ORGANIC SYNTHESES

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

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PREFACE TO VOLUME VIII

THE general plan of Organic Syntheses has been discussed in the prefaces of the previous volumes. In this volume are published two distinctly different methods of preparation for each of two compounds. The directions for producing β-chloropropionic acid first from acrolein and second from trimethylene chlorohydrin, and for producing trimethylacetic acid first from *tert*-butyl chloride and second from pinacolone, have been included. This has been deemed advisable since in some countries one raw material is more readily available than the other.

As the size of each volume must be limited there will necessarily be a delay in the publication of the directions submitted by contributors. Moreover, in certain instances, attempts by the editors to check the preparations have not met with immediate success. It is hoped, however, that former as well as new contributors will send in any preparations which may seem suitable for these publications.

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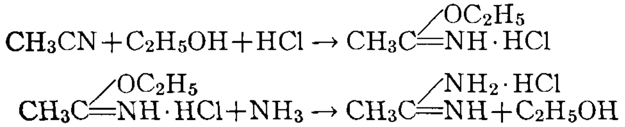
ORGANIC SYNTHESES

I

ACETAMIDINE HYDROCHLORIDE



$$CH_3CN + C_2H_5OH + HCl \rightarrow CH_3C\begin{array}{l}\diagup OC_2H_5\\ =NH\cdot HCl\end{array}$$

$$CH_3C\begin{array}{l}\diagup OC_2H_5\\ =NH\cdot HCl\end{array} + NH_3 \rightarrow CH_3C\begin{array}{l}\diagup NH_2\cdot HCl\\ =NH\end{array} + C_2H_5OH$$

Submitted by A. W. Dox.
Checked by Frank C. Whitmore.

1. Procedure

Dry hydrogen chloride (Org. Syn. **2**, 30) (Note 1) is passed into a solution of 100 g. (2.44 moles) of thoroughly dry acetonitrile (Note 2) in 113 g. of absolute ethyl alcohol (Note 1) contained in a 1-l. weighed suction flask (Note 3) surrounded by a freezing mixture of ice and salt, until an increase in weight of 95 g. (2.6 moles) is obtained. This requires about four hours (Note 4) but the time is diminished considerably if proper mechanical stirring is used. The flask is now tightly stoppered, the side arm being attached to a calcium chloride tube, and allowed to stand until the mixture has set to a solid mass of crystals. Usually this requires two or three days.

A solution of dry ammonia gas in absolute ethyl alcohol is prepared and titrated against standard hydrochloric acid, using methyl orange as the indicator. The solution should contain at least 9 per cent of ammonia by weight (Note 5).

The solid crystalline mass of acetimido ethyl ether hydrochloride is broken up and transferred to a dry mortar in which it is ground to a paste with 100 cc. of absolute alcohol and returned to the flask (Note 6). It is then stirred mechanically with an excess of the alcoholic ammonia solution (500 cc. of 9 per cent solution or an equivalent amount of a more concentrated solution). The crystals gradually dissolve and ammonium chloride separates. After stirring for three hours the ammonium chloride is filtered by suction and the filtrate evaporated on the steam bath to a volume of about 200 cc. when a considerable quantity of crystals separates. On cooling, the acetamidine hydrochloride separates in long colorless prisms. These are filtered by suction, washed with 10 cc. of cold alcohol, and dried in a desiccator over sulfuric acid. Concentration of the mother liquor gives a second crop. The product melts at 164–166° and is readily soluble in alcohol and in water. The yield varies from 185–210 g. (80–91 per cent of the theoretical amount). The product is somewhat deliquescent and should be kept in a tightly stoppered bottle.

2. Notes

1. The dryness of the reagents affects the yield seriously because of the ease with which the intermediate imido ether is hydrolyzed. The hydrogen chloride must be thoroughly dried by passing it through two wash bottles containing sulfuric acid. If the wash bottles are not effective, a tube containing glass beads mixed with phosphorus pentoxide should be used after the wash bottles. It is well to protect the side arm of the flask by means of a calcium chloride tube. The absolute alcohol used should be at least 99.5 per cent (Org. Syn. **5**, 56).

2. If commercial acetonitrile is used directly, the yields are poor. It should be dried over calcium chloride for at least a week, filtered, and distilled, the fraction boiling at 76–81° being used.

3. If a thinner flask is used, there is danger of its being cracked during the experiment.

4. If a proper safety bottle is placed between the drying train and the flask of acetonitrile, the treatment with hydrogen chloride does not require constant attention during this time.

5. When weaker solutions of ammonia were used, the yields were lower.

6. The grinding of the imido ether hydrochloride is very important, as lumps of this material become coated with ammonium chloride, which prevents the complete action of the ammonia.

3. Methods of Preparation

The only practical method of preparation is that of Pinner,[1] on which the present directions are based.

---

[1] Pinner, Ber. **16**, 1654 (1883); **17**, 178 (1884).

II

ALLYL CYANIDE

$$2CuSO_4 + 4NaCN \rightarrow 2CuCN + (CN)_2 + 2Na_2SO_4$$

$$CH_2{=}CHCH_2Br + CuCN \rightarrow CH_2{=}CHCH_2CN + CuBr$$

Submitted by J. V. Supniewski and P. L. Salzberg.
Checked by Frank C. Whitmore,
H. F. Herzog, and Gladys E. Woodward.

1. Procedure

A. *Preparation of Cuprous Cyanide.* (Note 1) — In a 6-l. round-bottom flask fitted with a stopper carrying a mechanical stirrer, a separatory funnel, and a gas exit tube leading to a good hood (Note 2), is placed a solution of 650 g. (2.6 moles) of crystallized copper sulfate in 4 l. of water. The flask is surrounded by an oil bath and heated to about 80°. The stirrer is started and a solution of 255 g. (5.2 moles) of sodium cyanide (Note 3) in 650 cc. of water is added from the separatory funnel over a period of about one-half hour. Then the mixture is boiled until no more cyanogen gas is evolved. This requires about five to ten minutes.

The cuprous cyanide, which begins to separate as a light tan precipitate as soon as any of the cyanide solution is added, is allowed to settle and the solution is decanted. The precipitate is filtered, then washed with water (1 l.) and finally with alcohol (500 cc.) and ether (300 cc.). After drying at 110° for about thirty-six hours, the product weighs 200–210 g. (85–90 per cent of the theoretical amount).

B. *Preparation of Allyl Cyanide.*— In a 1-l. round-bottom flask fitted with a condenser (Note 4) and a mechanical stirrer are placed 220 g. (1.83 moles) of allyl bromide (Note 5) and 170 g.

(1.9 moles) of dry cuprous cyanide (Note 6). The mixture is heated in a water bath and the stirrer rotated slowly by hand until the reaction starts (about fifteen to thirty minutes). When the reaction once begins, it becomes vigorous, and the heating bath must be replaced by a cooling mixture of ice and water in order to avoid loss of product through the condenser. After the vigorous reaction has subsided, the water bath is replaced, the mechanical stirrer is started and the mixture is heated until no more allyl bromide refluxes. This requires about one hour.

The condenser is then set for distillation and the allyl cyanide is distilled from the flask by heating it in an oil bath with stirring (Notes 7 and 8). Upon redistillation the allyl cyanide is pure and boils at 116–121° with almost no loss. The yield is 98–103 g. (80–84 per cent of the theoretical amount).

2. Notes

1. Technical cuprous cyanide dried at 110° gives as good results as the specially prepared substance.

2. The cyanogen evolved in this reaction should be led into a flue with good suction draft. It may be burned if a trap is placed in the system to allow the moisture to condense.

3. The ordinary technical sodium cyanide is used.

4. A very efficient condenser is needed as the mixture refluxes vigorously during the first part of the reaction. A condenser of the bulb type about 90 cm. long is satisfactory. If a less efficient condenser is used, the upper end should be fitted with a tube leading into an empty flask to catch any material forced out.

5. The allyl bromide (Org. Syn. 1, 3) should be dried over calcium chloride, filtered and redistilled, the fraction boiling at 69–71° being used.

6. The cuprous cyanide must be dry, as small amounts of moisture reduce the yield considerably (about 15 per cent). With some samples of technical cuprous cyanide a larger amount must be used.

7. Toward the end of this distillation it is advisable to connect with the suction to remove the last of the allyl cyanide from the solid residue in the flask.

8. The residue in the flask is very tarry. It is best removed by careful treatment with strong nitric acid, then with water, and finally with hot alcohol. If necessary, the treatment is repeated several times.

3. Methods of Preparation

Allyl cyanide has been found in oil of mustard[1] and has been prepared from allyl chloride and potassium cyanide,[2] allyl bromide and potassium cyanide,[3] allyl iodide and potassium cyanide[4] and silver cyanide.[5] The method described in the procedure is essentially that of Bruylants, who has shown that the yields are much better when dry cuprous cyanide is treated with allyl bromide.[6]

[1] Will and Körner, Ann. **125**, 273 (1863).

[2] Pinner, Ber. **12**, 2053 (1879).

[3] Pomeranz, Ann. **351**, 357 (1907); Lespieau, Compt. rend. **137**, 262 (1903); Lespieau, Bull. soc. chim. (3) **33**, 58 (1905).

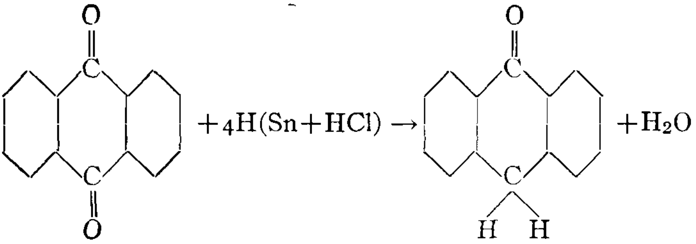
[4] Rinne and Tollens, Ann. **159**, 106 (1871).

[5] Lieke, Ann. **112**, 317 (1859).

[6] Bruylants, Bull. soc. chim. Belg. **31**, 175 (1922).

III

ANTHRONE



Submitted by Kurt H. Meyer.
Checked by J. B. Conant and W. C. Boyd.

1. Procedure

In a 2-l. round-bottom flask fitted with a reflux condenser, 105 g. (0.5 mole) of anthraquinone, m.p. 276–280° (corr.), is mixed with 100 g. (0.86 mole) of granulated tin, and 750 cc. of glacial acetic acid is added. The contents of the flask are heated to boiling, and in the course of two hours, 250 cc. of c.p. hydrochloric acid (sp. gr. 1.19) is added in 10 cc. portions to the boiling mixture. At the end of this time all of the anthraquinone should have gone into solution; if not, more tin and hydrochloric acid are added.

The liquid is filtered with suction through a Gooch crucible with a fixed porous plate (Note 1), and 100 cc. of water is added. The anthrone crystallizes at about 10°. After being dried on a porous plate, it melts at about 153° (corr.). The yield is 80 g. (82.5 per cent of the theoretical amount). On recrystallization from a 3 : 1 mixture (Note 2) of benzene and petroleum ether about 60 g. of anthrone melting at 154–155° (corr.) is obtained (62 per cent of the theoretical amount).

2. Notes

1. The liquid can also be filtered through a fluted filter paper, but this is slower.

2. The proportions do not make much difference as far as the yield is concerned, but the substance is more soluble in mixtures rich in benzene. About 10–12 cc. of the 3 : 1 mixture is required for each gram of anthrone. The anthrone may be more readily dissolved if it is added to the estimated quantity of hot benzene on the steam bath, and the petroleum ether is then added. About two-thirds of the mother liquor may be distilled off through a condenser and used in later runs. The residual mother liquor deposits about 12 g. of rather impure anthrone.

3. Methods of Preparation

Anthrone has been prepared by the reduction of anthraquinone with tin and hydrochloric acid,[1] and with aluminium bronze.[2]

---

[1] Meyer, Ann. **379**, 55 (1911).

[2] Eckert and Pollak, Monatsh. **38**, 12 (1917).

IV

APPARATUS FOR CATALYTIC REDUCTION

Submitted by Roger Adams and V. Voorhees.
Checked by Henry Gilman and S. A. Harris.

1. Procedure

I. *The Apparatus* (Fig. 1). A Prest-o-lite tank A from which the filling has been removed (Note 1), or any other similar tank of about 8–10 l. capacity, may be conveniently used as a container for hydrogen. The top of the tank contains two openings B and C. In B is welded a tube holding a gauge and valve, and through this tube the hydrogen from a large cylinder D is introduced into the tank. In C is welded another tube controlled by a needle valve. E is used for the vacuum, a manometer G being introduced into this system, and F for a tube leading to the reaction bottle H. These outlets are so arranged that it is possible to shut off the tank from either outlet and also to make a direct connection between the vacuum and the bottle H, leaving tank A out of the circuit. The connection between the tank A and the bottle H is a heavy taped rubber tube (Note 2) which is in turn connected to a glass tube inserted through the stopper of the bottle. The rubber tube and stopper should be high-grade and must be carefully boiled with alkali before being used (Note 3). The arrangement for shaking the bottle is shown in the diagram (Note 4). The driving pulley is connected to the reaction bottle by a wooden or preferably a metal rod. The rod in turn is attached by a yoke to a metal ring which circles the bottom of the bottle. The ring opens on the back side of the bottle and is held together by a wing-nut and bolt. In order to hold the stopper in the bottle when the latter is filled with hydrogen under pressure, a metal strip I is clamped tightly over the stopper. This strip is screwed to the long wooden bottle holder which extends between the bearings, and a short wooden piece which fits around the neck of the bottle is attached to the longer one by means of screws held by wing-nuts. This arrangement permits removal of the bottle from the apparatus without detaching the metal strip.

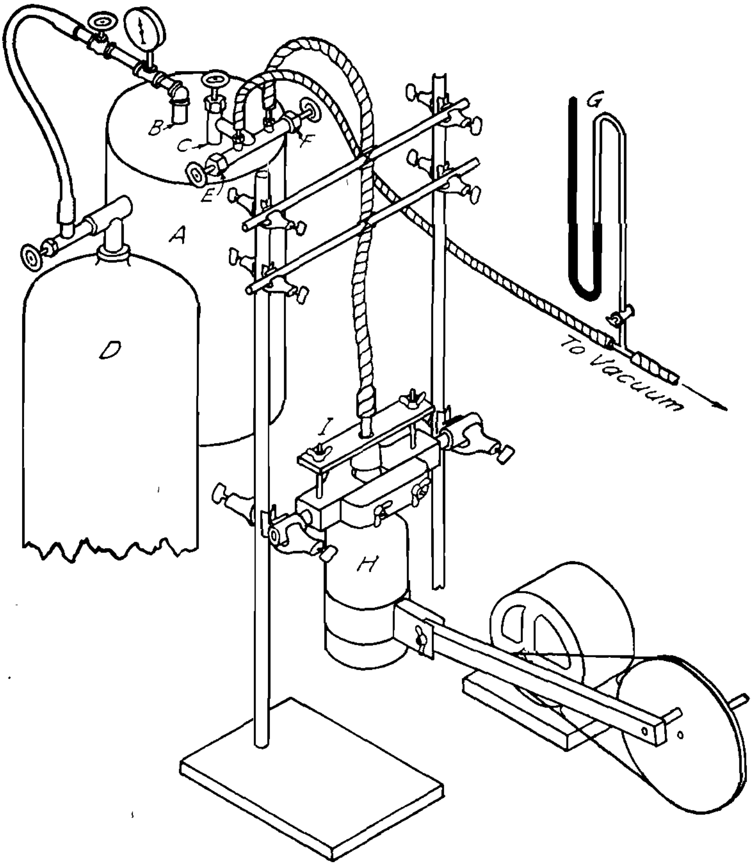


FIG. 1.

The chief precautions in setting up this reduction outfit are first, to have every piece free from catalytic poisons and second, to be certain that there are no leaks (Note 5). The latter are sometimes an annoying factor and the complete apparatus should be carefully tested before attempting any reductions for standardizing the hydrogen tank. The apparatus is put together in final form with the empty reduction bottle attached to the hydrogen tank exactly as it is arranged in a reduction. The tank is then filled with hydrogen until the gauge reads 2.5–3 atm. (40–45 lbs.) and the temperature of the tank recorded. The reading of the gauge is observed as soon as equilibrium is reached and the bottle is then shaken for six to eight hours. Observations are made of the drop in pressure, taking into account any change of temperature which may occur during this time. In general if the drop in pressure is less than 0.03 atm. (0.5 lb.) in the time indicated the apparatus may be considered sufficiently free from leaks for ordinary work.

For some reactions it is advantageous to heat the mixture, and the following arrangement is very satisfactory for this purpose. The bottle H is wrapped with moistened asbestos paper to a thickness of about 3 mm. and the paper is then allowed to dry. When the asbestos is thoroughly dry the bottle is wound with a coil of No. 24 Nichrome wire, beginning the coil at the bottom of the bottle and making the turns about 9 mm. apart. The wire is then covered with a 3 mm. layer of asbestos, which is moistened and allowed to dry, after which the wire is wound around the bottle in another coil from top to bottom. The second coil is covered with asbestos as before, and the ends of the wire are connected to the terminal wires from a source of current. These wires are led along the bottle to the neck and held by means of tape in order to avoid excessive shaking. A variable resistance in the circuit is used to regulate the temperature.

II. *Use of the Apparatus.*—The tank A is filled with hydrogen to a pressure of 3–3.5 atm. from the cylinder D (Note 6). The solution, in a suitable solvent, of the substance to be reduced is poured into the bottle H and the platinum oxide (p. 92)is added (Note 7). The bottle is attached to the apparatus and evacuated by opening valves E and F and closing C. In the case of low-boiling solvents, the evacuation is continued only until the solvent begins to boil; in other cases it is continued until the pressure as recorded by the manometer remains fairly constant. The valve E is then closed and hydrogen is admitted to the bottle H from the tank A by opening valve C (Notes 8 and 9). When the pressure in the bottle has become adjusted the pressure of the hydrogen and the temperature of the tank A are recorded. Shaking is started. Within a few minutes the brown platinum oxide turns black (see Note 5, p. 95) and the absorption of hydrogen begins. The shaking is continued until the theoretical amount of hydrogen has been absorbed. The hydrogen remaining in the bottle is removed, air is admitted and the mixture allowed to stand or, if necessary, shaken for a few minutes in order to aid the settling of the catalyst. In certain cases where the catalyst settles spontaneously at the end of the reduction it is not necessary to shake the mixture with air. The solution may be decanted from the main portion of the catalyst and a second reduction carried out. In cases where the catalyst cannot be used directly for another reduction (see Note 8, p. 97) the solution is filtered, preferably through an asbestos filter (Note 10) and fresh solvent is used for washing. The reduction product is isolated from the filtrate, usually by distilling off the solvent. The reduction of ethyl *p*-nitrobenzoate to ethyl *p*-aminobenzoate (p. 66) and benzalacetophenone to benzylacetophenone (p. 36) are described in detail in this volume.

III. *Standardization of the Apparatus.*—After making certain that there are no leaks in the apparatus (Note 5) the hydrogen tank may be standardized by reducing 11.6 g. (0.1 mole) of pure maleic acid (Note 11) dissolved in 150 cc. of 95 per cent alcohol using 0.1 g. of catalyst (p. 92). The reduction is carried out according to the procedure described in part II. Shaking of the mixture is continued until no more hydrogen is absorbed; the theoretical amount is absorbed by 0.1 mole of maleic acid within twenty or thirty minutes. The temperature of the tank is recorded. The decrease in pressure corresponds to 0.1 mole of hydrogen at the observed temperature. If the succinic acid is desired it may be recovered merely by filtering the platinum, evaporating the alcohol and crystallizing from about 10–15 cc. of boiling water. The yield of product is 10–11.5 g. (84–98 per cent of the theoretical amount) depending on the care used in crystallization.

2. Notes

1. The bottom of the tank is cut off, the filling removed, and the bottom welded on again.

2. A copper tube may be used for this connection but is less satisfactory since the shaking tends to wear it out at the joints.

3. It is advisable to boil the tube and stopper with several portions of 20 per cent sodium hydroxide until the solution is no longer colored yellow, after which the boiling is carried out several times with distilled water.

4. The motor, pulley and the supports for the reaction vessel must be attached firmly to a heavy wooden stand which will allow as little motion as possible in the apparatus during shaking, thus reducing to a minimum the possibility of the gradual formation of leaks.

