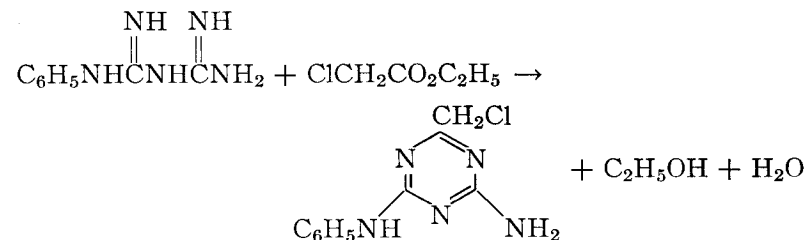


2-AMINO-4-ANILINO-6-(CHLOROMETHYL)-s-TRIAZINE

[s-Triazine, 2-amino-4-anilino-6-(chloromethyl)-]



Submitted by C. G. OVERBERGER and FRANCIS W. MICHELOTTI.¹
Checked by B. C. MCKUSICK and F. W. STACEY.

1. Procedure

Methanol (225 ml.) is placed in a 500-ml. two-necked flask equipped with a mechanical stirrer and a reflux condenser. Sodium (6.8 g., 0.30 g.-atom) in small pieces is dropped down the condenser into the stirred methanol. The resultant solution is cooled to room temperature, and 64 g. (0.30 mole) of 1-phenylbiguanide hydrochloride (Note 1) is added. The mixture is stirred at room temperature for 20 minutes. The sodium chloride that precipitates is separated on a Büchner funnel and washed with 25 ml. of methanol.

The combined filtrates, which contain 1-phenylbiguanide as the free base, are placed in a 500-ml. three-necked flask equipped with a mechanical stirrer, a drying tube containing calcium chloride, and a dropping funnel, and 36.8 g. (0.30 mole) of ethyl chloroacetate (Note 2) is added at room temperature with stirring. The mixture is stirred at room temperature for 14 hours, during which time 2-amino-4-anilino-6-(chloromethyl)-s-triazine precipitates as a white solid. After being separated by filtration and air-dried, the triazine weighs 37–40 g. and melts at 138–140°. The methanol filtrate is added to 500 ml. of cold water. The mixture is cooled in an ice bath with stirring for 2 hours and

filtered to remove an additional 10–12 g. of gray triazine, m.p. 140–142°. The total yield of crude product is 47–52 g.

The triazine is purified by recrystallizing it from 250 ml. of dioxane, using 2 g. of decolorizing carbon and filtering hot. The recrystallized triazine is dried for 5 hours at 60° (1–5 mm. pressure) in a vacuum oven (Note 3). It then weighs 31–33 g. (44–47%) (Note 4), m.p. 142–143° (Note 5).

2. Notes

1. 1-Phenylbiguanide hydrochloride can be obtained from American Cyanamid Company. If 1-phenylbiguanide itself is available, the triazine can be prepared in the same way by dissolving 53 g. (0.30 mole) of 1-phenylbiguanide in 250 ml. of methanol, adding 36.8 g. of ethyl chloroacetate, and proceeding as before. The same yield is obtained whether one starts with the free base or its hydrochloride.

2. Ethyl chloroacetate from Fisher Scientific Company was used.

3. The checkers found that less rigorous drying failed to remove all the dioxane.

4. An additional 3–5 g. of the triazine, m.p. 141–143°, can be obtained by concentrating the dioxane filtrate to about 60 ml. and cooling the concentrate.

5. 2-Chloromethyl-4,6-diamino-*s*-triazine can be prepared in 82% yield by stirring a mixture of biguanide and ethyl chloroacetate in methanol in the same way.

3. Methods of Preparation

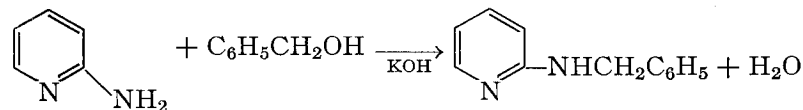
2-Amino-4-anilino-6-(chloromethyl)-*s*-triazine has been prepared from 1-phenylbiguanide and ethyl chloroacetate in the presence of sodium methoxide at –40°.² The present procedure is simpler and more convenient.

¹ Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York.

² Shapiro and Overberger, *J. Am. Chem. Soc.*, **76**, 97 (1954).

2-BENZYLAMINOPYRIDINE

(Pyridine, 2-benzylamino-)



Submitted by YAIR SPRINZAK.¹

Checked by MAX TISHLER and MATTHEW A. KOZLOWSKI.

1. Procedure

A 500-ml. Claisen flask with a 35-mm. indented side arm (Note 1) is attached downward to a Liebig condenser for distillation. A thermometer, held by a cork stopper, is inserted through the neck of the flask and adjusted so that its bulb is close to the bottom. The flask is heated by means of a mantle or air bath. To the flask are charged 94 g. (1.0 mole) of 2-aminopyridine (Note 2), 150 g. (1.39 moles) of benzyl alcohol, and 9 g. of potassium hydroxide. The mixture is heated to boiling and boiled vigorously enough to cause slow distillation of water accompanied by as little benzyl alcohol as possible (Note 3). The temperature of the boiling mixture rises gradually from 182° to 250° during a period of 30 minutes. The mixture is maintained at 250° for 3 minutes, then allowed to cool. The distillate amounts to 19–20 ml. of a water-rich layer and 2–4 ml. of a benzyl alcohol-rich layer.

The residual product is cooled to about 100° (Note 4) and poured into 250 ml. of water. The crystallized solid is crushed and collected on a 12-cm. Büchner funnel. Slight suction is applied at first, but, after most of the mother liquor has been removed, the crystals are pressed down with strong suction. The product is then washed thoroughly with water. After drying, the yield of colorless 2-benzylaminopyridine (Notes 5 and 6), m.p. 95–96°, amounts to 180–183 g. (98–99% of the theoretical amount). The product may be recrystallized from isopropyl alcohol with 90% recovery. For each gram of amine 3 ml. of

solvent is employed. The melting point of recrystallized material is 96.0–96.7° (cor.), lit.² m.p. 97–98°.

2. Notes

1. A short Vigreux column or any other short column for distillation may be used.

2. 2-Aminopyridine was obtained from Matheson, Coleman and Bell, Inc., East Rutherford, New Jersey.

3. If the reaction mixture is heated too strongly or the vapors are inadequately fractionated, correspondingly greater amounts of benzyl alcohol will distill, with concomitant loss of yield. The distillate should be clear, not milky.

4. If the product has partially solidified, it should be melted for easy handling.

5. By essentially the same procedure N,N'-dibenzyl-*p*-phenylenediamine has been obtained in 92% yield. The heating period requires 1 hour, and the final temperature is 260°.

6. N-Benzylaniline has been obtained in 90–94% yield by an appropriate modification³ of this method.

3. Methods of Preparation

For 2-benzylaminopyridine the methods of significance in the literature are condensation of 2-pyridinesulfonic acid and benzylamine,⁴ condensation of the alkali metal salts of 2-aminopyridine with benzyl chloride,⁵ reductive alkylation of 2-aminopyridine in the presence of benzaldehyde and formic acid,² oxidation of N-benzyl-N-pyridylaminoacetonitrile or N-benzyl-N-pyridylaminoacetaldoxime,⁶ and the method described here modified by use of an inert solvent.⁷

¹ The Weizmann Institute of Science, Rehovoth, Israel.

² Kaye and Kogon, *Rec. trav. chim.*, **71**, 309 (1952).

³ Sprinzak, *J. Am. Chem. Soc.*, **78**, 3207 (1956).

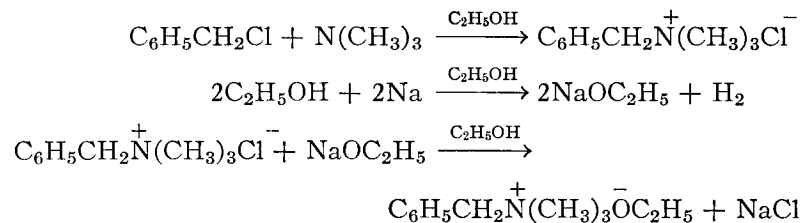
⁴ Mangini and Colonna, *Gazz. chim. ital.*, **73**, 313 (1943) [*C. A.*, **41**, 1224 (1947)].

⁵ Hutterer, Djerassi, Beears, Mayer, and Scholz, *J. Am. Chem. Soc.*, **68**, 1999 (1946).

⁶ Bristow, Charlton, Peak, and Short, *J. Chem. Soc.*, **1954**, (616).

⁷ Hirao and Hagashi, *J. Pharm. Soc. Japan*, **74**, 853 (1954) [*C. A.*, **49**, 10308 (1955)].

BENZYLTRIMETHYLAMMONIUM ETHOXIDE



Submitted by W. J. CROXALL, MARIAN F. FEGLEY, and H. J. SCHNEIDER.¹

Checked by JOHN C. SHEEHAN and M. GERTRUDE HOWELL.

1. Procedure

A 3-l. three-necked flask (flask *A*) is fitted with a nitrogen inlet, a reflux condenser protected by a soda-lime tube, and a reflux condenser fitted with a dropping funnel protected by a soda-lime tube.

A second 3-l. three-necked flask (flask *B*) is fitted with a gas-tight modified Hershberg stirrer (Note 1), a gas inlet tube, and an appropriately designed gas outlet tube bearing a thermometer and connections leading to a soda-lime tube and an open-end mercury manometer. All rubber stoppers and connections are wired in place with 16-gauge copper wire.

Sodium metal (69 g., 3 g. atoms) is introduced into flask *A*, which had been flushed previously with nitrogen (Note 2). Ethanol (1.2 kg.) (Note 3) is added at such a rate that a continuous reflux is maintained. After the sodium is completely dissolved, the solution is allowed to cool to room temperature. During this period the benzyltrimethylammonium chloride is prepared.

A solution of 379.5 g. (3 moles) of benzyl chloride (Note 4) dissolved in 750 g. of anhydrous ethanol (Note 3) is placed in flask *B*. The system is flushed with trimethylamine previously dried by passage through a soda-lime tower. The gas outlet is closed and connected to the manometer. Over a period of 80

minutes, 195 g. (3.3 moles) of trimethylamine (Note 5) is introduced with stirring. The reaction is exothermic and must be cooled to keep the temperature below 50°. After the amine addition is complete, the solution is kept at 50° under an amine pressure of 5 cm. of mercury above atmospheric pressure for 1 hour. The mixture is then cooled to room temperature under an amine atmosphere.

The inlet tube of flask *B* is replaced by a rubber stopper bearing a short glass outlet tube and a glass inlet tube which is connected to an appropriately designed glass siphon outlet tube extending to the bottom of flask *A*. Gentle suction applied to the outlet tube of flask *B* draws the ethoxide solution slowly into flask *B*. The benzyltrimethylammonium chloride solution is stirred throughout the addition of the sodium ethoxide. After the transfer of the sodium ethoxide is completed, the finely divided precipitate of sodium chloride is allowed to settle overnight. When the sodium chloride has completely settled, the stopper bearing the inlet and outlet tubes is replaced by a stopper bearing a 15-in. length of 19-mm. glass tubing which is attached in turn by a gum rubber connection to a clean, dry, 1-gal. bottle fitted with an inlet tube and an outlet tube protected by soda-lime. The bottle is flushed with nitrogen before use. The 15-in. tube is adjusted so that the bottom is approximately ½ in. above the level of the precipitated sodium chloride. With the open-end manometer sealed off by a screw clamp, nitrogen pressure is applied through the outlet tube of the flask until 1.7–1.9 kg. of supernatant liquor is forced from the flask into the bottle (Note 6). This solution contains 24–30% benzyltrimethylammonium ethoxide (2.1–2.7 moles), as determined by titration with 0.1 *N* hydrochloric acid, using methyl red as indicator. This represents a yield of 67–90%. An additional 270–400 g. of solution is obtained by filtration of the residual mixture under nitrogen. To ensure rapid filtration, a filter aid, such as Filtercel (Note 7), must be employed. The filtrate contains 24–30% benzyltrimethylammonium ethoxide (0.3–0.7 mole). The total yield is 89–100%. The solutions are stored under nitrogen and refrigeration in bottles sealed with rubber stoppers which are wired in place (Note 8).

Three hundred and thirty-five grams of the 25% ethanolic solution of benzyltrimethylammonium ethoxide (0.43 mole) is placed under nitrogen in a 3-l. three-necked flask equipped with a gas inlet tube, a gas-tight modified Hershberg stirrer (Note 1), and a gas outlet tube fitted with a thermometer. All stoppers and rubber connections are wired in place with 16-gauge copper wire. There is obtained by evaporation at 40° (Note 9) under reduced pressure (Note 10) 97 g. (0.40 mole) of the ethoxide containing an equivalent of ethanol. The vacuum is broken with dry nitrogen.

2. Notes

1. The stirrer is of the type designed by Hershberg,² but it has a single paddle of 16-gauge Nichrome wire.
2. A bubble counter is employed for indicating nitrogen flow.
3. The water content of the ethanol, determined by Karl Fischer analysis, is 0.02–0.10%.
4. Benzyl chloride is redistilled before use. The fraction collected at 40–41°/6 mm. is used.
5. The flask is disconnected periodically from the gas train and stirring mechanism for weighing.
6. In small-scale preparations (approximately 0.5 mole) centrifugation of the total mixture is a convenient method for separation of the product from sodium chloride.
7. Filtercel is supplied by Johns-Manville Corporation.
8. This method is more satisfactory than storage of the benzyltrimethylammonium ethoxide monoethanolate. The excess ethanol is removed as necessary.
9. The temperature is maintained by surrounding the flask with a warm water bath. Higher temperatures are not recommended because of the tendency of the quaternary ammonium ethoxide to decompose.
10. The bulk of the ethanol was removed by using a water pump (40–50 mm.) and collected in 1-l. and 200-ml. dry ice traps connected in series. The remaining ethanol was removed by using an oil pump protected with two 300-ml. Dry Ice traps.

3. Methods of Preparation

The procedure described is adapted from the preparation outlined by Meisenheimer.³ The method has been applied by the authors to the preparation of benzyltrimethylammonium methoxide, tetramethylammonium ethoxide, dibenzyltrimethylammonium methoxide, bisisopropylbenzyltrimethylammonium methoxide and benzyltriethylammonium ethoxide.

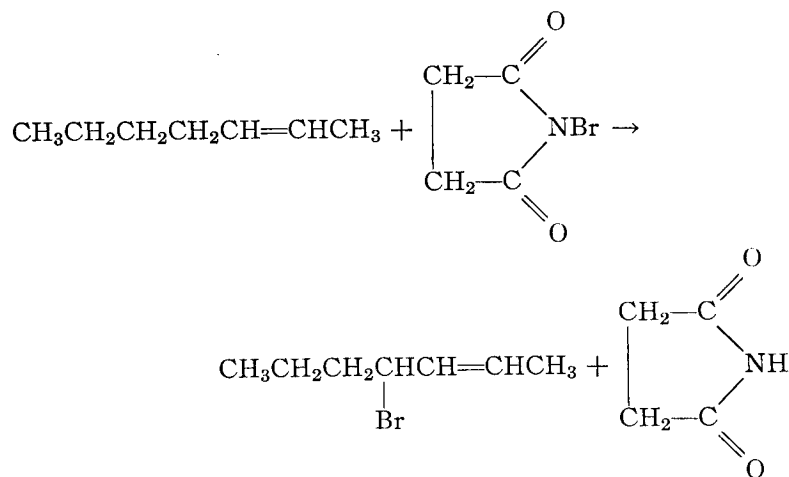
¹ Rohm and Haas Company, Philadelphia 37, Pennsylvania.

² Hershberg, *Ind. Eng. Chem., Anal. Ed.*, **8**, 313 (1936).

³ Meisenheimer and Bratring, *Ann.*, **397**, 295 (1913).

4-BROMO-2-HEPTENE

(2-Heptene, 4-bromo-)



Submitted by F. L. GREENWOOD, M. D. KELLERT, and J. SEDLAK.¹

Checked by JOHN D. ROBERTS and A. T. BOTTINI.

1. Procedure

In a 500-ml. round-bottomed flask fitted with a stirrer, nitrogen inlet tube, and reflux condenser are placed 40 g. (0.408 mole) of

2-heptene, 48.1 g. (0.272 mole) of N-bromosuccinimide, 0.2 g. of benzoyl peroxide, and 250 ml. of carbon tetrachloride (Note 1). The reaction mixture is stirred and heated under reflux in a nitrogen atmosphere for 2 hours (Note 2). The succinimide is removed by suction filtration, washed twice with 15-ml. portions of carbon tetrachloride and the carbon tetrachloride washings are combined with the filtrate (Note 3). The carbon tetrachloride solution is transferred to a 500-ml. Claisen flask modified so that the distilling arm carries a 25 x 300 mm. section packed with glass helices. The capillary is attached to a source of nitrogen and the carbon tetrachloride removed at 36–38°/190 mm. (Note 4).

The residue is transferred to a 125-ml. Claisen flask modified so that the distilling arm carries an 18 x 180 mm. section packed with glass helices. Nitrogen is led into the capillary, and, after a forerun of 1–3 g., there is collected 28–31 g. (58–64%) of 4-bromo-2-heptene, b.p. 70–71°/32 mm., n_D^{25} 1.4710–1.4715 (Note 5). A residue of 7–10 g. remains in the distilling flask (Note 6).

2. Notes

1. The 2-heptene was the pure grade material purchased from Phillips Petroleum Company, Bartlesville, Oklahoma. This olefin is comparable to material prepared by a Boord synthesis. The N-bromosuccinimide was obtained from Arapahoe Chemicals, Inc., Boulder, Colorado. The benzoyl peroxide was used as received from Distillation Products, Rochester, New York. The carbon tetrachloride was reagent grade, from J. T. Baker Chemical Company, Phillipsburg, New Jersey.

2. The reaction is not rapid, and benzoyl peroxide is necessary to effect reaction. Longer reflux times lead to darkening of the reaction mixture.

3. The succinimide recovered corresponded to 97–98% of the theoretical amount and analyzed for 0.4% active bromine.

4. Removal of the carbon tetrachloride at a lower pressure results in loss of product. Distillation at a pressure much above 200 mm. causes considerable darkening of the liquid. Carbon tetrachloride removed at the higher pressure gives no precipi-

tate with aqueous silver nitrate; this indicates the absence of product.

5. When first distilled, the product is nearly colorless. On standing under nitrogen in the refrigerator for several days, the material acquires a pale yellow color. Evidence for the identity of the product as 4-bromo-2-heptene is outlined in reference 3.

6. This includes the liquid wetting the helices as well as the small amount of dark residue in the flask.

3. Methods of Preparation

Ziegler and coworkers² indicated that allylic methylene groups undergo bromine substitution more readily than allylic methyl groups. This has been shown³ to be true, and the treatment of 2-heptene with N-bromosuccinimide gives rise to 4-bromo-2-heptene.

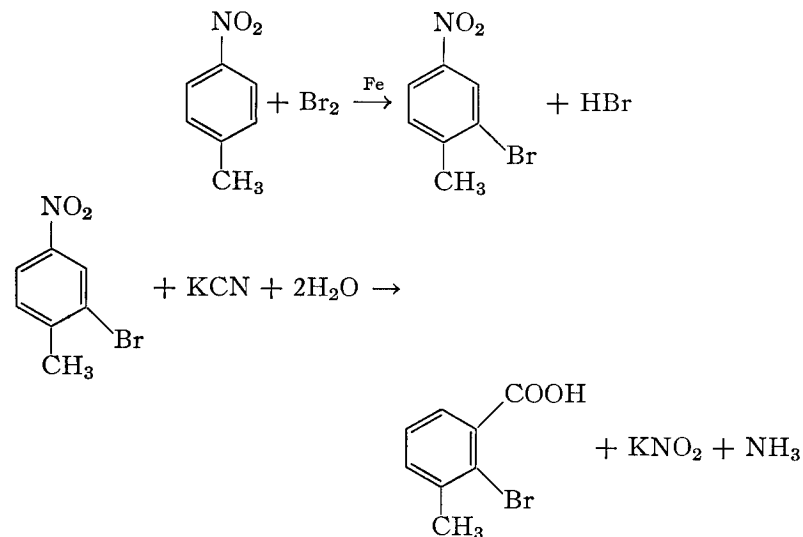
¹ Department of Chemistry, Tufts University, Medford, Massachusetts.

² Ziegler, et. al., *Ann.*, **551**, 80 (1942).

³ Greenwood and Kellert, *J. Am. Chem. Soc.*, **75**, 4842 (1953).

2-BROMO-3-METHYLBENZOIC ACID

(*m*-Toluic acid, 2-bromo-)



Submitted by J. F. BUNNETT and M. M. RAUHUT.¹

Checked by JOHN D. ROBERTS and MARC S. SILVER.

1. Procedure

A. *2-Bromo-4-nitrotoluene*. In a 200-ml. three-necked, round-bottomed flask provided with an efficient reflux condenser bearing a suitable trap for absorbing hydrogen bromide, a 100-ml. separatory funnel, and a ball-joint or mercury-sealed mechanical stirrer are placed 68.5 g. (0.5 mole) of *p*-nitrotoluene (Note 1) and 1.0 g. of iron powder. The mixture is heated to 75–80° by means of a water bath, vigorous stirring is begun, and 30.5 ml. (92.0 g., 0.57 mole) of bromine is added over the course of 30 minutes. After the addition of bromine is complete, the reaction mixture is maintained at 75–80° with continuation of stirring for an additional 1.5 hours.

The reaction mixture is poured with vigorous stirring into 750 ml. of ice-cold 10% sodium hydroxide solution, the solid is

allowed to settle, and the supernatant liquid is decanted. To the residue is added 250 ml. of glacial acetic acid, and the mixture is heated until the solid is completely melted. The two liquid phases are thoroughly mixed by stirring, the mixture is cooled to 5° in an ice bath, and the supernatant liquid is decanted. The product is then heated with 500 ml. of 10% acetic acid until molten, stirred thoroughly, and cooled to room temperature. The aqueous liquor is decanted, and the cycle is repeated with 500 ml. of 1% sodium hydroxide solution (Note 2). The solid 2-bromo-4-nitrotoluene is collected on a Büchner funnel and thoroughly washed with water. The moist product may be used directly in the next stage of the synthesis. It can be dried to yield 93–97 g. (86–90%) of light-brown material melting at 75–76°.

