 [3]	NH_3 −11 [3]	CH_3–NH_2 −5.5 [5] pyridine 33.5 [5]
81 ± 2.5 [1]				

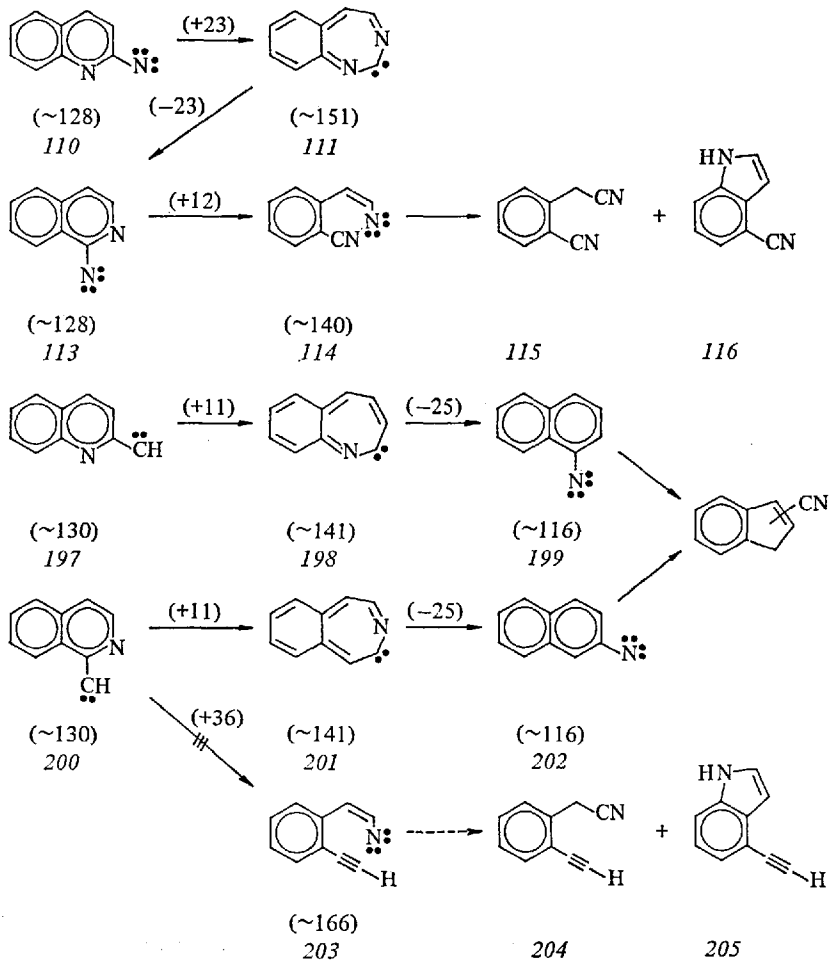
[1]) Ref. [16,17,18].
[2]) Ref. [125].
[3]) Ref. [126].
[4]) Ref. [104].
[5]) Ref. [14].

10—12 kcal/mol *higher* than the isosteric carbon compounds. Although ΔH_f^0(NH) is not known with precision, it is stated that it cannot be more than 94 kcal/mol [125]. Using the best values of Seal and Gaydon [125] and Stedman [125], ΔH_f^0(NH) = 90 kcal/mol, NH is some 10—15 kcal/mol more stable than would have been expected from the value for CH_2. That this conclusion is correct becomes even more probable when one compares CH and N (Table 26). The N atom has a heat of formation 29 kcal/mol *below* that of CH.

When one estimates the heats of formation of aromatic nitrenes and carbenes from those of NH and CH_2 with the aid of group additivity, the nitrenes will automatically become 10—15 kcal/mol more stable than the *isomeric* carbenes. These estimates are of necessity for the triplet species; we do not know the resonance energies in the singlets. Nor do we know the singlet-triplet splittings, which may be different in carbenes and nitrenes. We have, therefore, also performed semi-

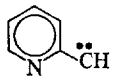
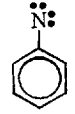
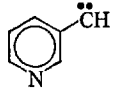
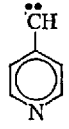
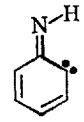
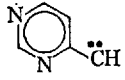
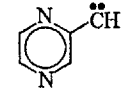
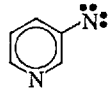
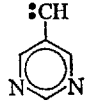
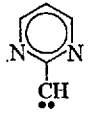
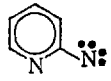
empirical calculations of the total energies of the singlet states of several carbenes and nitrenes (Table 27). The conclusion is the same: the nitrenes are always more stable than the isomeric carbenes [101,127].