The arrangement for shaking should be so made that the reaction bottle is agitated at a rate above which no difference in the speed of reduction is observed. In this laboratory the motor used is a 1/30 h.p., 1760 r.p.m., the pulley on the motor 2.5 cm. in radius, and the wooden driving pulley 7.5 cm. in radius. The distance from the center of the pulley to the hole for attaching the rod to the reaction bottle is 3.2 cm., the distance from the center of the pulley on the motor to the center of the driving pulley to the bottle attachment is 30 cm. Considerable latitude is possible in these measurements. Although the apparatus in Fig. 1 is readily set up in any laboratory, a more compact and more stable form is shown in Fig. 2. The uprights which support the bottle consist of 1.3 cm. (one-half inch) piping surmounted by T-couplings. The uprights, driving pulley, and motor are firmly screwed down to a heavy wooden stand. An apparatus similar to this can be purchased complete from the Standard Calorimeter Co., East Moline, Ill.

5. It is quite necessary that the welding of the tank is perfect and free from pin holes. Leaks frequently appear where the tubes are welded in the top of the tank. These may be eliminated by brazing the joints. A less satisfactory way is to use a cement of litharge and glycerol. This cement may also be used with success on leaky valves. Occasionally leaks occur in the rubber tubing or its connections with the bottle or tank, but these are unusual.

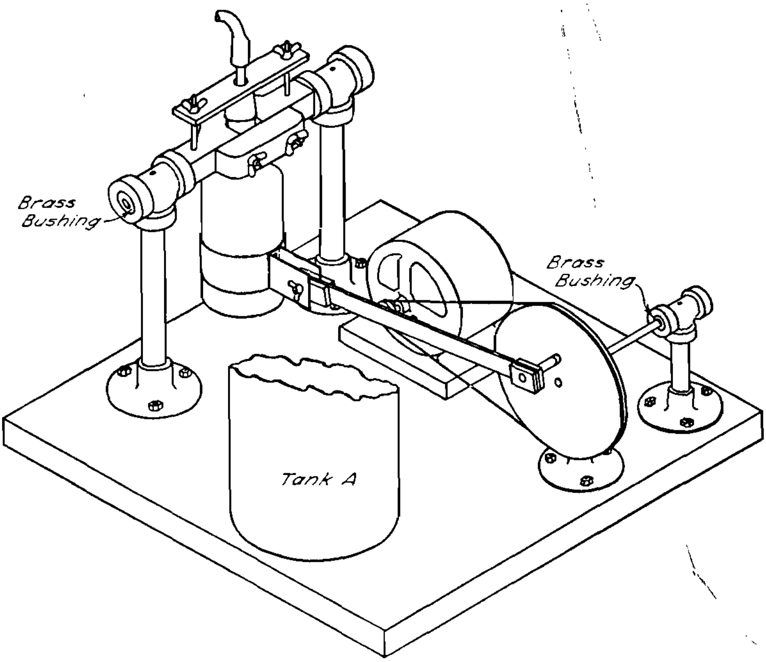


FIG. 2.

6. Electrolytic hydrogen was used in all experiments. This hydrogen is essentially free from all impurities except oxygen. Since oxygen in general has no harmful effect upon the reduction, no purification is necessary. If, however, oxygen-free hydrogen is needed, it must be passed over heated platinized asbestos.

7. This procedure may be varied in certain cases where it seems advantageous to reduce the platinum oxide to platinum black in the presence of the solvent alone (see Note 12, p. 98).

8. During the reductions it is usually advisable not to allow the pressure in the tank A to drop below about 2 atm. if the reduction is to be carried out in minimum time. When the gauge registers 2 atm. the tank is closed off from the reducing bottle and the pressure is increased to about 3–3.5 atm. by the admission of more hydrogen from D.

9. Ordinarily traces of air in the hydrogen have no deleterious effect upon the reductions. If in any experiment, absolute freedom from air is desired the bottle may be evacuated and refilled with hydrogen two or more times. In this way the air is all washed out of the bottle.

10. When paper filters are used the rapid suction of air through the paper in the presence of the catalyst often causes spontaneous combustion of the filter. Paper filters may be used, however, if care is taken to keep the filter covered with solvent while suction is being applied; just before the last portion of solvent has run through, the suction is stopped.

11. Instead of pure maleic acid, 10.6 g. (0.1 mole) of pure benzaldehyde may be used for the standardization. In this case 1 cc. of 0.1 molar ferrous sulfate is added to the mixture of benzaldehyde, alcohol and catalyst before the reduction is started (see Note 13, p. 98). The reduction is complete in fifteen to thirty minutes.

3. Forms of Apparatus

Other forms of catalytic reduction apparatus which may be used in the laboratory have been described in the following articles.[1]

---

[1] Paal and Amberger, Ber. **38**, 1390 (1905); Paal and Gerum, Ber. **41**, 813 (1908); Waser, Ueber Derivate des Cyclooctans (Promotionsarbeit) Zürich, 1911, p. 54; Willstätter and Hatt, Ber. **45**, 1472 (1912); Skita and Meyer, Ber. **45**, 3594 (1912); Stark, Ber. **46**, 2335 (1913); Boeseken, Van der Weide and Mom, Rec. trav. chim. **35**, 267 (1916); Rosenmund and Zetzsche, Ber. **51**, 580 (1918); Adams and Voorhees, J. Am. Chem. Soc. **44**, 1403 (1922); Klimont, Chem. Ztg. **46**, 275 (1922); Escourrou, Parfums France **26**, 88 (1925).

V

l-ARABINOSE

Hydrolysis of Mesquite Gum

Submitted by Ernest Anderson and Lila Sands.
Checked by H. T. Clarke and H. J. Bean.

1. Procedure

Five hundred grams of mesquite gum (Note 1) is dissolved (Note 2) in 3 l. of cold water in a 5-l. round-bottom flask; a cold solution of 125 g. of concentrated sulfuric acid in 80 cc. of water is added and the mixture warmed at 80° for six hours (Note 3) in a large water bath. The acid is neutralized by gradual addition of 140 g. of powdered calcium carbonate (Note 4), and the solution with excess calcium carbonate is heated in a boiling water bath for an hour to complete the neutralization. The calcium sulfate is filtered off and washed with about 2 l. of hot water. The filtrate is concentrated in an evaporating dish (Note 5) on the boiling water bath to a volume of 650–700 cc.

The solution is transferred to a 3-l. flask, using about 50 cc. of water for rinsing, and to it is added, with violent (Note 6) shaking, twice its volume (1400–1500 cc.) of 95 per cent ethyl alcohol. The solution is decanted from the gummy residue and the latter extracted three times with methyl alcohol under reflux, each time with 500 cc. of the solvent. In order to remove all the arabinose from the salts the precipitate is dissolved in 200–220 cc. of water, transferred to an evaporating dish, and 400 cc. of 95 per cent ethyl alcohol is stirred in with a heavy rod. The clear alcohol solution is decanted and the solid triturated twice with 300 cc. portions of methyl alcohol.

All the alcoholic extracts (both ethyl and methyl) are combined, shaken thoroughly, and 95 per cent ethyl alcohol added as long as any appreciable precipitate forms (Note 7). The solution is allowed to stand for some hours until it is clear, decanted, and concentrated in vacuo on a boiling water bath to a thin syrup (Note 8). Crystallization usually begins as soon as the syrup is cool though it is sometimes necessary to seed with arabinose.

After crystallization has begun 100 cc. of 95 per cent ethyl alcohol is stirred in, taking care not to precipitate any appreciable amount of gum. Crystallization is allowed to become complete in a cool place, occasionally stirring with a heavy rod. After about two days the crystalline arabinose is filtered off and washed with 200 cc. of 95 per cent ethyl alcohol. To secure further crops of arabinose from the mother liquor and washings, the solvent is distilled off under reduced pressure on the boiling water bath, and the residual gum dissolved in 200 cc. of hot methyl alcohol (Note 9). The solution is cooled, seeded with arabinose if necessary, set in the refrigerator for at least one day and the arabinose filtered off. After the first two crops of crystals have been secured, the organic salts that originally dissolved along with the arabinose begin to interfere with the crystallization. To remove these, the solvent is distilled off in vacuo on the boiling water bath, the residue dissolved in approximately 200 cc. of boiling methyl alcohol and 95 per cent ethyl alcohol added slowly with shaking until no more precipitate forms (about 40 cc. is necessary). The solution is allowed to cool and is decanted from the gummy salts; the solvent is then distilled from the sugar on the steam bath, finally under reduced pressure. The sugar is dissolved in a minimum volume of hot methyl alcohol, cooled, seeded with arabinose if necessary; set in the refrigerator to crystallize and the arabinose filtered off. If an appreciable amount of mother liquor is obtained, a fourth crop of crystals can be secured without again removing the gummy salts. In this way a total yield of 180–230 g. of crude arabinose can be obtained from the gum. The first two crops of crystals are easily obtained and amount to approximately 90 per cent of the total yield. The melting point of the crude sugar varies from 147 to 152°.

The crude powdered sugar is purified by heating 200 g. of it for forty-five minutes on the boiling water bath with 300 g. of glacial acetic acid,[1] allowing to cool, filtering off the arabinose, washing it with 500 cc. of 95 per cent ethyl alcohol in four portions, and drying at 50–60°. It then weighs about 182 g. and melts at 155–157°. It may be recrystallized from five times its weight of 76 per cent ethyl alcohol, with the use of 10 g. of decolorizing charcoal, Norite. The yield is about 127 g. and the melting point is 155–157°; the crystals are now perfectly colorless.

2. Notes

1. Mesquite gum is collected by the natives in the southwestern United States and northern Mexico. It is carried by most drug stores in this region and may be purchased from the Martin Drug Company of Tucson, Arizona.

2. If the mixture of mesquite gum and water is allowed to stand for ten hours with frequent shaking it will form a clear solution. If the mixture of gum and water is heated in the boiling water for an hour with frequent stirring the gum will also dissolve but the resulting solution is turbid.

3. Most of the arabinose is liberated during the first three hours' heating. The longer heating is necessary only in case the highest yield of arabinose is desired or the salts are to be used later for the preparation of galactose. No galactose is liberated by heating to 80° for six hours. However, some of this sugar is produced at 100° and seriously interferes with crystallization of the arabinose.

4. The solution is apt to foam over during neutralization. This may be prevented by adding to the foaming solution from time to time small amounts of *n*-butyl alcohol to break up the bubbles.

5. The solution may foam so badly that it is difficult to distil off the water under reduced pressure. In checking, it has

been found possible to do so if as much as 200–300 cc. of butyl alcohol has been added during neutralization.

6. If the mixture is merely gently shaken at this point much arabinose is contained with the precipitate, and the yield falls to as low as 30 per cent. of the amount obtained otherwise.

7. Appreciable amounts of organic salts dissolve during the extraction of the sugar and interfere seriously with the crystallization of the latter. Most of the salts are precipitated by addition of 95 per cent ethyl alcohol, leaving the sugar in solution.

8. If all the water is removed at this stage by heating the gum in vacuo for some time, the sugar will not crystallize readily.

9. Methyl alcohol, purified by distillation over quicklime, is the most satisfactory solvent for use in crystallizing the arabinose from the gummy mixture; ethyl alcohol at this stage usually causes the precipitation of a gum.

3. Methods of Preparation

The preparation of arabinose from various plant products has been repeatedly described in the literature. The most important sources are cherry gum,[2] beet pulp,[3] and as has recently been shown by the present authors,[4] mesquite gum. The chief advantages of the preparation from mesquite gum are that the material is readily available in large amounts, the process is simple, and the yield comparatively large. The present procedure is a modification of the original method of Anderson and Sands.

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[1] Hudson and Dale, J. Am. Chem. Soc. **39**, *322 (1917)*.

[2] Bauer, J. prakt. Chem. **34**, 46 (1886); Kiliani, Ber. **19**, 3029 (1886); cf. Browne, Handbook of Sugar Analysis, 548 (John Wiley, 1912).

[3] Gaertner, Z. Ver. deut. Zuckerind. **1919**, 232 [C. A. **14**, 1455 (1920)]; Harding, Sugar **24**, 656 *(1922)* [C. A. **17**, 1164 (1923)].

[4] Anderson and Sands, Ind. Eng. Chem. **17**, 1257 (1925).

VI

BENZALANILINE

$C_6H_5CHO + C_6H_5NH_2 \rightarrow C_6H_5CH{=}NC_6H_5 + H_2O$

Submitted by Lucius A. Bigelow and Harry Eatnough.
Checked by Henry Gilman and J. D. Robinson.

1. Procedure

In a 500-cc. three-neck, round-bottom flask provided with a mechanical stirrer is placed 106 g. (1 mole) of benzaldehyde (Note 1), and 93 g. (1 mole) of aniline is added with rapid stirring. After a few seconds a reaction occurs with evolution of heat and separation of water. The mixture is allowed to stand fifteen minutes and is then poured, with vigorous stirring, into 165 cc. of 95 per cent alcohol in a 600-cc. beaker. Crystallization begins in about five minutes, and the mixture is allowed to stand, first ten minutes at room temperature, and then thirty minutes in ice water. The almost solid mass is next transferred to a large Büchner funnel, filtered by suction, pressed out, and air dried. The yield of pure benzalaniline melting at 52° is 152–158 g. (84–87 per cent of the theoretical amount).

By concentrating the mother liquor to about half of its original volume at room temperature or lower, under reduced pressure by means of a water pump, an additional 10 g. of benzalaniline may be obtained. This is of good quality and melts at 51° (Note *2*).

2. Notes

1. Freshly distilled reagents must be used to obtain the yields described. Distillation through a column is recom-

mended. The benzaldehyde should be washed with 5 per cent sodium carbonate solution before being vacuum distilled.

2. Removal of the alcohol by distillation at ordinary pressure gives a much darker product.

3. Methods of Preparation

These are discussed in Org. Syn. 5, 13. The present method is simpler than that described there, and although the yields are approximately alike in the two methods, the product obtained here is purer. Excluding the drying of the crystals, the entire procedure may be completed in about two hours.

Benzalaniline has also been prepared by the condensation of aniline and benzaldehyde in dilute alcohol saturated with carbon dioxide.[1]

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[1] Pyl, Ber. **60**, 287 (1927).

VII

BENZOHYDROL

$$C_6H_5COC_6H_5+2H(Zn+NaOH) \rightarrow C_6H_5CHOHC_6H_5$$

Submitted by C. S. Marvel and N. A. Hansen.
Checked by J. B. Conant and G. M. Bramann.

1. Procedure

In a 3-l. three-neck, round-bottom flask fitted with a mechanical stirrer and a reflux condenser with a wide inner tube, are placed a solution of 200 g. (5 moles) of pure sodium hydroxide in 2 l. of 95 per cent alcohol (Note 1) and 200 g. (1.1 moles) of benzophenone (p. 26). The stirrer is started and the solution is heated to boiling until it has turned dark brown (about twenty minutes) (Note 2). To this brown solution 200 g. (about 2.6–3 moles) of technical zinc dust (about 85 per cent pure) is added over a period of twenty minutes. The solution is heated and stirred after all of the zinc has been added until the brown color has disappeared (usually about one hour). The hot solution is filtered and the residue is washed twice with a little hot alcohol (100 cc.). The filtrate is poured into five volumes of ice water acidified with about 425 cc. of concentrated hydrochloric acid (sp. gr. 1.19). The benzohydrol separates as a white crystalline mass and is filtered by suction. The yield of crude air-dried product melting at 65° is 192–200 g. (95–99 per cent of the theoretical amount). From 200 g. of crude product in 200 cc. of hot alcohol there is obtained, after cooling in an ice-salt mixture, filtering and drying, 140–145 g. of product melting at 68°. The benzohydrol remaining in the mother liquors may be precipitated with water.

1802

2. Notes

1. The directions in the literature usually call for the use of absolute alcohol and potassium hydroxide. The water present in ordinary alcohol does not interfere and sodium hydroxide can be substituted for potassium hydroxide. The alcoholic alkali is most easily prepared by dissolving the sodium hydroxide in 100 cc. of water and then adding 1900 cc. of absolute alcohol.

2. Unless the benzophenone is heated with the alcoholic alkali until a brown color is produced it is impossible to get a reduction. Several runs were made in which the alkali was dissolved in the hot alcohol, the benzophenone put in and the zinc dust added immediately in portions. No reduction took place.

3. Methods of Preparation

Benzohydrol has been obtained by reducing benzophenone with sodium amalgam,[1] with metallic calcium and alcohol,[2] with hydrogen in the presence of a catalyst,[3] with zinc, aluminium or sodium in strongly alkaline solutions,[4] with zinc dust and alcoholic potassium hydroxide solution,[5] and electrolytically.[6]

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[1] Linnemann, Ann. **125**, 230 (1863); **133**, 6 (1865).

[2] Marschalk, Ber. **43**, 642 (1910).

[3] Vavon, Compt. rend. **155**, 287 (1912).

[4] Böeseken and Cohen, Verhandel Akad. Wetenschappen Amsterdam, **16**, 91 (1913) [Chem. Zentr. **1915** (1), 1375.]

[5] Montagne, Rec. trav. chim. **25**, 402 (1906).

[6] Müller, Z. Electrochem. **16**, 240 (1910).

VIII

BENZOPHENONE

$$2C_6H_6+CCl_4(+AlCl_3) \rightarrow C_6H_5CCl_2C_6H_5+2HCl$$

$$C_6H_5CCl_2C_6H_5+H_2O \rightarrow C_6H_5COC_6H_5+2HCl$$

Submitted by C. S. Marvel and W. N. Sperry.
Checked by J. B. Conant and G. M. Bramann.

1. Procedure

In a 5-l. two-neck, round-bottom flask fitted with a good mechanical stirrer (Note 1), a separatory funnel, a thermometer, and a reflux condenser connected with a trap (Note 2) for absorbing the hydrogen chloride evolved, are placed 455 g. (3.4 moles) of anhydrous aluminium chloride (Note 3) and 1 l. (10.2 moles) of dry carbon tetrachloride (Note 4). The flask is surrounded by an ice bath (Note 5). The stirrer is started and when the temperature of the carbon tetrachloride has dropped to 10–15°, 50 cc. of dry thiophene-free benzene (Note 6) is added all at once. The reaction begins immediately as is indicated by the evolution of hydrogen chloride and a rising temperature. As soon as the reaction has started, salt is added to the ice in the cooling bath in order to get more effective cooling. When the temperature begins to fall after the reaction has started, a mixture of 550 cc. (a total of 6.7 moles) of thiophene-free benzene and 550 cc. (a total of 14.5 moles) of carbon tetrachloride is run in at such a rate that the temperature is kept between 5° and 10° (Note 4). If efficient cooling is maintained, this addition requires one to two hours. The stirring is continued for about three hours after the benzene-carbon tetrachloride solution has been added, while the temperature is held at about 10°. The stirring is then discontinued and the mixture is allowed to stand about twelve hours. During this time the mixture comes to room temperature. The stirrer is then again started and about 500 cc. of water is slowly added. External cooling is used in order that the water may be added more rapidly. The excess carbon tetrachloride usually refluxes during this part of the procedure. The reaction mixture is then first heated on a steam bath to remove most of the excess of carbon tetrachloride, then the mixture is distilled with steam to carry over the remaining carbon tetrachloride (Note 7), and to hydrolyze the benzophenone dichloride to benzophenone. The carbon tetrachloride comes over in about thirty minutes but the steam distillation is continued for about one hour to insure complete hydrolysis. The upper benzophenone layer is then separated from the aqueous layer and the latter is extracted with about 200 cc. of benzene. The benzene solution and the benzophenone are transferred to a 1-l. modified Claisen flask (Org. Syn. **1**, 40) for distillation. The benzene and any water that is present are removed under ordinary pressure and the benzophenone is distilled under reduced pressure (Note 8). The yield is 490–550 g. (80–89 per cent of the theoretical amount based on the benzene) of a product boiling at 187–190°/15 mm., and solidifying to a white solid melting at 47–48°. The material sometimes has a bluish tinge. This may be removed by moistening with benzene and centrifuging.

2. Notes

1. The stirrer should be very efficient as otherwise the aluminium chloride tends to cake on the sides of the flask. This makes cooling very difficult and thus increases the time necessary for the addition of the benzene-carbon tetrachloride mixture.

2. A convenient trap (Fig. 3) devised by John R. Johnson for the absorption of hydrogen chloride, or for the elimination of sulfur dioxide, hydrogen cyanide, etc., may be arranged as shown in the figure. The gases are led into a chamber in which a stream of water (from the reflux condenser in this case) flows downward into a large bottle. The bottle is provided with a

bent tube which serves as a siphon drain. The gases are thus brought into contact with a flowing stream of water so that the heat of solution is dissipated, and the level of the water in the lower bottle serves as a seal to prevent escape of the gases into the atmosphere. Water-insoluble gases are drawn out through the siphon drain directly into the sink.

If the gas chamber is of sufficient capacity there is practically no danger of water being drawn back into the reaction vessel, but care should be exercised when the reaction flask is cooled. For the reaction described here, a gas chamber about 2.5 cm. in diameter and 20–25 cm. in length was found to be satisfactory.