B. *2-Bromo-3-methylbenzoic acid*. *Caution! This procedure must be carried out in a hood with a good draft, because poisonous hydrogen cyanide gas is evolved.* In a 5-l. round-bottomed flask are placed 90 g. of potassium cyanide, 900 ml. of 2-ethoxyethanol (Note 3), 850 ml. of water, and the moist 2-bromo-4-nitrotoluene obtained above. A reflux condenser is attached, and the mixture is boiled for 16 hours (Note 4). To the hot, dark-red solution is then added 1.5 l. of water, and the mixture is acidified with concentrated hydrochloric acid. (*Caution! Hydrogen cyanide is evolved.*) The acidified mixture is boiled for 15 minutes to expel hydrogen cyanide and then allowed to cool to 35–40°. Five grams of diatomaceous earth is stirred in, and the mixture is filtered through a Büchner funnel precoated with a little diatomaceous earth. The solid is discarded, and the filtrate is extracted three times with 200-ml. portions of chloroform. The chloroform extracts are combined and extracted with three 100-ml. portions of 5% ammonium carbonate solution. The basic extracts are combined, acidified with concentrated hydrochloric acid, and cooled in an ice bath. The oil which first forms soon crystallizes.

The tarry solid is collected on a Büchner funnel, washed with 50 ml. of water, and dried. The dried solid is pulverized and boiled under reflux for 3 hours with 500 ml. of petroleum ether (b.p. 90–100°). The hot mixture is then filtered (fluted filter

paper), and the solid is discarded. The filtrate is allowed to cool to room temperature, and the 2-bromo-3-methylbenzoic acid is collected by filtration. The white acid when dry weighs 7.5–8.5 g. (7–8%, based on the *p*-nitrotoluene) and melts at 134–136° (Note 5).

2. Notes

1. Eastman Kodak Company practical grade *p*-nitrotoluene was used.

2. The hot mixture of 2-bromo-4-nitrotoluene and 1% sodium hydroxide solution should be stirred vigorously during cooling in order to avoid obtaining the product as a solid cake. If stirring is omitted, subsequent treatment is less convenient.

3. Commercial Cellosolve was used.

4. An electric heating mantle is a convenient heat source.

5. The submitters report 11–14 g. (10–13%) of material having m.p. 132–135°, which yields, after crystallization from benzene, 9–13 g. of product having m.p. 135–137°.

3. Methods of Preparation

Although 2-bromo-4-nitrotoluene has been obtained by several routes, it is most easily prepared by bromination of *p*-nitrotoluene.² The procedure given is adapted from that described by Cavill.³ 2-Bromo-3-methylbenzoic acid has not been prepared by any other means; evidence for its structure is presented elsewhere.⁴

¹ University of North Carolina, Chapel Hill, North Carolina.

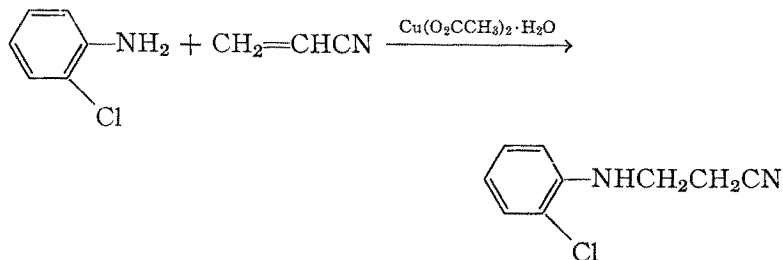
² Scheufelen, *Ann.*, **231**, 152 (1885); Lucas and Scudder, *J. Am. Chem. Soc.*, **50**, 244 (1928); Frejka and Vitha, *Publs. fac. sci. univ. Masaryk*, **20** (1925) [*Chem. Zentr.*, **96**, II, 1153 (1925)]; Higginbottom, Hill, and Short, *J. Chem. Soc.*, **1937**, 263; Truce and Amos, *J. Am. Chem. Soc.*, **73**, 3013 (1951).

³ Cavill, *J. Soc. Chem. Ind. (London)*, **65**, 124 (1926).

⁴ Bunnett and Rauhut, *J. Org. Chem.*, **21**, 936 (1956).

3-(*o*-CHLOROANILINO)PROPIONITRILE

(Propionitrile, 3-*o*-chloroanilino-)



Submitted by S. A. HEININGER.¹

Checked by JOHN C. SHEEHAN and ALMA M. BOSTON.

1. Procedure

A 500-ml. three-necked flask equipped with a stirrer, reflux condenser, and thermometer is charged with 255 g. (2.0 moles) of *o*-chloroaniline, 106 g. (2.0 moles) of acrylonitrile, and 10.2 g. (4.0% by weight of the amine) of cupric acetate monohydrate (Note 1). The mixture is then stirred and heated to reflux, beginning at about 95°. Refluxing is continued for 3.0 hours (Note 2), with the pot temperature rising to about 130° (Note 3).

The dark mixture is then transferred to a 500-ml. distilling flask fitted with a 15.2-cm. modified Vigreux column and the unchanged acrylonitrile (17–20 g.) collected at 100 mm. (water pump). The distillation is continued (vacuum pump) and the unchanged *o*-chloroaniline (110–120 g.), b.p. 57–60°/0.5 mm., is recovered. The 3-(*o*-chloroanilino)propionitrile (182–192 g.) is obtained as a colorless, somewhat viscous liquid, b.p. 139–141°/0.3 mm., n_D^{25} 1.5728–1.5735 (Note 4).

A pot residue of 30–35 g. remains (Note 5). The conversion of *o*-chloroaniline to 3-(*o*-chloroanilino)propionitrile is 50.5–53%, with a yield of 90–95% based on *o*-chloroaniline, and 53–65% based on acrylonitrile (Note 6).

2. Notes

1. The commercially available monohydrate form of cupric acetate was used. Anhydrous cupric acetate gives the same results. From 2% to 5% of catalyst by weight of the amine employed gives good yields of cyanoethylated products from a variety of anilines.

2. Slightly improved yields may be obtained by use of longer reaction times.

3. Maintaining the temperature at 100–110° for the same period of time gives equivalent results.

4. Physical constants for pure 3-(*o*-chloroanilino)propionitrile are: b.p. 139–141°/0.3 mm., n_D^{25} 1.5734, d_{25}^{25} 1.2103.

5. The residue consists mainly of polyacrylonitrile and copper or copper salts. It is slowly soluble in acetone, more readily soluble in polyacrylonitrile solvents such as dimethylformamide or dimethyl sulfoxide, especially when warmed.

6. An attempt to prepare 3-(*o*-chloroanilino)propionitrile by the Cymerman-Craig procedure (*o*-chloroaniline hydrochloride, diethylamine, and acrylonitrile)² gave no isolable product, with recovery of 75% of the *o*-chloroaniline as its acetyl derivative, m.p. 86–87°. Reported m.p. 87–88°.³ Thus representative *ortho*-substituted anilines can be cyanoethylated in much better yields by use of the cupric acetate catalyst than by the Cymerman-Craig route, which is known to be subject to steric interferences.⁴ Comparative yields for cyanoethylation of *o*-toluidine substantiate this conclusion; cupric acetate gave 62%, whereas Cymerman-Craig reported 25%.⁴ Bulky N-substituents appear to affect yields similarly: methyl-, ethyl-, *n*-propyl-, and isopropylanilines gave yields of 65%, 41%, 17.5%, and 0.5% by the exchange reaction,⁴ whereas, with cupric acetate, *n*-butylaniline was cyanoethylated in 68% yield.

3. Methods of Preparation

Cupric acetate is an efficient catalyst for the cyanoethylation of all but nitro-substituted aromatic amines. It is particularly effective with anilines which give poor yields by known methods,

i.e., those with substituents on the nitrogen atom or in the *ortho* position.

Other known catalysts for cyanoethylation of aromatic amines include acetic acid,^{5,6} acetic acid-cuprous chloride mixtures,^{7,8} aniline salts,⁹ and choline.¹⁰ 3-Anilinopropionitriles may also be prepared by an exchange reaction between the aniline hydrochloride and diethylaminopropionitrile.^{2,4}

¹ Research Department, Research and Engineering Division, Monsanto Chemical Company, Dayton, Ohio.

² Cymerman-Craig and Moyle, *Org. Syntheses*, **36**, 6 (1956).

³ Beilstein and Kurbatow, *Ann.*, **182**, 100 (1876).

⁴ Bates, Cymerman-Craig, Moyle, and Young, *J. Chem. Soc.*, **1956**, 388; and earlier papers.

⁵ Braunholtz and Mann, *J. Chem. Soc.*, **1952**, 3046.

⁶ Cookson and Mann, *J. Chem. Soc.*, **1949**, 67.

⁷ Smith and Yu, *J. Am. Chem. Soc.*, **74**, 1096 (1952).

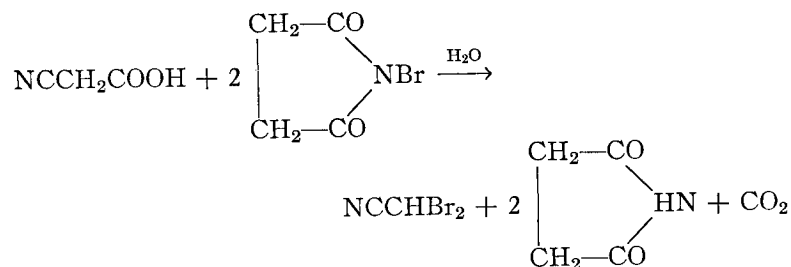
⁸ Braunholtz and Mann, *J. Chem. Soc.*, **1953**, 1817.

⁹ Bekhli and Serebrennikov, *J. Gen. Chem. U.S.S.R.*, **19**, 1553 (1949); [*C. A.*, **44**, 3448 (1950)].

¹⁰ Pietra, *Gazz. chim. ital.*, **86**, 70 (1956).

DIBROMOACETONITRILE

(Acetonitrile, dibromo-)



Submitted by JAMES W. WILT and JAMES L. DIEBOLD.¹

Checked by B. C. McKUSICK and H. E. KNIPMEYER.

1. Procedure

A solution of 63.8 g. (0.75 mole) of cyanoacetic acid (Note 1) in 750 ml. of cold water is placed in a 2-l. beaker. N-Bromo-

succinimide (267 g., 1.5 moles) (Note 2) is added in portions with good mechanical stirring over a period of about 6 minutes (Note 3). The slightly exothermic reaction which attends the separation of the dibromoacetonitrile as a heavy oil is completed in about 20 minutes, after which time the beaker is placed in an ice bath and allowed to cool for 2 hours (Note 4).

The precipitated succinimide is collected on a large Büchner funnel atop a 2-l. filter flask and is washed with six 50-ml. portions of methylene chloride. The lower organic layer in the filtrate is separated from the aqueous phase, which is extracted with two 25-ml. portions of methylene chloride. The organic layer and the extracts are combined, washed vigorously with 50 ml. of a 5% sodium hydroxide solution (Note 5) and three 80-ml. portions of water, and dried over 10 g. of anhydrous sodium sulfate for several hours in a flask wrapped with aluminum foil (Note 6).

The colorless dried oil is distilled through a 45-cm. Widmer column (Note 7). Most of the methylene chloride is removed by heating the contents of the distillation pot to 75° at atmospheric pressure. The pressure is then lowered to about 20 mm., and 112–129 g. (75–87%) of dibromoacetonitrile is collected as a colorless oil, b.p. 70–72°/20 mm., n_D^{25} 1.540–1.542, d_4^{20} 2.369 (Notes 8 and 9).

2. Notes

1. Commercial cyanoacetic acid (Eastman Kodak Company), m.p. 67–71.5°, about 98% pure, was found satisfactory for this preparation.

2. N-Bromosuccinimide obtained from Matheson, Coleman and Bell, Inc., as well as from Arapahoe Chemicals, Inc., was used as received. The N-chlorosuccinimide (see Note 9) was commercial material from Arapahoe Chemicals, Inc.

3. The N-bromosuccinimide should be added as rapidly as possible consistent with the foaming produced by evolution of carbon dioxide.

4. About one-third of the succinimide (50–53 g.) precipitates from the solution during the cooling period, thus rendering the subsequent purification of the nitrile easier. Sometimes the solu-

tion must be seeded to start the precipitation. The checkers found it necessary to store the mixture in a refrigerator overnight in order to obtain 50–53 g. of succinimide.

5. The basic aqueous phase becomes pink through action of the base on dibromoacetonitrile.

6. Pure dibromoacetonitrile is fairly stable to air and light, but traces of basic impurities cause it to become discolored (see Note 5). Protective shielding retards this coloration.

7. Unless an efficient column is used, some nitrile distils over with the methylene chloride. The checkers used a 120-cm. spinning-band column.

8. The product shows good shelf stability, but, as a precautionary measure, it is best stored under nitrogen in a sealed brown vessel. Dichloroacetonitrile (Note 9) is less sensitive and may be stored in an ordinary glass-stoppered brown bottle.

9. In exactly the same fashion, from 63.8 g. (0.75 mole) of cyanoacetic acid and 200.3 g. (1.5 moles) of N-chlorosuccinimide there may be obtained 45–54 g. (55–65%) of colorless dichloroacetonitrile, b.p. 110–112°/760 mm., n_D^{25} 1.439, d_4^{20} 1.369. Since this reaction is slightly slower, 30 minutes should be allowed for the reaction before chilling.

3. Methods of Preparation

Dibromoacetonitrile has been prepared by the dehydration of dibromoacetamide with phosphorous pentoxide^{2,3} and by the present method.⁴ An early report that dibromoacetonitrile can be obtained from cyanoacetic acid by treatment with bromine,⁵ a method similar to that described here, was later shown to be wrong.²

¹ Loyola University, Chicago, Illinois.

² Steinkopf, *Ber.*, **38**, 2694 (1905).

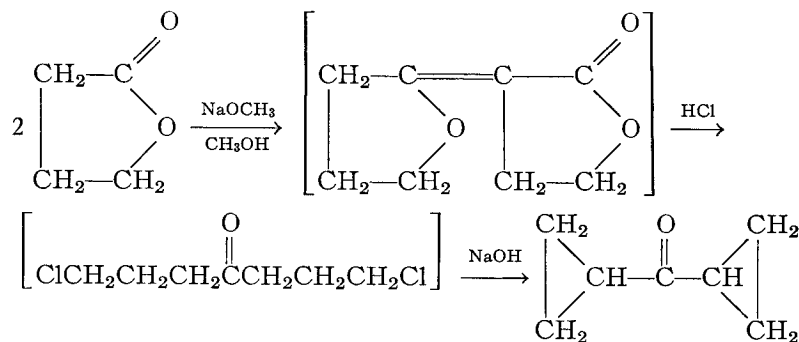
³ Ghigi, *Gazz. chim. ital.*, **71**, 641 (1941).

⁴ Wilt, *J. Org. Chem.*, **21**, 920 (1956).

⁵ van't Hoff, *Ber.*, **7**, 1382, 1571 (1874).

DICYCLOPROPYL KETONE

(Ketone, dicycloparyl)



Submitted by OMER E. CURTIS, JR., JOSEPH M. SANDRI,

RICHARD E. CROCKER, and HAROLD HART.¹

Checked by V. BOEKELHEIDE, R. TABER, and D. S. TARBELL.

1. Procedure

A solution of sodium methoxide is prepared from 50 g. (2.17 g. atoms) of freshly cut sodium and 600 ml. of absolute methanol (Note 1) in a 3-l. three-necked flask placed on a steam bath and equipped with a sealed stirrer (Note 2), dropping funnel, and a condenser set downward for distillation (Note 3). To the stirred solution is added in one portion 344 g. (4.0 moles) of γ -butyrolactone (Note 4), and the flask is heated until methanol distils at a rapid rate. After 475 ml. of methanol is collected, a filter flask or other suitable device equipped with a side arm is connected to the condenser. This receiver is surrounded by an ice bath, and reduced pressure from an aspirator is applied cautiously (frothing) with continuous stirring. An additional 50–70 ml. of methanol is collected in this way. The residue presumably is dibutyrolactone (Note 5).

The condenser is set for reflux, and the steam bath is replaced with a more potent source of heat (electric heating mantle, oil bath, or direct flame). Concentrated hydrochloric acid is added

with stirring, cautiously at first because a considerable amount of carbon dioxide is evolved. A total of 800 ml. of acid is added in about 10 minutes (Note 6). The mixture is heated under reflux with stirring for 20 minutes, then cooled in an ice bath (Note 7). A solution of 480 g. of sodium hydroxide in 600 ml. of water is added to the stirred mixture as rapidly as possible, without allowing the temperature to go above 50° (Note 8). The mixture is then heated under reflux for an additional 30 minutes.

The condenser is arranged for downward distillation, and a total of 650 ml. of ketone-water mixture is collected as distillate. Sufficient potassium carbonate is added to saturate the aqueous layer, and about 130 ml. of ketone is separated. The aqueous layer is extracted with three 100-ml. portions of ether, and the combined ether and ketone layers are dried over 25 g. of anhydrous magnesium sulfate. The product remaining after removal of the ether is distilled through an efficient column. The yield of dicyclopentyl ketone boiling at 72–74°/33 mm., n_D^{25} 1.4654, is 114–121 g. (52–55%) (Note 9).

2. Notes

1. Commercial sodium methoxide (117 g.) in 520 ml. of methanol may be used instead of metallic sodium.
2. The stirrer should be sturdy and capable of giving vigorous agitation.
3. It is desirable to have the condenser arranged for reflux during preparation of the methanolic sodium methoxide, if it is made from sodium metal.
4. Commercial lactone (available from General Aniline and Film Corporation, 435 Hudson Street, New York 14, New York) should be redistilled, b.p. 88–90°/12 mm., before use.
5. Dibutyrolactone can be isolated as a crystalline solid, m.p. 86–87°, from this residue.² The preparation can be interrupted at this point without jeopardizing the yield.
6. The color of the mixture changes from yellow through dark orange to dark reddish brown.
7. At this point, the following procedure may be used to prepare 1,7-dichloro-4-heptanone. To the cooled, stirred solution is

added 200 ml. of ether, which brings the dense dichloroketone to the upper layer. The latter is separated, and the acid layer is extracted with two 100-ml. portions of ether. The combined ether layers are dried over 25 g. of anhydrous calcium chloride. After removal of the solvent, the residue is distilled through an efficient column. The yield of 1,7-dichloro-4-heptanone, b.p. 106–110°/4 mm., n_D^{25} 1.4713, is 263–278 g. (72–76%). The material takes on a purple cast rapidly and should be stored in a refrigerator.

8. Considerable salt separates at this point but does not interfere with the subsequent steps.

9. According to the submitters, a similar procedure can be applied to substituted lactones; di-(2-methylcyclopentyl) ketone, b.p. 65–67°/7 mm., n_D^{25} 1.4600, has been made from γ -valerolactone in 50% yield.

3. Methods of Preparation

This procedure is a modification of one recently described in the literature.³ The first step is based on early work of Fittig⁴ and Volhard⁵ as modified by Spencer and Wright.² The third step, ring closure of a γ -haloketone, is well known.^{5,6} Dicyclopentyl ketone was reported to form in small amounts from the decarboxylation of cyclopropanecarboxylic acid over thoria,⁷ but there is some doubt³ about the product. Dicyclopentyl ketone is available in research quantities from the Aldrich Chemical Company, Milwaukee 12, Wisconsin, and from Columbia Organic Chemicals, Inc., Columbia, South Carolina.

¹ Department of Chemistry, Michigan State University, East Lansing, Michigan.

² Spencer and Wright, *J. Am. Chem. Soc.*, **63**, 1281 (1941).

³ Hart and Curtis, Jr., *J. Am. Chem. Soc.*, **78**, 112 (1956).

⁴ Fittig, *Ann.*, **256**, 50 (1889); Fittig and Stöm, *Ann.*, **267**, 191 (1892).

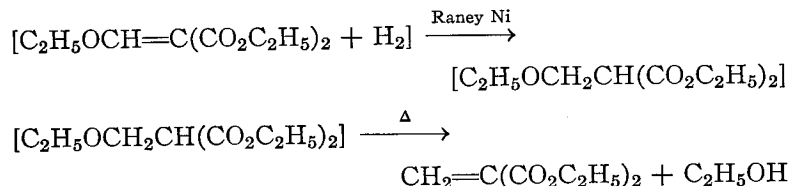
⁵ Volhard, *Ann.*, **267**, 78 (1892).

⁶ *Org. Syntheses*, **31**, 74 (1951).

⁷ Michiels, *Bull. soc. chim. Belges*, **24**, 396 (1910) [*Chem. Zentr.*, **82**, I, 66 (1911)].

DIETHYL METHYLENEMALONATE

(Malonic acid, methylene-, diethyl ester)

Submitted by WAYNE FEELY and V. BOEKELHEIDE.¹

Checked by MAX TISHLER, BARBARA P. BIRT, and ARTHUR A. PATCHETT.

1. Procedure

A solution of 108 g. (0.5 mole) of diethyl ethoxymethylenemalonate (Note 1) in 100 ml. of commercial absolute alcohol is placed in an apparatus for high-pressure hydrogenation together with 10 g. of Raney nickel catalyst (Note 2). The pressure in the bomb is raised to 1000–1500 lb. with hydrogen, and the temperature is adjusted to 45° (Note 3). The bomb is shaken, and the reaction is allowed to proceed for 12–20 hours, during which time 0.5 mole of hydrogen is absorbed.

The apparatus is allowed to cool to room temperature, the pressure is released, and the catalyst is removed by filtration. Concentration of the filtrate under reduced pressure at room temperature yields a colorless oil (Note 4).

The residual oil is transferred to a distillation flask (Note 5), and the flask is carefully warmed with a small flame (Note 6). After a fore-run of ethanol is collected, the variable transformer controlling the heating tape is set at a voltage to give an internal temperature in the distilling head of 80–100° before distillation. The flask is then heated to effect slow distillation at atmospheric pressure. About 10–13 g. of fore-run is collected before the temperature of the distillate vapor reaches 200°. The main fraction (68–71 g., 79–82%) is collected between 200° and 216°

as a colorless oil. For most purposes, the fore-run is sufficiently pure that it can be combined with the main fraction to give an over-all yield of 78–81 g. (91–94%) (Note 7). Diethyl methylenemalonate polymerizes on standing to a white solid, from which the monomer can be recovered by slow distillation. The diethyl methylenemalonate should be distilled just prior to use (Note 8).

2. Notes

1. Diethyl ethoxymethylenemalonate can be prepared by the method of Parham and Reed.² The submitters used diethyl ethoxymethylenemalonate obtained commercially from Kay-Fries Chemicals Inc., 180 Madison Avenue, New York 16, New York.

2. Raney nickel catalyst can be prepared by the method of Mozingo.³ The submitters used Raney nickel catalyst obtained commercially from the Gilman Paint and Varnish Company, Chattanooga, Tennessee.

3. At higher temperatures (about 70°) the diethyl ethoxymethylmalonate formed tends to eliminate ethanol, forming diethyl methylenemalonate which is hydrogenated to diethyl methylmalonate.

4. This oil, n_D^{20} 1.4254, is presumably diethyl ethoxymethylmalonate, as evidenced by its infrared and ultraviolet absorption spectra. It is relatively stable and can be stored at room temperature without change. If the concentration of the filtrate under vacuum is carried out by heating on a steam bath instead of by keeping it at room temperature, the diethyl ethoxymethylmalonate undergoes elimination of ethanol to some extent, giving diethyl methylenemalonate directly. The yield of diethyl methylenemalonate obtained eventually is not altered by this procedure.