On this basis one can understand some reactivity differences between *isosteric* nitrenes and carbenes. The quinolyl- and isoquinolyl carbenes and nitrenes are compared in Scheme 7. 2-Quinolylnitrene (*110*) and 2-quinolylcarbene (*197*) are analogous in that both expand and contract, rearranging to *113* and *199*, respectively (cf. Section V.2). However, 1-isoquinolylcarbene (*200*) is not analogous to 1-isoquinolylnitrene (*113*), for no acetylenic ring opened products, *204*—205 were observed. The estimated enthalpies of formation and reaction (cf. Table 14) are indicated in parentheses in Scheme 7. To the extent that differences in activation energies are proportional to differences in reaction enthalpy (Bell-Evans-Polanyi Principle), the thermochemistry explains the reactions. Thus, ring expansion in 1-isoquinolylnitrene (*113*) is endothermic by ca. 23 kcal/mol, but ring opening



Scheme 7

Table 27. $-E_{tot}$ (eV) Calculated for isomeric carbenes and nitrenes [1]

	CNDO/2	EH		CNDO/2	EH		CNDO/2	EH
	1568.703	606.187		1568.093	605.138		1571.946	607.890
	1568.616	606.135		1568.088	604.452			
	1568.432	605.809		1567.563	604.881			607.101
	1670.644			1670.053				
	1670.651			1669.661			1674.000	
	1670.845			1670.141			1674.135	
	1670.925			1669.930			1674.036	615.877
				1670.055				

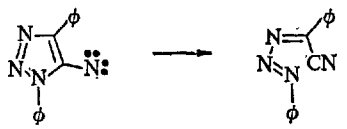
[1]) Ref. [101,127]) EH = Extended Hückel; geometries were not optimized; all C—C = C—N = 1.1 Å; all species are singlets.

only by 12 kcal/mol. By contrast, ring expansion in 1-isoquinolylcarbene (*200*) is endothermic by only ca. 11 kcal/mol, whereas ring opening requires ca. 36 kcal/mol.

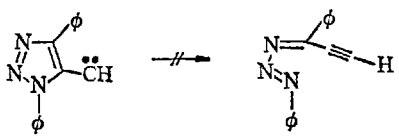
The difference is twofold: (1) the higher heat of formation of an acetylene over a nitrile (ca. 26 kcal/mol[14]) makes ring opening in a carbene unfavorable; (2) the lower heat of formation of a nitrene compared with an *isomeric* carbene makes ring expansion more favorable in carbenes than in nitrenes.

Using similar arguments it can be understood why 2-pyrimidylcarbenes [Eqs. (66) and (68)] and pyrazinylcarbene [Eq. (69)] expand, while the isosteric nitrenes do not (Section IV. 5.—6.). The alternative is ring opening or ring contraction to acetylenes.The 2-pyrimidylcarbenes enjoy the same stabilizing 4-electron 3-center bonding as 2-pyrimidylnitrene [57] (see *157*, p. 226), but the lower electronegativity of carbon compared with nitrogen makes this stabilization less pronounced, and the carbenes do in fact expand [Eq. (68)]. The carbene expansion will be less endothermic then the nitrene expansion, since C=N bonds are formed in the former; N=N bonds in the latter.

It is also known that 1,4-diphenyl-5-(1,2,3-triazolyl)nitrene (*206*) undergoes ring opening in solution, whereas the carbene *207* only gives normal intermolecular carbene reactions [128].



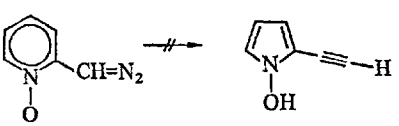
206



207

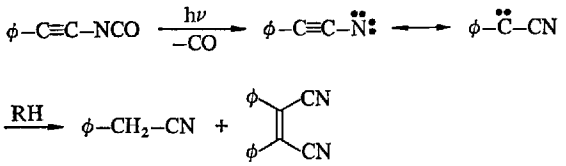
2-Azidopyridine *N*-oxides (*208*) undergo ring contraction to 2-cyano-1-hydroxypyrroles (*209*) in solution [129]. The reaction is formally analogous to the ring contraction in pyridylnitrenes (Section IV.1) but probably does not involve nitrenes [129]. In any case, analogous acetylenes have not been obtained from the corresponding diazomethane *210* [130].

208 *209*



210

It is possible to stabilize a carbene sufficiently, so that it becomes more stable than an isomeric nitrene. Cyanocarbene (NC—C̈H) is expected to be more stable than ethynylnitrene (:N̈—C≡CH) due to the lower heat of formation of the cyano-group. There is experimental evidence for this: attempts to generate phenyl-ethynylnitrene led only to products derived from phenylcyanocarbene [131] [Eq. (72)].