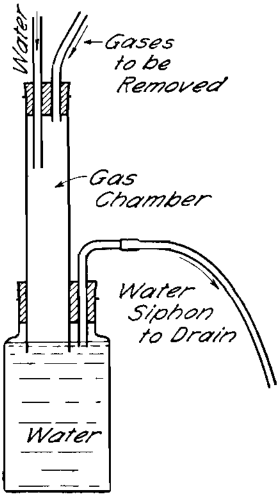

FIG. 3.

3. A good grade of technical anhydrous aluminium chloride was used to obtain the results given in the procedure. The yield falls off considerably when the quality of this reagent is not good.

4. No difference in yield is noticed in using the ordinary "pure" grade of carbon tetrachloride and the sulfur-free C.P. grade. It is easily dried by distilling the commercial product and rejecting the first 10 per cent of the distillate.

5. It is necessary to allow the reaction to start before packing in an ice-salt mixture. If the temperature is too low (below 10°) the reaction does not start. After the reaction has started, the cooling should be as efficient as possible so that the mixture of benzene and carbon tetrachloride may be added in the minimum amount of time. If the temperature drops below 5° the reaction is too slow. If the temperature goes above 10° there is increasing formation of tarry matter and lowering of the yield.

6. The yield is 5 to 10 per cent lower if the ordinary technical grade of benzene is used. The benzene is dried in the same manner as the carbon tetrachloride (Note 4).

7. About 1050–1150 cc. of carbon tetrachloride is recovered. This contains a small amount of benzene. However, it may be used in a succeeding run if it is dried over calcium chloride and distilled. No difference in the yield is noticed when recovered carbon tetrachloride is used.

8. There is considerable tendency for the benzophenone to foam over during the early part of the vacuum distillation and care must be taken to prevent this.

3. Methods of Preparation

Benzophenone has been prepared by the distillation of calcium benzoate,[1] by the action of benzoyl chloride on benzene in the presence of aluminium chloride,[2] by the action of phosgene on benzene in the presence of aluminium chloride,[3] by the action of carbon tetrachloride on benzene in the presence of aluminium chloride followed by hydrolysis.[4]

[1] Peligot, Ann. **12**, 41 (1834); Chancel, **72**, 279 (1849).

[2] Friedel and Crafts, Ann. chim. phys. (6), **1**, 510 (1884); Böeseken, Rec. trav. chim., **19**, 21 (1900); Olivier, **37**, 205 (1917); Norris, Thomas and Brown, Ber. **43**, 2959 (1910); Rubidge and Qua, J. Am. Chem. Soc. **36**, 735 (1914).

[3] Friedel and Crafts, Ann. chim. phys. (6) **1**, 518 (1884); Friedel, Crafts and Ador, Ber. **10**, 1854 (1877).

[4] Böeseken, Rec. trav. chim. **24**, 3 (1905); Gomberg and Jickling, J. Am. Chem. Soc. **37**, 2577 (1915).

IX

BENZOYLHYDROPEROXIDE

$$(C_6H_5CO)_2O_2+C_2H_5ONa \rightarrow C_6H_5COO_2Na+C_6H_5CO_2C_2H_5$$
$$C_6H_5COO_2Na+H_2SO_4 \rightarrow C_6H_5COO_2H+NaHSO_4$$

Submitted by M. TIFFENEAU.
Checked by ROGER ADAMS and F. E. KENDALL.

1. Procedure

IN a 5-l. round-bottom flask, fitted with an efficient mechanical stirrer and surrounded by an ice-salt mixture, is placed a solution of 121 g. (0.5 mole) of pure dry finely-powdered benzoylperoxide (m.p. 104°) (Note 1) in about 1.5 l. of dry toluene. The temperature should be below −5°. A solution of sodium ethylate, prepared by dissolving 23 g. (1 mole) of sodium in 500 cc. of absolute alcohol, and cooled to 0°, is introduced from a separatory funnel while the mixture is vigorously stirred. This operation should not require more than eight or ten minutes. The liquid whitens and thickens considerably on account of the formation of sodium benzoylperoxide.

After the sodium ethylate has been added, the sodium benzoylperoxide is dissolved by pouring 2 l. of ice water into the flask, while continuing the stirring and keeping the mixture cold (Note 2). When there remains no more than a trace of sodium benzoylperoxide, as evidenced by the fact that addition of a small quantity of ice water produces no further clarification, the toluene layer is separated in a previously cooled separatory funnel. The aqueous solution is extracted with ether which takes up the ethyl benzoate, the ether is separated, and the aqueous portion placed in the original flask surrounded by the cooling mixture. The liquid should be clear and absolutely free from unchanged benzoylperoxide.

The solution is cooled to 0° and then a cold solution of 54 g. of sulfuric acid (sp. gr. 1.84) in 50 cc. of water (slightly more than the theoretical amount) is slowly introduced from the separatory funnel during vigorous stirring. The solution becomes turbid and whitens as a result of the formation of the hydroperoxide, but no solid should appear. There should be no evolution of gas. Oxygen is evolved if the cooling is insufficient. The hydroperoxide appears in the form of a thick oil. The mixture is poured into a separatory funnel and extracted three times with 250-cc. portions of cold chloroform (Note 3) which dissolves the hydroperoxide. The chloroform is poured into a graduated cylinder, the volume noted, then poured into a carefully dried flask containing anhydrous sodium sulfate. The yield is 750–820 cc. of a solution containing 40 g. of benzoylhydroperoxide (90 per cent of the theoretical amount) (Notes 4 and 5). The use of this reagent in oxidation reactions is illustrated by the formation of styrene oxide from styrene (p. 84).

2. Notes

1. The benzoylperoxide used was analyzed by dissolving 1 g. in 25 cc. of dry ether and adding 2 cc. of 5 per cent sodium ethylate solution, keeping the temperature below −5°. The ether solution was extracted with exactly 100 cc. of cold water and an aliquot part of the aqueous extract taken. To this was added 2 cc. of 5 per cent potassium iodide and 2 cc. of dilute hydrochloric acid and the liberated iodine was titrated with 0.1 N sodium thiosulfate solution. The peroxide analyzed 90 per cent pure.

2. Generally it is noticed that a little of the benzoylperoxide remains undissolved, causing a turbidity in the bottom of the flask. This does not interfere with the reaction.

3. Ethereal solutions of the hydroperoxide are as stable as

chloroform solutions, but have been found to be notably less active.

4. Determination of active oxygen: The equation

$$C_6H_5COO_2H + 2\,KI + HCl \rightarrow C_6H_5CO_2K + I_2 + KCl + H_2O$$

shows that 16 g. of active oxygen correspond to 2 x 127 g. of iodine. Suppose for simplicity that a solution of sodium thiosulfate which is exactly 0.1 N is available. One cc. of this solution, containing 0.158 g. of sodium thiosulfate, corresponds to 0.0008 g. of active oxygen. Let v be the total volume of the chloroform solution of benzoylhydroperoxide prepared. For titration, 0.5 cc. of this solution is taken and several drops of dilute hydrochloric acid added. If n cc. of thiosulfate is required to absorb the iodine set free, the weight of active oxygen may be found from the following equation: $p = nv\,\frac{.0008}{0.5}$ or $p = \frac{nv}{625}$.

5. The yield is calculated upon the benzoylperoxide content of the material used. A decrease in the size of the run decreases the yield of benzoylhydroperoxide. A run using 20 g. of benzoylperoxide gave a yield of 65 per cent of the theoretical amount.

6. A recent publication by Hibbert and Burt[1] has modified Tiffeneau's directions, particularly in regard to the order of addition of the reacting substances. Tiffeneau adds the sulfuric acid to the sodium benzoylperoxide while Hibbert and Burt use the reverse procedure. The latter investigators state "benzoylhydroperoxide is very unstable in the presence of alkali, and its preparation must therefore be carried out in such a manner that no trace of sodium hydroxide is in solution when the free hydroperoxide is liberated. This is practically impossible when separation is effected by adding the acid to the aqueous solution of the sodium benzoylperoxide. When the latter is precipitated in ether solution by the action of sodium ethylate on the benzoylperoxide, the sodium salt always carries down with it a small amount of the ethylate and the latter during the acidification process yields sufficient free alkali to bring about a decomposition of the hydroperoxide as fast as it is formed. The reverse order is therefore employed."

Hibbert and Burt dissolved the benzoylperoxide in dry ether, cooled to −5° and added the calculated amount of a 10 per cent sodium ethylate solution, maintaining the low temperature during the procedure. Sufficient ice water was added to give a clear solution, the ether containing the ethyl benzoate separated and the aqueous sodium benzoylperoxide solution added slowly with stirring to twice the necessary amount of cold 20 per cent sulfuric acid (reaction mixture always at 0°). The oily layer of benzoylhydroperoxide was then extracted three times with chloroform and the extract dried over anhydrous sodium sulfate.

This procedure was carried out by the checkers and compared with Tiffeneau's procedure. Tiffeneau's directions seem preferable for the following reasons. There was much less tendency to form an emulsion when the sodium salt was extracted with ether. The emulsion in Hibbert's methods was frequently persistent and the solution became warm before the aqueous solution could be separated from the ether, thus causing decomposition. A 10 per cent solution of sodium ethylate is difficult to handle for it crystallizes and cannot be added from a separatory funnel. If more alcohol is added the tendency toward formation of the emulsion is increased.

It seems to the checkers that if any free alkali were present with the sodium benzoylperoxide this would certainly be neutralized first when acid is added before any free benzoylhydroperoxide is formed. At any rate the yields by both procedures were excellent.

7. Evaporation of a chloroform solution of benzoylhydroperoxide under reduced pressure yields a paste containing 20–30 per cent of hydroperoxide. On further evaporation this decomposes into benzoic acid. A chloroform solution of benzoylhydroperoxide when carefully dried over anhydrous sodium sulfate at 0° may be kept exposed to light at room temperature for a number of days without appreciable decomposition. In order to obtain benzoylhydroperoxide free from the reagents used in its preparation, it is necessary to extract the product with chloroform, such extraction resulting in a loss of about 10 per cent.

3. Methods of Preparation

Benzoylhydroperoxide has always been prepared by the action of sodium ethylate on benzoylperoxide and subsequent acidification with dilute sulfuric acid.[2]

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[1] Hibbert and Burt, J. Am. Chem. Soc. **47**, 2240 (1925).

[2] Baeyer and Villiger, Ber. **33**, 858, 1569 (1900).

X

BENZYLACETOPHENONE

$$C_6H_5CH{=}CHCOC_6H_5+H_2(Pt) \rightarrow C_6H_5CH_2CH_2COC_6H_5$$

Submitted by ROGER ADAMS, J. W. KERN and R. L. SHRINER.
Checked by HENRY GILMAN and S. A. HARRIS.

1. Procedure

A SOLUTION of 20.8 g. (0.1 mole) of benzalacetophenone (Note 1) (Org. Syn. **2**, 1) in 150 cc. of C.P. ethyl acetate (Note 2) is placed in the reaction bottle of the catalytic reduction apparatus (p. 10) and 0.2 g. of platinum oxide catalyst (p. 92) is added. The apparatus is evacuated, then filled with hydrogen, and the mixture shaken with hydrogen until 0.1 mole has been absorbed. The time required is usually about fifteen to twenty-five minutes (Note 3). The platinum is filtered off and the solvent removed from the filtrate by distillation. The benzylacetophenone is recrystallized from about 25 cc. of alcohol and melts at 72–73°. The yield is 17–20 g. (81–95 per cent of the theoretical amount).

2. Notes

1. The benzalacetophenone should be freshly recrystallized from alcohol just before using and should melt at 57°.

2. Owing to the comparatively slight solubility of benzalacetophenone in alcohol, ethyl acetate is used as a solvent during the reduction.

3. If 0.1 g. of catalyst is used the reduction requires about three hours; an increase in catalyst to 0.5 g. causes the reduction to take place in three or four minutes. The exact time depends

to a considerable extent on the grade of benzalacetophenone used and it is not certain that the very purest will necessarily be reduced in the shortest time.

3. Methods of Preparation

Benzylacetophenone has been prepared by the reduction of benzalacetophenone with zinc and acetic acid[1] and catalytically with palladium and hydrogen;[2] by the reduction of β-duplobenzylidene acetophenone monosulfide;[3] by the oxidation of the corresponding carbinol with chromic acid;[4] by the hydrolysis of ethyl benzyl benzoylacetate;[5] from acetophenone and benzyl chloride by the action of sodamide;[6] and from benzoic and hydrocinnamic acids using as catalysts manganese oxide[7] and ferric oxide.[8]

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[1] Schneidewind, Ber. **21**, 1325 (1888); Harries and Hübner, Ann. **296**, 327 (1897).

[2] Straus and Grindel, Ann. **439**, 294 (1924).

[3] Fromm, Ber. **41**, 3648 (1908).

[4] Bauer, Compt. rend. **154**, 1094 (1912).

[5] Perkin and Stenhouse, J. Chem. Soc. **59**, 1007 (1891).

[6] Claisen, Ber. **38**, 698 (1905); Haller and Bauer, Compt. rend. **149**, 8 (1909).

[7] Sabatier and Mailhe, Compt. rend. **158**, 835 (1914).

[8] Mailhe, Bull. soc. chim. (4) **15**, 325 (1914).

XI

BENZYLANILINE

$$C_6H_5CH_2Cl + C_6H_5NH_2 \rightarrow C_6H_5CH_2NHC_6H_5 + HCl$$

Submitted by F. G. Willson and T. S. Wheeler.
Checked by Henry Gilman and R. McCracken.

1. Procedure

A 1500-cc. flask is fitted with a reflux condenser, a mechanical stirrer, and a 200-cc. separatory funnel. In the flask are placed 372 g. (4 moles) of aniline (Note 1), 105 g. (1.25 moles) of sodium bicarbonate (Note 2) and 100 cc. of water. The flask and contents are then heated on a steam bath to 90–95°, and 127 g. (1 mole) of benzyl chloride (Note 3) is run in slowly from the separatory funnel, vigorous agitation being maintained. The addition of benzyl chloride should take not less than one and one-half to two hours, and the reaction is complete in four hours.

The mixture is then cooled, filtered with suction, the layers of water and organic liquid separated, and the latter washed with saturated salt solution (Note 4). The amines are then dried by shaking with about 20 g. of anhydrous sodium sulphate, and again filtered with suction. The excess of aniline is removed by vacuum distillation (Note 5) using a modified Claisen flask with a fractionating side arm (Org. Syn. **1**, 40). The aniline distils at 81°/12 mm., and then the temperature rises quickly to the boiling point of benzylaniline, 180°/12 mm. or 190°/16 mm. When the temperature has risen to within about 5° of the boiling point of the benzylaniline, the receiver is again changed and the benzylaniline collected from 170–200°/12 mm., practically all boiling at 178–180°/12 mm. The aniline recovered amounts to 250–260 g. (89–92 per cent of the theoretical amount), and the yield of benzylaniline is 155–160 g. (85–87 per cent of the theoretical amount based on the benzyl chloride). The product solidifies on cooling and melts at 33–36°. It is practically colorless and sufficiently pure for most synthetic purposes. A pure compound melting at 36° may be obtained by crystallizing the product from about 100 cc. of ligroin (b.p. 85–90°). The solution is cooled in a freezing mixture to cause crystallization, the crystals filtered with suction, washed with a little cold ligroin, pressed, and dried. The recovery is about 90 per cent of the original product.

2. Notes

1. Benzylaniline reacts with benzyl chloride to form dibenzylaniline. If the proportion of aniline used is less than that given, the yield of benzylaniline is lowered, and separation rendered more difficult.

2. Sodium bicarbonate is used on account of its high purity and convenience in handling. An equivalent amount of the normal carbonate may be substituted, but reagents of stronger basicity increase the proportion of high-boiling by-products.

3. The benzyl chloride should be freshly distilled and collected at 176–178°.

4. Saturated salt solution is used here in preference to water, as separation of the liquids is more rapid and clean.

5. The aniline may also be quite satisfactorily removed by distillation under atmospheric pressure, using an efficient fractionating column, the distillation being interrupted when the thermometer in the still head registers 235°.

6. Benzylaniline distils without appreciable decomposition at atmospheric pressure at 298–300°. It assumes, however, a yellow color, and separation from any higher-boiling impurities is more difficult than when distillation is carried out under reduced pressure.

3. Methods of Preparation

Fleischer[1] prepared benzylaniline by heating aniline with benzyl chloride at 160°. This reaction may be very violent and always leads to mixtures. Bernthsen and Trompetter[2] reduced thiobenzanilide with zinc and hydrochloric acid or sodium amalgam, while O. Fischer[3] reduced benzalaniline with sodium and alcohol, to benzylaniline. Knoevenagel[4] obtained a 32 per cent yield of benzylaniline from benzyl alcohol and aniline in the presence of iodine. Ullmann[5] describes the preparation of benzylaniline from benzyl chloride and excess of aniline at low temperatures.

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[1] Fleischer, Ann. **138**, 225 (1866).

[2] Bernthsen and Trompetter, Ber. **11**, 1760 (1878).

[3] Fischer, Ann. **241**, 330 (1887).

[4] Knoevenagel, J. prakt. Chem. (2) **89**, 32 (1914).

[5] Ullmann, " Enzyklopädie der technischen Chemie " (Urban and Schwarzenberg, Berlin) I, 445 (1914).

XII

p-BROMODIPHENYL

$$p\text{-BrC}_6\text{H}_4\text{N}_2\text{Cl} + \text{C}_6\text{H}_6 + \text{NaOH} \rightarrow$$
$$p\text{-BrC}_6\text{H}_4\text{C}_6\text{H}_5 + \text{N}_2 + \text{NaCl} + \text{H}_2\text{O}$$

Submitted by M. Gomberg and W. E. Bachmann.
Checked by C. S. Marvel and L. T. Sandborn.

1. Procedure

Forty-three grams (0.25 mole) of *p*-bromoaniline (Note 1) and 20 cc. of water are warmed in a 400-cc. beaker until the bromoaniline melts, and then 50 cc. of concentrated hydrochloric acid (sp. gr. 1.19) is added with mechanical stirring. The mixture is heated and stirred until solution is practically complete (Note 2). The beaker is then set in a dish of ice water and the solution is stirred as it cools in order to precipitate the *p*-bromoaniline hydrochloride in fine crystals. A few small pieces of ice are added and the cold (about 0–5°) suspension is diazotized with a solution of 18 g. of sodium nitrite in 36 cc. of water to an end point with starch-iodide paper.

The diazotized solution is poured into a 1.5-l. wide-mouth flask or bottle which is surrounded by ice water. Three hundred cc. of cold benzene is now poured into the diazonium solution, and by means of a good stirrer the two liquids are intimately mixed. The mixture, which is at the temperature of melting benzene, is now ready for the addition of alkali.

To this well-stirred mixture is added 58 cc. of 5 N sodium hydroxide solution over a period of one-half to three-quarters of an hour. This may be added drop by drop from a separatory funnel or in portions of a few cubic centimeters. The addition of the alkali causes the formation of a yellow precipitate which, on being stirred into the benzene, reacts with the latter and gives *p*-bromodiphenyl. If too much of this reactive " oxide " is precipitated at one time, some of it may decompose to a dark-brown product. The alkali is, therefore, added at such a rate that the amount of precipitate is at no time greater than can readily react with the benzene, and the stirring must be efficient. The temperature during the reaction is kept at about 5°; when all the alkali has been added, the mixture is allowed to warm to room temperature.

If an emulsion has formed, it may be broken by acidifying with hydrochloric acid, whereupon two clear layers are obtained. The benzene solution may be dried and then fractionated or preferably, it may be steam distilled. In the latter case it is transferred to a 1-l. Claisen flask, the flask is set in an oil bath (Note 3) and the benzene distilled. Steam is then passed in, and after the last of the benzene is removed, the *p*-bromodiphenyl distils with the steam. The temperature of the oil bath is held at 170° in order to hasten the distillation. The product solidifies in the condenser and receiving flask. There is obtained 23–24 g. of *p*-bromodiphenyl which melts at 85–86.5°.

The crude product is usually yellow or orange in color. The color may be readily removed by dissolving the crude product in 200 cc. of hot ethyl alcohol and treating this solution with 5 g. of zinc dust and about 5 cc. of concentrated hydrochloric acid (sp. gr. 1.19). This solution is then filtered and the *p*-bromodiphenyl allowed to crystallize. This gives a white product melting at 89.5–90°. The yield is 20–21 g. (34–35 per cent of the theoretical amount).

2. Notes

1. The *p*-bromoaniline used was somewhat colored and melted at 62.5–63°.

2. The volume of the diazonium solution is kept as small as possible in order that the proportion of benzene to water may be as large as possible. The bromoaniline does not completely dissolve in this quantity but is entirely converted to the salt.