5. The distillation apparatus is shown in Fig. 1. The upper part of the flask and the short column are wrapped in electrical heater tape, which is operated during distillation of the product.

6. The elimination of ethanol is slightly exothermic. It is advisable to heat the flask cautiously with a small flame until the reaction starts and then to remove the flame until the reaction subsides.

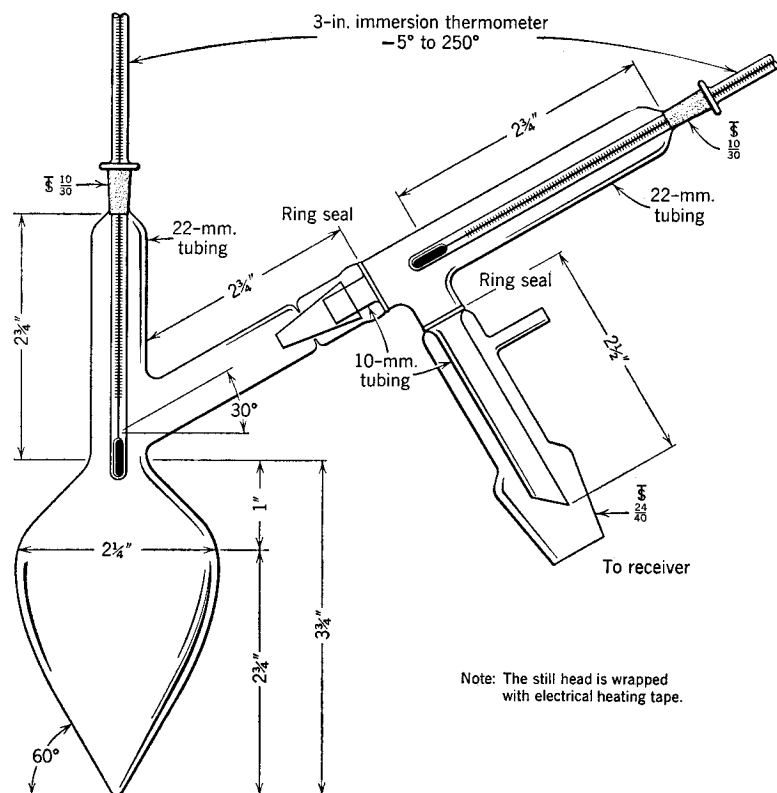


FIG. 1.

7. The fore-run has a refractive index (usually about n_D^{22} 1.4154) lower than that of the main fraction (about n_D^{22} 1.4250). The combined fractions show refractive indices in the range n_D^{22} 1.4210–1.4259.

8. When the solid polymer from the above preparation was slowly distilled to recover diethyl methylenemalonate, there was obtained 57 g. of colorless oil, b.p. 210–216°/730 mm., n_D^{20} 1.4220.

3. Methods of Preparation

Diethyl methylenemalonate was first prepared by Perkin⁴ from formaldehyde and malonic ester. An alternative procedure involving the reaction of methylene chloride or iodide with

sodiummalonic ester was developed by Tanatar.⁵ Diethyl methylenemalonate is also formed when hexaethyl pentane-1,1,3,3,5,5-hexacarboxylate is treated with methylene iodide and sodium ethoxide.⁶ Bachman and Tanner⁷ have prepared diethyl methylenemalonate by both vapor and liquid phase reactions of formaldehyde and diethyl malonate in the presence of various catalysts.

¹ Department of Chemistry, University of Rochester, Rochester, New York.

² Parham and Reed, *Org. Syntheses*, Coll. Vol. **3**, 395 (1955).

³ Mozingo, *Org. Syntheses*, Coll. Vol. **3**, 181 (1955).

⁴ Perkin, *Ber.*, **19**, 1053 (1886).

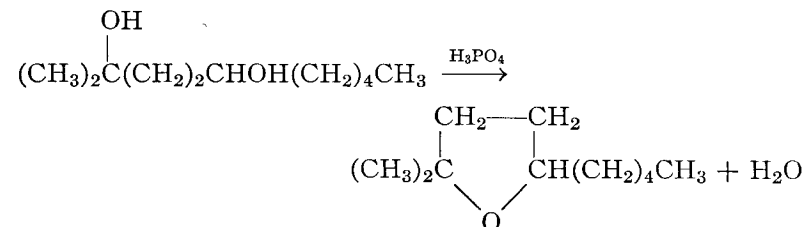
⁵ Tanatar, *Ann.*, **273**, 48 (1893).

⁶ Bottomley and Perkin, *J. Chem. Soc.*, **77**, 294 (1900).

⁷ Bachman and Tanner, *J. Org. Chem.*, **4**, 493 (1939).

5,5-DIMETHYL-2-*n*-PENTYLTETRAHYDROFURAN

(Furan, tetrahydro-2,2-dimethyl-5-pentyl-)



Submitted by J. COLONGE and R. MAREY.¹

Checked by V. BOEKELHEIDE and H. KAEMPFFEN.

1. Procedure

In a 100-ml., three-necked, round-bottomed flask, fitted with a sealed mechanical stirrer, a reflux condenser, and a thermometer reaching to the bottom of the flask, are placed 37.6 g. (0.2 mole) of 2-methyl-2,5-decanediol² and 17 g. of 85% phosphoric acid. The limpid liquid obtained is heated and maintained at 125° for 40 minutes. Then the acidic lower layer is discarded,

and the organic layer is washed with three or four 50-ml. portions of lukewarm distilled water.

Distillation of the resulting crude oil using a simple fractionating column gives 32–33 g. (94–97%) of pure 5,5-dimethyl-2-*n*-pentyltetrahydrofuran as a colorless liquid boiling at 31–33°/1.5 mm.; n_D^{25} 1.4257 (Note 1).

2. Note

1. The submitters have also prepared 5,5-dimethyl-2-heptyltetrahydrofuran (n_D^{25} 1.4360) by a similar dehydration of 2-methyl-2,5-undecanediol obtained from the reaction of methylmagnesium bromide and γ -undecanoic lactone.

3. Methods of Preparation

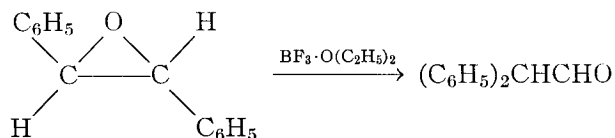
There is no previous report on the preparation of 5,5-dimethyl-2-*n*-pentyltetrahydrofuran.

¹ École de Chimie Industrielle de Lyon and Établissement Descollonges Frères (Lyon).

² *Org. Syntheses*, **38**, 41 (1958).

DIPHENYLACETALDEHYDE

(Acetaldehyde, diphenyl-)



Submitted by DONALD J. REIF and HERBERT O. HOUSE.¹

Checked by M. S. NEWMAN and W. H. POWELL.

1. Procedure

In a 1-l. separatory funnel is placed a solution of 39.2 g. (0.2 mole) of *trans*-stilbene oxide (Note 1) in 450 ml. of reagent benzene. To the solution is added 13.2 ml. (0.1 mole) of boron tri-

fluoride etherate (Note 2). The solution is swirled, allowed to stand for 1 minute (Note 3), and then washed with two 300-ml. portions of water. The organic layer is separated, and the benzene is removed by distillation (Note 4). The residual crude aldehyde is purified by distillation under reduced pressure. The product, collected at 115–117°/0.6 mm., amounts to 29–32 g. (73–83%), n_D^{25} 1.5875–1.5877 (Note 5).

2. Notes

1. The *trans*-stilbene oxide² should be free from *trans*-stilbene, since the stilbene, if present, is not altered by the reaction conditions and will contaminate the final product.

2. A practical grade of boron trifluoride etherate, purchased from Eastman Kodak Company, was redistilled before use. The pure etherate boils at 126°.

3. Longer reaction times result in a marked decrease in the yield of diphenylacetaldehyde.

4. The submitters found that distillation of the benzene solution is necessary to obtain an anhydrous product. If the benzene solution is dried over magnesium sulfate and the benzene removed under reduced pressure, the diphenylacetaldehyde is contaminated with water.

5. The product obtained by this procedure, when treated with 2,4-dinitrophenylhydrazine,³ produced the 2,4-dinitrophenylhydrazone of diphenylacetaldehyde, m.p. 146.8–147.8°, in 94% yield.

3. Methods of Preparation

Diphenylacetaldehyde has been prepared by the isomerization of 1,2-dihydroxy-1,2-diphenylethane either thermally⁴ or in the presence of sulfuric acid^{5–7}, oxalic acid,⁸ or acetic anhydride.⁹ The aldehyde has also been produced by the reaction of 2,2-diphenyl-2-hydroxyethyl ether with sulfuric acid^{7,8} or oxalic acid,^{8,10} by the reaction of hydrochloric acid with 2-amino-1,1-diphenylethanol,¹¹ by the reaction of hydrobromic acid with 2-diethylamino-1,1-diphenylethanol,¹² by the hydrolysis of β,β -diphenylvinyl ethyl ether,¹³ by the thermal rearrangement of

deoxybenzoin,¹⁴ and by the hydrolysis and decarboxylation of the glycidic ester obtained from ethyl chloroacetate and benzophenone.¹⁵ Diphenylacetaldehyde has also been prepared by the isomerization of *trans*-stilbene oxide in the presence of sodium bisulfite¹⁶ or the isomerization of either *cis*- or *trans*-stilbene oxide in the presence of boron trifluoride etherate.³ The procedure chosen illustrates the ready isomerization of substituted ethylene oxides to carbonyl compounds. The procedure is applicable to substituted epoxides in which one of the carbon atoms of the oxirane ring is bonded either to two other carbon atoms or to an aromatic nucleus or a carbon-carbon double bond.

¹ Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

² *Org. Syntheses*, **38**, 83 (1958).

³ House, *J. Am. Chem. Soc.*, **77**, 3070 (1955).

⁴ Ramart-Lucas and Salmon-Legagneur, *Compt. rend.*, **186**, 1848 (1928).

⁵ Henze and Leslie, *J. Org. Chem.*, **15**, 901 (1950).

⁶ Tiffeneau, *Compt. rend.*, **142**, 1537 (1906); *Ann. chim. (Paris)*, [8]**10**, 322 (1907).

⁷ Stoermer, *Ber.*, **39**, 2288 (1906).

⁸ Danilov and Venus-Danilova, *Ber.*, **59B**, 1032 (1926).

⁹ Tiffeneau, *Compt. rend.*, **150**, 1181 (1910).

¹⁰ Behal and Sommelet, *Bull. soc. chim. France*, [3]**31**, 300 (1904).

¹¹ Thomas and Bettzieche, *Z. physiol. Chem.*, **140**, 261 (1924).

¹² Sou, *Bull. fac. sci. univ. franco-chinoise Peiping*, **1935**, No. 5, 1 [*C. A.*, **30**, 4463 (1936)].

¹³ Buttenberg, *Ann.*, **279**, 324 (1894).

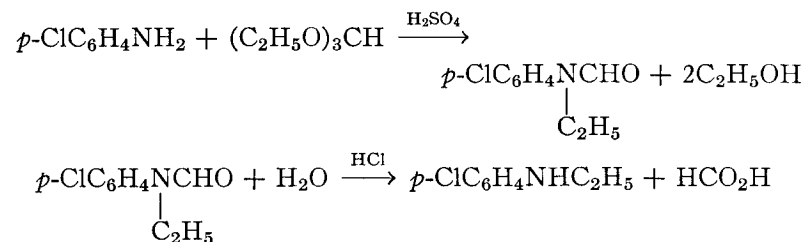
¹⁴ Brueur and Zincke, *Ann.*, **198**, 141 (1879).

¹⁵ Ecary, *Ann. chim. (Paris)*, [12]**3**, 445 (1948).

¹⁶ Klager and Kessler, *Ber.*, **39**, 1753 (1906).

N-ETHYL-*p*-CHLOROANILINE

(Aniline, *p*-chloro-N-ethyl-)



Submitted by ROYSTON M. ROBERTS and PAUL J. VOGT.¹

Checked by JAMES CASON and MILTON FINGER.

1. Procedure

A. *N-Ethyl-p-chloroformanilide*. In a 300-ml. round-bottomed flask, equipped with a side tubulature just large enough to accommodate a thermometer, are placed 63.8 g. (0.50 mole) of *p*-chloroaniline and 111 g. (0.75 mole) of triethyl orthoformate (Note 1), and then 2.0 g. (0.02 mole) of concentrated sulfuric acid is added with mixing. The flask is attached to a 30-cm. column 2 cm. in diameter packed with glass helices (Note 2), which is surmounted by a distillation head equipped with a thermometer and condenser. A thermometer is connected through a slip joint made from a short section of rubber tubing to the side tubulature so that its bulb is in the reaction mixture; then the flask is heated in an oil bath. When the temperature of the oil bath reaches 115–120°, the reaction mixture begins to boil, and ethanol soon begins to distil at a vapor temperature of 78–80° at the top of the column. During the course of about 1 hour the bath temperature is raised to about 175°. This promotes a steady distillation of ethanol at a rate which begins to decrease after 30 minutes. The amount of ethanol that distils (70–75 ml.) is always in excess of the stoichiometric amount. Finally, the reaction mixture is kept in the oil bath at 175–180° for 30 minutes (Note 3); an additional small amount of volatile material distils during this time.

After the reaction mixture has cooled somewhat the flask is disconnected from the column, a Claisen head is attached, and the product is distilled at reduced pressure (Note 4). After a fore-run of about 20 g. (not readily condensed below 40 mm. pressure), the faintly yellow product is collected at 124–126°/3 mm., weight 73–79 g. (80–86%), n_D^{25} 1.5525–1.5540 (Note 4).

B. *N-Ethyl-p-chloroaniline*. In a 500-ml. round-bottomed flask are placed 70 g. (0.38 mole) of *N*-ethyl-*p*-chloroformanilide and 170 ml. of 10% hydrochloric acid. The mixture is heated under reflux for 1 hour, cooled, then neutralized, and finally made basic with 15% potassium hydroxide solution. The lower layer of *N*-ethyl-*p*-chloroaniline is separated, and the aqueous layer is saturated with potassium carbonate and extracted with two 200-ml. portions of ether. The ether extracts are combined with the bulk of the product, washed with two 100-ml. portions of water, and then dried over calcium chloride. After the ether has been removed by distillation, the residue is distilled at reduced pressure from a 125-ml. Claisen flask. *N*-Ethyl-*p*-chloroaniline is collected at 108–110°/5 mm. or 149–150°/40 mm., n_D^{25} 1.5650–1.5661, weight 52–55 g. (87–92%) (Note 5).

2. Notes

1. The checkers used, without purification, white label grades of *p*-chloroaniline and triethyl orthoformate from Eastman Organic Chemicals; the submitters used triethyl orthoformate from Kay-Fries Chemicals Inc., New York.

2. It is most convenient to make connections with standard taper joints. The checkers used with equal satisfaction a 50-cm. column randomly packed with short sections of glass tubing.

3. The submitters report that during this heating period the temperature of the reaction mixture may rise as high as 185–190° on account of an exothermic reaction; however, the checkers did not observe this temperature rise of the reaction mixture. The submitters also report that in some of the preparations mentioned in Note 5 the reaction is more exothermic and the temperature may rise as high as 244°, but this does not cause difficulty.

4. The submitters distilled the product through the 30-cm. packed column which was wrapped with a heating tape for this purpose. If this is done, there are collected about 20 g. of recovered triethyl orthoformate at 65–67°/40 mm. and about 2 g. of ethyl *N*-*p*-chlorophenylformimidate at 82–83°/40 mm., followed by the product, which has n_D^{25} 1.5559. The checkers obtained the same results when this distillation was carried out through a fractionating column; however, the yield and properties of *N*-ethyl-*p*-chloroaniline obtained from this material were the same as those of amine obtained from material distilled through a Claisen head.

5. This method is suitable for the mono-*N*-alkylation of other primary aromatic amines. Trimethyl and triethyl orthoformate are commercially available, and other alkyl orthoformates can be obtained readily from them by transesterification.² The following have been prepared in a similar manner by the submitters.³

Product	Yield, %	B.P., °C./mm.	n_D (t , °C)
<i>N</i> -Methylaniline	44	104–105/40	1.5701 (22)
<i>N</i> -Ethylaniline	66	92–93/16	—
<i>N</i> -Isoamylaniline	58	149–151/40	1.5212 (25)
<i>N</i> -Methyl- <i>m</i> -toluidine	67	120–121/40	1.5557 (25)
<i>N</i> -Ethyl- <i>m</i> -toluidine	69	125–127/40	1.5451 (23)
<i>N</i> -Methyl- <i>p</i> -chloroaniline	77	141–142/40	1.5799 (25)

3. Methods of Preparation

N-Ethyl-*p*-chloroaniline has been prepared by alkylation of *p*-chloroaniline with ethyl bromide^{4,5} and by reduction of aceto-*p*-chloroanilide with lithium aluminum hydride.⁶ The present procedure, which is based on the results of an investigation by Roberts and Vogt,³ is a convenient general method for preparation of pure *N*-alkyl aromatic amines.

¹ Department of Chemistry, University of Texas, Austin, Texas.

² Alexander and Busch, *J. Am. Chem. Soc.*, **74**, 554 (1952); Roberts, Higgins, and Noyes, *J. Am. Chem. Soc.*, **77**, 3801 (1955).

³ Roberts and Vogt, *J. Am. Chem. Soc.*, **78**, 4778 (1956).

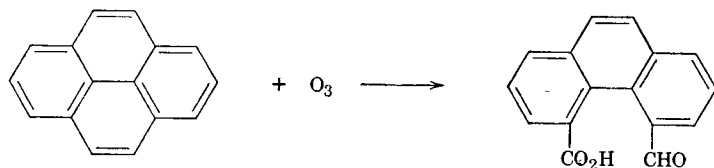
⁴ Hofmann, *Ann.*, **74**, 143 (1850).

⁵ Crowther, Mann, and Purdie, *J. Chem. Soc.*, **1943**, 58.

⁶ Bory and Mentzer, *Bull. soc. chim. France*, **1953**, 814.

5-FORMYL-4-PHENANTHROIC ACID

(4-Phenanthroic acid, 5-formyl-)



Submitted by R. E. DESSY and M. S. NEWMAN,¹
 Checked by J. D. ROBERTS and D. I. SCHUSTER.

1. Procedure

A solution of 25 g. (0.125 mole) of pyrene (Note 1) in 100 ml. of dimethylformamide (Notes 2 and 3) is treated with a 50% excess of ozone (Note 4). The solution of the ozonide is added at a moderate rate, with stirring, to 500 ml. of 1% aqueous acetic acid. The suspension is allowed to stand overnight (Note 5), and the resulting solid is collected by filtration and washed with water.

The moist solid is suspended in 200 ml. of 10% aqueous potassium hydroxide solution, and the suspension is boiled for 5 minutes. The hot solution is filtered, and the remaining solid is again extracted, using 100 ml. of potassium hydroxide solution.

To the dark-brown combined filtrates is added 100 ml. of potassium hypochlorite solution (Note 6), and the resulting solution is permitted to stand overnight. The mixture is then heated on a steam bath for 4 hours. The resulting orange solution is filtered while hot, and 100 ml. of 35% sodium hydroxide solution is added. The solution is cooled to 5°, the resulting solid is collected by filtration and washed with a small amount of saturated sodium chloride solution.

The moist sodium salt is digested with 50 ml. of cold 6 *N* hydrochloric acid, and after several hours the mixture is filtered and the resulting solid acid dried.

The crude acid is dissolved in 100 ml. of boiling dimethylformamide, and 100 ml. of hot glacial acetic acid is added. Water is added to the hot solution until it becomes cloudy, and then just enough dimethylformamide is added to render the solution clear again. It is cooled to 5°, and the resulting acid collected by filtration and washed with glacial acetic acid. Upon drying, 10–11.5 g. (32–38%) of 5-formyl-4-phenanthroic acid (Note 7), melting at 272–276° (Note 8), is obtained.

2. Notes

1. Technical pyrene, Reilly Tar and Chemical Corp., was employed. Purification did not improve the over-all yield, and purer pyrene is not sufficiently soluble in dimethylformamide.

2. Freshly distilled dimethylformamide should be employed. The yields with the technical grade solvent were very erratic.

3. Complete solution is attained by heating the mixture for 5 minutes on a steam bath.

4. An ozonizer similar to that described by Henne and Perilstein² was employed. At an oxygen flow rate of 30 l./hr. it produced about 30 millimoles of O₃ per hour (3% conversion). Under these conditions the ozonization of 25 g. of pyrene requires about 6 hours.

5. Filtration of the hydrolyzate immediately after decomposition is difficult because of the fine nature of the solid. Upon standing, coagulation takes place to yield a granular brown solid.

6. The potassium hypochlorite solution was prepared³ from the calcium hypochlorite sold by Mathieson Chemical Corporation under the trade name HTH. If the HTH reagent used is not fresh, it is found that subsequent heating of the filtrate with the potassium hypochlorite solution does not result in an orange solution. The solution remains dark brown, and the product is distinctly brown. The yield is not affected.

7. Unpublished experiments indicate that 5-formyl-4-phenanthroic acid exists mainly in the cyclic hydroxylactone form.

8. The checkers found that the melting point depends on the rate of heating. A reproducible melting point was obtained if

the sample was placed in the bath at 270° and the temperature raised at the rate of two degrees per minute.

3. Methods of Preparation

The only reported method of preparation of 5-formyl-4-phenanthroic acid is by the reaction described here.⁴

¹ The Ohio State University, Columbus, Ohio.

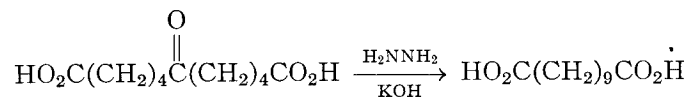
² Henne and Perilstein, *J. Am. Chem. Soc.*, **65**, 2183 (1943).

³ Newman and Holmes, *Org. Syntheses*, **17**, 66 (1937).

⁴ Vollmann, Becker, Corell, and Streeck, *Ann.*, **531**, 65 (1937).

HENDECANEDIOIC ACID

(Undecanedioic acid)



Submitted by LOIS J. DURHAM, DONALD J. MCLEOD, and JAMES CASON.¹

Checked by N. J. LEONARD, D. H. DYBVIG, and K. L. RINEHART, JR.