(72)

Aminocarbene (N̈H$_2$—C̈H) is probably more stable than methylnitrene (:N̈—CH$_3$) due to stabilization by the amine lone pair [132], but H$_2$N—CH$_2$—C̈H would be ca. 9 kcal/mol less stable than :N̈—CH$_2$—CH$_3$ (cf. values in Table 26).

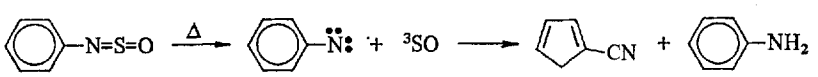
8. Spin State

In this account little has been said about the spin states of the carbenes and nitrenes which react, and it has been tacitly assumed that rearrangement occurs from singlet states, whereas amine and azobenzene formation most probably occurs from triplets. Since we are dealing with thermal reactions, the law of spin conservation [133] would predict that the first-formed species are singlets. However, this is claimed not to be absolutely necessary, for the direct formation of triplets,

$$^1R_2C{=}N_2 \rightarrow {}^3R_2C{:} + {}^1N_2 \qquad (73)$$

is allowed by overall (space × spin) symmetry [134] [Eq. (73)].

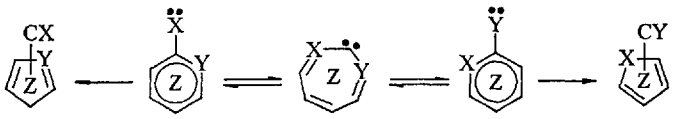
The direct generation of triplet phenylnitrene from (singlet) phenylsulphinyl-amine is certainly an allowed reaction, since the ground state of SO is a triplet [135]. The reaction occurs, and both aniline and cyanocyclopentadiene is formed [136].



Although the yield of the latter is low (4% at 1000 °C) it is not very much lower than from phenyl azide (Table 19). Since ring contraction in arylcarbenes and -nitrenes requires high activation energies (temperatures of 600—800 °C) it is of little importance in which state the initial species is formed. The activation energies are probably higher than the singlet-triplet splittings, and rapid intersystem crossing can take place prior to ring contraction.

VI. Conclusion

Acrylcarbenes and arylnitrenes undergo two major kinds of isomerization, namely ring expansion and ring contraction:



X, Y, Z = CH or N

The ring expansion proceeds *via* bicyclic intermediates when these are stabilized relative to the carbenes, but the formation of such intermediates is not a prerequisite for the reaction. The expanding carbenes and nitrenes show both electrophilic and nucleophilic properties, and the ease of expansion can be predicted from a qualitative consideration of HOMO and LUMO energies, and general organic chemistry. The activation energies for ring expansion are often, but not always, lower than those for ring contraction. Both expansion and contraction is accelerated in heteroaromatic systems, where both the carbenes, the nitrenes, and the rings are more electrophilic, and LUMO energies are lower. Hetarylcarbenes rearrange efficiently to (het)arylnitrenes, the latter being thermodynamically more stable.

There are at least two mechanisms of ring contraction: direct and indirect. The direct contraction can yield either N-nitriles (in pyrazinyl- and 2-pyrimidylnitrenes) or C-nitriles [in 3-cyano-2-pyridylnitrene, *102* (Eq. (34)]. The indirect contraction takes place via iminocyclohexadienylidenes (in phenyl- and 2-naphthylnitrenes), or methylenecyclohexadienylidenes (in phenylcarbene). The cyclohexadienylidenes are themselves formed from — and in equilibrium with — 1*H*-benzazirine and benzocyclopropene, respectively. Ring contraction is favored by high temperature or precursors which decompose with high activation energies, thus producing chemically activated ("hot") species. The ring contraction is strongly exothermic, so that the final products are chemically activated too, and they isomerize by CN- and alkyl shifts. The energies involved in gas-phase isomerizations of carbenes and nitrenes are often higher than the singlet-triplet splittings, so that the initial spin state of the species may be without importance.

The stimulus to this work originated in Copenhagen [137]. The work was performed in Canberra and Lausanne. I thank Professors Rolf Gleiter, Hans Jörg Lindner (Technische Hochschule Darmstadt), Wilfrid D. Crow (Canberra), and my students, Célestin Thétaz, Raymond Harder, Nguyen Mong Lân, and Dr. Claude Mayor for exciting and stimulating collaboration. The financial support of the Schweizerische Nationalfonds zur Förderung der Wissenschaftlichen Forschung under Projects No. 2.241.70 (Prof. H. Dahn) and 2.258.074 is gratefully acknowledged. The manuscript was read and criticized by Drs. Edeline (née) Byrne and John F. McGarrity.

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