3. There is some tendency toward foaming during the steam distillation. To avoid this the flask should be submerged almost completely in the oil bath.

3. Methods of Preparation

p-Bromodiphenyl has been obtained along with some of the ortho derivative from the bromination of diphenyl.[1] However, according to Schlenk,[2] the product so obtained is contaminated with some *p*, *p*′-dibromodiphenyl which is very difficult to remove. Bamberger obtained *p*-bromodiphenyl from the action of benzene on solid *p*-bromobenzene diazoanhydride.[3] The method described in the procedure has recently been described in the literature.[4]

[1] Schultz, Ann. **174**, 207 (1874).

[2] Schlenk, Ber. **46**, 1477 (1913).

[3] Bamberger, Ber. **29**, 470 (1896).

[4] Gomberg and Bachmann, J. Am. Chem. Soc. **46**, 2339 (1924).

XIII

m-BROMONITROBENZENE

$C_6H_5NO_2+Br_2(Fe) \rightarrow m\text{-}BrC_6H_4NO_2+HBr$

Submitted by JOHN R. JOHNSON and C. G. GAUERKE.
Checked by FRANK C. WHITMORE and T. OTTERBACHER.

1. Procedure

IN a 3-l. three-neck, round-bottom flask, provided with an efficient reflux condenser bearing an outlet tube held above a surface of water, a 100-cc. separatory funnel, and a mercury-sealed mechanical stirrer (Note 1), is placed 270 g. (2.2 moles) of freshly distilled dry nitrobenzene (Note 2). The joints in the apparatus are made of asbestos paper covered with water glass (Org. Syn. 5, 9). The flask is heated in an oil bath maintained at 135–145°, and 26 g. of iron powder and 180 cc. (3.5 moles) of dry bromine (Note 3) are added in the following manner: Eight grams of iron powder (" ferrum reductum ") (Note 4) is added through the side neck to the stirred nitrobenzene. From the separatory funnel 60 cc. of bromine is added at such a rate that the bromine vapors do not traverse the condenser. This addition requires about one hour, and the mixture is stirred and heated for another hour before the addition of a second portion of iron and bromine. Two portions, each of 8 g. of iron powder and 60 cc. of bromine, are added under the same conditions as the first addition, and the mixture is stirred and heated for one hour between the completion of one addition and the beginning of another. The evolution of hydrogen bromide slackens considerably toward the last of the heating, and there is practically no more bromine vapor condensed.

A final addition of 2 g. of iron powder is made, and the heating continued for one hour longer.

The reaction product, which is a dark reddish-brown liquid, is poured or siphoned (Note 5) into 1.5 l. of water to which 50 cc. of a saturated solution of sodium bisulfite has been added (Note 6). The mixture is distilled with steam (Org. Syn. **2**, 80) and the first portion of the distillate is collected separately to remove a small amount of unchanged nitrobenzene. It is necessary to collect about 12 l. of distillate in order to obtain all of the *m*-bromonitrobenzene. The yellow crystalline solid is filtered with suction and pressed well on the funnel to remove water and traces of nitrobenzene. The yield of crude product varies from 270–340 g. (60–75 per cent of the theoretical amount). It melts at 51.5–52° and boils at 117–118°/9 mm. This product is satisfactory for most purposes. If a purer material is desired, the crude *m*-bromonitrobenzene may be distilled under reduced pressure. The recovery on purification is about 85 per cent. Brühl recorded the b.p. as 138°/18 mm. and the m.p. as 56° for pure *m*-bromonitrobenzene.[1]

2. Notes

1. With small amounts, up to 90 g. of nitrobenzene, mechanical stirring is not essential, and occasional shaking is sufficient.

2. The nitrobenzene is dried by distillation under atmospheric or reduced pressure, by rejecting the first 5 per cent of the distillate.

3. The bromine is dried by shaking with an equal volume of concentrated sulfuric acid and separating.

4. A number of other forms of iron were used, but none gave as good results as the " ferrum reductum."

5. If a series of successive runs is to be made, it is convenient to siphon the reaction product, and carry out a second preparation in the same apparatus without dismantling it.

6. The sodium bisulfite is added to remove any free bromine. A large excess should not be used as secondary reactions may occur during the steam distillation.

3. Methods of Preparation

m-Bromonitrobenzene has been obtained through *m*-nitrobenzene diazonium salts[2] and by elimination of the amino group from 4-bromo-2-nitroaniline.[3] It has been prepared by the bromination of nitrobenzene in the presence of various catalysts.[4]

The procedure given is adapted from that described by Wheeler and McFarland.[5]

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[1] Brühl, Z. physik. Chem. **22**, 379 (1897).

[2] Griess, Phil. Trans. Roy. Soc. London **154**, III, 711 (1864); Jahresber. **1866**, 457; Fittig and Mager, Ber. **8**, 364 (1875).

[3] Wurster, Ber. **6**, 1543 (1873); Wurster and Grubenmann, Ber. **7**, 416 (1874).

[4] Scheufelen, Ann. **231**, 165 (1885).

[5] Wheeler and McFarland, Am. Chem. J. **19**, 366 (1897).

XIV

tert-BUTYL CHLORIDE

tert-$C_4H_9OH + HCl \rightarrow$ *tert*-$C_4H_9Cl + H_2O$

Submitted by JAMES F. NORRIS and ALANSON W. OLMSTED.
Checked by HENRY GILMAN and L. L. HECK.

1. Procedure

IN a 500-cc. separatory funnel are placed 74 g. or 95 cc. (1 mole) of *tert*-butyl alcohol (Note 1) and 247 cc. (3 moles) of C.P. concentrated hydrochloric acid (sp. gr. 1.19). After shaking, the layers are allowed to separate (fifteen to twenty minutes) and the upper layer is drawn off and washed first with a 5 per cent sodium bicarbonate solution, then with water until neutral to moist litmus paper (Note 2). The chloride is treated with 10 g. of calcium chloride and shaken thoroughly, then transferred to a 125-cc. distilling flask. It is then distilled, using a long water condenser. The fraction boiling at 49.5–52° weighs 72–82 g. (78–88 per cent of the theoretical amount).

2. Notes

1. As it is difficult to prepare *tert*-butyl alcohol free from water, 84 g. of the constant boiling mixture of the alcohol and water can be used. This mixture boils at 80°, contains 88.24 per cent alcohol when the distillation is carried out at 760 mm., and can be readily obtained by distilling a sample of the dilute alcohol.
2. The chloride is very slowly hydrolyzed by cold water.

3. Methods of Preparation

tert-Butyl chloride has been prepared by passing hydrogen chloride into the alcohol kept cold in a freezing mixture,[1] and by distilling a mixture of the alcohol and a large excess of concentrated hydrochloric acid.[2] The method given is an improvement of the latter as it takes less time and largely avoids loss of the very volatile product by reducing the number of operations involved.

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[1] Boedtker, Bull. soc. chim. (3) **31**, 965 (1904).

[2] Norris, Am. Chem. J. **38**, 642 (1907).

XV

γ-CHLOROBUTYRONITRILE

$$ClCH_2CH_2CH_2Br + KCN \rightarrow ClCH_2CH_2CH_2CN + KBr$$

Submitted by Charles F. H. Allen.
Checked by C. S. Marvel and C. G. Gauerke.

1. Procedure

In a 2-l. three-neck, round-bottom flask, fitted with a stirrer, a reflux condenser and a separatory funnel are placed 82 g. (1.2 moles) of potassium cyanide (95 per cent) (Note 1) and 100 cc. of water. The mixture is warmed and stirred until the cyanide is completely dissolved. To this solution is added 350 cc. of 95 per cent alcohol, followed by 158 g. (1 mole) of trimethylene chlorobromide (Note 2), and the mixture is heated under a reflux condenser (best on a water bath) with stirring for about one and one-half hours.

The solution is cooled and then diluted with 450 cc. of water. The oily layer of chloronitrile is collected in about 80 cc. of chloroform and separated from the water solution. The chloroform solution is washed with about 125–150 cc. of calcium chloride solution (prepared by adding one volume of water to an equal volume of a saturated solution of crystallized calcium chloride) and once with 125–150 cc. of water, and then dried over fused calcium chloride.

The dried solution is then fractionally distilled in a modified 100-cc. Claisen flask (Org. Syn. 1, 40). The chloroform is removed by distilling at ordinary pressure until the temperature reaches 120° (Note 3). The remainder may be fractionated under ordinary pressure but it is better to use reduced pressure.

After two or three distillations the yield of pure product boiling at 93–96°/26 mm. (Notes 4 and 5) is 42–49 g. (60–70 per cent of the theoretical amount based on the chlorobromide used, or 40–47 per cent based on the total amount of chlorobromide taken). (Notes 5 and 6.)

2. Notes

1. An equivalent amount (58 g., 1.2 moles) of sodium cyanide dissolved in 90 cc. of water may be used instead of the potassium salt without materially altering the yields.

2. The trimethylene chlorobromide used boiled at 142–147°. It may be prepared in 75–85 per cent yields from trimethylene chlorohydrin (p. 112) by the general method for the preparation of alkyl bromides described in Org. Syn. 1, 1.

3. The chloroform fraction has a very strong odor of isonitrile. Only a trace is noted in the redistilled product.

4. When the distillation is carried out under ordinary pressures (about 745 mm.) the product boils at 194–197°.

5. The lower boiling fraction is mainly unchanged trimethylene chlorobromide and amounts to 15–20 g. It may be refractionated or used directly in a subsequent run. The high boiling residue is mainly trimethylene cyanide. If the residues from several runs are combined and redistilled an average of 6–7 g. per run of product boiling at 160–165°/26 mm. is obtained.

6. Larger runs have been made and the yields are proportional; thus a five-mole run gives 210–245 g. of chlorobutyronitrile and 30–35 g. of trimethylene cyanide.

3. Methods of Preparation

γ-Chlorobutyronitrile has always been prepared by the action of potassium cyanide on trimethylene chlorobromide.[1]

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[1] Henry, Compt. rend. **101**, 1158 (1885); Bull. soc. chim. (2) **45**, 341 (1886); Gabriel, Ber. **23**, 1771 (1890); **42**, 1252 (1909); Conant, Segur and Kirner, J. Am. Chem. Soc. **46**, 1884 (1924).

XVI

β-CHLOROPROPIONIC ACID

$$CH_2=CHCHO+HCl \rightarrow CH_2ClCH_2CHO$$

$$CH_2ClCH_2CHO+O(HNO_3) \rightarrow CH_2ClCH_2CO_2H$$

Submitted by C. Moureu and R. Chaux.
Checked by C. S. Marvel and L. F. Martin.

1. Procedure

In a tared Erlenmeyer flask surrounded by an ice-salt bath is placed 100 g. (1.78 moles) of acrolein (Org. Syn. **6**, 1) (Note 1). When the temperature has dropped to -10 to $-15°$ a current of dry hydrogen chloride (Org. Syn. **6**, 64) is passed into the acrolein until it shows a gain in weight of 65 g. (1.78 moles). This requires about two hours. The product thus obtained is a clear, viscous, slightly yellow liquid which becomes very turbid and dark colored on standing one or two days (Note 2).

The oxidation of the crude β-chloropropionaldehyde is carried out in a 200-cc. flask fitted with a cork stopper held by a clamp about 2 cm. above the opening of the neck. The stopper carries a mechanical stirrer, a separatory funnel, a thermometer and a glass delivery tube about 10 mm. in diameter which is connected to a water pump. The space between the stopper and the flask is closed by winding a strip of asbestos paper around it (Note 3).

In the flask is placed 64 g. of fuming nitric acid (sp. gr. 1.49) (Note 4), the stirrer is started and about one-sixth (Note 5) of the crude β-chloropropionaldehyde is added (Note 6) very slowly through the separatory funnel. About 1 cc. of the aldehyde is added to the acid. The temperature remains constant for one or two minutes and then slowly rises. As the oxidation begins, oxides of nitrogen are evolved and are drawn off by means of the water pump. When the temperature of the reaction mixture reaches about 30° (Note 7), the flask is immersed in a water bath (at about 15–20°) and the rate of addition of the aldehyde is regulated so that the temperature of the reaction mixture is about 30–35°. After the addition of the last of the portion of the aldehyde, stirring is continued until the temperature drops below 25°. This oxidation requires about twenty-five minutes.

The products of six successive oxidations are combined in a 1-l. long-neck flask. Oxides of nitrogen are often evolved but there is no danger of a violent reaction. The entire quantity of liquid is heated gradually on a water bath until the bath is boiling. This should be done under a hood as large quantities of oxides of nitrogen are evolved. After about an hour and a half the oxidation is complete and a yellow-brown liquid remains.

The liquid is placed in a modified Claisen flask (Org. Syn. 1, 40) and distilled (Note 8) on an oil bath with a water pump, care being taken to protect the manometer (placed in shunt in order to avoid the passage of a current of vapors) by a tube containing solid sodium hydroxide. A water condenser 40–50 cm. long should be used. At first oxides of nitrogen are evolved and it is difficult to obtain a low pressure. Then the pressure drops (to about 20–25 mm.) and nitric acid distils at 40–70°. When the distillation has nearly stopped, the temperature of the bath is raised until the boiling point of the distilling vapors reaches 100°. This fraction weighs 160–170 g. and is nitric acid having a sp. gr. of 1.25–1.30. It may contain a small amount of acrylic acid. The condenser is now removed from the apparatus, a distilling flask attached as receiver, and the residue is fractionated at 20 mm., collecting about 4–5 g. boiling up to 105° and 116–125 g. of β-chloropropionic acid boiling at 105–107° (60–65 per cent of the theoretical amount). The product melts at 35–40° (purest acid melts at 42°). The fraction boiling below 105° contains a large proportion of β-chloropropionic acid and should be redistilled with a subsequent run.

2. Notes

1. The acrolein used by the checker was that obtained by distilling the commercial material (stabilized by hydroquinone) purchased from Poulenc Frères.

2. β-Chloropropionaldehyde is a very unstable substance which polymerizes rapidly especially in the presence of traces of hydrochloric acid. The crude material must be oxidized without delay as standing before oxidation will cause a lowering of the yield.

3. This constitutes a safety device, since it prevents diffusion of the oxides of nitrogen, but in case the reaction becomes violent it permits a free expansion of a sudden wave of gases.

4. The concentration and purity of the fuming nitric acid is of considerable importance. It should have a sp. gr. of not less than 1.49 and should leave no residue on distillation.

5. It is not advantageous to work with larger quantities as an explosive reaction is liable to occur if stirring is stopped.

6. It is absolutely necessary to introduce the aldehyde into the nitric acid. When the reverse is attempted the reaction starts slowly but soon becomes explosive.

7. The temperature interval most favorable for the reaction is 30–35°.

8. The reaction mixture may also be worked up by pouring it into water and extracting the β-chloropropionic acid with ether. This is less satisfactory as the nitric acid is lost and some of the β-chloropropionic acid remains in the water.

3. Methods of Preparation

β-Chloropropionic acid has been prepared by the hydrolysis of ethylene cyanohydrin with hydrochloric acid,[1] and by the oxidation of β-chloropropionaldehyde [2] or of trimethylene chlorohydrin [3] by nitric acid.

---

[1] Jacobs and Heidelberger, J. Am. Chem. Soc. **39**, 1466 (1917).

[2] Krestownikow, Ber. **12**, 1487 (1879); Moureu, *Bull.* soc. chim. (3) **9**, 388 (1893); Ann. chim. phys. (7) **2**, 157 (1894); Moureu and Chaux, Bull. soc. chim. (4) **35**, 1360 (1924).

[3] Rojahn, Ber. **54*B***, 3116 (1921); Adams and Marvel, Organic Chemical Reagents, Univ. of Ill. Bulletin, vol. 20, no. 8, p. 14 (1922); Powell, J. Am. Chem. Soc. **46**, 2879 (1924).

XVII

β-CHLOROPROPIONIC ACID

$ClCH_2CH_2CH_2OH + 2O(HNO_3) \rightarrow ClCH_2CH_2CO_2H + H_2O$

Submitted by SARGENT G. POWELL.
Checked by C. S. MARVEL and STANLEY G. FORD.

1. Procedure

IN a 1-l. wide-mouth, narrow bottle immersed in running water and fitted with a 3-hole rubber stopper holding a mechanical stirrer, a separatory funnel and a reflux condenser is placed 220 g. of concentrated nitric acid (sp. gr. 1.42). The condenser should be connected with a hood or trap to catch the oxides of nitrogen liberated during the oxidation. The stirrer is started and 50 g. (0.52 moles) of trimethylene chlorohydrin (p. 112) is added from the separatory funnel during the course of one hour. Stirring is continued for half an hour longer. During this part of the oxidation the reaction vessel is cooled with running water. The reaction is completed by warming the reaction mixture on a steam-bath for one hour.

The β-chloropropionic acid is best isolated by direct distillation under reduced pressure (Note 1) using a 250-cc. modified Claisen flask (Org. Syn. 1, 40). The nitric acid is collected up to 100°/20 mm. using a water condenser. The condenser is then removed and the residual β-chloropropionic acid is fractionated, collecting as pure product the portion boiling at 105–107°/20 mm. The yield is 31–31.5 g. (54–55 per cent of the theoretical amount) (Note 2). The product solidifies on cooling and melts at 41–41.5°.

2. Notes

1. About 130 cc. of nitric acid (sp. gr. 1.27) is obtained. If desired the oxidation mixture may be diluted with water and the β-chloropropionic acid extracted with ether and distilled. Some material is lost in the water by this procedure.

2. Larger runs may be carried out without lowering the yield. When a run of four times that described was made, the time of adding the trimethylene chlorohydrin was only doubled.

3. Methods of Preparation

These are given on p. 56.

XVIII

DIBENZOYLMETHANE

(Phenyl-α-hydroxystyrylketone)

$$C_6H_5CHBrCHBrCOC_6H_5 + 2NaOCH_3 \rightarrow C_6H_5C(OCH_3){=}CHCOC_6H_5 + 2NaBr + CH_3OH$$

$$C_6H_5C(OCH_3){=}CHCOC_6H_5 + H_2O \rightarrow C_6H_5C(OH){=}CHCOC_6H_5 + CH_3OH$$

$$C_6H_5C(OH){=}CHCOC_6H_5 \rightleftarrows C_6H_5COCH_2COC_6H_5$$

Submitted by CHARLES F. H. ALLEN.
Checked by ROGER ADAMS and G. R. YOHE.

1. Procedure

IN a 2-l. round-bottom flask, fitted with a stirrer and a reflux condenser, and surrounded by a cold water bath, are placed 184 g. (0.5 mole) of benzalacetophenone dibromide (Note 1) and 165 cc. of absolute methyl alcohol (Notes 2 and 3). A solution of sodium methylate, previously prepared by dissolving 23.2 g. of sodium (1.01 moles) in 230 cc. of absolute methyl alcohol, is added slowly through the condenser, stirring being begun as soon as the mass is fluid enough. When the addition has been completed, the whole is heated to boiling and refluxed for three hours. To the brown liquid is then added 140 cc. of water to dissolve the precipitated sodium bromide, and enough concentrated hydrochloric acid (sp. gr. 1.19) to acidify the solution, when the color changes to a light yellow and an oil separates. The acid solution is refluxed two hours longer, then cooled in ice-water, stirring rapidly to cause formation of small crystals (Note 5); the latter are separated by filtration and washed once with 50 cc. of cold 50 per cent alcohol and then with water until free from acid. The yield (Note 1) of the crude, air-dried dibenzoylmethane, m.p. 76–78°, is 66–69 g. (59–61 per cent of the theoretical amount) (Note 4). The crude product is quite pure but if desired it may be recrystallized from 160 cc. of hot 95 per cent alcohol. The first crop weighs 58–62 g. (m.p. 77–78°) and on partial evaporation of the solvent a less pure second crop of 2–3 g. (m.p. 74–75°) can be obtained.

2. Notes

1. The yield depends largely upon the quality of the dibromide. The product which gave the results described in the procedure was prepared by dissolving 208 g. (1 mole) of benzalacetophenone (Org. Syn. **2**, 1) in 600 cc. of carbon tetrachloride, cooling the solution in an ice bath and adding with stirring 160 g. (1 mole) of bromine. After the reaction was complete the dibromide was filtered off and washed with two 250-cc. portions of hot alcohol. The product obtained in this way melted at 156–157° and weighed about 310 g.

2. If ordinary methyl alcohol is used, the yields agree with the lower figures. The diketone is also contaminated by an oily substance that persists through several recrystallizations. The presence of water favors the elimination of bromine and regeneration of the unsaturated ketone.

3. The use of ethyl alcohol results in an inferior product, m.p. 63–65°.

4. The use of steel spatulas should be avoided, as traces of iron salts cause the product to be of a reddish color. This can be removed either by a vacuum distillation, or by dissolving in concentrated sulfuric acid and reprecipitating by pouring the acid solution upon cracked ice.