1. Procedure

A 500-ml. round-bottomed flask is attached by a well-lubricated ground-glass joint to a reflux condenser with a side take-off having a stopcock which may be opened to permit distillation. In the flask are placed 170 ml. of commercial diethylene glycol and 30 g. (0.46 mole) of potassium hydroxide (U.S.P., or reagent grade, 85%). This mixture is heated carefully (*Caution! Note 1*) until the potassium hydroxide begins to melt and go into solution; then the heat is removed intermittently until the exothermic dissolution is completed. After the solution has been cooled to 80–100°, the condenser is removed and there are added to the flask 35 g. (0.152 mole) of 6-ketohendecanedioic acid ² and 22 ml. (22.4 g., 0.38 mole) of commercial 85% hydrazine hydrate. The condenser is immediately replaced, and the mixture is

warmed cautiously until any exothermic reaction is complete and then heated under reflux for 1 hour.

A thermometer is suspended through the condenser by copper wire so that the bulb is in the heated liquid, the stopcock of the take-off attachment is opened, and the mixture is distilled sufficiently slowly so that the froth does not rise out of the flask. When the liquid temperature has reached 205–210° (after about 30 ml. of distillate has been collected), the stopcock in the take-off is closed, the thermometer is removed, and the mixture is heated under reflux for 3 hours. If the temperature is checked during this heating period, it is usually found to be in the range 190–200°.

At the end of the heating period the reaction mixture is cooled to about 100–110° (at lower temperatures a gelatinous precipitate separates) and is then poured into 150 ml. of water contained in a 1-l. Erlenmeyer flask. An additional 100 ml. of water is used to rinse the reaction flask. The diluted mixture is acidified to Congo red by slow addition of 6 *N* hydrochloric acid as the mixture is stirred vigorously to ensure conversion of any precipitated potassium salt to the free acid. The mixture is then cooled by tap water for at least 30 minutes (Note 2). The white precipitate is collected by suction filtration, transferred to a beaker, and is heated with about 250 ml. of water until the solid has melted (Note 3). As the mixture is cooled, it is stirred vigorously by hand until the oil has resolidified. After the mixture has been cooled again, the precipitated acid is collected by suction filtration, washed with water, and dried (Note 4). The yield of hendecanedioic acid, m.p. 110.5–112° (Note 5), is 28.5–30.6 g. (85–93%).

2. Notes

1. When the temperature becomes high enough for the potassium hydroxide to melt under the diethylene glycol, solution occurs rapidly with evolution of heat sufficient to drive material out of the top of the condenser if the source of external heat is not removed immediately. For this reason it is wise not to add the compound being reduced until after solution has been accom-

plished; moreover, in the case of keto acids there is some evidence that yields are lowered somewhat if the acid is added before solution of the potassium hydroxide. Since diethylene glycol does not present a serious fire hazard, this initial heating is probably best done with a small flame which may be easily removed quickly. Subsequent heating with an electric mantle is recommended.

2. Somewhat higher yields appear to be obtained when the mixture is allowed to stand overnight.

3. Remelting the solid acid over water removes occluded impurities, including salt and diethylene glycol. Moreover, acid which has crystallized in lumps is dried faster than the initial fine precipitate.

4. The submitters suggest recrystallization from benzene as a means of purification.

5. The acid is probably polymorphic,³ since the melting point varies somewhat with the rate of heating and a solidified melt remelts more sharply than do the original crystals.

3. Methods of Preparation

Hendecanedioic acid has been prepared by hydrolysis of the corresponding dinitrile, obtained from 1,9-dibromononane or 1,9-diiodononane;⁴⁻⁶ by oxidation of 11-hydroxyhendecanoic acid;^{7,8} by the Arndt-Eistert synthesis from 9-carbethoxynonanoyl⁹ and nonanedioyl chloride;¹⁰ and by the Willgerodt reaction on undecylenic acid.¹¹ The present method, previously described briefly,^{12,13} appears to represent the most convenient preparation of dibasic acids having an odd number of carbon atoms greater than ten. It has been applied to several other dibasic acids.¹⁴

¹ Department of Chemistry, University of California, Berkeley, California.

² Durham, McLeod, and Cason, *Org. Syntheses*, **38**, 38 (1958).

³ Dupré la Tour, *Ann. phys.*, **18**, 199 (1932).

⁴ von Braun and Danziger, *Ber.*, **45**, 1970 (1912).

⁵ Chuit, *Helv. Chim. Acta*, **9**, 264 (1926).

⁶ Arosenius, Stållberg, Stenhagen, and Tägtström-Eketorp, *Arkiv Kemi Mineral. Geol.*, **26A**, No. 19 (1948) [*C. A.*, **44**, 3883 (1950)].

⁷ Walker and Lumsden, *J. Chem. Soc.*, **79**, 1191 (1901).

⁸ Verkade, Hartman, and Coops, *Rec. trav. chim.*, **45**, 373 (1926).

⁹ Kawasaki, *J. Pharm. Soc. Japan*, **70**, 485 (1950) [*C. A.*, **45**, 5624 (1951)].

¹⁰ Canonica and Bacchetti, *Atti accad. nazl. Lincei Rend. Classe sci. fis. mat. e nat.*, **10**, 479 (1951) [*C. A.*, **48**, 6377 (1954)].

¹¹ Pattison and Carmack, *J. Am. Chem. Soc.*, **68**, 2033 (1946).

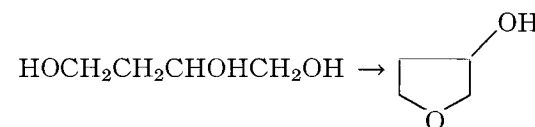
¹² Cason, Taylor, and Williams, *J. Org. Chem.*, **16**, 1187 (1951).

¹³ Canonica and Bacchetti, *Atti accad. nazl. Lincei Rend. Classe sci. fis. mat. e nat.*, **15**, 278 (1953) [*C. A.*, **49**, 8121 (1955)].

¹⁴ Blomquist, Johnson, Diuguid, Shillington, and Spencer, *J. Am. Chem. Soc.*, **74**, 4203 (1952).

3-HYDROXYTETRAHYDROFURAN

(Furan, 3-hydroxy-1,2,3,4-tetrahydro-)



Submitted by HANS WYNBERG and A. BANTJES.¹

Checked by JOHN C. SHEEHAN and GREGORY L. BOSHART.

1. Procedure

A 500-ml. flask is charged with 318 g. (3 moles) of 1,2,4-trihydroxybutane (Note 1) and 3 g. of *p*-toluenesulfonic acid monohydrate. A few Carborundum boiling chips are added, the flask is equipped with a 30.5-cm. Vigreux column, condenser, and receiver arranged for vacuum distillation, and the contents are heated, with swirling, to dissolve the acid (Note 2). The flask is then heated in a bath held at 180–220° so that 300–306 g. of distillate, b.p. 85–87°/22 mm., is collected over a period of 2–2.5 hours (Note 3). The colorless liquid obtained is refractionated, the same apparatus being used, and two fractions are collected: the first, 50–60 g., b.p. 42–44°/24 mm., n_D^{25} 1.3343, is mainly water. After a negligible intermediate fraction, 215–231 g. (81–88%) of pure 3-hydroxytetrahydrofuran, b.p. 93–95°/26 mm., n_D^{25} 1.4497, d_4^{20} = 1.095, is collected (Note 4).

2. Notes

1. Supplied by the General Aniline and Film Corporation.
2. Considerable darkening occurs even when the acid is well dispersed. The yield appears not to be affected.

3. Other temperatures are: b.p. 75–77°/16 mm.; 90–92°/28 mm. This first distillate contains 14% ($\pm 3\%$) of water as determined by interpolation of the refractive indices.

4. Calcd. $M_D = 21.64$. Found: 21.72. As obtained by this single fractionation the submitters found the alcohol to be analytically pure: Calcd. for $C_4H_8O_2$: C, 54.53; H, 9.14. Found: C, 54.74; H, 9.32. Others have reported: b.p. 50°/1 mm., n_D^{18} 1.4486, $d_4^{20} = 1.090$,² and b.p. 81°/13 mm., $d^{18} = 1.07$, n_D^{18} 1.4478.³

3. Methods of Preparation

3-Hydroxytetrahydrofuran has been obtained during the preparation of 1,2,4-trihydroxybutane,³ by hydrolysis of 4-chloromethyl-1,3-dioxane² and by acid catalyzed dehydration of 1,2,4-trihydroxybutane.⁴ The present procedure is similar to that described by Reppe.⁴

¹ Department of Chemistry, Tulane University, New Orleans, Louisiana.

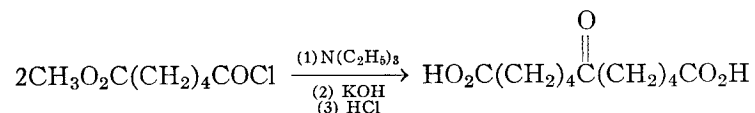
² Price and Krishnamurti, *J. Am. Chem. Soc.*, **72**, 5335 (1950).

³ Pariselle, *Ann. chim. (Paris)*, [8]**24**, 315 (1911).

⁴ Reppe, *Ann.*, **596**, 1 (1955), see p. 112; DBP 841 592 (1942), BASF (H. Krzika, E. Woldan).

6-KETOHENDECANEDIOIC ACID

(Undecanedioic acid, 6-oxo-)



Submitted by LOIS J. DURHAM, DONALD J. McLEOD, and JAMES CASON.¹

Checked by N. J. LEONARD, D. H. DYBVIC, and K. L. RINEHART, JR.

1. Procedure

In a 1-l. three-necked flask fitted with a sealed mechanical stirrer, a 125-ml. dropping funnel, a thermometer, and a drying tube filled with calcium chloride, are placed 500 ml. of dry ben-

zene (Note 1) and 89.3 g. (0.5 mole) of δ -carbomethoxyvaleryl chloride (Note 2). The thermometer is adjusted to extend into the stirred liquid but not into the path of the stirrer. The mixture is cooled, with stirring, to 3–5° in an ice bath, then 50.6 g. (0.5 mole) of triethylamine (Note 3) is added as rapidly as is consistent with keeping the temperature of the reaction mixture below 25° (3–5 minutes). When the mildly exothermic reaction has subsided, the ice bath is removed and a warm water bath is used to raise the temperature of the reaction mixture to 33–35° during 10–15 minutes. A heavy white precipitate of triethylamine hydrochloride separates. After the reaction mixture has been warmed to about 35°, the water bath is removed and stirring is continued without heating for 30 minutes.

The reaction mixture is filtered (Note 4) with suction, and the amine salt is washed with about 200 ml. of benzene. The filtrate and washings are combined and transferred to a 1-l. round-bottomed flask, benzene is removed at reduced pressure, and to the residue is added 500 ml. of 2 *N* aqueous potassium hydroxide. This mixture is heated under reflux for 4 hours, by which time the solution should become completely homogeneous. The cooled solution is extracted with three 100-ml. portions of ether, then acidified to Congo red with concentrated hydrochloric acid (approximately 95 ml.). After the solution has been cooled in ice for at least 1 hour, the precipitated white solid is collected by suction filtration, washed with water, and recrystallized from a minimal amount of hot water (105–125 ml. required at about 90°). The yield of colorless 6-ketohendecanedioic acid, m.p. 108–109° (Note 5) is 35–37 g. (60–64%).

2. Notes

1. A quantity of thiophene-free benzene is conveniently dried by distilling about one-fourth of it, then cooling the residue with protection from moisture by use of a calcium chloride tube.

2. This ester acid chloride is prepared by allowing 100 g. (0.63 mole) of redistilled commercial methyl hydrogen adipate (b.p. 155–156°/7 mm., 172–173°/13 mm.) to stand overnight at room temperature with 150 g. (1.25 moles) of thionyl chloride.

A Claisen head is attached, and the thionyl chloride is removed at aspirator pressure on a steam bath. A pump is attached, and the ester acid chloride is distilled; the yield is at least 94 g. (84%), b.p. 114–115°/1 mm.

3. Triethylamine purified by drying over sodium hydroxide pellets and distilling from α -naphthyl isocyanate was found to give no better results than amine which had been distilled through a half-meter Vigreux column and collected over the range 89.5–90°.

4. Frequently the flocculent precipitate of triethylamine hydrochloride is filtered with some difficulty; accordingly, a sufficiently large Büchner funnel should be used for the filtration.

5. Titration of this acid gives an equivalent weight in the range 115–116 (theory, 115). The highest melting point recorded for this acid is 111°.²

3. Methods of Preparation

6-Ketohendecanedioic acid has been prepared by the reactions described,^{3,4} by the dialkylation of diethyl acetonedicarboxylate with ethyl γ -iodobutyrate in the presence of sodium ethoxide followed by hydrolysis and decarboxylation,^{2,5} and by the permanganate oxidation of 6-(1'-cyclohexenyl)-1-hexene.⁶ The present method is a simplification of the procedure originally described by Sauer.³ This method is practical for the preparation of symmetrical keto dibasic acids and esters.⁷

¹ Department of Chemistry, University of California, Berkeley, California.

² English, *J. Am. Chem. Soc.*, **63**, 941 (1941).

³ Sauer, *J. Am. Chem. Soc.*, **69**, 2444 (1947).

⁴ Cason, Taylor, and Williams, *J. Org. Chem.*, **16**, 1187 (1951).

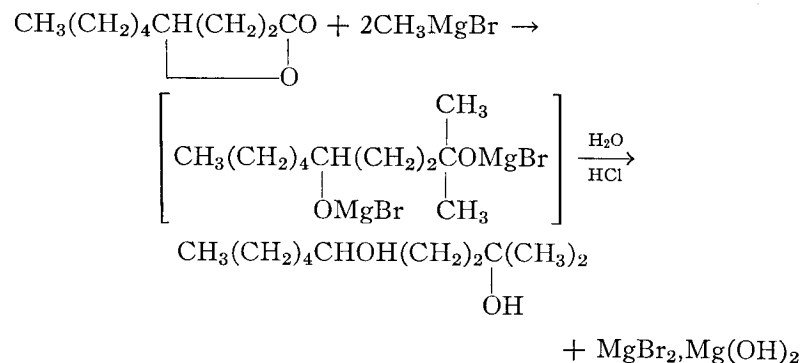
⁵ Leonard and Goode, *J. Am. Chem. Soc.*, **72**, 5404 (1950).

⁶ Kreuchunas, *J. Am. Chem. Soc.*, **75**, 4278 (1953).

⁷ Blomquist, Johnson, Diuguid, Shillington, and Spencer, *J. Am. Chem. Soc.*, **74**, 4203 (1952).

2-METHYL-2,5-DECANEDIOL

(2,5-Decanediol, 2-methyl-)



Submitted by J. COLONGE and R. MAREY.¹

Checked by V. BOEKELHEIDE and H. KAEMPFFEN.

1. Procedure

A 2-l. flask containing 1.0 l. of anhydrous ether (Note 1) is fitted with a stopper bearing an inlet tube dipping below the surface of the ether and an outlet tube protected by a calcium chloride drying tube. After the ether has been cooled thoroughly in an ice-salt bath, the flask is placed on a balance and cold methyl bromide (Note 2) is introduced through the inlet tube until the gain in weight is 200 g. (2.1 moles).

In a 3-l. three-necked flask, equipped with a sealed mechanical stirrer, reflux condenser, and a pressure-equalizing separatory funnel (Note 3), are placed 48 g. (2 g.-atoms) of magnesium turnings, 500 ml. of anhydrous ether, and a small crystal of iodine. The cold methyl bromide solution is transferred to the separatory funnel and slowly added, with stirring. The reaction starts spontaneously, and the remainder of the methyl bromide is added at a rate such that the solution boils gently under reflux. Generally, the addition is complete at the end of 1–2 hours and all the magnesium should be dissolved. After the stirred solu-

tion of methylmagnesium bromide is well cooled by using an ice bath, a solution of 78.0 g. (0.5 mole) of γ -nonanoic lactone (Note 4) in 100 ml. of dry ether is added slowly over a period of 30 minutes. When the addition is complete, the mixture is placed on a steam bath and boiled under reflux for 2 hours. Then the condenser is arranged for downward distillation (Note 5), and the ether is removed.

To the thick, syrupy residue is added 200 ml. of benzene, and, after the solution is cooled in an ice bath and the condenser is set for reflux, 350 ml. of water is slowly added through the separatory funnel, with stirring. This is followed by the cautious addition of 325 ml. of a 20% solution of hydrochloric acid, and stirring is continued until all the precipitate dissolves. The organic layer is then separated, and the aqueous layer and flask are washed with 50 ml. of benzene. The combined benzene extracts are washed successively with water, a 5% solution of sodium carbonate, and again with water. Concentration of the benzene solution gives 88.5 g. of an oily residue. Careful fractional distillation (Note 6) of this residue gives, after a fore-run, 53.0 g. (57%) of the pure 2-methyl-2,5-decanediol boiling at 65–69°/2 mm., n_D^{25} 1.4420.

2. Notes

1. Commercial anhydrous ether should be dried over sodium or sodium hydride before use.

2. Commercial methyl bromide (Eastman Kodak Company, Rochester, New York) was used without purification.

3. The separatory funnel is fitted to an adapter tube extending to the bottom of the flask so that the methyl bromide solution is introduced below the surface of the mixture. A drying tube is placed in the condenser outlet.

4. Commercial γ -nonanoic lactone (Aldrich Chemical Co., Milwaukee, Wisconsin) was purified by distillation prior to use. The refractive index of the pure lactone is n_D^{25} 1.4449.

5. As the removal of ether proceeds, the viscous solution becomes difficult to stir and stirring may be stopped without harm.

6. The checkers found that an ordinary Vigreux column was ineffective in separating lower-boiling impurities. An efficient

fractionating column 1 m. in length and of 5 mm. I.D. gave excellent results. The infrared spectrum of the product gave no evidence of impurities.

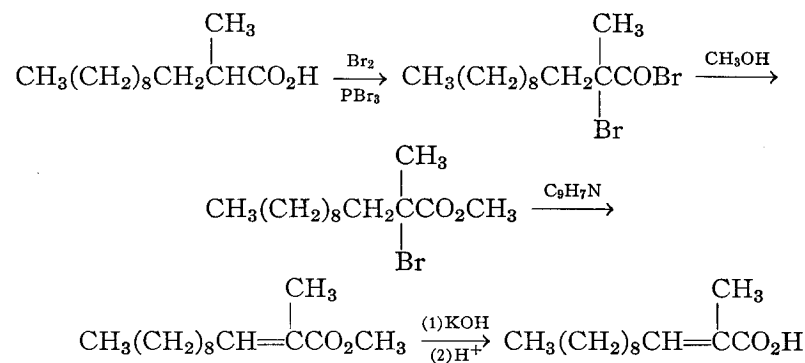
3. Methods of Preparation

The preparation of 2-methyl-2,5-decanediol has not been described elsewhere in the literature.

¹ École de Chimie Industrielle de Lyon and Établissement Descollonges Frères (Lyon).

trans-2-METHYL-2-DODECENOIC ACID

(trans-2-Dodecenoic acid, 2-methyl-)



Submitted by C. FREEMAN ALLEN and MAX J. KALM.¹

Checked by WILLIAM S. JOHNSON and H. W. WHITLOCK, JR.

1. Procedure

Caution! The bromination and debromination steps should be carried out in a hood.

Thirty grams (0.14 mole) of 2-methyldodecanoic acid is brominated exactly as described in the preparation of 2-methylene-dodecanoic acid.² The crude product, after the 18-hour heating period, is allowed to cool; then 56 ml. (1.4 moles) of commercial absolute methanol is added at such a rate that the exothermic re-

action is kept under control (Note 1). The resultant pale-orange two-phase mixture is heated under reflux with stirring for 15 minutes, cooled, and diluted with 150 ml. of water containing about 2 g. of sodium sulfite. The bromo ester is extracted with two portions (75 ml. and 25 ml.) of petroleum ether (Note 2). The extracts are combined, washed with water, and dried over anhydrous sodium sulfate. The solvent is removed by flash distillation of the filtered solution from a 250-ml. flask heated on a steam bath, and the last traces of solvent are eliminated by reducing the pressure with a water aspirator. The crude bromo ester remaining amounts to 41.5–42.5 g. and is thermally unstable to distillation at reduced pressure.

The crude bromo ester is mixed with 82.5 ml. (0.70 mole) of pure quinoline (Note 3) in a 250-ml. round-bottomed flask equipped with an air condenser, and the mixture is heated for 3 hours with an oil bath maintained at 160–170°. The black mixture is cooled, treated with 150 ml. of 20% hydrochloric acid, then shaken thoroughly with 200 ml. of petroleum ether (Note 2) until most of the tarry material has dissolved (Note 4). The aqueous phase is separated and washed with an additional 200 ml. of petroleum ether, and the combined organic extracts are washed with 10% hydrochloric acid and then with water. This washing cycle is repeated until the washes are colorless (two acid washes usually suffice); finally, the petroleum ether solution is washed once more with water. The organic layer is dried over anhydrous sodium sulfate, the solvent is flash-distilled as described above, and the residual liquid ester is distilled through a 61-cm. Podbielniak-type column (Note 5). The colorless unsaturated ester (Note 6) distils at 153–154°/14.5 mm. after a small fore-run. The yield is 22–27 g. (70–85.5% based on 2-methyldodecanoic acid), n_D^{25} 1.4520–31, λ_{\max} 214 m μ , ϵ 12,300, in hexane (Note 7), λ_{\max} 217 m μ , ϵ 12,800, in 95% ethanol.

The ester is hydrolyzed by heating under reflux for 1.5 hours with 50 ml. of 95% ethanol and 4.4 g. of 85% potassium hydroxide (0.066 mole) for each 10 g. (0.044 mole) of ester. Two-thirds of the ethanol is removed by distillation; then the residue is diluted with five volumes of water and acidified to Congo red with 5 *N* sulfuric acid. The organic acid is extracted with two

150-ml. portions of petroleum ether (Note 2), washed with water, and dried over anhydrous sodium sulfate. The petroleum ether is removed from the extracts by flash distillation as described above, and the residual acid is distilled at reduced pressure through a 61-cm. Podbielniak-type column (Note 5). The 2-methyl-2-dodecenoic acid, distilling at 166–168°/3 mm., is obtained in 68–83% over-all yield (20–24.5 g. from 22–27 g. of ester) (Notes 8 and 9), m.p. 28.5–32° to 29.5–32.4°, λ_{\max} 218 m μ , ϵ 12,900, in hexane (Note 7), λ_{\max} 216–217 m μ , ϵ 12,800, in 95% ethanol.

2. Notes

1. About 20 minutes is required. It may be desirable to cool the flask during the addition.

2. Commercial hexane, b.p. 65–68°, from petroleum fractionation is satisfactory.

3. Eastman Kodak Company white label *synthetic* quinoline was used. The use of coal tar quinoline introduces non-extractable aromatic impurities which contaminate the product.

4. The tarry material apparently consists of quinoline salts and some insoluble polymers.

5. A simplified Podbielniak column was employed.³ Other columns of comparable efficiency should be suitable.

6. This methyl *trans*-2-methyl-2-dodecenoate is contaminated with 10–15% of methyl 2-methylenedodecanoate. Little, if any, *cis* isomer, which boils at the same temperature as the methylene isomer, is present. The methylene ester, which boils less than 10° below the desired isomer, can be separated by careful fractionation through an efficient column such as the 1.5-m. simple Podbielniak-type column.³ The esters are more easily fractionated than are the higher-boiling acids.