5. The mother liquor contains only 2–3 g. more of the diketone, which can be separated as the copper derivative by shaking an ethereal extract with a saturated aqueous solution of copper acetate.

3. Methods of Preparation

Dibenzoylmethane has been prepared by the hydrolysis of dibenzoyl acetic acid;[1] by the slow spontaneous decomposition of acetyl dibenzoyl methane;[2] by the action of metallic sodium,[3] sodium ethylate,[3] sodium methylate,[4] alchoholic potash,[4] or sodamide[5] on mixtures of acetophenone and ethyl benzoate; and by the action of alcoholic potash,[6] sodium methylate,[7] or sodium ethylate[8] on benzalacetophenone dibromide.

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[1] Baeyer and Perkin, Ber. **16**, 2134 (1883); Perkin, J. Chem. Soc. **47**, 250 (1885).

[2] Claisen, Ann. **291**, 83 (1896).

[3] Claisen, Ann. **291**, 52 (1896).

[4] Bülow and von Sicherer, Ber. **34**, 2372 (1901).

[5] Claisen, Ber. **38**, 696 (1905).

[6] Wislicenus, Ann. **308**, 219 (1899); See Abell, J. Chem. Soc. **101**, 1002 (1912).

[7] Pond, Maxwell and Norman, J. Am. Chem. Soc. **21**, 964 (1899).

[8] Sluiter, Rec. trav. chim. **24**, II, 368 (1905).

XIX

DI-*o*-NITROPHENYL DISULFIDE

$$2\ o\text{-}ClC_6H_4NO_2 + Na_2S_2 \rightarrow o\text{-}NO_2C_6H_4SSC_6H_4NO_2 + 2NaCl$$

Submitted by Marston T. Bogert and Arthur Stull.
Checked by Frank C. Whitmore, W. F. Singleton and F. E. Smith.

1. Procedure

In a 3-l. round-bottom flask fitted with a reflux condenser are placed 360 g. (1.5 moles) of crystalline sodium sulfide (Note 1) and 1.5 l. of 95 per cent alcohol. The flask is heated on a steam bath until the sulfide dissolves. Then 48 g. (1.5 moles) of finely ground sulfur is added, and the heating is continued until the sulfur has dissolved, forming a brownish red-solution of sodium disulfide (Note 2). A solution of 315 g. (2 moles) of *o*-chloronitrobenzene (Note 3) in 500 cc. of 95 per cent alcohol is prepared in a 5-l. round-bottom flask fitted with a reflux condenser. The sodium disulfide solution is added slowly to this solution through a funnel placed in the top of the reflux condenser. The addition should be slow until the violence of the reaction abates somewhat. The mixture is then heated on a steam bath, gently at first (Note 4), and then at full heat for two hours. After cooling, it is filtered by suction. The mixture of the organic disulfide and the sodium chloride is transferred to a 1-l. beaker and stirred thoroughly with 500 cc. of water to remove the sodium chloride. It is then filtered by suction and the crystalline residue is washed on the filter with 100 cc. of alcohol to remove any *o*-chloronitrobenzene. The product melting at 192–195° weighs 180–210 g. (58–66 per cent of the theoretical amount).

2. Notes

1. Crystals as dry as possible should be selected. If desired, an equivalent amount of analyzed fused sodium sulfide may be used. In this case, solution takes a longer time. Since an excess of sodium sulfide is added, slight inaccuracies in the amount used are not important.

2. In case a small amount of sodium disulfide separates in a layer at the bottom, it should be taken up with a little more alcohol and added to the chloronitrobenzene solution.

3. Commercial *o*-chloronitrobenzene containing 95–98 per cent of the ortho compound was used.

4. If too much heat is applied at first, the reaction becomes very violent.

3. Methods of Preparation

Di-*o*-nitrophenyl disulfide was first prepared by the action of hydriodic acid on *o*-nitrobenzene sulfochloride.[1] It has also been prepared by the reduction of *o*-nitrobenzene sulfinic acid with hydrogen bromide;[2] by the reduction of ethyl-*o*-nitrophenylsulfonacetate with ammonium sulfide;[3] and by the deamination of 4,4′-diamino-2,2′-dinitrodiphenyldisulfide.[4] The procedure given is the method of Blanksma[5] as elaborated by Wohlfahrt.[6]

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[1] Cleve, Ber. **20**, 1534 (1887).

[2] Fries and Schürmann, Ber. **47**, 1199 (1914).

[3] Claasz, Ber. **45**, 1021 (1912).

[4] Müller, Z. f. Farbenind. **5**, 357 [Chem. Zentr. **1906, II**, 1587].

[5] Blanksma, Rec. trav. chim. **20**, 127 (1901).

[6] Wohlfahrt, J. prakt. Chem. (2) **66**, 553 (1902).

XX

ETHYL *p*-AMINOBENZOATE

$$p\text{-}NO_2C_6H_4CO_2C_2H_5 + 3H_2(Pt) \rightarrow p\text{-}NH_2C_6H_4CO_2C_2H_5 + 2H_2O$$

Submitted by ROGER ADAMS and F. L. COHEN.
Checked by HENRY GILMAN and S. A. HARRIS.

1. Procedure

A SOLUTION of 19.5 g. (0.1 mole) of ethyl *p*-nitrobenzoate (Note 1) in 150 cc. of 95 per cent alcohol is placed in the reaction bottle of the catalytic reduction apparatus (p. 10) and 0.2 g. of platinum oxide catalyst (p. 92) is added. The mixture is shaken with hydrogen until three molecular equivalents have been absorbed. The time required is about seven minutes. The platinum is filtered off and the alcohol removed from the filtrate by distillation. The ethyl *p*-aminobenzoate, recrystallized from about 40 cc. of ether, melts at 89–90°. The yield is 15–16.5 g. (91–100 per cent of the theoretical amount).

2. Notes

1. The ethyl *p*-nitrobenzoate should be freed from acid and recrystallized from alcohol until it melts at 57°.

3. Methods of Preparation

Ethyl *p*-aminobenzoate has been prepared by the esterification of *p*-aminobenzoic acid[1] and by the reduction of ethyl *p*-nitrobenzoate with ammonium sulfide.[2] Although commercially the reagent used is usually iron and water in presence of a little acid, in the laboratory the catalytic reduction as described in the procedure is by far the most convenient.

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[1] Salkowski, Ber. **28**, 1921 (1895); Vorländer and Meyer, Ann. **320**, 135 (1902).

[2] Limpricht, Ann. **303**, 278 (1898).

XXI

ETHYL BENZOYLFORMATE

$$C_6H_5CHOHCO_2H + O(KMnO_4) \rightarrow C_6H_5COCO_2H + H_2O$$

$$C_6H_5COCO_2H + C_2H_5OH(H_2SO_4) \rightarrow C_6H_5COCO_2C_2H_5 + H_2O$$

$$C_6H_5COCO_2C_2H_5 + NaHSO_3 \rightarrow C_6H_5COH(SO_3Na)CO_2C_2H_5$$

$$C_6H_5COH(SO_3Na)CO_2C_2H_5 + H_2SO_4 \rightarrow C_6H_5COCO_2C_2H_5 + NaHSO_4 + SO_2 + H_2O$$

Submitted by B. B. CORSON, RUTH A. DODGE,
S. A. HARRIS, and R. K. HAZEN.
Checked by C. S. MARVEL and F. E. KENDALL.

1. Procedure

IN a 12-l. earthenware crock equipped with an efficient stirrer and a strong motor are placed 375 g. (2.5 moles) of mandelic acid (Org. Syn. **6**, 58) and 500 cc. of water. The stirrer is started, and a cool solution of 110 g. (2.8 moles) of sodium hydroxide (or 115 g. of technical sodium hydroxide) in 500 cc. of water is added. This is followed by the addition of 2000 g. of cracked ice and then after a few minutes by 275 g. (1.74 moles) of finely ground U.S.P. potassium permanganate in portions over a period of half an hour. The mixture is stirred for one and a half hours, the temperature being maintained at −2 to −4°. About 5 kg. of ice is necessary. At the end of one and a half hours the mixture is tested for excess permanganate by placing a drop on a piece of filter paper; there is formed a black or brown center of manganese dioxide, a greenish ring around this, and an outer ring which is colorless in the absence and pink in the presence of excess permanganate. Any excess is removed by adding ethyl alcohol, generally about 200–300 cc.

When the permanganate has been destroyed, the stirrer is stopped and the manganese dioxide allowed to coagulate for an hour. The mixture is filtered through two 20-cm. Büchner funnels, the filter cakes washed with 1000 cc. of water (Note 1) and sucked dry again (Note 2). The filtrate is evaporated to 800–1000 cc. over a free flame. While the volume of solution is large, two 30-cm. evaporating dishes are used, but toward the end the two solutions are combined in one dish. The evaporation requires two to three hours. Sometimes a little manganese dioxide will be coagulated during the evaporation and this should be removed by filtration.

The yellowish solution is transferred to a 3-l. round-bottom wide-neck flask and cooled with running water while 300 cc. of concentrated sulfuric acid is added slowly from a separatory funnel. This acidification process requires thirty minutes and the temperature should not rise much above 25°. The liquid froths and about 30 g. of benzoic acid separates but it is not filtered. Extraction of the reaction mixture with 200 cc. portions of ether until 1500 cc. of extract has been collected is now carried out in a separatory funnel. The ether is distilled on a steam bath from a 1-l. round-bottom wide-neck flask connected with a water condenser, the extract being added from a separatory funnel as fast as the ether distils. After most of of the ether has been removed, the heating is continued for an additional half hour.

The crude liquid acid (about 300 g.) is cooled with running water and 15 cc. of concentrated sulfuric acid is added; the clear yellow oil becomes cloudy. The acid is esterified by the method described in Org. Syn. 3, 54, with the following changes: all three flasks, the alcohol flask, the trap, and the esterification flask are 1-l. round-bottom wide-neck flasks. The alcohol flask and the trap are set on adjacent steam baths. The esterification flask is placed in an oil bath which is heated by a free flame. A safety tube leads from the alcohol flask and dips under 7.5 cm. of mercury contained in a side-arm tube.

This mercury safety valve avoids all dangers which might result from the development of excess pressure within the system (Note 3). The temperature of the esterification mixture is kept at 105–110° and ethyl alcohol vapor is passed through until 500 cc. of distillate has been collected. This requires about three hours. The distillate consists of alcohol, water, and a little ether.

The crude ester is cooled, an equal volume of benzene is added, then the free acid is neutralized by shaking with about 250 cc. of a 10 per cent solution of sodium carbonate (Note 4). The benzene solution is poured into 1300 cc. of a saturated solution of sodium bisulfite (about 60 g. of technical sodium bisulfite per 100 cc.), contained in a wide-neck bottle equipped with an efficient stirrer, and the mixture stirred for two and a half hours. The mixture soon warms up a little and becomes semi-solid. It is filtered through a 20-cm. Büchner funnel and carefully washed, first with 200 cc. of a saturated solution of sodium bisulfite, finally with two 150-cc. portions of benzene (Notes 5 and 6). The white pearly flakes of the sodium bisulfite addition product are transferred to a 3-l. round-bottom wide-neck flask equipped with a mechanical stirrer and containing 700 cc. of water, 175 cc. of concentrated sulfuric acid, and 500 cc. of benzene. The flask is heated on a steam bath under a hood, the temperature being kept at 55°, and the mixture is stirred for thirty minutes (Note 7). The solution is then poured into a separatory funnel, the benzene separated and the water layer extracted with a 200-cc. portion of benzene. The combined benzene solution is shaken with excess of 10 per cent sodium carbonate solution to remove free acid and sulfur dioxide (Note 8). The benzene is washed with a little water and then dried over anhydrous potassium carbonate (Note 9). The benzene is distilled at ordinary pressure over a free flame from a 500-cc. Claisen flask, the solution being added from a separatory funnel as fast as the benzene distils. It is advisable to distil the ester under reduced pressure although it can be done under ordinary pressure. The fraction distilling around 118°/5 mm., 130°/10 mm., 138°/15 mm., 148°/25 mm., 155°/35 mm., or

254°/760 mm., is collected. The yield of ethyl benzoylformate is 155–175 g. (35–40 per cent of the theoretical amount). (Note 10).

2. Notes

1. In order to wash the manganese dioxide cake it must be removed from the funnel and stirred into a thin paste with water.

2. It is advisable not to stop the experiment until after filtration since manganese dioxide slowly oxidizes benzoylformic acid to benzoic acid.

3. If it is necessary to generate the steam from a can or similar contrivance, the steam generator should be connected with a safety tube dipping under 20–25 cm. of mercury.

4. The sodium carbonate solution contains 8–15 g. of unesterified acid which can be easily recovered by acidification with concentrated hydrochloric acid followed by extraction with ether.

5. The benzene contains 80 g. of impure ethyl benzoate boiling at 180–260° and containing about 20 per cent of ethyl benzoylformate. In the case of the methyl ester the benzene contains 60 g. of impure methyl benzoate, boiling at 170–250°, and containing about 20 per cent of methyl benzoylformate.

6. If the stirring is not very efficient the benzene layer should be stirred with the bisulfite solution a second time.

7. Longer contact with acid tends to hydrolyze the ester. The reaction should be performed under a hood since considerable sulfur dioxide is generated.

8. This sodium carbonate solution contains about 4 g. of impure benzoylformic acid.

9. The potassium carbonate holds some ester which may be recovered by adding water and separating the ester layer.

10. The methyl ester is easily made by substituting methyl for ethyl alcohol. It boils at 250–255°/760 mm. The yield is about 175 g. (43 per cent of the theoretical amount).

11. This work was done with the aid of a grant from the

Cyrus M. Warren fund of the American Academy of Arts and Sciences.

3. Methods of Preparation

Ethyl benzoylformate has been prepared by the direct esterification of the acid[1] and by the action of oxides of nitrogen on an alcoholic suspension of indigo.[2] The acid has been prepared by many different reactions but the most practical are the hydrolysis of benzoyl cyanide,[3] the oxidation of acetophenone[4] and the oxidation of mandelic acid.[5]

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[1] Claisen, Ber. **10**, 846 (1877); **12**, 629 (1879); Simon, Ann. chim. phys. (7) **9**, 529 (1896); Kailan, Monatsh. **28**, 1204 (1907); Acree, Am. Chem. J. **50**, 392, 393 (1913).

[2] Posner and Aschermann, Ber. **53*B***, 1931 (1920).

[3] Claisen, Ber. **10**, 429, 844 (1877); **12**, 626 (1879); Buchka, Ber. **20**, 395 (1887); Simon, Ann. chim. phys. (7) **9**, 508 (1896).

[4] Glücksmann, Monatsh. **11**, 248 (1890); Claus and Neukranz, J. prakt. Chem. (2) **44**, 80 (1891).

[5] Hunaeus and Zincke, Ber. **10**, 1489 (1877); Acree, Am. Chem. J. **50**, 391 (1913).

XXII

ETHYL CYANOACETATE

$$ClCH_2CO_2Na + NaCN \rightarrow CNCH_2CO_2Na + NaCl$$

$$CNCH_2CO_2H + C_2H_5OH \rightarrow CNCH_2CO_2C_2H_5 + H_2O$$

Submitted by J. K. H. Inglis.
Checked by C. S. Marvel, W. F. Tuley and S. V. Puntambeker.

1. Procedure

In a 5-l. round-bottom flask 500 g. (5.3 moles) of chloroacetic acid is dissolved in 700 cc. of water. The solution is warmed to 50° and neutralized with anhydrous sodium carbonate of which about 290 g. (2.6 moles) is required (a slight excess of sodium carbonate is not disadvantageous). Meanwhile 294 g. (5.8 moles) of sodium cyanide (97 per cent) is dissolved in 750 cc. of water warmed to 55°. The sodium cyanide solution is then added to the sodium chloroacetate solution, which has been cooled to room temperature, with rapid mixing of the two solutions and cooling under the water tap. The temperature rapidly rises; when it reaches 95° the solution should be cooled by adding 200 cc. of cold water and this repeated, if necessary, until the temperature no longer rises (Note 1). The solution is heated to the boiling point and boiled for five minutes (Note 2), and finally cooled with running water for a half hour.

The solution is filtered if not clear, and the cyanoacetic acid is set free (hood) by adding with thorough stirring 600 cc. (a slight excess) of commercial hydrochloric acid (sp. gr. 1.156). The solution is evaporated on a water bath at 60–70° (Note 3) under a pressure of 20–30 mm. and the evaporation continued until practically no more distillate (Note 4) comes over. To the residue is added 600 cc. of 95 per cent alcohol. The solution is filtered (Note 5) from the sodium chloride, and the residue is washed with another 500-cc. portion of alcohol.

On evaporating the alcoholic solution under reduced pressure from a water bath held at 50–60° (Note 6) the residue weighs about 540 g. A mixture of 600 cc. of absolute alcohol and 10 cc. of concentrated sulfuric acid (Note 7) is then added. The mixture is then heated on the water bath under a reflux condenser for three hours. The excess of alcohol and some of the water formed are removed by distillation under reduced pressure and the residue again heated for two hours with 300 cc. of absolute alcohol and an additional 4 cc. of concentrated sulfuric acid. The alcohol is removed by distillation under reduced pressure, and when the ester has cooled to room temperature, the sulfuric acid is neutralized with a concentrated solution of sodium carbonate; the ester (upper layer) is separated, and the aqueous solution extracted with ether, or preferably benzene; about one-tenth of the yield is in the extract. The combined products are placed in a 1-l. distilling flask and distilled under reduced pressure after the solvent and alcohol and water have been removed. The ester is collected at 94–99°, chiefly at 97–98°/16 mm. (Note 8). The yield of a product analyzing about 97–98 per cent ethyl cyanoacetate amounts to 474–492 g. (77–80 per cent of the theoretical amount) (Note 9).

2. Notes

1. If the reaction between the cyanide and chloroacetate becomes too vigorous, hydrogen cyanide is set free and partly changed to brown material and a corresponding amount of glycollate is formed.

2. The color at this stage should be yellow or a light brown.

3. If the mixture is heated to a higher temperature there is a considerable loss due to decomposition of the cyanoacetic acid.

4. Toward the end of the distillation, hydrochloric acid should be present in the distillate if excess was added in the first place. During the addition of the hydrochloric acid the excess of cyanide is decomposed, giving off hydrogen cyanide.

5. It is much easier to remove the salt by means of a centrifuge. If this method is used the salt should be washed first with 500 cc. and then with 250 cc. of alcohol.

6. The solution containing mineral acid must not be evaporated at a high temperature or ethyl malonate will be formed.

7. The addition of sulfuric acid will probably produce a slight precipitate, but this may be ignored if the original treatment with hydrochloric acid was properly carried out.

8. Ethyl cyanoacetate boils at 97°/16 mm., 101°/19 mm., 107°/27 mm.

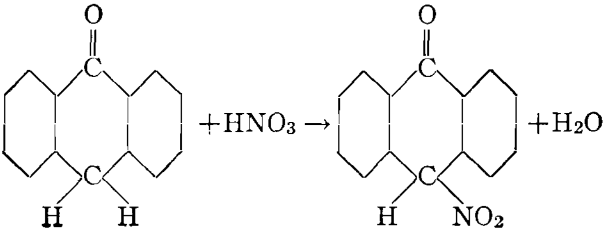
9. The product was analyzed for nitrogen by the Kjeldahl method.

3. Methods of Preparation

The method described differs from that given in Org. Syn. 3, 53 mainly in the use of hydrochloric acid in place of sulfuric acid, in the liberation of the cyanoacetic acid from the sodium salt and in the simplified esterification process. These are slight but very important differences and make the procedure much easier to carry out in the laboratory. Moreover, the yields are higher.

XXIII

NITROANTHRONE



Submitted by Kurt H. Meyer.
Checked by J. B. Conant and W. C. Boyd.

1. Procedure

In a 1-l. beaker equipped with a separatory funnel, a mechanical stirrer, and a thermometer, 20 g. (0.1 mole) of anthrone (p. 8) is dissolved in 300 cc. of glacial acetic acid. While the mixture is kept at 60° and stirred, a solution of 7 cc. of fuming nitric acid (sp. gr. 1.5) in 50 cc. of glacial acetic acid is run in during one hour.

On cooling (to about 10°) 15 g. of nitroanthrone separates out in long yellowish-white needles. After the addition of 100 cc. of water to the mother liquor 6 g. more, somewhat darker in color, crystallizes in three to four hours.

On recrystallization from about 300 cc. of a 1 : 1 benzene-petroleum ether (40–60°) mixture, 16.5 g. of nitroanthrone melting at 140° (corr.) is obtained (67 per cent of the theoretical amount) (Note 1).

2. Notes

1. By dissolving in hot alkali (about 300 cc. of water and 30 g. of sodium hydroxide per gram of nitroanthrone) and precipitat-

ing with acid below 10°, the red nitroanthranol may be obtained, which on standing slowly changes back to the nitroanthrone.

3. Methods of Preparation

Nitroanthrone has been prepared by the nitration of anthracene in isobutyl alcohol,[1] and by the nitration of anthrone.[2]

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[1] Perkin and Mackenzie, J. Chem. Soc. **61**, 868 (1892); Meisenheimer and Connerade, Ann. **330**, 177 (1904).

[2] Meyer and Sander, Ann. **396**, 149 (1913).

XXIV

m-NITROPHENOL

$$m\text{-}NO_2C_6H_4NH_2 + H_2SO_4 + HNO_2 \rightarrow NO_2C_6H_4N_2OSO_3H$$

$$NO_2C_6H_4N_2OSO_3H + H_2O \rightarrow m\text{-}NO_2C_6H_4OH + N_2 + H_2SO_4$$

Submitted by R. H. F. MANSKE.
Checked by H. T. CLARKE and H. R. BRETHEN.

1. Procedure

IN a 4-l. beaker is placed 210 g. of finely powdered *m*-nitroaniline (Note 1). A cold mixture of 450 cc. of water and 330 cc. of concentrated sulfuric acid is added with hand or mechanical stirring and then about 800 g. of finely crushed ice. When a homogeneous mixture has resulted, a solution of 105 g. of sodium nitrite in 250 cc. of water is added rapidly over a period of eight to ten minutes at the bottom of the mixture through a separatory funnel (Note 2) until a permanent color is given to starch-iodide paper (about 25–30 cc. of nitrite solution remains unused). The temperature during diazotization should be maintained at 0–5°. Stirring is continued for five to ten minutes longer and the solution allowed to settle for another five minutes. A heavy crystalline deposit of *m*-nitrobenzene diazonium sulfate settles at the bottom of the beaker, from which the supernatant liquid is decanted (Note 3).

While the diazotization is in progress 1 l. of concentrated sulfuric acid is added to 750 cc. of water in a 5-l. round-bottom flask and the mixture heated to boiling (160°) with a large ring burner. The liquor from the diazotization is then added from a separatory funnel at such a rate that the acid mixture boils very vigorously. About fifty minutes is required for this addition. The crystalline diazonium sulfate is then added in small portions at such a rate that the evolved nitrogen does not cause loss of material by excessive foaming. Boiling is continued for a few minutes longer and the contents of the flask are poured into a large beaker (Note 4) set in running cold water, and vigorously stirred to obtain a homogeneous crystal magma.

When completely cold, the nitrophenol is filtered, thoroughly pressed out, drained with suction, and washed with several portions of iced water, 450 cc. in all being used. It is spread on large sheets of filter paper and dried in a warm room. As thus prepared it has a yellowish brown appearance with darker particles intermixed. The yield is 170–180 g. (81–86 per cent of the theoretical amount) (Note 5).

It may be purified by recrystallization from hot hydrochloric acid, as recommended in Org. Syn. **3**, 87, but on account of the difficulty of filtration this procedure is satisfactory on a small scale only. It is preferably distilled in 200-g. lots from a 500-cc. Claisen flask under 10–15 mm. pressure, b.p. 160–165°/12 mm. It is important that no air inlet be used to prevent bumping, since under these conditions it partly sublimes and causes trouble by stopping up the connections. A filter or distilling flask is used as a receiver and only a short but wide bore (10 mm.) air condenser is necessary. This product is pale yellow and melts at 95–96°. The yield from 200 g. of crude product is 180–185 g.

2. Notes

1. The *m*-nitroaniline used in these experiments was a commercial specimen of 98.4 per cent purity. A less pure specimen did not give a greatly decreased yield.

The *m*-nitroaniline may also be added to the mixture prepared by adding the ice to the diluted acid, but this procedure is not quite so satisfactory.

2. The addition of the sodium nitrite solution should be as rapid as possible. If added too rapidly, however, considerable foaming occurs.

3. The filtration of this solution is slow and usually unnecessary. Occasionally undetermined impurities are present and then washing of the diazonium salt with iced water by decantation, followed by filtration, becomes desirable.

4. In the first part of the addition the solution remains pale yellow to brown but when the solution becomes saturated with the nitrophenol the latter separates as a dark oil which is not filtered off. The final volume of the solution is about 3.5 l. and the boiling temperature about 120°.

5. By using the same molecular proportions the following *m*-nitrophenols were prepared in equally good yields from the corresponding *m*-nitroanilines: 3-methoxy-5-nitrophenol and 3-nitro-4,6-xylenol. In the former case it is advisable to use slightly more ice in the diazotization and add the diazonium solution to a mixture of equal volumes of sulfuric acid and water.

3. Methods of Preparation

m-Nitrophenol has recently been made in the laboratory of one of the editors by boiling *m*-nitrophenetole (from phenacetin by nitration, hydrolysis, and diazotization in alcohol) with hydrobromic acid, a method which is better than that given in Org. Syn. 3, 87, but far inferior to the present method.

XXV

PHENYLETHYLENE

(Styrene)

$$C_6H_5CH=CHCO_2H \rightarrow C_6H_5CH=CH_2+CO_2$$

Submitted by T. W. Abbott and John R. Johnson.
Checked by H. T. Clarke and M. R. Brethen.

1. Procedure

In a 500-cc. flask fitted with a 24-cm. fractionating column (Notes 1 and 4) attached to a water-jacketed condenser, are placed 148 g. (1 mole) of dry powdered cinnamic acid, 2 g. of hydroquinone and several small pieces of clay plate. One-half gram of hydroquinone is also placed in the flask in which the distillate is to be collected (Note 2). The acid is rapidly heated over a wire gauze with a free flame until phenylethylene begins to distil, the heating being regulated so that the temperature of the vapors at the head of the column never exceeds 130°, and mainly remains below 120° (Notes 3 and 4). The cinnamic acid refluxes, but very little should escape and collect in the condenser. The decomposition is complete in three and one-half to five hours, when no more phenylethylene distils and the temperature at the head of the column rises rapidly. The distillate consists of a straw-colored oil and a little water; a dark tarry residue (50–60 g.) remains in the reaction flask. About 100 cc. of water is added to the distillate and the aqueous mixture is distilled. The phenylethylene is easily volatile with steam and separates in the distillate as a colorless oil. The oil (45–48 g.) is separated, dried with a small amount of calcium chloride, and carefully distilled under diminished pressure, cooling the condenser and receiver to 0–5° by means of iced (or very cold) water. The phenylethylene is collected at 44–46°/40 mm. or 60–63°/60 mm. (Note 5). The yield is 40–42 g. (38–41 per cent of the theoretical amount) (Note 6).

2. Notes

1. The column consists of a glass tube of 13–14 mm. internal diameter, 24 cm. long from lower end to the side arm, which has an internal diameter of 7 mm. It is important that these dimensions be observed in order to avoid polymerization of the product. It has been found in checking that better results are obtained by making indentations in the tube at frequent intervals and at different angles; these tend to reduce the number of cinnamic acid particles which are carried over with the vapor. A column of the Vigreux type would no doubt also be suitable.

2. An anti-oxygen such as catechol or hydroquinone is used to prevent polymerization. Hydroquinone should be added in the ratio of one part per thousand unless the phenylethylene is to be used immediately.[1]

3. If the temperature of the escaping vapor rises above 130° appreciable amounts of cinnamic acid pass into the condenser and the yield falls materially.

4. If the fractionating column does not have the exact dimensions designated in Note 1 the temperature of the vapors at the head of the column will vary from those given. However, no difficulty will arise in obtaining the yield of product indicated if the general directions for heating the cinnamic acid, so as to avoid the carrying of the cinnamic acid into the distillate, are followed.

5. Phenylethylene should not be distilled under atmospheric pressure since the temperature (146°) required for the distillation causes a considerable loss by polymerization. The decomposition of cinnamic acid cannot be effected by distillation under diminished pressure, since the acid under these conditions distils below the temperature required for decomposition (approximately 300°).

6. On increasing the scale of the preparation, the yield is somewhat higher.

3. Methods of Preparation

The method given is that of Böeseken and Bostet.[2] Phenylethylene has also been prepared by the addition of hydrobromic or hydriodic acid to cinnamic acid and subsequent treatment with alkali.[3] This method is stated to give higher yields but it requires more time and reagents. Phenylethylene has been prepared from phenylmethyl carbinol by distillation of the benzoic ester or by the action of phosphoric acid;[4] also by distilling β-phenylethyl phenyl acetate.[5] Phenylethylene may be prepared from ethyl benzene by pyrogenic decomposition,[6] or by conversion into phenyldibromoethane and treatment of the latter with magnesium.[7]

[1] Moureu and Dufraisse, Bull. soc. chim. (4), **31**, 225 (1922).

[2] Böeseken and Bastet, Rec. trav. chim. **32**, 190 (1913); Ostromislensky, U. S. pat. 1,541,176 [C. A. **20**, 424 (1926)].

[3] Fittig and Binder, Ann. **195**, 131 (1879).

[4] Klages and Allendorff, Ber. **31**, 1003, 1298 (1898).

[5] Hibbert and Burt, J. Am. Chem. Soc. **47**, 2240 (1925).

[6] Ostromislensky and Shepard, U. S. pat. 1,541,175 [C. A. **20**, 424 (1926)].

[7] v. Braun and Moldänke, Ber. **54**, 618 (1921).

XXVI

PHENYLSUCCINIC ACID

$$C_6H_5CH{=}C(CN)CO_2H + C_2H_5OH + HCl \rightarrow C_6H_5CH{=}C(CN)CO_2C_2H_5 + HCl + H_2O$$

$$C_6H_5CH{=}C(CN)CO_2C_2H_5 + NaCN + HCl \rightarrow C_6H_5CH(CN)CH(CN)CO_2C_2H_5 + NaCl$$

$$C_6H_5CH(CN)CH(CN)CO_2C_2H_5 + 5H_2O + 2HCl \rightarrow C_6H_5CH(CO_2H)CH_2CO_2H + C_2H_5OH + CO_2 + 2NH_4Cl$$

Submitted by ARTHUR LAPWORTH and WILSON BAKER.
Checked by J. B. CONANT and MILDRED EVANS.

1. Procedure

A. *Esterification of α-Cyano-β-Phenylacrylic Acid:* — In a 200-cc. round-bottom flask fitted with a reflux condenser, 50 g. of dry α-cyano-β-phenylacrylic acid (Org. Syn. 7, 20) is boiled for four and a half hours with 100 cc. of absolute alcohol containing 3–4 g. of anhydrous hydrogen chloride. The resulting solution is filtered rapidly while hot and allowed to stand overnight. Long, flat, colorless prisms separate which are filtered off with suction, washed with a little cold alcohol and dried in air. A further small quantity may be obtained by working up the mother liquor. The melting-point of the ethyl α-cyano-β-phenylacrylate is 50° and the yield 46.5–53 g. (82–94 per cent of the theoretical amount).

B. *Addition of Sodium Cyanide to Ethyl α-Cyano-β-phenylacrylate:*—Twenty grams of cyanophenylacrylic ester is treated with 40 cc. of 50 per cent alcohol and 10 g. of finely powdered sodium cyanide. The mixture becomes warm and the ester rapidly dissolves, the reaction being completed by heating on the steam bath for two minutes. To this is added 200 cc. of water and the resulting clear, colorless solution of the addition product is decomposed with hydrochloric acid. This causes the precipitation of ethyl α, β-dicyano-β-phenylpropionate as a yellowish oil, which on standing overnight and being stirred vigorously, or seeded if possible, sets to a yellowish solid mass. This is filtered off with suction and washed with cold water.

C. *Hydrolysis of Ethyl α, β-Dicyano-β-phenyl Propionate:* — The product thus obtained is hydrolyzed by boiling under a reflux condenser for four hours with 80 cc. of concentrated hydrochloric acid (sp. gr. 1.19). The substance goes into solution and this clear solution, on cooling, deposits phenylsuccinic acid in small crystals which are nearly colorless. These are filtered off, washed with cold water and dried. The yield of product melting at 164–166° is 17.6–18.4 g. (91–95 per cent of the theoretical amount based on the weight of ester used) (Notes 1 and 2).

2. Notes

1. The phenylsuccinic acid, if slightly off color, may be recrystallized easily from a hot water solution by rapid cooling. Five grams is dissolved in 400 cc. of hot water and then 60 cc. more of hot water is added. This solution is filtered and cooled in ice water with stirring until crystals separate. After standing the crystals are filtered off. The yield is 4.5 g. (90 per cent) of product melting at 167°.

2. The quantities of material used may be doubled from (B) on, in which case the refluxing in (C) requires at least a half hour longer for complete solution. One run with double quantities yielded 32.6 g.

3. Methods of Preparation

Phenylsuccinic acid has been prepared by the action of potassium cyanide and alcohol upon α-chlorostyrene;[1] by the reaction of ethoxyphenylmaleic anhydride and fuming hydriodic acid at 165°; [2] by the hydrolysis of phenylcyanopropionic acid, obtained by heating ethyl benzylidene malonate and aqueous potassium cyanide; [3] by the action of potassium cyanide on ethyl benzalmalonate and saponification of the product with potassium hydroxide; [4] by the addition of hydrogen cyanide to ethyl benzylidene acetoacetate in the presence of piperidine, followed by hydrolysis; [5] by the action of sulfuric acid on β-benzoyl-α-phenylpropionic acid oxime;[6] by the hydrolysis with hydrochloric acid of ethyl α, β-dicyano-β-phenylpropionate, obtained from sodium ethyl cyanoacetate and mandelonitrile; [7] by the hydrolysis of the addition product of hydrogen cyanide and ethyl-α-cyano-β-phenylacrylate.[8]

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[1] Rügheimer, Ber. **14**, 428 (1881).

[2] Volhard and Henke, Ann. **282**, 83 (1894).

[3] Bredt and Kallen, Ann. **293**, 348 (1896).

[4] Wegscheider and Hecht, Monatsh. **24**, 417 (1903).

[5] Knoevenagel, Ber. **37**, 4069 (1904).

[6] Hann and Lapworth, J. Chem. Soc. **85**, 1365 (1904).

[7] Higson and Thorpe, J. Chem. Soc. **89**, 1471 (1906).

[8] Lapworth and McRae, J. Chem. Soc. **121**, 1704 (1922).

XXVII

PLATINUM CATALYST FOR REDUCTIONS

(Platinic Oxide)

$$H_2PtCl_6 + 6NaNO_3 \rightarrow Pt(NO_3)_4 + 6NaCl + 2HNO_3$$

$$Pt(NO_3)_4 \rightarrow PtO_2 + 4NO_2 + O_2$$

$$PtO_2 + H_2O \rightarrow PtO_2 \cdot H_2O$$

Submitted by Roger Adams, V. Voorhees, and R. L. Shriner.
Checked by Henry Gilman and S. A. Harris.

1. Procedure

In a porcelain casserole (a Pyrex beaker may be used) is prepared a solution of 3.5 g. (Note 1) of a commercial c.p. chloroplatinic acid (Note 2) in 10 cc. of water and to this is added 35 g. of c.p. sodium nitrate (Note 3). The mixture is evaporated to dryness by heating gently over a Bunsen flame while stirring with a glass rod. The temperature is then raised, 350–370° being reached within about ten minutes. Fusion takes place, brown oxides of nitrogen are evolved, and a precipitate of brown platinum oxide gradually separates. During this procedure foaming often occurs, in which case the mass must be more vigorously stirred and an additional flame directed at the top of the reaction mixture. If the burner under the casserole is removed when foaming starts, the top of the fused mass solidifies and foaming may become sufficient to carry material over the sides of the casserole. By the end of fifteen minutes, when the temperature has reached about 400°, the evolution of gas has greatly decreased. At the end of twenty minutes the temperature should be 500–550°. At this point the vigorous evolution of oxides of nitrogen has practically ceased and a gentle evolution of gas takes place. The temperature is held at this point (best with the full force of the burner directly on the casserole) until about thirty minutes have elapsed, when the fusion should be complete. This temperature (500–550°) is most satisfactory for the fusion (Note 4) in order to obtain a catalyst of maximum activity and minimum lag (Note 5). The temperature indicated is generally attained in this laboratory by the use of one ordinary Bunsen burner turned on as high as possible; where the gas pressure is lower a Meker burner may be necessary. The mass is allowed to cool and is then treated with 50 cc. of water. The brown precipitate settles to the bottom and can be washed by decantation once or twice, then filtered (preferably through a hardened filter paper on a Gooch crucible) and washed on the filter until practically free from nitrates. If the fusion has been properly carried out no difficulty is encountered in this procedure; but if the temperature of fusion has not been high enough or has not been maintained for a sufficiently long time the precipitate tends to become colloidal on addition of water and does not filter well; moreover under these conditions, the yield of product and its activity as a catalyst are diminished. Sometimes the precipitate becomes colloidal only when practically all of the nitrates are removed; in this case it is better to stop washing as soon as the colloid starts to form, since small traces of the salt do not affect the efficiency of the catalyst. The filtrates should be tested for platinum and saved if any is present (Note 6). The oxide is either used directly, or more generally it is dried in a desiccator and portions of the dried material weighed out for reductions. The yield is 1.57–1.65 g. (95–100 per cent of the theoretical amount) (Notes 4 and 7). The use of platinum oxide is illustrated in the reduction of ethyl *p*-nitrobenzoate to ethyl *p*-aminobenzoate (p. 66) and of benzalacetophenone to benzylacetophenone (p. 36).

The platinum black by reduction of the oxide may sometimes be used a second, third or even more times in the reduction of certain compounds merely by reactivating (Note 8) with air or oxygen. A spent catalyst must be reworked (Note 9) along with the platinum recovered from filtrates (Note 6), filter papers (Note 10) and the casserole (Note 11). In the use of platinum-oxide platinum black for reductions, certain types of compounds require different physical conditions from others in order to obtain the best results in each case and factors such as the following must be taken into consideration: the temperature, the medium in which the reduction of platinum oxide to platinum black occurs (Note 12), the effect of traces of inorganic salts (Note 13), the solvent employed (Note 14). Palladous-oxide palladium black has been used for catalytic reduction, and in some cases has proved a more efficient catalyst than the platinum-oxide platinum black though generally this has not been found true (Note 15).

2. Notes

1. If a considerable quantity of platinum oxide is desired it is more satisfactory to prepare several runs of the size indicated than one large run, since spattering and the evolution of gases make large amounts inconvenient to handle. The activity of the catalyst appeared in certain cases to decrease after standing for several weeks and therefore the oxide should preferably be prepared as required.

2. Commercial c.p. chloroplatinic acid varies somewhat in its purity. In this work that from the Mallinckrodt Chemical Works, St. Louis, was used and gave very satisfactory results. Since small amounts of impurities in the catalyst are important factors in the rate of reduction of certain types of compounds, this question of impurities in the chloroplatinic acid must be taken into account (Note 13). In a large proportion of the reductions studied, platinum oxide prepared from the chloroplatinic acid mentioned gave as good results as that from spectroscopically pure chloroplatinic acid made according to the directions of Wichers.[1]

If only platinum metal is available this is dissolved in aqua regia and evaporated to dryness several times with hydrochloric acid, until free from nitrates (Note 9) and the product purified according to the method of Wichers.

3. U.S.P. sodium nitrate could probably be used in place of the C.P. grade in most instances, but in one type of reduction at least (that of aminophenols to cyclic amino alcohols) the small amount of impurities in the U.S.P. grade affected the activity of the catalyst.

4. The relation of temperature of fusion to the properties of the catalyst produced was determined[3c] by carrying out the fusion at various temperatures which were recorded by stirring continuously with a thermocouple encased in a Pyrex glass tube, and reading the temperature on a pyrometer. The product prepared at lower temperatures is usually light brown in color and has a greater tendency to become colloidal on washing. The catalyst prepared at intermediate temperatures is brown in color and at 600° has a very deep brown color. The color may vary even when the catalyst is prepared under conditions which are essentially the same, but if the temperature indicated in the procedure is used the oxide will be satisfactory.

The products prepared at temperatures below 450° and above 600° have a lower activity and require a greater length of time for reduction to platinum black than those prepared at temperatures between 450° and 600°.

If the fusion temperature is about 300°, the yield of platinum oxide is very low, at higher temperatures the yield increases, and at temperatures of 450° and higher it is practically quantitative. With a proper fusion a slightly lower yield than quantitative is generally not due to non-precipitation of the platinum but to loss by spattering and to deposition of a small amount on the casserole.