A significant fraction of the α,β -unsaturated ester is transformed into an unidentified material of similar molecular weight when stored for several weeks in contact with air. The contaminant cannot be separated by ordinary distillation. The acid is much more stable to storage.

7. Optically pure hexane is preferred to ethanol as a solvent for absorption measurements below about 220 m μ . Commercial

hexane from petroleum fractionation can usually be rendered optically pure by stirring overnight twice with 15% fuming sulfuric acid (1 lb. of the acid to about 3 l. of hexane), followed by a wash with 5% aqueous sodium hydroxide and distillation from sodium hydroxide pellets.

8. The carbon-carbon double bond is not isomerized to a detectable extent during saponification of the ester or distillation of the acid; thus the 2-methyl-2-dodecenoic acid will have the same isomeric composition as the sample of ester from which it was obtained, and it consists entirely of α,β -unsaturated isomers.

9. *trans*-2-Methyl-2-dodecenoic acid, freed from isomeric impurities by fractionation through a 1.5-m. Podbielniak-type column, distilled at 146–147°/1.4 mm., λ_{\max} 217 m μ , ϵ 14,500, in hexane. Since several consecutive fractions showed these properties, they are believed to represent the properties of the pure isomer. The quantity of such material recovered is entirely dependent on the efficiency of the column and the distillation procedure. Pure samples of solid acids may be readily secured by crystallization. Those prepared⁴ by this procedure include: 2-methyl-2-eicosenoic acid, m.p. 66.3–67.6°, λ_{\max} 217 m μ , ϵ 13,490, in 54% yield; 2-methyl-2-hexacosenoic acid, m.p. 85.4–86.2°, λ_{\max} 217 m μ , ϵ 14,000, in 20% yield; 2,4-dimethyl-2-pentacosenoic acid, m.p. 69.5–70.3°, λ_{\max} 218 m μ , ϵ 14,550, in 19% yield. The lowered yields arise from difficulties in purification of the higher molecular weight isomers.

3. Methods of Preparation

2-Methyl-2-dodecenoic acid has been prepared by bromination of methyl 2-methyldodecanoate with N-bromosuccinimide, followed by dehydrobromination with quinoline and saponification of the ester.⁵ The present procedure is an adaptation of the method of Cason, Allinger, and Williams.⁵

¹ Department of Chemistry, University of California, Berkeley, California.

² *Org. Syntheses*, **38**, 47 (1958).

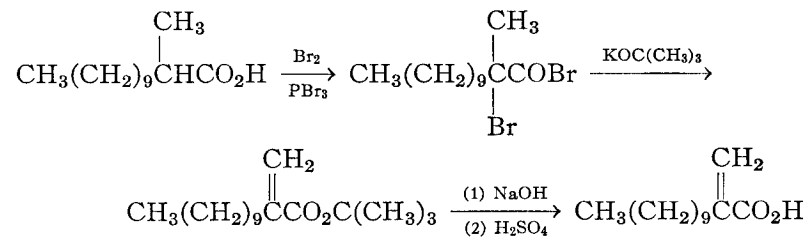
³ Cason and Rapoport, *Laboratory Text in Organic Chemistry*, p. 237, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1950.

⁴ Cason and Kalm, *J. Org. Chem.*, **19**, 1836 (1954).

⁵ Cason, Allinger, and Williams, *J. Org. Chem.*, **18**, 842 (1953).

2-METHYLENEDODECANOIC ACID

(Dodecanoic acid, 2-methylene-)



Submitted by C. FREEMAN ALLEN and MAX J. KALM.¹

Checked by WILLIAM S. JOHNSON and KENNETH L. WILLIAMSON.

1. Procedure

Caution! The bromination step should be carried out in a hood, and appropriate precautions should be employed in handling potassium (Note 1).

A 250-ml. three-necked flask fitted (glass joints) with a sealed mechanical glass stirrer, an addition funnel, and a reflux condenser capped with a calcium chloride drying tube is charged with 30.0 g. (0.140 mole) of 2-methyldodecanoic acid (Note 2) and 13.7 ml. (0.144 mole) of phosphorus tribromide (Note 3). Stirring is commenced, and 14.6 ml. (0.284 mole) of dry bromine (Note 4) is introduced slowly from the addition funnel until the reaction mixture retains a deep bromine coloration. The addition requires about 10 minutes to this stage (Note 5). The remainder of the bromine is then added all at once, and the flask heated in a bath maintained at 85–90° (Note 6) for 1.5 hours. An additional 3.6 ml. (0.07 mole) of bromine is then added and the heating at 85–90° continued for 18 hours. The mixture is cooled to room temperature and poured into a 1-l. separatory funnel containing about 150 ml. of water and 200 g. of cracked ice. The transfer is completed with the addition of 150 ml. of benzene, and the separatory funnel is shaken vigorously for

about 10 minutes, during which time most of the ice melts and the originally denser organic phase becomes the upper phase. The aqueous layer is separated and washed with 100 ml. of benzene, while the organic layer is vigorously shaken with another 200-ml. portion of ice water. This ice-water wash is also shaken with the 100-ml. portion of benzene and is then discarded. The combined benzene extracts are filtered through anhydrous sodium sulfate to remove suspended water; then the benzene and residual bromine are removed under reduced pressure (water aspirator) at a bath temperature of 70° or below (Note 7). The crude bromo acyl bromide is added slowly, at room temperature, to a solution of 13.7 g. (0.35 g. atom) of potassium metal (Note 1) in 300 ml. of dry *tert*-butyl alcohol (Note 1) contained in a well-dried 1-l. flask fitted with a reflux condenser that is protected from moisture with a calcium chloride drying tube. The resultant suspension is heated at reflux for 1 hour, cooled, and diluted with three volumes of water. The mixture, containing insoluble *tert*-butyl 2-methylenedodecanoate, is extracted with two 100-ml. portions of low-boiling petroleum ether (Notes 8 and 9). The combined petroleum ether extracts are washed with water and filtered through anhydrous sodium carbonate into a distilling flask from which the solvent is flash-distilled. The residual *tert*-butyl 2-methylenedodecanoate is then distilled through a 61-cm. Podbielniak-type column (Note 10) at 129–130°/3.0 mm.; the yield is 18.5–21 g. of semipurified ester, n_D^{25} 1.4405–1.4413 (Notes 11 and 12).

The *tert*-butyl 2-methylenedodecanoate is hydrolyzed by heating under reflux with ethanolic potassium hydroxide for 6 hours; 40 ml. of 95% ethanol and 3.7 g. (0.056 mole) of 85% potassium hydroxide are used for each 10 g. (0.037 mole) of the ester. The hydrolysis mixture is cooled, diluted with three volumes of water, and extracted with two 100-ml. portions of petroleum ether which are discarded. The aqueous phase is acidified to Congo red with 5 *N* sulfuric acid, and the 2-methylenedodecanoic acid is extracted with two 150-ml. portions of low-boiling petroleum ether (Note 8). These extracts are combined, washed with three 100-ml. portions of water to insure complete removal of *tert*-butyl alcohol, and dried by filtration through anhydrous sodium

sulfate. The solvent is removed by flash distillation, and the acid is subjected to rapid distillation from a Claisen flask (Note 13). 2-Methylenedodecanoic acid containing less than 5% of 2-methyl-2-dodecenoic acid is collected at 149–151°/1.7 mm., m.p. about 32°, λ_{\max} 209 m μ , ϵ 7800, in hexane (Note 14). The yield is 10.5–12 g. (35–41% from 2-methyldodecanoic acid), not including the acid obtained on acidification of the dehydrohalogenation mixture (Note 9).

2. Notes

1. The precautions for handling potassium and the procedure for preparing anhydrous potassium *tert*-butoxide have already been described.²

2. 2-Methyldodecanoic acid was prepared as follows according to the method of Cason, Allinger, and Williams.³ A three-necked flask fitted with a sealed mechanical stirrer, dropping funnel, and efficient reflux condenser is charged with 1.4 l. of absolute ethanol; then, while stirring, 48.3 g. (2.1 g. atoms) of sodium metal is added gradually in small pieces. The dropping funnel is charged with 383 g. (2.2 moles) of diethyl methylmalonate (Matheson, Coleman and Bell) which is added to the sodium ethoxide solution over a period of about 20 minutes; then the mixture is boiled under reflux for 5 minutes. The dropping funnel is charged with 442 g. (2.0 moles) of *n*-decyl bromide (Eastman Kodak Company, white label brand) which is added to the mixture as rapidly as is allowed by the exothermic reaction. After the addition is complete (about 20 minutes), the mixture is boiled under reflux for 2 hours, then neutralized with a few drops of glacial acetic acid. About two-thirds of the alcohol is removed by distillation, and 2 l. of water is added to the residue. The organic phase is separated, and the aqueous phase extracted with three 250-ml. portions of benzene. The organic phase and extracts are combined, washed with water, and dried over anhydrous sodium sulfate. The residue obtained upon evaporation of the solvent is treated with a solution of 447.5 g. of 85% potassium hydroxide pellets in 3.5 l. of 95% ethanol and the mixture heated at reflux, with stirring, for 4 hours. About two-

thirds of the solvent is removed by distillation, 3 l. of water is added, followed by sufficient (about 2 l.) 6 *N* sulfuric acid (cooling is necessary) to bring the *pH* of the solution to 1–2. The organic phase is separated, and the aqueous phase (containing some precipitated sulfates) is extracted with two portions of ether. The organic phase and extracts are combined, washed with water, then with saturated sodium chloride solution, and finally dried over anhydrous sodium sulfate. The residue obtained upon evaporation of the ether is heated at 180–190°, at which temperature decarboxylation occurs smoothly over a 20-minute period. The material is then distilled from a modified Claisen flask. The yield of product, b.p. 159–161°/4.4 mm., is 262–318 g. (61–74%), n_D^{25} 1.4404–1.4408.

3. Phosphorus tribromide (Eastman Kodak Company, white label brand) was freshly distilled before use. The full molar equivalent accelerates the desired α -bromination.

4. Bromine is conveniently dried over phosphorus pentoxide, then filtered into the addition funnel through a plug of glass wool.

5. The first mole equivalent of bromine reacts with the phosphorus tribromide to form the solid pentabromide which, in turn, is rapidly consumed in the formation of the acyl bromide.

6. The temperature is critical. At lower temperatures the reaction is very slow, and at higher temperatures partial dehydrobromination and subsequent allylic bromination result in contamination of the product with dienoic acid, as evidenced by the characteristic intense absorption at 275 $m\mu$ in hexane.

7. Higher temperatures at this point tend to promote dehydrobromination under the acidic conditions with the formation of 2-methyl-2-dodecenoic acid.

8. Commercial hexane from petroleum fraction (b.p. 65–68°) is satisfactory.

9. Acidification of the alkaline aqueous layer to Congo red with 5 *N* sulfuric acid liberates 2–4 g. of crude 2-methylenedodecanoic acid which can be isolated by extraction with petroleum ether as described below. Distillation of such material gave a product which did not crystallize readily.

10. A simplified Podbielniak column⁴ was employed. Other columns of comparable efficiency should be suitable.

11. If the distillation is carried out in a Claisen flask, the final product is impure, apparently contaminated with about 10% of 2-methyl-2-dodecenoic acid.

12. Pure *tert*-butyl 2-methylenedodecanoate may be isolated by refractionation of this product through an efficient column. The yield in such an experiment was 15–17 g. of material with n_D^{25} 1.4400.

13. Fractionation through a column results in some isomerization.

14. 2-Methylenedodecanoic acid, free from any isomeric impurities, can be obtained by recrystallization from acetone. The pure acid is recovered in over 70% yield, m.p. 33.3–34.2°, λ_{max} 210 $m\mu$, ϵ 7500, in hexane. It is very difficult to obtain pure methylene acid from Claisen-distilled *tert*-butyl ester (cf. Note 11).

3. Methods of Preparation

This preparation is based on the method of Cason, Allinger, and Williams.³

¹ Department of Chemistry, University of California, Berkeley, California.

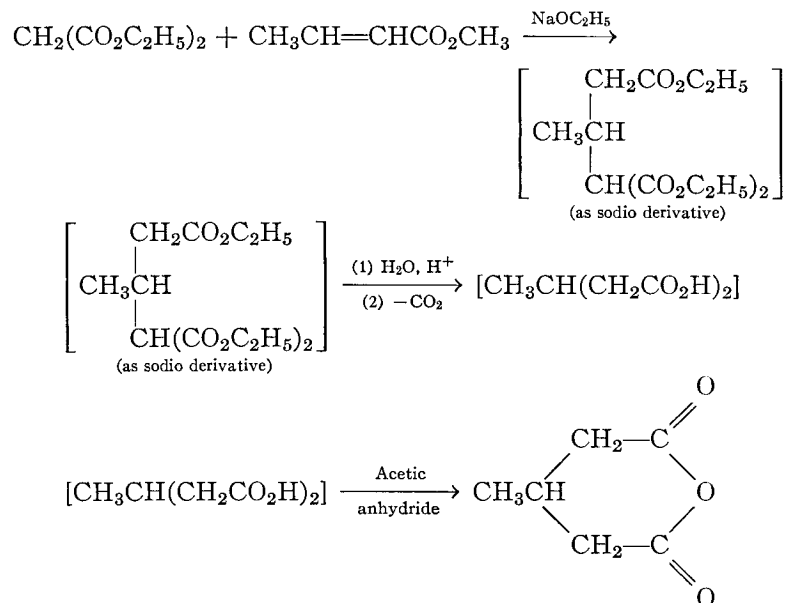
² *Org. Syntheses*, **30**, 18 (1950).

³ Cason, Allinger, and Williams, *J. Org. Chem.*, **18**, 842 (1953).

⁴ Cason and Rapoport, *Laboratory Text in Organic Chemistry*, p. 237, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1950.

β-METHYLGLUTARIC ANHYDRIDE

(Glutaric anhydride, 3-methyl-)

Submitted by JAMES CASON.¹

Checked by B. C. McKUSICK, R. D. SMITH, and W. R. HATCHARD.

1. Procedure

A. *Triethyl 2-methyl-1,1,3-propanetricarboxylate* (not isolated). A 1-l. three-necked flask is fitted with a mechanical stirrer, a reflux condenser protected by a calcium chloride tube, and a 250-ml. dropping funnel. All parts of the apparatus should be scrupulously dry. Three hundred milliliters of anhydrous ethanol (Note 1) is placed in the flask, and 14.1 g. (0.61 g. atom) of clean sodium, cut in pieces as large as will easily pass through a neck of the flask, is added rapidly. The neck of the flask is immediately closed, and the mixture is stirred until all the sodium has dissolved; the cooling bath is removed, and heat is applied if the reaction becomes sluggish at the end.

After all the sodium has dissolved, a mixture of 115 g. (0.72 mole) of diethyl malonate (Note 2) and 60 g. (0.60 mole) of methyl crotonate (Note 2) is added from the separatory funnel. This addition is made as rapidly as is consistent with keeping the exothermic reaction under control. After the exothermic reaction has subsided, the mixture is heated for 1 hour under reflux with stirring. An oil bath is recommended for heating. At the end of the heating period the condenser is changed to a position for distilling, and the temperature of the oil bath is raised sufficiently to distil alcohol fairly rapidly from the stirred mixture. Distillation is continued until most of the alcohol has been distilled. There is left a residue of the sodio derivative of triethyl 2-methyl-1,1,3-propanetricarboxylate (Note 3). If water is added to obtain the free ester, considerable heat is generated and cooling must be adequate to prevent partial hydrolysis of the ester by the alkali liberated. For present purposes there is no advantage in attempting isolation of the ester, and the residue is processed as described below.

B. *β-Methylglutaric anhydride*. The residue described above is cooled in an ice bath during the successive addition of 200 ml. of water and 450 ml. of concentrated hydrochloric acid. The resultant mixture is heated under reflux, with stirring, for 8 hours (Note 4). The condenser is again set for distillation, the bath temperature is raised, and, with continued stirring, water and alcohol are distilled. The bath is finally heated to 180–190° until gas evolution ceases (usually about 1 hour).

The stirrer is removed, 125 ml. of technical acetic anhydride is added to the residue, and, after thorough mixing, the mixture is heated on a steam bath for 1 hour. The condenser protected by a calcium chloride tube is left attached, and the other necks of the flask are closed. At the end of the heating period salt is removed from the cooled reaction mixture by filtering it with suction, using a filter aid mat, into a 250-ml. Claisen flask. The reaction vessel and filter are washed with a few milliliters of acetic acid.

The combined filtrate and washings are distilled at reduced pressure, using a water pump, until all acetic acid and acetic anhydride have been removed. An oil pump is then connected,

and the distillation is continued. β -Methylglutaric anhydride is collected at 118–122°/3.5 mm. The yield of semisolid anhydride (Note 5) is 46–58 g. (60–76%) (Note 6).

2. Notes

1. Commercial absolute ethanol from a freshly opened bottle is often satisfactory. Otherwise it can be dried by treatment with sodium,² sodium ethoxide and diethyl phthalate,³ magnesium methoxide,⁴ or aluminum *tert*-butoxide.⁵

2. Because commercial diethyl malonate is likely to contain small amounts of water and acid, it should be distilled from a Claisen flask at reduced pressure before use. The material used should be collected over a two- or three-degree range. The boiling point of malonic ester is 98°/20 mm.

Commercial methyl crotonate is rather impure and should be distilled at atmospheric pressure through a simple Vigreux or packed column which is 40–60 cm. in length. The fraction used should be collected over a two-degree range, and 70–85% of material boiling in such a range may usually be obtained from the commercial product. The boiling point is 117–118°.

3. Because of transesterification, the ester is principally the triethyl ester.

4. Sometimes the mixture becomes homogeneous after 3–5 hours, and heating can be stopped. At other times oily material remains even after 8 hours, but nothing is gained by further heating.

5. Pure β -methylglutaric anhydride melts at 46°.⁶ The β -methylglutaric anhydride obtained in this preparation varies in its appearance at 25° from an almost completely crystalline mass to a mixture of about one-third solid and two-thirds liquid. However, the submitter has found that product of either appearance can be converted to methyl hydrogen β -methylglutarate in 80–85% yield. Further purification is troublesome, and the product of the present procedure is pure enough for most purposes.

6. The submitter has obtained yields of 85–90%.

3. Methods of Preparation

β -Methylglutaric anhydride is obtained from the acid, which has been prepared by condensation of acetaldehyde with cyanoacetamide.^{7,8} The present method, which is a simplification of that published by Ställberg-Stenhagen,⁹ gives a higher yield and is much better adapted to the preparation of large quantities.

¹ Department of Chemistry, University of California, Berkeley, California.

² Kaufmann and Dreger, *Org. Syntheses*, Coll. Vol. 1, 259 (1941).

³ Manske, *Org. Syntheses*, Coll. Vol. 2, 155 (1943).

⁴ Marvel and Hager, *Org. Syntheses*, Coll. Vol. 1, 249 (1941).

⁵ Adkins and Gillespie, *Org. Syntheses*, Coll. Vol. 3, 672 (1955).

⁶ Darbishire and Thorpe, *J. Chem. Soc.*, 87, 1717 (1905).

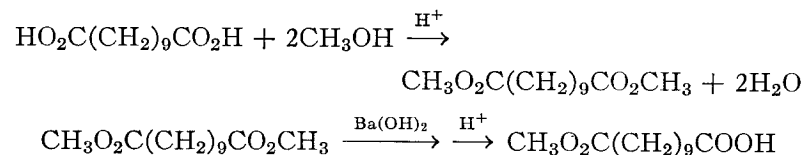
⁷ Day and Thorpe, *J. Chem. Soc.*, 117, 1465 (1920).

⁸ Kent and McElvain, *Org. Syntheses*, Coll. Vol. 3, 591 (1955).

⁹ Ställberg-Stenhagen, *Arkiv Kemi Mineral. Geol.*, 25A, No. 10 (1947) [*C. A.*, 42, 5851 (1948)].

METHYL HYDROGEN HENDECANEDIOATE

(Undecanedioic acid, monomethyl ester)



Submitted by LOIS J. DURHAM, DONALD J. MCLEOD, and JAMES CASON.¹

Checked by N. J. LEONARD, D. H. DYBVIG, and K. L. RINEHART, JR.

1. Procedure

Dimethyl hendecanedioate is prepared by heating 23 g. (0.106 mole) of hendecanedioic acid² under reflux for 2 hours with a solution of 8 ml. of concentrated sulfuric acid in 80 ml. of methanol. After the reaction mixture has been diluted with 3 volumes of water, it is extracted with two 75-ml. portions of benzene. The benzene extracts are washed successively with 250-ml. portions of water, 5% aqueous sodium carbonate solution, and

water. After benzene has been removed under reduced pressure, the residue (Note 1) is transferred to a 250-ml. Erlenmeyer flask containing 127 ml. of a 0.915 *N* solution of barium hydroxide (0.058 mole) in commercial anhydrous methanol (Note 2). The flask is immediately closed with a soda-lime tube and swirled to mix the solution. The barium salt of the half ester begins to precipitate after about 2 minutes.

After the flask has been allowed to stand at room temperature (20–25°) for at least 17 hours (Note 3), the barium salt is collected by suction filtration and washed with about 20 ml. of methanol (Note 4). The moist barium salt is shaken for a few minutes in a separatory funnel with a mixture of 100 ml. of 4 *N* hydrochloric acid and 100 ml. of ether. The aqueous layer, together with any precipitated barium chloride, is removed and extracted again with 100 ml. of ether. The two ether extracts are combined and washed with three 100-ml. portions of water, the solvent is removed, and the residue (Note 5) is distilled through a half-meter column (Note 6). There is essentially no fore-run (see Note 4). The pure half ester is collected at 165–168°/2 mm., weight 14.6–15.7 g. (60–64%), m.p. 44–46° (Note 7).

2. Notes

1. The submitters state that the residue may be distilled to give dimethyl hendecanedioate in 98% yield (25.5 g.).

2. An approximately 1.0 *N* solution of *anhydrous* barium hydroxide in methanol is prepared, and the exact normality is determined by titration. The checkers employed 143 ml. of an 0.814 *N* solution of barium hydroxide in anhydrous methanol. This procedure is not suitable for making ethyl esters on account of the low solubility of barium hydroxide in ethanol.

3. Periodic titration of aliquots of the reaction mixture has shown that after 16 hours about 95% of the original barium hydroxide has reacted.

4. If an insufficient amount of methanol is employed to wash the precipitate, a considerable quantity of recovered diester, b.p. ca. 145°/2 mm., is obtained as a fore-run in the fractional distillation of the product. The diester may be recovered by dilution of the filtrate with water and extraction.

5. The crude product obtained directly from the barium salt is 90–95% half ester, and the remainder is diacid. This material may be used directly in reactions where small amounts of diacid are not objectionable; however, distillation is necessary in order to obtain a pure sample of half ester. This distillation is simplified because there is no lower-boiling diester and only a small amount of higher-boiling diacid.

6. The submitters used a simple type of Podbielniak column.³ The checkers used a 122-cm. column of similar design.

7. Titration of this half ester gives an equivalent weight, within experimental error, of the calculated value of 230.3. The yield in this preparation may be regarded as close to theoretical on the basis of recovery and re-use of diacid and diester.

3. Methods of Preparation

Methyl hydrogen hendecanedioate has been reported as a by-product in the ozonolysis of methyl 11-dodecenoate,⁴ but the only preparative procedure reported is that presently described.⁵ Half esters have usually been prepared by partial esterification⁶ and direct fractional distillation of the three products of the reaction; however, some modification⁷ of this procedure is required for the higher-boiling half esters. The present method^{5,8} is considerably less laborious than the partial esterification procedure, and is a particular advantage for higher-boiling esters where a prolonged fractional distillation at high temperatures permits disproportionation of the half ester. This method is not satisfactory for lower-molecular-weight half esters, for their salts are too soluble in methanol. Sebacic acid gives satisfactory results by this method; azelaic acid, poor results; and lower-molecular-weight dibasic acids fail to give significant amounts of half ester.

¹ Department of Chemistry, University of California, Berkeley, California.

² Durham, McLeod, and Cason, *Org. Syntheses*, **38**, 34 (1958).

³ Cason and Rapoport, *Laboratory Text in Organic Chemistry*, p. 237, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1950.

⁴ Lycan and Adams, *J. Am. Chem. Soc.*, **51**, 625 (1929).

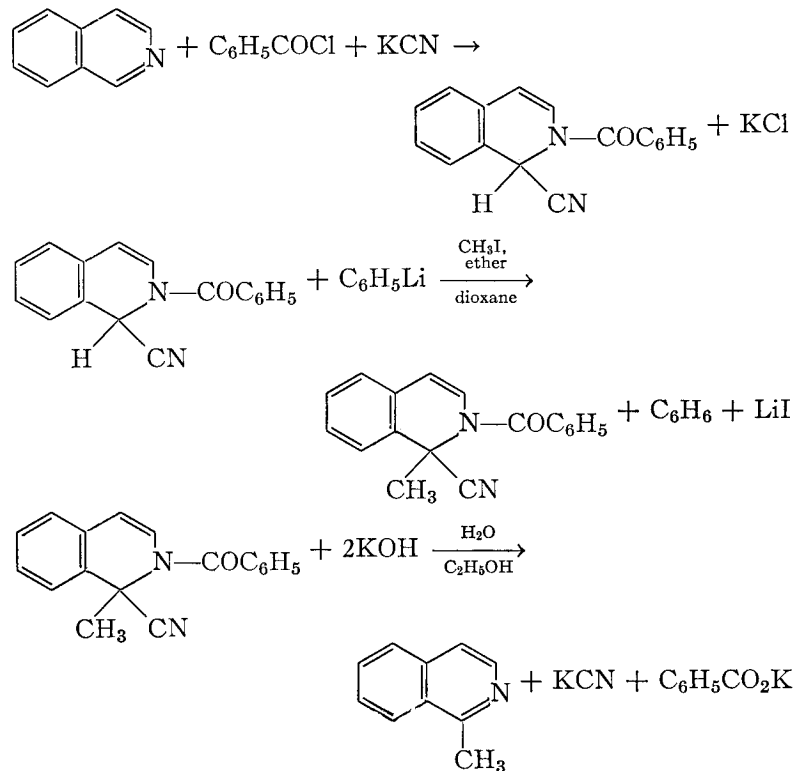
⁵ Cason, Taylor, and Williams, *J. Org. Chem.*, **16**, 1187 (1951).

⁶ Swann, Oehler, and Buswell, *Org. Syntheses*, Coll. Vol. **2**, 276 (1943).

⁷ Jones, *J. Am. Chem. Soc.*, **69**, 2350 (1947).

⁸ Signer and Sprecher, *Helv. Chim. Acta*, **30**, 1001 (1947).

1-METHYLISOQUINOLINE

Submitted by J. WEINSTOCK and V. BOEKELHEIDE.¹

Checked by N. J. LEONARD, TERRY W. MILLIGAN, and WILLIAM R. SHERMAN.

1. Procedure

Caution! All the operations should be carried out in a well-ventilated hood because of the toxic nature of hydrogen cyanide and the cyanide solutions.

A. *1-Cyano-2-benzoyl-1,2-dihydroisoquinoline*² (*Reissert's compound*³) (*Note 1*). In a 5-l. three-necked flask equipped with a Hershberg stirrer, a dropping funnel, and a condenser is placed a

solution of 391 g. (6.0 moles) of potassium cyanide in 2.5 l. of water and 258 g. (2.0 moles) of isoquinoline (freshly distilled from zinc dust). The mixture is maintained below 25° by immersion in an ice bath (*Note 2*). The stirrer is started, and, when the isoquinoline has formed an emulsion with the aqueous solution, 562 g. (4.0 moles) of benzoyl chloride is added over 3 hours. The stirring is continued another hour or until the Reissert's compound has separated as small, hard, tan spheres. The reaction mixture is cooled further in the ice bath, and the product is collected on a large Büchner funnel. It is washed on the funnel with successive portions of 400 ml. of water, 400 ml. of 3 *N* hydrochloric acid, and 500 ml. of water. The product is then recrystallized from 2–3 l. of commercial absolute ethanol using 2.5 g. of activated carbon to effect partial decolorization of the solution. The hot filtration to remove the carbon is done by means of a heated Büchner funnel. The filtrate is cooled in an ice bath and filtered when cold. Long standing in the presence of the supernatant liquid causes the adsorption of dark material by the product. The cream-colored crystals which separate are collected on a Büchner funnel, washed with 100 ml. of cold 95% ethanol, and dried in air overnight. The yield of dry 1-cyano-2-benzoyl-1,2-dihydroisoquinoline, m.p. 125–127°, sufficiently pure for use in the next step, is 303–400 g. (58–77%).

B. *2-Benzoyl-1-cyano-1-methyl-1,2-dihydroisoquinoline*. A 3-l. round-bottomed flask, a 500-ml. dropping funnel, a condenser, and a stirrer are dried in an oven and then arranged so that a nitrogen atmosphere can be maintained in the flask with the use of a mercury bubbler. The apparatus is flushed with dry nitrogen for 1 hour, and 83.5 g. (0.32 mole) of 1-cyano-2-benzoyl-1,2-dihydroisoquinoline, 350 ml. of dry dioxane (*Note 3*), and 100 ml. of anhydrous ether are added. The stirrer is started, and, when the solid is dissolved completely, the flask is immersed in an ice-salt bath at –10°. Then 450 ml. of a 0.78 *N* ether solution of phenyllithium (0.35 mole) (*Note 4*) is added dropwise, with stirring, during 30 minutes. The reaction mixture turns a deep red, and as the addition is continued a red solid separates. Ten minutes after the addition is complete 56.2 g. (0.40 mole) of methyl iodide is added, and the reaction mixture

is stirred in the cold for 2 hours, then overnight at room temperature. The reaction mixture is transferred to a separatory funnel and washed with three 50-ml. portions of water. The organic solution is filtered, and the solvent is removed under reduced pressure. If the residue does not crystallize immediately upon evaporation of the solvent, crystallization may be induced by scratching the sides of the flask and cooling. The crystals are transferred to a Büchner funnel, washed on the funnel with 50 ml. of cold 95% ethanol, and dried. The yield of dry 2-benzoyl-1-cyano-1-methyl-1,2-dihydroisoquinoline in the form of cream-colored crystals, m.p. 120–122°, is 62–63 g. (71–72%) (Note 5).

C. *1-Methylisoquinoline*. In a 500-ml. round-bottomed flask equipped with a reflux condenser are placed 62.2 g. (0.227 mole) of 2-benzoyl-1-cyano-1-methyl-1,2-dihydroisoquinoline, 50 ml. of 95% ethanol, and a solution of 32.0 g. (0.57 mole) of potassium hydroxide in 100 ml. of water. The mixture is heated under reflux for 1.5 hours, during which time the solid dissolves and the solution becomes homogeneous. After the solution has cooled, it is extracted with four 75-ml. portions of ether. The combined ethereal extracts are washed with two 25-ml. portions of water and dried with anhydrous magnesium sulfate. After removal of the drying agent by filtration and of the solvent by concentration under vacuum, the residue is distilled under reduced pressure to give 24–26 g. (74–80%) of colorless 1-methylisoquinoline, b.p. 81°/1 mm.; n_D^{25} 1.6102, n_D^{20} 1.6119 (Note 6).

2. Notes

1. This is essentially the procedure of Padbury and Lindwall.²
2. If the mixture is not kept cold during the addition of the benzoyl chloride, the product is likely to be highly colored.
3. The dioxane is dried as described by Fieser.⁴ It is kept in a glass-stoppered bottle sealed with wax. The ether is commercial anhydrous ether dried over sodium wire.
4. A convenient preparation of phenyllithium is described by Wittig.⁵ The ethereal solution may be titrated by adding an aliquot to water and titrating to the methyl orange end point with standardized hydrochloric acid.

5. Another 10 g. (11%) of impure 2-benzoyl-1-cyano-1-methyl-1,2-dihydroisoquinoline may be obtained by adding water to the cold mother liquor until it becomes turbid. The mixture is heated until the turbidity disappears, and the resulting solution is cooled slowly, then refrigerated. The additional product obtained by this method is contaminated with Reissert's compound and should not be used in the next step if pure 1-methylisoquinoline is desired.

6. This method may be used to prepare other 1-substituted isoquinolines. The submitters have prepared 1-benzylisoquinoline and 1-butyloisoquinoline by this method.⁶

3. Methods of Preparation

1-Methylisoquinoline has been prepared by the catalytic dehydrogenation of 1-methyl-3,4-dihydroisoquinoline prepared by the Bischler-Napieralski reaction, which involves treating β -phenylethylacetamide with a strong dehydrating reagent at elevated temperatures.^{7–12} 1-Methyl-3,4-dihydroisoquinoline has been prepared from β -phenylethylacetamide by using polyphosphoric acid, and the same reagent produced some 1-methylisoquinoline from N-acetyl-*dl*-phenylalanine.¹³ 1-Methylisoquinoline has also been prepared from β -phenyl- β -hydroxyethylacetamide by using phosphorus pentoxide,¹⁴ and by cyclization of the Schiff base obtained from acetophenone and aminoacetal¹⁵ or from α -phenylethylamine and glyoxalsemiacetal.¹⁶

¹ Department of Chemistry, University of Rochester, Rochester, New York.

² Padbury and Lindwall, *J. Am. Chem. Soc.*, **67**, 1268 (1945).

³ Reissert, *Ber.*, **38**, 3427 (1905).

⁴ Fieser, *Experiments in Organic Chemistry*, 2nd ed., p. 369, D. C. Heath and Co., Boston, 1941.

⁵ Wittig, *Newer Methods of Preparative Organic Chemistry*, p. 576, Interscience Publishers, Inc., New York, 1948; see also *Org. Syntheses*, Coll. Vol. **3**, 757 (1955).

⁶ Boekelheide and Weinstock, *J. Am. Chem. Soc.*, **74**, 660 (1952).

⁷ Whaley and Hartung, *J. Org. Chem.*, **14**, 650 (1949).

⁸ Leonard and Boyer, *J. Am. Chem. Soc.*, **72**, 2980 (1950).

⁹ Späth, Berger, and Kuntara, *Ber.*, **63B**, 134 (1930).

¹⁰ Burrows and Lindwall, *J. Am. Chem. Soc.*, **64**, 2430 (1942).

¹¹ Dey and Ramanathan, *Proc. Natl. Inst. Sci. India*, **9A**, 193 (1943).

¹² Pietet and Kay, *Ber.*, **42**, 1973 (1909).

¹³ Snyder and Werber, *J. Am. Chem. Soc.*, **72**, 2962 (1950).

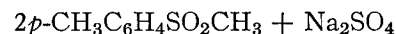
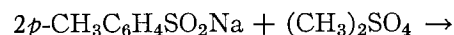
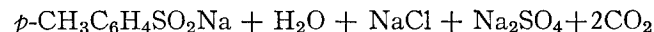
¹⁴ Mills and Smith, *J. Chem. Soc.*, **121**, 2724 (1922); Pictet and Gams, *Ber.*, **43**, 2384 (1910).

¹⁵ Pomeranz, *Monatsh. Chem.*, **15**, 299 (1894).

¹⁶ Schlittler and Müller, *Helv. Chim. Acta*, **31**, 914 (1948).

METHYL *p*-TOLYL SULFONE

(Sulfone, methyl *p*-tolyl)



Submitted by L. FIELD and R. D. CLARK,¹

Checked by JOHN C. SHEEHAN and M. GERTRUDE HOWELL.

1. Procedure

In a 4-l. beaker (Note 1) provided with a mechanical stirrer and thermometer are placed 600 g. (4.76 moles) of anhydrous sodium sulfite, 420 g. (5.0 moles) of sodium bicarbonate, and 2.4 l. of water. The mixture is heated on a hot plate at 70–80° and is maintained at this temperature by switching the hot plate off occasionally, while 484 g. (2.54 moles) of *p*-toluenesulfonyl chloride (Note 2) is added in portions of 5–10 g., with stirring, during 3 hours. When addition is complete, the mixture is heated and stirred at 70–80° for 1 hour (Note 3). The mixture is then removed from the hot plate and allowed to stand for 4 to (preferably) 10 hours.

The solid sodium *p*-toluenesulfinate which separates is collected by filtration and mixed with 400 g. (4.76 moles) of sodium bicarbonate and 490 g. (370 ml., 3.88 moles) of dimethyl sulfate (Note 4) in a 3-l. three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, and a 1-l. separatory funnel containing 925 ml. of water. Water (75–100 ml.) is added from the separatory funnel to make the mixture fluid enough for stirring. The remainder of the water is then added

dropwise, with stirring, during 3 hours. The mixture is then heated under reflux for 20 hours.

After the mixture is cooled to 75°, 200 ml. of benzene is added (Note 5). The mixture is stirred briefly, and the liquid is decanted from the solid into a 5-l. separatory funnel. The aqueous layer is separated and extracted again with 200 ml. of benzene. The aqueous layer is then returned to the separatory funnel, and the solid in the reaction flask is washed in with it by means of 2 l. of water. The mixture is shaken with 200-ml. portions of benzene until all solid has dissolved (usually three portions of benzene suffice). All the benzene extracts are combined and dried with 20 g. of anhydrous calcium chloride. The drying agent is removed by filtration and washed with two 20-ml. portions of benzene. Benzene is removed from the filtrate by distillation under reduced pressure (Note 6), and the solid which separates is dried further at about 10 mm. and room temperature to constant weight. The yield (Note 2) of methyl *p*-tolyl sulfone is 298–317 g. (69–73%), m.p. 83–87.5°. Further purification is generally unnecessary, but, if desired, the product may be recrystallized from carbon tetrachloride or ethanol-water (1:1). The submitters state that the method may be extended to the preparation of methyl phenyl sulfone and, presumably, of methyl aryl sulfones generally (Note 7).

2. Notes

1. A porcelainized metal bucket is a convenient alternative.
2. The submitters used Eastman Kodak Company practical grade; although the solid is somewhat oily, the m.p. is 66–68°. The checkers used *p*-toluenesulfonyl chloride purchased from Matheson, Coleman and Bell and obtained a yield of 78–82%.
3. The volume at the end of the heating period should not exceed 2.4 l. If, after 1 hour of heating, the volume exceeds 2.4 l., the mixture is heated longer.
4. Eastman Kodak Company practical grade was used, b.p. 69–70°/10 mm. Dimethyl sulfate is toxic and must be handled with caution. This part of the preparation should be run in a hood with provision for containing the contents should breakage

occur. It is unlikely that any dimethyl sulfate survives the 20-hour reflux period however, and the submitters reported that no difficulty whatever was encountered in handling the mixture after this point without special precautions; nevertheless, they recommend that the possible presence of dimethyl sulfate be borne in mind. Ammonia is a specific antidote for dimethyl sulfate and should be at hand to destroy any accidentally spilled. A solution of a detergent in dilute ammonia water may be used to clean glassware used in transfers. For hazards, see Sax.²

5. Extraction with benzene improves the yield somewhat but offers the more important advantage of permitting effective drying of the sulfone when it is to be used in metallation reactions. If this advantage is not sought, the reaction mixture simply can be allowed to cool to room temperature and let stand until crystallization is complete (2–3 hours). The solid is then collected by filtration and washed with water (about six 200-ml. portions) until the washings give no precipitate with barium chloride solution. The yield is 272 g. (63%); it can be increased by 12.6 g. (66%) by extraction of the mother liquor and wash water. The sulfone thus obtained contains only 0.25% of benzene-insoluble material and has m.p. 86.5–87.5°.

6. If the benzene is removed at a temperature not exceeding 50°, the sulfone is obtained as well-formed crystals.

7. According to the submitters, methyl phenyl sulfone³ is obtained similarly from benzenesulfonyl chloride in 66–69% yields, m.p. 86–88°.

3. Methods of Preparation

Methyl *p*-tolyl sulfone has been prepared by oxidation of methyl *p*-tolyl sulfide with hydrogen peroxide^{4,5} or ruthenium tetroxide,⁶ by alkylation of sodium *p*-toluenesulfinate with methyl iodide^{7,8} or with methyl potassium sulfate,⁹ by decarboxylation of *p*-tolylsulfonylacetic acid,⁷ by thermal decomposition of tetramethylammonium *p*-toluenesulfinate,¹⁰ by reaction of *cis*-bis-(*p*-tolylsulfonyl)-ethene with sodium hydroxide (low yield),¹¹ by the reaction of methanesulfonyl chloride with toluene in the presence of aluminum chloride (mixture of isomers),¹² by

reaction of alkali with 3-*p*-tolylsulfonyl-7-hydroxynaphtho- α -pyrone,¹³ and by heating allyl *p*-tolyl sulfone with sodium hydroxide.¹⁴

The method described here is that of Field and Clark.³ It involves preparation of sodium *p*-toluenesulfinate by the procedure of Oxley et al.⁸ and alkylation by modification of a method used by Baldwin and Robinson¹⁵ for the preparation of methyl phenyl sulfone.

¹ Department of Chemistry, Vanderbilt University, Nashville, Tennessee.

² Sax, *Handbook of Dangerous Materials*, p. 147, Reinhold Publishing Corporation, New York, 1951.

³ Field and Clark, *J. Org. Chem.*, **22**, 1129 (1957).

⁴ Zincke and Frohneberg, *Ber.*, **43**, 837 (1910).

⁵ Gilman and Beaber, *J. Am. Chem. Soc.*, **47**, 1449 (1925).

⁶ Djerassi and Engle, *J. Am. Chem. Soc.*, **75**, 3838 (1953).

⁷ Otto, *Ber.*, **18**, 154 (1885).

⁸ Oxley, Partridge, Robson, and Short, *J. Chem. Soc.*, **1946**, 763.

⁹ Otto and Artmann, *Ann.*, **284**, 300 (1895).

¹⁰ Meyer, *Chem. Zentr.*, **80**, 1800 (1909).

¹¹ Truce and McManis, *J. Am. Chem. Soc.*, **76**, 5745 (1954).

¹² Truce and Vriesen, *J. Am. Chem. Soc.*, **75**, 5032 (1953).

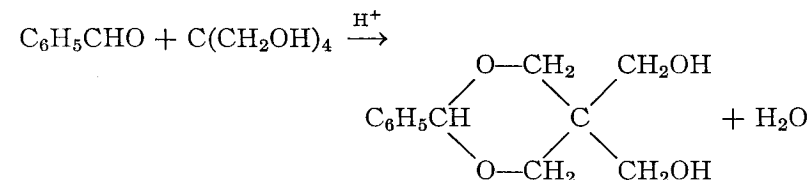
¹³ Tröger and Dunkel, *J. prakt. Chem.*, **104**, 311 (1922).

¹⁴ Backer, Strating, and Drenth, *Rec. trav. chim.*, **70**, 365 (1951).

¹⁵ Baldwin and Robinson, *J. Chem. Soc.*, **1932**, 1445.

MONOBENZALPENTAERYTHRITOL

(Pentaerythritol, monobenzal-)



Submitted by C. H. ISSIDORIDES and R. GULEN.¹

Checked by M. S. NEWMAN and ARLEN B. MEKLER.

1. Procedure

In an open 3-l. three-necked flask are placed 180 g. (1.32 moles) of pentaerythritol (Note 1) and 1.3 l. of water. The flask is fitted with an efficient mechanical stirrer and a graduated dropping funnel containing 147 g. (1.38 moles) of benzaldehyde (Note 2). The mixture in the flask is heated until all the solid dissolves and is then allowed to cool undisturbed (Note 3).

When the solution has cooled to room temperature, stirring is started and 6.6 ml. of concentrated hydrochloric acid is added through the open neck of the flask, followed by 30 ml. of benzaldehyde from the dropping funnel. When the precipitate of monobenzalpentaerythritol starts forming, dropwise addition of benzaldehyde is begun (Note 4). After the addition of benzaldehyde is completed, the mixture is stirred for an additional 3 hours (Note 5). The precipitate is collected (Note 6) on a Büchner funnel and washed with ice-cold water which has been made slightly alkaline by addition of sodium carbonate. The solid is transferred to a 3-l. round-bottomed flask, 1 l. of water (slightly alkaline with sodium carbonate) is added, and the mixture is heated to 100° (Note 7). After about 10 minutes at this temperature the hot mixture is filtered quickly through a fluted filter paper (Note 8). The solid remaining on the filter paper is washed with 50 ml. of hot water (made slightly alkaline with sodium carbonate) (Note 9). The combined aqueous filtrates are cooled in an ice bath for several hours, and the crystals are collected on a Büchner funnel and dried. The dry product is heated under reflux for 15 minutes in an Erlenmeyer flask with 200 ml. of toluene, and the hot mixture is allowed to cool to room temperature, with continuous agitation (stirring rod) to prevent formation of hard lumps. Finally, the mixture is cooled in an ice bath for 5 hours, and the solid product is collected on a Büchner funnel and dried (Note 10). The yield of monobenzalpentaerythritol melting at 134–135° is 215–227 g. (73–77%).

2. Notes

1. Eastman Kodak Company white label pentaerythritol was used. The checkers used a commercial sample obtained from the Heyden Chemical Corporation.

2. The third neck may be left open and used later for addition of hydrochloric acid and for introduction of the thermometer.