5. The brown oxide is a heavy granular powder which settles to the bottom of the solution in the bottle in which the reduction is carried out (p. 10). It must be reduced to platinum black before it becomes a catalyst for the reduction. When the hydrogen is admitted and the bottle shaken the brown oxide becomes black and whips up into a fine suspension. The time necessary for the change of the oxide to platinum black is called the lag. The time of lag varies usually from several seconds to two or three minutes, depending upon the conditions under which

the platinum oxide is reduced to platinum black. In general the lag is short provided the reduction of the oxide is carried out merely in the presence of solvent; if carried out in the presence of solvent and substance to be reduced, as is more frequently the case, the character of the substance being reduced has a considerable effect, and sometimes a lag of ten to fifteen minutes occurs. In experiments where foreign salts are added as promoters or poisons the lag varies widely, though generally within a maximum of ten to fifteen minutes; exceptions occur and it was found that the lag was forty to sixty minutes more when the platinum oxide was reduced in the presence of a little sodium nitrite and an alcoholic solution of benzaldehyde. It is probable also that the temperature at which the platinum oxide is formed from the chloroplatinic acid and the solvent present have some effect on the ease with which it is reduced to platinum black.

6. It is advisable to test for platinum in all the filtrates before discarding any of them, since there is sometimes a tendency for small amounts of platinum to remain in solution. A very satisfactory and delicate test for platinum, described by Wöhler,[2] consists in making the solution acid with hydrochloric acid and adding a few drops of stannous chloride. A yellow color develops when platinum is present and a brown color when it is in large amount. If any doubt exists as to whether or not the solution is yellow, it should be shaken with a small amount of ether; the yellow color concentrates in the ether layer, indicating the presence of platinum. From the sodium nitrate filtrates a large proportion of the platinum can be recovered by adding excess of formaldehyde and sodium hydroxide and heating. Upon standing, platinum black separates and may be filtered and worked up with other platinum black residues. The platinum which still remains in solution after this precipitation can be recovered by acidifying the solution and heating with zinc.

7. Quantitative analyses show the oxide to be $PtO_2.H_2O$.[3c] It usually contains a very small amount of glaze from the casserole, but this does not affect its use or activity. The oxide

dissolves only slightly in hot aqua regia even after long heating; it is insoluble in boiling concentrated nitric acid and only slightly, or at least only slowly, soluble in boiling concentrated hydrochloric acid. Constant-boiling hydrobromic acid, on the other hand, dissolves it completely in the cold with the evolution of bromine and the formation of a solution of bromoplatinic acid from which the red potassium salt can be readily precipitated or the solution may be evaporated and the residue used directly in a subsequent fusion.

8. The platinum-oxide platinum black, like any other platinum black, gradually loses its activity with use. In the reduction of certain types of compounds, notably aldehydes the catalyst can be revivified by shaking with air or oxygen for a few minutes.[3b] Frequently this must be done in order to have the reduction go to completion and often it is desirable to do so during a reduction so as to increase the rate of reaction. In other reductions attempted reactivation as described results in the complete inactivation and frequently the coagulation of the catalyst. In reducing certain substances, the catalyst tends to coagulate in lumps during the reduction, particularly toward the end of the reduction. In these instances reworking of catalyst is necessary (Note 9) before it can be used satisfactorily for a second run. On the other hand in the reduction of many substances, the catalyst does not coagulate, but after the reduction is complete it gradually settles if allowed to stand, and the supernatant liquid may be decanted; when a second run is made with this catalyst it is frequently not much inferior to new catalyst and forms a fine suspension as soon as shaking is again started.

9. Platinum residues may be reworked by dissolving them in aqua regia, filtering, evaporating the filtrate to dryness, taking up with a little water and fusing with sodium nitrate. If organic matter is present in the chloroplatinic acid, as is generally the case when recovered platinum is used, it will be oxidized during the fusion and, excepting in cases requiring a spectroscopically pure platinum, seems to have no deleterious effect. Repeated

reworking does seem to cause an accumulation of poison in the catalyst and under these conditions it should be purified as described by Wichers.[1]

10. There is always a certain amount of the oxide which adheres to the filter paper during filtration, so that these papers should be ignited and the residue added to any platinum catalyst which has already become inactive and requires redissolving and reprecipitation (Note 9).

11. The thin film of oxide which remains in the casserole is dissolved by treating with a little constant-boiling hydrobromic acid (Note 7); the solution obtained may then be evaporated and the residue added to the next fusion mixture.

12. In certain reductions it is an advantage to reduce the platinum oxide to platinum black by shaking with hydrogen in the presence of solvent only, before the substance to be reduced is added to the mixture. More often the catalyst is reduced in the presence of the substance to be reduced; with aldehydes for example the platinum black is usually more finely divided and generally more active if prepared in presence of the aldehyde.

13. Certain inorganic salts have the effect of promoting or retarding the action of the catalyst.[3 b, d, e, g, h, i, j, k, l] Thus in the reduction of aldehydes, iron salts in mere traces have a remarkable effect in increasing the rate of reduction and in inhibiting the tendency of the catalyst to lose its activity. To a lesser extent manganese, nickel, and other salts have the same effect. On the other hand, with the majority of substances studied, the effect of these salts is to retard the reduction.

14. The solvent used is an important factor influencing the rate of reduction[3e] and no generalization can be made beyond the one that alcohol, either 95 per cent or absolute has proved to be the best solvent for most of the compounds thus far studied. Ethyl acetate and glacial acetic acid may be used to advantage in some cases.

15. Palladous oxide,[3f] PdO, may be prepared by the fusion of palladous chloride with sodium nitrate, and is an effective catalyst in hydrogenation, the most active form being produced when the fusion temperature is 600°.

3. Methods of Preparation

Platinic oxide has been prepared previously by the interaction of platinic chloride and excess sodium hydroxide.[4] Since the catalyst itself is platinum black, the other methods for its preparation are given below.

Platinum black has been prepared chiefly by the reduction of chloroplatinic acid with formaldehyde;[5] the details have been improved by Willstätter and Hatt;[6] Willstätter and Waldschmidt-Leitz,[7] and by Feulgen.[8]

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[1] Wichers, J. Am. Chem. Soc. **43**, 1268 (1921).

[2] Wöhler, Chem. Ztg. **31**, 938 (1907).

[3] Articles in this field are (*a*) Voorhees and Adams, J. Am. Chem. Soc. **44**, 1397 (1922); (*b*) Carothers and Adams, **45**, 1071 (1923); (*c*) Adams and Shriner, **45**, 2171 (1923); (*d*) Kaufmann and Adams, **45**, 3029 (1923); (*e*) Carothers and Adams, **46**, 1675 (1924); (*f*) Shriner and Adams, **46**, 1683 (1924); (*g*) Carothers and Adams, **47**, 1047 (1925); (*h*) Pierce and Adams, **47**, 1098 (1925); (*i*) Kern, Shriner and Adams, **47**, 1147 (1925); (*j*) Heckel and Adams, **47**, 1712 (1925); (*k*) Tuley and Adams, **47**, 3061 (1925); (*l*) Adams and Garvey, **48**, 477 (1926); (*m*) Hiers and Adams, Ber. **59**, 162 (1926); (*n*) Adams, Cohen and Rees, J. Am. Chem. Soc. **49**, 1093 (1927); (*o*) Hiers and Adams, **49**, 1099 (1927); (*p*) Carothers and Jones, **47**, 3051 (1925). A study of ketones as yet unpublished has indicated that reductions are more satisfactory when no solvent is used.

[4] Wöhler, Z. anorg. Chem. **40**, 434 (1904); Bellucci, Z. anorg. Chem. **44**, 171 (1905); Wöhler and Frey, Z. Elektrochem. **15**, 132 (1909).

[5] Loew, Ber. **23**, 289 (1890).

[6] Willstätter and Hatt, Ber. **45**, 1472 (1912).

[7] Willstätter and Waldschmidt-Leitz, Ber. **54**, 113 (1921).

[8] Feulgen, Ber. **54**, 360 (1921).

XXVIII

SODIUM *p*-ARSONO-N-PHENYLGLYCINAMIDE

(Tryparsamide)

$$p\text{-}H_2O_3AsC_6H_4NH_2 + ClCH_2CONH_2 + NaOH \rightarrow p\text{-}H_2O_3AsC_6H_4NHCH_2CONH_2 + NaCl + H_2O$$

$$p\text{-}H_2O_3AsC_6H_4NHCH_2CONH_2 + 2NaOH \rightarrow p\text{-}Na_2O_3AsC_6H_4NHCH_2CONH_2 + 2H_2O$$

Submitted by W. A. Jacobs and M. Heidelberger.
Checked by Roger Adams and L. F. Martin.

1. Procedure

To a solution of 130 g. (0.6 mole) of arsanilic acid (Org. Syn. **3**, 13) in 600 cc. (0.6 mole) of normal sodium hydroxide is added 52 g. (0.62 mole) of sodium bicarbonate and 70 g. (0.75 mole) of chloroacetamide (Org. Syn. **7**, 16). The mixture is heated on a water bath to 90–100° and a steady evolution of carbon dioxide occurs. At the end of two hours, when gas evolution has practically ceased, the mixture is cooled to 40° C., stirred vigorously and 150 cc. of 1 : 1 hydrochloric acid poured in rapidly. *p*-Arsonophenylglycinamide crystallizes at once and, after cooling to room temperature, is filtered by suction and washed once with 2 per cent hydrochloric acid (Note 1), then with cold water. The crude product thus obtained is contaminated with some arsanilic acid and possibly other products. These are removed during purification. The crude product is suspended in about 400 cc. of water and with vigorous stirring, treated carefully with 25 per cent aqueous sodium hydroxide until solution is just complete. At this point the mixture is still acid to litmus and an excess of sodium hydroxide is to be avoided to prevent decomposition of the product. About 15 g. of boneblack is added, the mixture stirred for five minutes without heating and filtered. The filtrate is treated during vigorous stirring with 100 cc. of 1 : 1 hydrochloric acid and the pure acid at once separates. After cooling, it is filtered by suction and washed thoroughly with small portions of ice-cold water until the filtrate is practically halogen-free (Note 2).

The acid, without drying, is suspended in about 200 cc. of distilled water and with vigorous stirring, cautiously (Note 3) treated with 25 per cent sodium hydroxide solution until dissolved and the solution reacts neutral to litmus. The solution is then filtered through folded filter paper which should be free from soluble calcium salts, otherwise the filtrate will remain clouded by a suspension of the calcium salt. The clear, faintly yellow or colorless filtrate is then vigorously stirred and treated with 1.5 volumes of 95 per cent alcohol. Crystallization is induced by rubbing with a rod and then an additional volume of alcohol is added. The mixture should be allowed to cool to about 20° and stand for at least two hours to complete the precipitation of the salt, which is then filtered by suction and washed thoroughly with 85 per cent alcohol. The salt is then air-dried. The yield is 73–77 g. (38–40 per cent of the theoretical amount).

2. Notes

1. From this filtrate approximately 15–30 g. of arsanilic acid may be recovered by just neutralizing to Congo Red with sodium hydroxide.

2 If the free acid is desired it may be obtained by drying the product at this stage. The yield of free acid is about 100 g. (60 per cent of the theoretical amount).

3. If sodium hydroxide is added too rapidly some solid precipitates which does not redissolve.

3. Methods of Preparation

This procedure for the preparation of tryparsamide has been described in the literature.[1]

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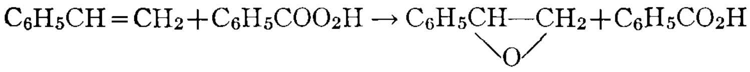
[1] Jacobs and Heidelberger, J. Am. Chem. Soc. **41**, 1590 (1919); U. S. pat. 1,280,119 [C.A. **12**, 2658 (1918)].

XXIX

STYRENE OXIDE



$$C_6H_5CH{=}CH_2+C_6H_5COO_2H \rightarrow C_6H_5\underset{\diagdown O \diagup}{CH{-}CH_2}+C_6H_5CO_2H$$

Submitted by Harold Hibbert and Pauline Burt.
Checked by Roger Adams and F. E. Kendall.

1. Procedure

To a solution of 42 g. (0.33 mole) of benzoylhydroperoxide (p. 30) in 500 cc. of chloroform is added 30 g. (0.3 mole) of styrene (b.p. 141–143°) (p. 84). The solution is kept at 0° for twenty-four hours and is shaken frequently during the first hour. At the end of twenty-four hours, titration of an aliquot part of the solution shows that only the excess of benzoylhydroperoxide remains (Note 1).

The benzoic acid is removed from the chloroform solution by shaking with an excess of 10 per cent sodium hydroxide solution, the alkali is removed by washing with water, and the chloroform solution is dried with anhydrous sodium sulfate. It is then fractionated through an efficient distilling column (Org. Syn. 1, 40). Removal of the chloroform leaves a practically colorless liquid which distils at 188–192° (uncorr.) (Note 2). The yield is 24–26 g. (70–75 per cent of the theoretical amount).

2. Notes

1. The benzoylhydroperoxide may be analyzed by mixing with an excess of acidified potassium iodide and titrating the liberated iodine with sodium thiosulfate (p. 31).

2. If the styrene oxide is distilled over a free flame some

decomposition takes place, indicated by the formation of water. This is not observed if the product is distilled from an oil bath.

3. Methods of Preparation

Styrene oxide has previously been prepared by the action of iodine, water and mercuric oxide on styrene.[1] A description of Hibbert's method [2] using benzoylhydroperoxide has appeared in the literature.

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[1] Fourneau and Tiffeneau, Compt. rend. **140**, 1596 (1905).

[2] Hibbert and Burt, J. Am. Chem. Soc. **47**, 2240 (1925).

XXX

TRIMETHYLACETIC ACID

$$(CH_3)_3CCl+Mg \rightarrow (CH_3)_3CMgCl$$

$$(CH_3)_3CMgCl+CO_2 \rightarrow (CH_3)_3CCO_2MgCl$$

$$(CH_3)_3CCO_2MgCl+H_2O \rightarrow (CH_3)_3CCO_2H+MgOHCl$$

Submitted by S. V. PUNTAMBEKER and E. A. ZOELLNER.
Checked by J. B. CONANT and A. HAROLD BLATT.

1. Procedure

IN a 3-l., three-neck, round-bottom flask, fitted with a mechanical stirrer and mercury seal, a 500-cc. separatory funnel and an efficient reflux condenser, is placed 61 g. (2.5 moles) of magnesium turnings or powder (Note 1). The magnesium is then covered with 200 cc. of anhydrous ether. Five cc. of pure *tert*-butyl chloride (with a crystal or two of iodine) is added to start the reaction. Stirring is begun and a solution of 227 g. (2.5 moles) of pure *tert*-butyl chloride (p. 50) in 1100 cc. of anhydrous ether is dropped slowly (Note 2) on the magnesium during six to eight hours. The reaction is practically complete when all the halide has been added, but stirring should be continued for fifteen minutes longer.

The reaction mixture is now surrounded by an ice and salt mixture. The separatory funnel is replaced by a two-hole rubber stopper containing a thermometer (bulb immersed in the reaction mixture) and a glass tube the outer end of which is connected to a mercury trap (Note 3). When the temperature of the reaction mixture has fallen to 0°, the condenser is replaced by a tube 10 mm. in diameter and adjusted so the end is 50 mm. above the surface of the reaction mixture. The reaction mixture is stirred and carbon dioxide is added through this tube directly from a cylinder after passing through two bottles containing concentrated sulfuric acid. The carbon dioxide is added as rapidly as it is used up. The temperature is controlled by the rate of stirring and should not go above +8°. After two and one-half to three hours the temperature falls below 0°. Then the addition is continued for one-half hour under a pressure of 45 mm. (Note 3). The temperature falls to −3° to −5° at the end of this time and the reaction is complete.

After surrounding the flask with ice, the reaction mixture is hydrolyzed (Note 4) with 25 per cent sulfuric acid. The reaction mixture is transferred to a 2-l. separatory funnel and the ether layer separated (Note 4). The water layer is extracted with four 100-cc. portions of ether. The combined ether extracts are then washed with four 100-cc. portions of 25 per cent sodium hydroxide solution to remove the trimethylacetic acid from the ether.

The aqueous alkaline extract is heated to 100° to remove ether and volatile impurities. The solution is then cooled with ice and acidified with 25 per cent sulfuric acid, and the organic acid separated. The water layer is distilled from a 2-l. flask until no more oily solution comes over. The distillate is saturated with salt and the acid layer is separated. This water layer together with the low boiling fraction from distillation of the crude trimethylacetic acid is distilled and the distillate salted out as before.

The combined acid layers are distilled from a 250-cc. Claisen flask connected to an air condenser, which in turn is connected to a side-arm flask cooled by running water. The trimethylacetic acid is collected at 162–165°/atm. press., 110–112/124 mm. The yield, which depends somewhat on the form of magnesium, is 157–162 g. (61–63 per cent of the theoretical amount based on *tert*-butyl chloride) when ordinary magnesium turnings are used and 177–178 g. (69–70 per cent) when 200-mesh magnesium powder is used. The acid melts at 34–35°.

2. Notes

1. The yield of product depends to a considerable extent upon the form of magnesium used. Either the finer commercial grade of turnings should be used or the 30 to 200-mesh powdered magnesium that is kept in a tightly stoppered bottle when not in use. The powdered magnesium makes possible a 5–8 per cent increase in yield.

2. The rate of addition of the halide solution is important. The slower the rate the better the yield. A delivery constant should be determined of the separatory funnel so that the solution can be added uniformly over a period of six to eight hours.

3. The mercury trap enables the operator to adjust the flow of the carbon dioxide according to the rate of absorption, and to apply a pressure of 45 mm. during the last half-hour. The pressure itself has practically no effect. The trap consists merely of a narrow glass test-tube containing mercury, and the tube is made to extend beneath the surface.

4. The hydrolysis of the reaction mixture and subsequent separation of the acid is the procedure given by Gilman and Parker (Org. Syn. **5**, 25). Sulfuric acid should be added during the hydrolysis as long as any particles of magnesium are present. The water layer does not become clear, due to solidification of the organic acid.

3. Other Methods of Preparation

See p. 110.

XXXI

TRIMETHYLACETIC ACID

$$(CH_3)_3CCOCH_3+4NaOH+3Br_2 \rightarrow$$
$$(CH_3)_3CCO_2Na+3H_2O+CHBr_3+3NaBr$$
$$(CH_3)_3CCO_2Na+H_2SO_4 \rightarrow (CH_3)_3CCO_2H+NaHSO_4$$

Submitted by L. T. Sandborn and E. W. Bousquet.
Checked by F. C. Whitmore and T. Otterbacher.

1. Procedure

In a 5-l. round-bottom flask fitted with a mechanical stirrer is placed a solution of 330 g. (8 moles) of stick sodium hydroxide (U.S.P.) in 2.8 l. of water and the solution is cooled to 0° in an ice-salt bath. To the well-stirred solution 480 g. (3 moles) of bromine is added from a separatory funnel at such a rate as to keep the temperature below 10° (Note 1) (fifteen to twenty minutes). The solution is cooled again to 0° and 100 g. (1 mole) of pinacolone (Org. Syn. **5**, 91) is added from a separatory funnel, keeping the temperature below 10°. After the solution is decolorized (about an hour) it is stirred for three hours at room temperature.

The flask is then fitted with a separatory funnel and a condenser for distillation, and heated with a Meker burner to steam distil the bromoform and carbon tetrabromide (Notes 2 and 3).

The burner is then removed, the mixture is cooled to 50°, and 400 cc. of concentrated sulfuric acid (Note 4) is added through the separatory funnel. The heat of neutralization causes some trimethylacetic acid to distil with water. When all the acid is added the flask is heated again and the trimethylacetic acid comes over with about 400 cc. of water. When all of the trimethylacetic acid (70-80 cc.) has distilled, a liquid heavier than water begins to come over. The distillation is stopped and the acid separated from the water in a separatory funnel and dried either with calcium chloride or by distilling with benzene which carries over all water (Note 5). The trimethylacetic acid is further purified by distillation under reduced pressure. It boils at 75–78°/20 mm. and the yield is 63–65 g., melting at 34–35°.

The water layer is extracted with two 100-cc. portions of ether. The combined ether solutions are dried with calcium chloride, the ether distilled, and the residue fractionated under reduced pressure, using a modified Claisen flask (Org. Syn. 1, 40). Ten to twelve grams may be obtained in this way. The total yield is 72-75 g. (71–74 per cent of the theoretical amount).

2. Notes

1. The temperature must be kept low during the reaction to prevent formation of sodium bromate.

2. The reaction between sodium hydroxide and tribromopinacolone is not complete at room temperature. Heating in this manner, rather than separation in the cold, results in an increase of 10–15 per cent in the yield.

3. The bromoform passes over with the steam rather rapidly. In some runs some carbon tetrabromide was also obtained. Toward the end of the steam distillation a heavy oil that is more or less of a lachrymator may come over. This is undoubtedly brominated pinacolone. The bromoform may be purified by vacuum distillation. One run gave 115 g. of product, boiling at 78-79°/22 mm.