3. The temperature of the solution should not be allowed to go below 25°; otherwise pentaerythritol will precipitate.

4. The addition should take about 2.5 hours. The temperature of the mixture should be kept at 25–29°.

5. If stirring is continued for a substantially longer period, the yield of monobenzalpentaerythritol is somewhat decreased.

6. The product should be collected immediately, as losses result if there is delay at this point.

7. The mixture should be stirred continuously during the heating. The use of a mechanical stirrer is recommended.

8. Use of a steam-heated funnel is recommended.

9. The solid remaining finally on the filter paper may be recrystallized from 1-butanol to give 1–2 g. of dibenzalpentaerythritol melting at 159–160°.

10. The product and the toluene in the Erlenmeyer flask form a solid mass which is difficult to remove. The operation is made easier by adding 70 ml. of ice-cold toluene to the flask and stirring, before transferring the product to the Büchner funnel. One or two additional 20-ml. portions of cold toluene may be used to remove the product completely.

3. Methods of Preparation

The procedure described is based on the method of E. Bograchov.²

¹ American University of Beirut, Beirut, Lebanon.

² E. Bograchov, *J. Am. Chem. Soc.*, **72**, 2268 (1950).

MONOBROMOPENTAERYTHRITOL

(1,3-Propanediol, 2-bromomethyl-2-hydroxymethyl-;
pentaerythritol monobromohydrin)



Submitted by S. WAWZONEK, A. MATAR, and C. H. ISSIDORIDES.¹

Checked by CHARLES C. PRICE and G. VENKAT RAO.

1. Procedure

In a 3-l. two-necked flask (Note 1) fitted with a dropping funnel and a reflux condenser are placed 200 g. (1.47 moles) of pentaerythritol, 1.5 l. of glacial acetic acid, and 17 ml. of 48% hydrobromic acid (Note 2). After a reflux period of 1.5 hours, 170 ml. of 48% hydrobromic acid is added and the solution is heated under reflux for an additional 3 hours. At the end of this time 96 ml. of 48% hydrobromic acid is added and the heating under reflux is continued for 3 hours. The solution is distilled under reduced pressure to remove as much of the acetic acid and the water as possible, first on a steam bath and finally for 15 minutes in an oil bath at 140–150°, as the pressure is reduced to 10 mm. The viscous residue is transferred to a 2-l. flask and treated with 750 ml. of 98% ethanol and 50 ml. of 48% hydrobromic acid. The flask is provided with an efficient fractionating column (Note 3), and the solution is fractionated slowly until about 500 ml. of distillate is collected. Then a second 750-ml. portion of ethanol is added, and the fractionation is continued slowly until 750 ml. more distillate is collected (Note 4). Finally, the flask is fitted with a Claisen head and a condenser set for downward distillation, and the remaining alcohol is removed as completely as possible under reduced pressure.

Benzene (500 ml.) is added to the residue and distilled at atmospheric pressure. The last traces of benzene are removed by heating for 15 minutes in an oil bath at 150°, as the pressure is reduced to 8 mm. The same procedure is repeated, using a

second 500-ml. portion of benzene (Note 5). The viscous residue is then heated under reflux for several hours with 500 ml. of dry ether, with frequent shaking, until it becomes white and granular (Note 6). After cooling thoroughly, the ether is decanted, and the solid is washed twice with two 200-ml. portions of dry ether. The solid is powdered thoroughly and dried in a vacuum desiccator. The dry solid is then extracted exhaustively in a Soxhlet extractor with 600 ml. of dry ether (Note 7). The ether extract is cooled overnight in an ice bath, and the precipitated monobromopentaerythritol is collected by filtration and washed with two 200-ml. portions of cold, dry ether. The yield of crude product melting at 72–73° is 145–160 g. (49–54% of the theoretical). One recrystallization from a mixture of 3 parts of chloroform and 2 parts of ethyl acetate by volume raises the melting point to 75–76°, recovery 75–85%.

2. Notes

1. For best results the flask should have standard-taper, ground-glass fittings.

2. Eastman Kodak Company white label pentaerythritol and 48% hydrobromic acid were used.

3. A 40-cm. column packed with glass beads is satisfactory.

4. The fractionation should be carried out slowly to ensure complete alcoholysis of the bromoacetate. The boiling point during the collection of the first 500 ml. of distillate remains constant at around 72°, corresponding to the ethanol-ethyl acetate azeotrope.

5. The purpose of this operation is to remove completely the water present in the product. Toluene may be substituted for benzene.

6. If the product has a tendency to form a hard mass, it is advisable to break up the solid with a stirring rod.

7. The extraction is very slow and requires several hours for completion, depending upon the rate of refluxing of the ether. Usually crystals of the monobromopentaerythritol begin to deposit on the walls of the extraction flask after the first hour. At the end of the extraction 30–35 g. of unchanged pentaerythritol

remains in the extraction thimble. Dibromopentaerythritol, formed as a side product, is present in the ether washings.

3. Methods of Preparation

Monobromopentaerythritol has been prepared by the action of 66% hydrobromic acid on pentaerythritol in glacial acetic acid² and by the action of 66% hydrobromic acid on pentaerythritol³ at 120°. The procedure described is a modification of the method of Beyaert and Hansens.³

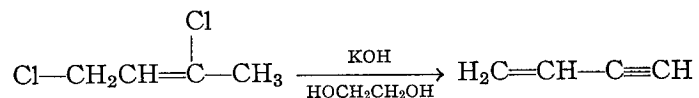
¹ State University of Iowa, Iowa City, Iowa.

² Beyaert and Hansens, *Natuurw. Tijdschr. (Ghent)*, **22**, 249 (1940) [*C. A.*, **37**, 5373 (1943)].

³ Barbieri and Matti, *Bull. soc. chim. France* [5]5, 1565 (1938).

MONOVINYLACETYLENE

(1-Buten-3-yne)



Submitted by G. F. HENNION, CHARLES C. PRICE, and
THOMAS F. McKEON, JR.¹

Checked by MAX TISLER and JOHN E. ALLEGRETTI.

1. Procedure

A 2-l. three-necked flask, heated by a Carbowax bath, is equipped with a motor-driven Trubore stirrer, Teflon paddle, Trubore bearing (Note 1), a Friedrichs condenser, and a 250-ml. dropping funnel. The dropping funnel is connected to the flask by a 24/40 ground-glass joint with a side arm made of 7-mm. tubing. The side arm is connected through a calcium chloride drying tower and a bubbler to a nitrogen tank.

The top of the condenser is connected to a horizontal tube (ca. 2 x 25 cm.) partially filled with granular anhydrous calcium chloride. The horizontal tube is then connected to a 100-ml.

graduated cylinder immersed in an acetone-Dry Ice mixture for collection of the product. The cylinder is also equipped with an escape tube protected by a calcium chloride drying tube.

Four hundred grams of powdered technical potassium hydroxide flakes (Note 2) is placed in the flask, and 500 ml. of ethylene glycol is added. This mixture is stirred vigorously while adding 100 ml. of *n*-butyl Cellosolve (Note 3). The system is swept with a rapid stream of nitrogen for 15–20 minutes while the temperature of the oil bath is raised to 165–170°. The flow of nitrogen is then reduced to a rate just sufficient to maintain an atmosphere of nitrogen in the system.

One hundred and twenty-five grams of 1,3-dichloro-2-butene (1.0 mole) (Note 4) is added at a rate of about 3 drops per second. Addition should be complete in 0.75–1 hour (Note 5). During the addition the temperature of the oil bath is maintained at 165–170° (Note 6), and the reaction mixture is stirred vigorously. Heating is continued for 1 hour after the addition of dichlorobutene is complete.

The yield of crude product obtained is 31.2 g. (39 ml., 60.0%) (Notes 7 and 8). The crude product may be purified by distillation through a low-temperature column (Note 9) to yield 22.4–24.8 g. (28–31 ml., 43.8–47.8%) of monovinylacetylene, b.p. 0–6° (Note 10). The storage of monovinylacetylene in the presence of oxygen has been reported to lead to explosive compounds. It is therefore suggested that the product be stored under an inert atmosphere.

2. Notes

1. An oil-sealed stirrer was found unsuitable because the pressure drop through the system was greater than the pressure drop across the oil-sealed stirrer. The Trubore stirrer and bearing were purchased from Ace Glass Inc., Vineland, New Jersey.

2. The potassium hydroxide was weighed as flakes, then ground rapidly with a mortar and pestle to roughly the consistency of granulated sugar, and added as soon as possible to the reaction flask to minimize moisture uptake. The flakes may be used directly without grinding, the only difference being that the mixture of potassium hydroxide, glycol, and Cellosolve should be

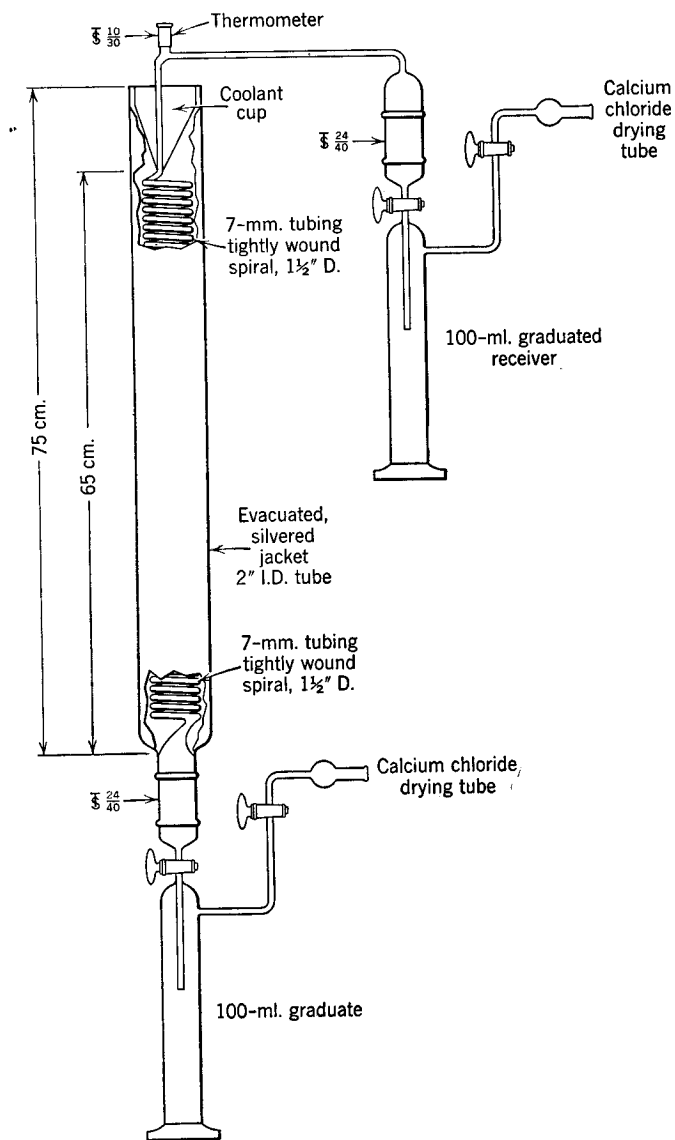


FIG. 2. Low-temperature distillation column.

heated for a slightly longer time before any dichlorobutene is added in order to allow as complete a dispersion as possible.

3. The butyl Cellosolve is added to control the foaming during the reaction.

4. The dichlorobutene used was Eastman Kodak Company technical grade. Distillation before use was not observed to increase the yields.

5. The rate of addition is very important. If the time of addition of 1 mole of dichlorobutene goes much beyond 1 hour, the yield will decrease noticeably.

6. This is apparently an optimum temperature. Lower temperatures lead to lower yields, while higher temperatures do not change the yield appreciably.

7. The calculations of yields are based on $d^{-80} = 0.8$ extrapolated from data at higher temperature.²

8. The preparation also has been run on a 2-mole scale, using double the quantities specified in a 3-l. flask. The yields obtained were comparable to those obtained on the 1-mole scale.

9. The low-temperature column shown in Fig. 2 was 75 cm. long, made of 7-mm. glass tubing. The entire column was surrounded by an evacuated, silvered jacket. The column, for the lower 60 cm., was a tightly coiled spiral (3.8 cm. diameter). The remaining length was straight and was surrounded by a coolant cup in which liquid of any temperature could be placed to control the refluxing temperature. For the purpose, a calcium chloride-water-Dry Ice mixture was used to keep the temperature of the cup at approximately -5 to 0° . The vapor from the column was condensed and collected in a graduated cylinder immersed in an acetone-Dry Ice bath (Note 10). The major features of infrared spectra of the vapor from redistilled product are summarized in Table I (Note 11).

10. Warming the still pot with 60° water was necessary to distil all the volatile gases toward the end of the distillation.

11. The spectrum of the fractionated monovinylacetylene was comparable, in band peaks and intensities, with previously reported spectra. A previously reported band at 5.8μ , however, was not found in any of the samples, suggesting that an impurity was present in the sample previously reported.

TABLE I

THE MAJOR BANDS FOR THE INFRARED SPECTRUM OF
MONOVINYLAETHYLENE GAS

(350 mm. pressure, 5-cm. cell)

Wavelength, μ	Absorption, %	Wavelength, μ	Absorption, %
3.02	93	6.20	87
3.22	62	7.0-7.15	33
3.30	67	7.9-8.1	98
4.73	9	9.17	49
5.13	19	9.37	18
5.41	59	10.2-11.2	99
5.46	52	13.67	27
5.80	—		

3. Methods of Preparation

Monovinylacetylene has been prepared by the decomposition of a diquaternary ammonium base,³ by the dimerization of acetylene,⁴ and by the dehydrohalogenation of dihalobutenes in liquid ammonia.⁵ The last method produces a metal salt. The procedure described has been published.⁶

¹ University of Notre Dame, Notre Dame, Indiana.

² Kuchinskaya and Anitina, *Khim. Referat. Zhur.*, **2**, No. 5, 65 (1939) [*C. A.*, **34**, 2783 (1940)].

³ Willstatter and Wirth, *Ber.*, **46**, 535 (1913).

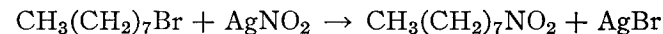
⁴ Nieuwland, Calcott, Downing, and Carter, *J. Am. Chem. Soc.*, **53**, 4197 (1931).

⁵ Croxall and Van Hook, U. S. Patent 2,623,077 (December 23, 1952, to Rohm and Haas Co.); *J. Am. Chem. Soc.*, **76**, 1700 (1954).

⁶ Hennion, Price and McKeon, *J. Am. Chem. Soc.*, **76**, 5160 (1954).

1-NITROOCTANE

(Octane, 1-nitro-)



Submitted by N. KORNBLUM and H. E. UNGNADE.¹

Checked by JOHN C. SHEEHAN and M. GERTRUDE HOWELL.

1. Procedure

1-Bromoöctane (96.5 g., 0.5 mole) (Note 1) is added dropwise during 2 hours to a stirred suspension of silver nitrite (116 g., 0.75 mole) (Note 2) in 150 ml. of dry ether (Mallinckrodt anhydrous), contained in a 500-ml. three-necked round-bottomed flask equipped with dropping funnel, reflux condenser, and a sealed Hershberg-type stirrer (Trubore) and immersed in a 1-gal. Dewar flask filled with ice and water (Note 3). The mixture is stirred for 24 hours in an ice bath. The bath is removed, and stirring is continued at room temperature (26–28°) until the supernatant liquor gives a negative test for halides (approximately 40 hours, Notes 4 and 5).

The silver salts are removed by filtration, slurried with two 100-ml. portions of dry ether, and the ether washings are added to the ethereal solution of reaction products (Note 6). The combined ethereal solutions are distilled at atmospheric pressure through a 2 x 45 cm. column packed with 4-mm. Pyrex helices (Note 7). The residue remaining after removal of the ether is fractionated under reduced pressure. The yellow liquid distilling at 37°/3 mm. has n_D^{20} 1.4127–1.4129 and weighs 11.3 g. (14%); this is 1-octyl nitrite. It is followed by an interfraction of b.p. 38–70°/3 mm., n_D^{20} 1.4133–1.4320, yield 6.83 g., which contains some nitrite, some 1-octanol, and a little 1-nitroöctane. Finally, pure, colorless 1-nitroöctane distils at 66°/2 mm., n_D^{20} 1.4321–1.4323, yield 59.6–63.6 g. (75–80%) (Notes 8 and 9).

2. Notes

1. 1-Bromoöctane b.p. 50–51°/0.8 mm., n_D^{20} 1.4526, was employed.

2. Silver nitrite can be prepared as follows: silver nitrate (169.9 g., 1 mole) dissolved in 500 ml. of distilled water is added in small portions, with vigorous shaking, to a solution of 76 g. (1.1 mole) of sodium nitrite, dissolved in 250 ml. of distilled water contained in a 1-l. Erlenmeyer flask. (These operations are best carried out under a yellow safelight or, in any case, with minimum exposure to light.) Then the mixture is allowed to stand in the dark for 1 hour. The yellow precipitate is then collected by filtration with suction, suspended in 250 ml. of distilled water, and again filtered. The washing is repeated twice, and the product is collected by filtration and dried to constant weight in a vacuum desiccator over potassium hydroxide pellets; yield 134 g. (86%). The silver nitrite drying process can be facilitated by washing the material with methanol.

3. It is preferable to carry out the entire reaction in a dark room equipped with a yellow safelight. The reaction mixture should be protected from moisture by means of drying tubes.

4. The stirrer is stopped, and the precipitate is allowed to settle. Unchanged alkyl halide is detected in the supernatant liquor by the Beilstein test (copper wire spiral) or by adding a few drops of the ethereal solution to alcoholic silver nitrate.

5. According to the submitters, with primary straight-chain bromides the time needed to reach a negative test for halide is 24 hours at 0° followed by 48 ± 12 hours at room temperature. When primary straight-chain iodides are employed, the reaction time is shorter: 24 hours at ice temperature followed by 36 ± 12 hours at room temperature.

6. It is more difficult to remove an alcohol from the corresponding nitroalkane than it is to separate the nitrite ester and the nitroalkane. Minimal exposure to a moist atmosphere is, therefore, desirable since anhydrous ether is hygroscopic and nitrite esters hydrolyze readily, especially if a little acid is present.

7. A column of high efficiency is undesirable because of the thermal instability of the nitrite, and a column of lesser efficiency

cannot accomplish a complete separation of the products. The column used by the submitters was equipped with a total condensate, partial take-off head with small holdup.

8. 1-Nitroöctane is completely soluble in aqueous alkali. It is converted to a crystalline colorless sodium salt on shaking with 20% aqueous sodium hydroxide, and this salt dissolves completely on adding enough water to make the solution 10% aqueous base. That the nitro compound is free from nitrate is shown by the absence of the infrared absorption bands at 6.15, 7.85 and 11.6 μ characteristic of nitrate esters.

9. A recent study² has shown that this is a general reaction for primary straight-chain bromides and iodides; in contrast, primary chlorides fail to react. Primary bromides and iodides having branched chains also give excellent yields of nitro compounds, especially if the branching is not on the carbon *alpha* to the one holding the halogen (Table I).

TABLE I
YIELDS OF NITRO COMPOUNDS

Halide	RNO ₂ , %	Halide	RNO ₂ , %
<i>n</i> -Butyl Br	73	<i>n</i> -Octyl I	83
<i>n</i> -Butyl I	74	<i>Iso</i> amyl Br	72
<i>n</i> -Hexyl Br	76	<i>Iso</i> amyl I	78
<i>n</i> -Hexyl I	78	<i>Isobutyl</i> Br	18
<i>n</i> -Heptyl Br	79	<i>Isobutyl</i> I	59
<i>n</i> -Heptyl I	82	<i>Neopentyl</i> I	0
<i>n</i> -Octyl Br	80		

The reaction of silver nitrite with secondary halides gives yields of nitroparaffins in the vicinity of 15%, while with tertiary halides the yields are even lower (0–5%). There is no question that the reaction of silver nitrite with alkyl halides is useful only for the synthesis of primary nitroparaffins.

3. Methods of Preparation

The present procedure is based on a recently published paper.² 1-Nitroöctane has previously been prepared from 1-iodoöctane and silver nitrite,³ from octane by boiling with nitric acid,^{4,5} and

from 1-nitroöctylene by catalytic hydrogenation.⁶ 1-Nitroöctane has also been obtained from *n*-octyl *p*-toluenesulfonate and sodium nitrite in 17% yield.⁷

¹ Department of Chemistry, Purdue University, Lafayette, Indiana.

² Kornblum, Taub, and Ungnade, *J. Am. Chem. Soc.*, **76**, 3209 (1954).

³ Eichler, *Ber.*, **12**, 1883 (1879).

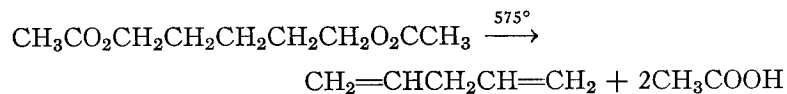
⁴ Worstall, *Am. Chem. J.*, **20**, 213 (1898); **21**, 228 (1899).

⁵ Urbanski and Slon, *Roczniki Chem.*, **17**, 161 (1937) [*C. A.*, **31**, 6190 (1937)].

⁶ de Mauny, *Bull. soc. chim. France*, **7**, 133 (1940) [*C. A.*, **34**, 5413 (1940)].

⁷ Drahowzal and Klamann, *Monatsh. Chem.*, **82**, 975 (1951).

1,4-PENTADIENE



Submitted by R. E. BENSON and B. C. MCKUSICK.¹

Checked by N. J. LEONARD and A. G. COOK.

1. Procedure

The apparatus (Fig. 3) is similar to that described in previous volumes.^{2,3} It consists of a Pyrex glass reaction tube, 90 cm. long by 45 mm. in outside diameter, mounted vertically in an electric furnace about 50 cm. long. Attached to the top of the tube are a graduated dropping funnel (Note 1), an inlet tube for nitrogen, and a thermocouple well extending to the bottom of the heated section and holding a movable thermocouple. The entire heated section, which begins 10 cm. from the top of the tube, is packed with Pyrex glass rings 10 mm. in outside diameter by about 10 mm. in length held in place by a plug of glass wool supported by indentations in the tube. The lower end of the tube is attached to a 1-l. round-bottomed flask immersed in an ice bath and having a side arm from which vapors pass successively through a trap immersed in an ice bath and a trap immersed in a bath of Dry Ice and acetone. Each trap is capable of holding about 200 ml. of liquid. The temperature of the hottest part of the tube,

which is located near the middle of the heated section, is raised to $575^\circ \pm 10^\circ$ while nitrogen (Note 2) is passed successively through a flowmeter and the tube at a rate of 4–6 l./hr. Under these conditions (Note 3), 658 g. (645 ml., 3.5 moles) of 1,5-pentanediol diacetate (Note 4) is added to the tube over a period of 3.5 hours. The contents of the three receivers are combined and distilled at atmospheric pressure through a 15-cm. indented Claisen-type still head; the condenser is cooled with ice water, and the receiver is immersed in an ice bath. The fraction boiling at $25\text{--}55^\circ$, wt. 170–190 g., is redistilled through a 60-cm. column packed with glass helices or a column of similar efficiency to give 150–170 g. (63–71%) of 1,4-pentadiene, b.p. $26\text{--}27.5^\circ/760\text{ mm.}$, n_D^{25} 1.3861–1.3871 (Note 5).