4. An equivalent amount of hydrochloric acid may be used without affecting the yield.

5. The trimethylacetic acid is dried very easily by distilling with about 50 cc. of benzene at ordinary pressure until all of the water is removed and then the residue is distilled under reduced pressure.

3. Methods of Preparation

Trimethylacetic acid may be made by the hydrolysis of *tert*-butyl cyanide with weak hydrochloric acid at 100°.[1] It is also obtained by oxidation of trimethylpyroracemic acid with silver oxide or potassium dichromate and sulfuric acid,[2] by oxidation of *tert*-butylethylene with permanganate solution,[3] or by oxidation of dimethyl 2,2-propanol with chromic acid.[4] Schroeter reports the formation of trimethylacetic acid by rearrangement of the oxime of trimethylacetophenone to give the anilide of trimethylacetic acid, which can be hydrolyzed to give the acid.[5]

The method given in these directions [6] may be modified by using potassium hypochlorite [7] or chromic acid [8] as the oxidizing agent.

The directions given in Exp. XXX by the reaction of *tert*-butyl magnesium chloride and carbon dioxide are an improvement on those described by Bouveault.[9]

[1] Butlerow, Ann. **165**, 322 (1873).

[2] Glücksmann, Monatsh. **10**, 777 (1889).

[3] Fomin and Sochanski, Ber. **46**, 247 (1913).

[4] Franke, Monatsh. **34**, 1900 (1913).

[5] Schroeter, Ber. **44**, 1206 (1911).

[6] Richard and Langlais, Bull. soc. chim. (4) **7**, 464 (1910).

[7] Böeseken, Rec. trav. chim. **29**, 99 (1910).

[8] Friedel and Silva, Ber. **6**, 146, 826 (1873).

[9] Bouveault, Compt. rend. **138**, 1108 (1904).

XXXII

TRIMETHYLENE CHLOROHYDRIN

$$HOCH_2CH_2CH_2OH + HCl \rightarrow ClCH_2CH_2CH_2OH + H_2O$$

Submitted by C. S. MARVEL and H. O. CALVERY.
Checked by H. T. CLARKE and M. R. BRETHEN.

1. Procedure

A 100-cc. round-bottom wide-mouth flask (or a large test-tube 18 cm. long and 4.5 cm. wide) is fitted with a rubber stopper carrying a separatory funnel, a thermometer, an inlet tube reaching almost to the bottom of the flask and an outlet tube leading to a condenser set for downward distillation. A receiver consisting of a suction flask is attached tightly to the end of the condenser and the side arm of the receiver is attached to a reflux condenser. A tube is led from the top of the condenser to the hood in order to take care of excess hydrogen chloride during the distillation, or better the apparatus described in Note 2, p. 27, is used. About 25–30 cc. of trimethylene glycol (b.p. 210–215°) is placed in the flask and heated by means of an oil or metal bath to 150–170°. A *very* rapid stream of dry hydrogen chloride (Note 1) is now led into the hot glycol through the inlet tube. A reddish distillate consisting of water, trimethylene chlorohydrin, hydrogen chloride and some unchanged glycol begins to distil. As rapidly as the glycol is used up in the reaction flask, more is added from the separatory funnel. It is always advisable to keep the amount of material in the reaction flask as small as possible. The rate at which the hydrogen chloride is passed through the flask controls the reaction and also has a marked effect on the yield (Note 2). The best results are obtained by passing in the gas rapidly enough to use up 2–3 cc. of trimethylene glycol in one minute. The process is continuous and can be run indefinitely without changing the apparatus. The weight of crude distillate from 1800 g. of trimethylene glycol is usually 2300–2500 g.

To obtain the trimethylene chlorohydrin, the distillate from this operation is heated for about one hour on a steam bath in order to drive out most of the excess hydrogen chloride. The distillate is then fractionated under reduced pressure (Note 3) in a modified Claisen flask (Org. Syn. 1, 40). The fractionating side arm should be 25 cm. in length. The fractions collected under 10 mm. are: to 55°, 55–57°, 57–65°, 65–85°, 85–105°, residue.

Before a further fractionation is carried out, the residue is discarded; the portion boiling at 85–105°, consisting chiefly of unchanged trimethylene glycol, is set aside for use in a later preparation; the low-boiling portion up to 55° consisting mainly of water and hydrogen chloride with some trimethylene chloride (Note 4) and trimethylene chlorohydrin, is neutralized carefully with powdered sodium carbonate. Two layers form and the upper containing the chlorohydrin is separated, dried over anhydrous potassium carbonate and again replaced as the portion boiling up to 55°. Another complete fractional distillation, carried out in the usual way, is now made except that the highest fraction boils at 65–85°/10 mm.

The material boiling above 65°/10 mm. is chiefly trimethylene glycol and is used in a succeeding experiment. The final yield of trimethylene chlorohydrin (Note 5) boiling at 60–64°/10 mm. is 835–1000 g. from 1800 g. of trimethylene glycol (50–60 per cent of the theoretical amount), and 400–450 g. of trimethylene glycol is recovered.

2. Notes

1. The hydrogen chloride may be generated by any method desired. Since a large quantity of gas is required, the procedure described (Org. Syn. **2**, 29) is rather expensive. A more satisfactory arrangement is to half fill a 12-l. flask with a paste of salt and concentrated hydrochloric acid and run into this com-

mercial sulfuric acid. The gas is dried by a single wash bottle of sulfuric acid.

If sulfuric and hydrochloric acids are used then for the conversion of 1800 g. of trimethylene glycol, a 20-l. bottle half-filled with concentrated sulfuric acid is treated with concentrated hydrochloric acid introduced through a tube reaching to the bottom. The hydrochloric acid is added at the rate of 30–40 drops per minute. Two charges of sulfuric acid are needed and a total of about 24 kg. of hydrochloric acid.

2. The yield of chlorohydrin is largely determined by the rate at which the reaction is carried out. A very rapid stream of hydrogen chloride is absolutely essential for obtaining the yields mentioned. Moreover, it is very important to keep as small an amount of glycol as possible in the reaction flask. If larger amounts of glycol are present at any one time, the yield of product is lowered and considerable tar is produced.

3. Trimethylene chlorohydrin cannot be distilled under atmospheric pressure without some decomposition. The fractionation can be carried out at ordinary pressures when the fractions collected are up to 125°, 125–158°, 158–164°, 164–190°, 190–210° and residue. This procedure is less desirable as some hydrogen chloride is evolved and the product turns dark on standing.

4. The portion boiling up to 55°/10 mm., obtained after the second fractionation, was washed with concentrated sulfuric acid, then water, and finally dried and distilled. A certain amount of trimethylene chloride was sometimes obtained, boiling at 115–120° and amounting to about 30 per cent of the total fraction.

5. The chlorohydrin contains a very small amount (less than 0.5 per cent) of water-insoluble material, which is probably trimethylene chloride and di-γ-chloropropyl ether.

3. Methods of Preparation

Trimethylene chlorohydrin has been prepared from trimethylene glycol by the action of dry hydrogen chloride under various conditions; [1] by the action of aqueous hydrochloric acid; [2] and by the action of sulfur chloride.[3] It has also been prepared from γ-chloropropyl acetate and methyl alcoholic hydrochloric acid.[4]

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[1] Reboul, Ann. chim. phys. (5) **14**, 493 (1878); Malengreau and Lebailly, Z. physiol. Chem. **67**, 37 (1910); Karvonen, Ann. acad. sci. Fennicae [A], **3**, 1 (1912) [Chem. Zentr. **1912**, II, 1271]; Derick and Bissell, J. Am. Chem. Soc. **38**, 2481 (1916); Karvonen, Ann. acad. sci. Fennicae [A], **5**, 1 (1914) [C.A. **14**, 2176 (1920)].

[2] Norris and Mulliken, J. Am. Chem. Soc. **42**, 2095 (1920); Hultman, Davis, and Clarke, J. Am. Chem. Soc. **43**, 369 (1921).

[3] Derick and Bissell, J. Am. Chem. Soc. **38**, 2481 (1916).

[4] Henry, Bull. Acad. roy. Belg. cl. sci. **8**, 738 (1906).

XXXIII

TRIPHENYLAMINE

$$2(C_6H_5)_2NH+2C_6H_5I+K_2CO_3 \rightarrow 2(C_6H_5)_3N+2KI+H_2O+CO_2$$

Submitted by F. D. Hager.
Checked by Henry Gilman and R. McCracken.

1. Procedure

In a 2-l. three-neck, round-bottom flask, fitted with a very efficient mechanical stirrer, a 100-cc. separatory funnel and a large air-cooled reflux condenser (Note 1), the upper part of which is bent downwards and attached to a vertical water condenser, are placed 176 g. (1.04 moles) of ground diphenylamine (Note 2), 204 g. (1 mole) of iodobenzene, 1 l. of nitrobenzene (Note 3), 138 g. (1 mole) of finely powdered anhydrous potassium carbonate and 5 g. of copper powder (Note 4).

The reaction mixture is then stirred very vigorously and boiled at such a rate that the nitrobenzene condenses in the upper third of the air-cooled reflux condenser and flows back in an almost steady stream. The water formed in the reaction passes over, together with a small amount of nitrobenzene and iodobenzene, and is condensed by the water-cooled condenser. This distillate is freed of water by shaking with a small quantity of sodium sulfate and returned at intervals through the separatory funnel to the reaction flask. Heating is continued for about twenty-four hours or until the reaction is complete, as is evidenced by the non-evolution of water (Note 5).

The reaction mixture is allowed to cool somewhat and is then transferred to a 5-l. flask, and the nitrobenzene together with a little of the excess diphenylamine is removed by steam distillation. During distillation the flask should be heated to prevent excessive condensation of steam (Note 6). Steam distillation should be continued until a liter of distillate contains less than 5 cc. of water-insoluble material (Note 7).

The reaction mixture is cooled and the crude amines which separate are collected on a suction funnel and washed twice with 400-cc. portions of water. The filtrate and washings should be saved for the recovery of iodine (Note 8). The precipitate on the funnel is transferred to a 2-l. beaker, dissolved in about 1 l. of benzene, filtered, and the benzene-insoluble part washed three times with 75-cc. portions of benzene. The benzene solution and washings are combined and separated mechanically from as much water as is possible. The water is then completely removed by distilling until the distillate comes over clear. If necessary, dry benzene is added to the solution in order to have a final volume of about 1200 cc.

When the water is entirely removed, the benzene solution is cooled and an excess of dry hydrogen chloride is passed into it to precipitate the diphenylamine as the hydrochloride (Note 9).

After standing about three hours, the diphenylamine hydrochloride is filtered and washed with benzene (Note 10). The benzene is distilled from the filtrate (Note 11) and the residual triphenylamine is transferred to a 500-cc. modified Claisen flask (Org. Syn. 1, 40) and distilled under reduced pressure. The first fraction consists of some benzene, then the temperature rises rapidly and a few cubic centimeters of deeply colored distillate comes over just before the amine fraction, which is collected at 195–205°/10–12 mm. The distillate is a yellow liquid which soon solidifies to a light yellow solid. The side arm of the distilling flask should be of rather large bore (about 10 mm.) to prevent clogging by the amine which solidifies. The crude product weighs 220–235 g. and melts at 120–124°.

In order to obtain a pure product the amine is dissolved in about 700 cc. of boiling ethyl acetate under a reflux condenser. When the amine has dissolved the solution is rapidly cooled and stirred, whereupon the amine separates in almost white crystals. Further crops of crystals may be obtained on concentrating the solution and cooling. The last portions may be colored, but one crystallization from ethyl acetate gives a nearly colorless product (Note 12). The total yield of pale yellow product which melts at 126° is 200–210 g. (82–85 per cent of the theoretical amount) (Note 13).

2. Notes

1. The air condenser used here was 65 cm. long and of 13 mm. bore and the vertical water condenser, 40 cm. in length. Cork stoppers were used and it was found desirable to protect their exposed surfaces by coating them with water glass, allowing these to dry, and then coating with lead foil. It is best to boil the mixture on a sand bath and to cover with asbestos that part of the flask not immersed in the sand.

2. Technical diphenylamine which has been vacuum distilled and collected over a 5° range (159–164°/4 mm.) is satisfactory.

3. The nitrobenzene should not contain any free acid. Should there be free acid present, it can be removed by shaking with solid potassium carbonate.

4. " Natur Kupfer C " is a good catalyst, but ordinary copper bronze may be used.

5. The time required for the completion of reaction varies with the rate of stirring. When the stirring is very vigorous most of the water comes over within twelve hours.

6. This heating should be done carefully, preferably on a sand bath, because of the danger of breaking the flask due to the caking of some undissolved potassium carbonate.

7. In general, about 8–10 l. of aqueous distillate is required, and practically all but about 25 cc. of the nitrobenzene is recovered. It is recommended that the removal of nitrobenzene by steam distillation be fairly complete in order to avoid a gummy residue.

8. Most of the iodine can be recovered as potassium iodide mixed with some potassium carbonate. A little cuprous iodide is also present.

9. The hydrogen chloride is introduced through a delivery tube at least 25 mm. in diameter and about 10 cm. under the

surface of the liquid. If the gas is introduced rapidly enough and the mixture occasionally stirred there is little trouble with clogging of the delivery tube.

10. The crude diphenylamine may be recovered by decomposing the hydrochloride with water and filtering the mixture.

11. A large amount of hydrogen chloride is evolved during the distillation and some provision must be made to keep it out of the room.

12. Because of the lesser solubility of triphenylamine in ethyl alcohol this solvent may be used advantageously in washing the crystals and in recrystallizing small amounts of the compound.

13. N-Phenyl carbazole may be made in an analogous manner by using carbazole in place of diphenylamine. If stirring and heating are both very vigorous, twelve hours suffice for the reaction. The yield of purified product is about 88 per cent and the compound melts at 88–89°. The crystals, when crushed, emit a strong violet light.

3. Methods of Preparation

This procedure is a modification of the method of Goldberg and Nimerovsky.[1] Triphenylamine has also been prepared by the treatment of aniline or diphenylamine with potassium and then bromobenzene[2] and by the action of sodium on diphenylamine and bromobenzene.[3]

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[1] Goldberg and Nimerovsky, Ber. **40**, 2452 (1907).

[2] Merz and Weith, Ber. **6**, 1514 (1873).

[3] Heydrich, Ber. **18**, 2156 (1885).

LATER REFERENCES TO PREPARATIONS IN PRECEDING VOLUMES

(The following references are to methods of possible preparative value that have been described during 1926. The numbers in parentheses following the name of a compound refer to the volume and page of Organic Syntheses).

Acrolein (**6**, 1):

By heating glycerol with anhydrous magnesium sulfate. Evans and Hass, J. Am. Chem. Soc. **48**, 2703 (1926).

Benzene sulfonyl chloride (1, 21):

From sodium benzene sulfonate and chlorosulfonic acid. Rodionov, Bull. soc. chim. (4) **39**, 305 (1926).

Benzil (1, 25):

By the oxidative catalytic dehydration of benzoin. Zetzsche and Zala, Helvetica Chim. Acta **9**, 288 (1926).

Benzilic acid (1, 29):

By heating benzil in toluene with sodamide and treatment with water. Kasiwagi, Bull. Chem. Soc. Japan **1**, 66 (1926) [C. A. **20**, 2491 (1926)].

***n*-Butyl *n*-butyrate** (5, 23):

A by-product in the preparation of butyraldehyde by the dehydrogenation of butyl alcohol with a copper catalyst. Legg and Bogin, U. S. pat. 1,580,143 (1926) [C. A. **20**, 1813 (1926)].

Ethyl Bromide (1, 6):

From ethyl *p*-toluene sulfonate and potassium bromide. Rodionov, Bull. soc. chim. (4) **39**, 305 (1926).

Ethyl oxalate (2, 22, **and** 5, 59):

(*a*) To oxalic acid is added sufficient alcohol to remove as the azeotropic mixture all of the water formed in the reaction and then the mixture is heated until the water is removed. CONTZEN-CROWET, Bull. soc. chim. Belg. **35**, 165 (1926).

(*b*) Essentially the method given in Organic Syntheses. WAHL, Bull. soc. chim. (4) **37**, 713 (1925).

2-Furancarboxylic acid and 2-Furylcarbinol (**6**, 44):

By heating furfural in toluene with sodamide. KASIWAGI, Bull. Chem. Soc. Japan **1**, 66 (1926) [C. A. **20**, 2491 (1926)].

Furfural (**1**, 49):

(*a*) From peanut hulls. DE BELSUNCE, Bull. mat. grasses **1926**, 1.

(*b*) By the oxidative catalytic dehydration of furfuralcohol. ZETZSCHE and ZALA, Helvetica Chim. Acta **9**, 288 (1926).

d-**Glutamic acid** (**5**, 63):

(*a*) By the electrolysis of beet sugar residues. TAKAYAMA, Brit. pat. 233,196 (1924) [C. A. **20**, 675 (1926)].

(*b*) By the hydrolysis of the residues from alcoholic fermentation. IKEDA, U. S. pat. 1,582,472 (1926) [C. A. **20**, 1996 (1926)].

(*c*) From acrolein through γ-aldehydobutyric acid. KEIMATSU and SUGASAWA, J. Pharm. Soc. Japan **531**, 369 (1925) [C. A. **20**, 2824 (1926)].

Mesityl oxide (1, 53):

(*a*) From acetone and sulfuric acid. YLLNER, Svensk. Kem. Tids. **37**, 227 (1925) [C. A. **20**, 739 (1926)].

(*b*) From acetone and phosphorus oxychloride. GASOPOULOS, Ber. **59**, 2188 (1926).

Myristic acid (**6**, 66):

An improvement over the general procedure given in organic syntheses is described. VERKADE and COOPS, Rec. trav. chim. **46**, 528. (1927).

Phenylacetic acid (**2**, 63):

By the action of carbon dioxide on benzyl magnesium bromide. IVANOV, Bull. soc. chim. (4) **37**, 287 (1925).

Phenylacetylene (**2**, 67):

By the action of sodamide on styrene dibromide and on α-bromostyrene. BOURGUEL, Ann. chim. (10) **3**, 225, 228 (1925).

Pinacol hydrate (**5**, 87):

A general study of the reduction of acetone to pinacol. CALVERT, India Rubber Rev. **26**, No. 9, 48 (1926).

Quinone (**2**, 85):

By the oxidation of hydroquinone in 60 per cent acetic acid with chromic acid. CRAVEN and DUNCAN, J. Chem. Soc. **127**, 1489 (1925).

1,2,3-Tribromopropane (**5**, 99):

By the bromination of 1,2-dibromopropane in the presence of iron. TAPLEY and GIESY, J. Am. Pharm. Assoc. **15**, 173 (1926).

ADDITIONS AND CORRECTIONS FOR PRECEDING VOLUMES

(The numbers in parentheses following the name of a compound, refer to a number and page of "Organic Syntheses.")

Cyclohexylcarbinol (**6**, 22). In the preparation of cyclohexylcarbinol as described in Vol. **6**, 22, a high-boiling by-product, the cyclohexylcarbinol acetal of formaldehyde, is sometimes obtained. The by-product becomes the main product if the steam distillation of the reaction mixture is omitted. The by-product can usually be avoided if twice the calculated amount to decompose the Grignard reagent of 10 per cent sulfuric acid is added to the reaction mixture before steam distillation is carried out. The acetal which may be present is thus hydrolyzed.

If acetal has been isolated, it may best be hydrolyzed by boiling with an equivalent weight of ethyl alcohol and concentrated hydrochloric acid (2 cc. for each 50 cc. of alcohol used) for four or five hours, then distillation of the ethyl alcohol, and treatment with water.

Ketene (**4**, 39). It has been found that the formation of acetanilide from ketene and aniline takes place more satisfactorily if the ketene is passed directly into excess aniline without any dry ether present. The excess aniline may then be removed by vacuum distillation until the temperature of the vapors is 10–15° higher than the boiling point of aniline. An alternative plan is to remove excess aniline by dilute hydrochloric acid, to filter the acetanilide and to wash with water.

Phenylacetylene (**2**, 67). It is stated in the directions that the distilling flask is heated until a temperature of 200° is reached and at that temperature the potassium hydroxide which is used is molten. The potassium hydroxide usually available contains sufficient moisture so that it will liquefy at 200°. If pure dry potassium hydroxide is used, it is necessary to add a little water so that the fusion point will be lowered to the point indicated.

Another contributor has offered the suggestion that just as good yields can be obtained if the eutectic of sodium hydroxide and potassium hydroxide is employed, under which conditions the alkali is molten at 200° and the reaction takes place very readily.

AUTHOR INDEX

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