2. Notes

1. A Hershberg dropping funnel⁴ modified by addition of a pressure-equalizing arm (Fig. 3) makes it easy to add the diacetate at a constant rate.

2. A dry, oxygen-free grade of commercial nitrogen is used. Nitrogen can be omitted without diminishing the yield by more than a few per cent.

3. As the addition of the diacetate begins, the temperature of

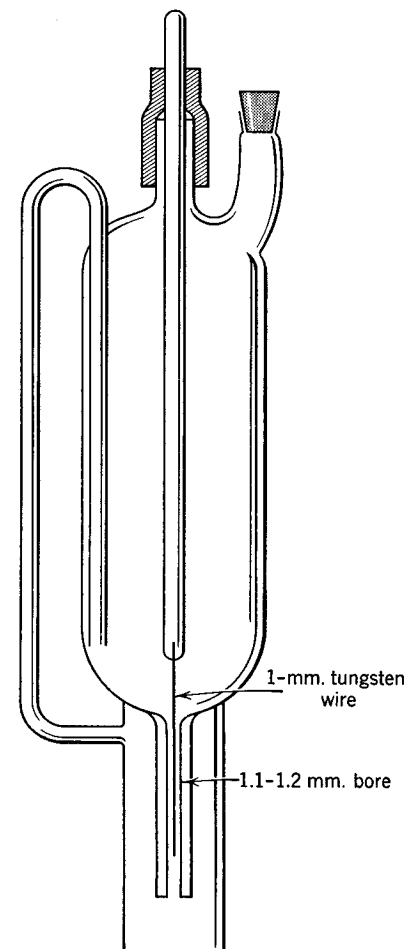


FIG. 3.

the hottest part of the tube (the location of which generally shifts lower at this time) decreases, necessitating an increase in current in the electric furnace.

4. 1,5-Pentanediol diacetate,^{5,6} b.p. 85–90°/0.9 mm., n_D^{25} 1.4253, is obtained in 92–94% yield by adding a 10% excess of acetic anhydride to 1,5-pentanediol⁷ at 120–140°, refluxing the mixture for 2 hours, and distilling it at reduced pressure. The practical grade of 1,5-pentanediol sold by the Eastman Kodak Company may be used.

5. The residue from the first distillation is a mixture of acetic acid, 4-penten-1-ol acetate, and 1,5-pentanediol diacetate. Another 15–35 g. (6–15%) of 1,4-pentadiene can be obtained by passing the residue through the pyrolysis tube under the conditions described above.

3. Methods of Preparation

1,4-Pentadiene has been prepared by the interaction of allyl bromide and vinyl bromide in the presence of magnesium,⁸ by the pyrolysis of 1,5-pentanediol diacetate^{5,6} or 4-penten-1-ol acetate,^{6,9} and by the reaction of α -allyl- β -bromoethyl ethyl ether with zinc.^{10,11} The present procedure is based on the work of Schniepp and Geller⁵ and of Paul and Tchelitcheff.⁶

¹ Chemical Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware.

² Ratchford, *Org. Syntheses*, Coll. Vol. **3**, 30 (1955).

³ Bourns, Embleton, and Hansuld, *Org. Syntheses*, **34**, 79 (1954).

⁴ Hershberg, *Org. Syntheses*, Coll. Vol. **2**, 129 (1943).

⁵ Schniepp and Geller, *J. Am. Chem. Soc.*, **67**, 54 (1945).

⁶ Paul and Tchelitcheff, *Bull. soc. chim. France*, [5]**15**, 108 (1948).

⁷ Kaufman and Reeve, *Org. Syntheses*, Coll. Vol. **3**, 693 (1955).

⁸ Kogerman, *J. Am. Chem. Soc.*, **52**, 5060 (1930).

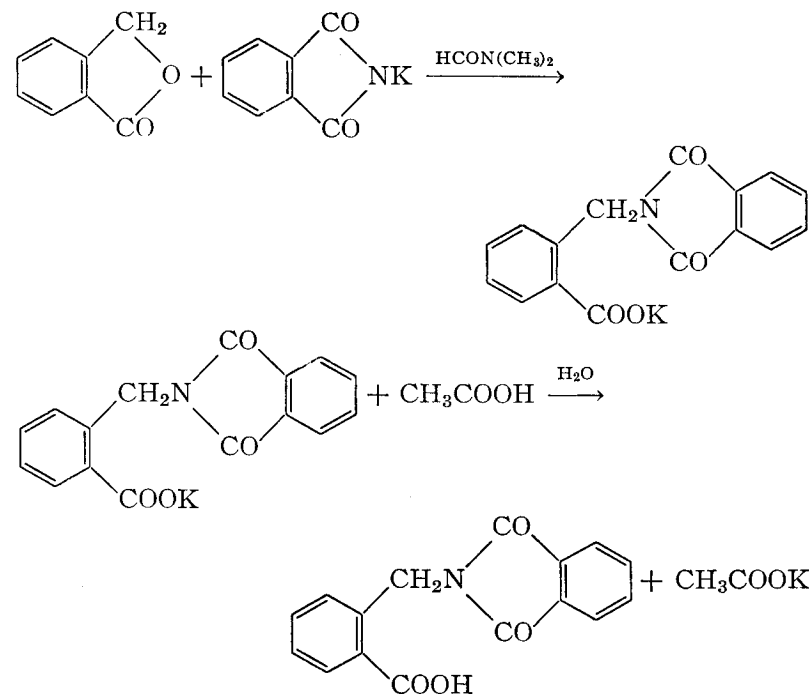
⁹ Paul and Normant, *Bull. soc. chim. France*, [5]**11**, 367 (1944).

¹⁰ Shoemaker and Boord, *J. Am. Chem. Soc.*, **53**, 1505 (1931).

¹¹ Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.*, **58**, 146 (1936); Elsner and Wallsgrove, *J. Inst. Petrol.*, **35**, 259 (1949).

α -PHTHALIMIDO-*o*-TOLUIC ACID

(*o*-Toluic acid, α -phthalimido-)



Submitted by J. BORNSTEIN, P. E. DRUMMOND, and S. F. BEDELL.¹

Checked by JOHN C. SHEEHAN and Y. L. YEH.

1. Procedure

A 2-l. three-necked round-bottomed flask, fitted with a sealed stirrer and a reflux condenser carrying a drying tube, is charged with 100 g. (0.75 mole) of phthalide (Note 1), 150 g. (0.81 mole) of potassium phthalimide (Note 2), and 500 ml. of dimethylformamide (Note 3). The stirred suspension is heated under reflux by means of an electric mantle for 5 hours; the deep blue solution is then cooled to room temperature (Note 4). A solu-

tion of 300 ml. of glacial acetic acid in 500 ml. of water is added in one portion to the stirred reaction mixture, and the resulting yellow suspension, which becomes slightly warm, is stirred for an additional 30 minutes.

The precipitate is separated by suction filtration, pressed on the funnel, and washed successively with three 100-ml. portions of water and two 100-ml. portions of 95% ethanol. The product is transferred to a 1-l. Erlenmeyer flask, boiled for 10 minutes with 400 ml. of 60% ethanol with occasional stirring, filtered hot, washed twice with 50-ml. portions of 95% ethanol, and then dried in an oven at 90–100° for 6–12 hours. The crude α -phthalimido-*o*-toluic acid, which weighs 140–155 g., is divided into two equal portions, and each portion is dissolved in boiling propionic acid (Note 5). Each solution is treated with 1 tablespoon of Norit and filtered through an electrically heated gravity funnel. The filtrates are allowed to cool slowly to room temperature and are then refrigerated overnight. The crystals from the two portions are collected by suction filtration in one funnel and washed on the funnel with 400 ml. of 95% ethanol. The product is dried over potassium hydroxide in a vacuum desiccator. The yield of nearly white crystals of α -phthalimido-*o*-toluic acid is 126–141 g. (60–67% based on phthalide), m.p. 265.0–266.5°.

2. Notes

1. The phthalide was prepared according to *Organic Syntheses*² and was also purchased from Aldrich Chemical Company. The commercial product (200 g.) was recrystallized in 50-g. portions from 1.5 l. of water, the mother liquor from the first crop being employed for recrystallization of the subsequent portions. Each portion was treated with 2 tablespoons of Norit, filtered hot, allowed to cool to room temperature with occasional stirring, and then cooled to 5° before collecting the crystals which were washed on the funnel with small quantities of cold water. Final drying was effected in a vacuum desiccator containing phosphorus pentoxide.

2. Eastman Kodak Company potassium phthalimide (200 g.) was digested with 450 ml. of boiling acetone for 15 minutes,

filtered hot, washed on the funnel with 100 ml. of acetone, and dried at 100° for 6 hours.

3. The dimethylformamide was obtained from Eastman Kodak Company and was used without further purification.

4. The reaction mixture is most conveniently cooled by allowing it to stand at room temperature overnight. Occasionally the potassium salt of α -phthalimido-*o*-toluic acid precipitates at this point, but this does not interfere with the subsequent operations.

5. Approximately 1.33 l. of propionic acid is required for 78 g. of the crude α -phthalimido-*o*-toluic acid. Glacial acetic acid may be used as the solvent, but considerably larger volumes are required than when propionic acid is employed. This step should be carried out in a hood, since hot propionic acid vapors are very irritating.

3. Methods of Preparation

The present procedure is that described by the submitters.³ α -Phthalimido-*o*-toluic acid has also been prepared by the acidolysis of the corresponding ethyl ester, obtained from the reaction of ethyl α -bromo-*o*-toluate with potassium phthalimide.³

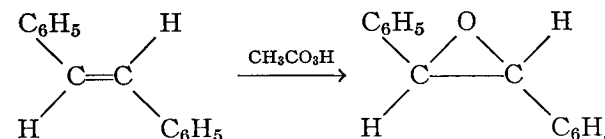
¹ Department of Chemistry, Boston College, Chestnut Hill, Massachusetts.

² *Org. Syntheses*, Coll. Vol. 2, 526 (1943).

³ Bornstein, Bedell, Drummond, and Kosloski, *J. Am. Chem. Soc.*, 78, 83 (1956).

trans-STILBENE OXIDE

(α,α' -Epoxybibenzyl)



Submitted by DONALD J. REIF and HERBERT O. HOUSE.¹

Checked by MELVIN S. NEWMAN and DONALD K. PHILLIPS.

1. Procedure

In a 1-l. three-necked flask equipped with stirrer, dropping funnel, and thermometer is placed a solution of 54 g. (0.3 mole) of *trans*-stilbene (Note 1) in 450 ml. of methylene chloride. The methylene chloride solution is cooled to 20° with an ice bath, and then the cooling bath is removed. A solution of peracetic acid (0.425 mole) in acetic acid (Note 2) containing 5 g. of sodium acetate trihydrate is added dropwise and with stirring to the reaction mixture during 15 minutes. The resulting mixture is stirred for 15 hours, during which time the temperature of the reaction mixture is not allowed to rise above 35° (Notes 3 and 4). The contents of the flask are poured into 500 ml. of water, and the organic layer is separated. The aqueous phase is extracted with two 150-ml. portions of methylene chloride, and the combined methylene chloride solutions are washed with two 100-ml. portions of 10% aqueous sodium carbonate and then with two 100-ml. portions of water. The organic layer is dried over magnesium sulfate, and the methylene chloride is distilled, the last traces being removed under reduced pressure. The residual solid is recrystallized from methanol (3 ml./g. of product) to yield 46–49 g. (78–83%) of crude *trans*-stilbene oxide, m.p. 66–69° (Note 5). An additional recrystallization from hexane (3 ml./g. of product) sharpens the melting point of the product to 68–69°. The yield is 41–44 g. (70–75%).

2. Notes

1. *trans*-Stilbene (Eastman Kodak Company) may be used directly. A slightly higher yield is obtained if the stilbene is crystallized once from alcohol.

2. Approximately 40% peracetic acid in acetic acid is available (Becco Chemical Division, Food Machinery and Chemical Corporation, Buffalo 7, New York). Sodium acetate is added to neutralize a small amount of sulfuric acid which is present in the commercial product. The peracetic acid concentration should be determined by titration.² The peracetic acid solution used by the submitters contained 0.497 g. (0.00655 mole) of peracid per

milliliter. Consequently 65 ml. (0.425 mole) of this solution was used in the reaction.

3. Without further cooling, the temperature of the reaction mixture usually rises to 32–35° after 1–2 hours and then gradually falls.

4. The progress of the epoxidation can be followed by measuring periodically the optical density of the reaction mixture at 295 m μ . The reaction time and temperature specified in the procedure were found to reduce the optical density of the reaction mixture at 295 m μ (and, accordingly, the *trans*-stilbene concentration) to less than 3% of its initial value. If more than this amount of unchanged *trans*-stilbene remains in the crude product, it cannot be removed by recrystallization from either methanol or hexane. Even after repeated crystallization the melting point of the product does not rise above 66–67°. Pure *trans*-stilbene oxide can be isolated from such a mixture if the mixture is treated with additional peracetic acid to convert the remaining *trans*-stilbene to *trans*-stilbene oxide.

5. This melting point and yield are obtained after the crystalline product which separates from methanol has been dried under reduced pressure for 12 hours. This drying process is unnecessary if the product is subsequently to be recrystallized from hexane.

3. Methods of Preparation

trans-Stilbene oxide has been prepared by the reaction of silver oxide with the methiodide of 1,2-diphenyl-2-dimethylaminoethanol,^{3,4} by the reaction of hydrazine with hydrobenzoin,⁵ and by the reaction of peracetic acid^{6,7} or perbenzoic acid⁸ with *trans*-stilbene. The procedure described illustrates the use of a commercially available peracetic acid solution for the epoxidation of carbon double bonds. Since the reaction of *trans*-stilbene and other olefins conjugated with aromatic nuclei with peracids is slow, the procedure for the epoxidation of unconjugated olefins should be modified by the use of a lower reaction temperature, a shorter reaction time, and a longer period of time for the addition of the peracid.

¹ Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

² Greenspan and MacKellar, *Anal. Chem.*, **20**, 1061 (1948).

³ Read and Campbell, *J. Chem. Soc.*, **1930**, 2377.

⁴ Rabe and Hallensleben, *Ber.*, **43**, 884 (1910).

⁵ Müller and Kraemer-Willenberg, *Ber.*, **57B**, 575 (1924).

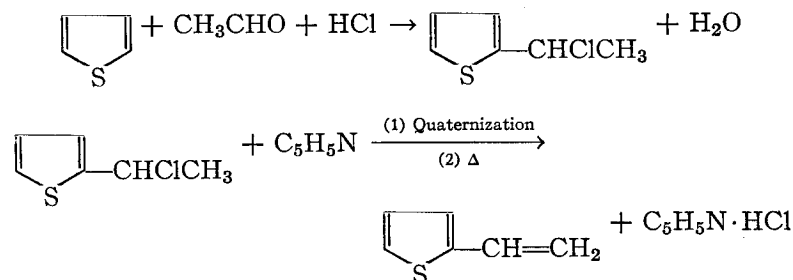
⁶ Böseken and Elsen, *Rec. trav. chim.*, **47**, 694 (1928).

⁷ Böseken and Schneider, *J. prakt. Chem.*, **131**, 285 (1931).

⁸ Tiffeneau and Levy, *Bull. soc. chim. France*, [4]**39**, 763 (1926).

2-VINYLTHIOPHENE

(Thiophene, 2-vinyl-)



Submitted by W. S. EMERSON and T. M. PATRICK, JR.¹

Checked by MAX TISHLER, P. TISHLER, and F. W. BOLLINGER.

1. Procedure

A 2-l. three-necked flask is fitted with a thermometer, a stirrer, a gas inlet tube which will reach beneath the surface of the liquid, and a vent. The flask is placed in a bath of acetone to which Dry Ice can be added. To the flask are charged 336 g. (318 ml., 4.0 moles) of thiophene (Note 1), 176 g. (177 ml., 1.33 moles) of paraldehyde, and 300 ml. of concentrated hydrochloric acid. While this mixture is stirred and maintained at 10–13° (Note 2) by means of Dry Ice, gaseous hydrogen chloride is bubbled in. At the end of 25 minutes the solution is saturated (Note 3).

The contents of the flask are poured onto 300 g. of ice, the layers

are separated, and the organic portion is washed three times with 200-ml. portions of ice water (Note 4). The organic layer is added, with some cooling (Note 5), to 316 g. (322 ml., 4.0 moles) of pyridine and 2.0 g. of α -nitroso- β -naphthol in a 1-l. distilling flask. The aqueous layer is extracted with two 100-ml. portions of ether, and the combined ethereal extract is used to wash each aqueous wash in turn (Note 6). The ethereal layer is concentrated on the steam bath under a stream of nitrogen and combined with the organic mixture in the distilling flask. The mixture is allowed to stand for 1.5 hours before distillation. The distillation is performed under reduced nitrogen pressure. The distillate is collected over 1.0 g. of α -nitroso- β -naphthol in an ice-cooled receiver at successively lower pressures ending at 125°/50 mm. (Note 7). The distillate is poured onto a mixture of 400 g. of ice and 400 ml. of concentrated hydrochloric acid. The layers are separated, and the organic portion is washed successively with 100-ml. portions of 1% hydrochloric acid, water, and 2% ammonia.

The organic layer is filtered through 1 cm. of anhydrous magnesium sulfate on a sintered-glass funnel into a 500-ml. distilling flask. The aqueous layer is extracted with two 100-ml. portions of ether which are combined and used to extract the aqueous washes. The ethereal layer is washed with 50 ml. of saturated salt solution and filtered through the same funnel into a fresh suction flask. The funnel is finally washed with two 50-ml. portions of ether. The ethereal washes are concentrated on a steam bath under nitrogen (Note 8) and combined with the filtrate in the distilling flask. The filtrate is fractionally distilled under nitrogen through a 2-cm. column, 35 cm. high, packed with 6-mm. glass helices (Note 9). The column is jacketed and provided with a heater inside the jacket to minimize heat losses during distillation. The receiver is cooled in an ice bath, and the distillate is collected in three fractions, thiophene 45.6–27.9 g., b.p. 36°/150 mm.–35°/100 mm. (Note 10), intermediate 11.8–4.8 g., b.p. 35°/100 mm.–80°/98 mm., and 2-vinylthiophene (Notes 11 and 12) 191.3–224.0 g., b.p. 65–67°/50 mm., n_D^{25} 1.5701, lit.² b.p. 65.5–66.5°/48 mm., lit.³ n_D^{25} 1.4698. The yield is 50–55% of the theoretical amount based on the thiophene consumed.

The undistilled residue amounts to about 27 g. and the distillate in the Dry Ice-acetone trap to about 4 g.

2. Notes

1. Specific gravities at 25° were used to determine the volumes of reagents. Eastman Kodak Company thiophene, b.p. 83–85°, n_D^{25} 1.5252, and U.S.P. paraldehyde were used.

2. The submitters used an ice-salt bath, but the checkers found a Dry Ice-acetone bath more convenient and almost indispensable. Temperature control is important. Small deviations from the prescribed range result in a lower yield.

3. When the solution is saturated, copious fumes of hydrogen chloride are evolved from the vent. The reaction should not be continued beyond this point. With an ice-salt bath the time required for addition of hydrogen chloride was 35 minutes.

4. The yield will be much lower if the washing process is not carried out quickly.

5. If the mixture is too cold, the quaternization reaction will be delayed. On the other hand, if no cooling is provided, the reaction mixture may boil over spontaneously because of the exothermic nature of the reaction. Heat cracks the quaternary compound to 2-vinylthiophene which, if not removed by distillation, may undergo thermal polymerization.

6. Omission of this ethereal extraction will reduce the quoted yield by about 2 per cent.

7. At this temperature and pressure volatilization of pyridine hydrochloride occurs. Passage of vapors during the distillation through a Dry Ice-acetone trap yields 8.8 g. of thiophene contaminated with its original odoriferous impurities and 2.2 g. of an aqueous layer, both of which were discarded.

8. Omission of this ethereal extraction will reduce the quoted yield by about 6 per cent.

9. A packed column is essential to achieve the degree of fractionation required.

10. The distillation is conducted so as to keep the pot temperature below 90° until about 90% of the product has been distilled. This is done to minimize thermal polymerization of the product.

11. If the intermediate and product fractions are not to be used immediately, α -nitroso- β -naphthol is added as a stabilizer.

12. 5-Chloro-2-vinylthiophene and 5-bromo-2-vinylthiophene have been prepared in 47% and 35% yields, respectively, by essentially the same procedure.

3. Methods of Preparation

2-Vinylthiophene has been prepared by the dehydration of α -(2-thienyl)ethanol,³⁻⁵ by the condensation of vinyl chloride with 2-thienylmagnesium bromide in the presence of cobaltous chloride,⁶ and by the dehydrochlorination of α -(2-thienyl)ethyl chloride.⁷

¹ Monsanto Chemical Co., Dayton 7, Ohio.

² Schick and Hartough, *J. Am. Chem. Soc.*, **70**, 1646 (1948).

³ Mowry, Renoll, and Huber, *J. Am. Chem. Soc.*, **68**, 1105 (1946).

⁴ Kuhn and Dann, *Ann.*, **547**, 293 (1941).

⁵ Nazzaro and Bullock, *J. Am. Chem. Soc.*, **68**, 2121 (1946).

⁶ Strassburg, Gregg, and Walling, *J. Am. Chem. Soc.*, **69**, 2141 (1947).

⁷ Emerson and Patrick, *J. Org. Chem.*, **13**, 729 (1948).

SUBJECT INDEX

(This cumulative index comprises material from Volumes 30-38; for previous volumes see Collective Volumes 1, 2, and 3.)

Names in small capital letters refer to the titles of individual preparations. A number in ordinary bold-face type denotes the volume. A page number in bold-face italics indicates that the detailed preparative directions are given or referred to; entries so treated include principal products and major by-products, special reagents or intermediates (which may or may not be isolated), compounds mentioned in the text or Notes as having been prepared by the method given, and apparatus described in detail or illustrated by a figure. Page numbers in ordinary type indicate pages on which a compound or subject is mentioned in connection with other preparations. For example, Allylbenzene, **31**, 85, *86* indicates that allylbenzene is mentioned on page 85, and that directions for its preparation are given on page 86, of Volume 31.

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ORGANIC SYNTHESSES

AN ANNUAL PUBLICATION OF SATISFACTORY
METHODS FOR THE PREPARATION
OF ORGANIC CHEMICALS

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Additions, corrections, and improvements to the preparations previously published are welcomed and should be directed to the Secretary.

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