

ORGANIC SYNTHESSES

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

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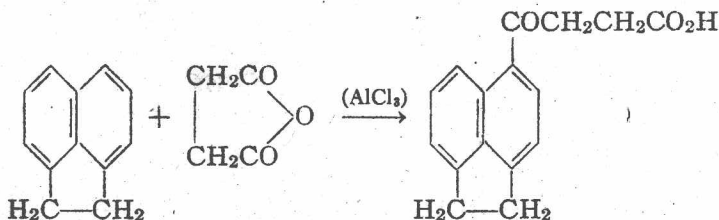
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ORGANIC SYNTHESSES

β -(3-ACENAPHTHOYL)-PROPIONIC ACID.

(Propionic Acid, β -3-Acenaphthenylcarbonyl-)



Submitted by L. F. FIESER.

Checked by W. W. HARTMAN and A. WEISSBERGER.

1. Procedure

In a 3-l. round-bottomed, three-necked flask (Note 1), 100 g. (0.65 mole) of pure acenaphthene (Note 2) and 72 g. (0.72 mole) of succinic anhydride (Org. Syn. 15, 93) are dissolved by warming in 600 cc. of nitrobenzene. The flask is clamped in a large ice bath. Through the central opening is inserted a mercury-sealed mechanical stirrer. A second opening is connected to a gas trap (Org. Syn. 14, 2) and also carries a thermometer, while the third is for the introduction of aluminum chloride. After the mixture has been cooled to about 0° , 195 g. (1.46 moles) of aluminum chloride is added in small portions in the course of one hour, keeping the temperature below 5° . Stirring is continued at 0° for four more hours, after which time the mixture is allowed to stand for at least twelve hours so that the ice melts and the clear red solution gradually comes to room temperature.

The flask is cooled by immersion in a slush of ice and water, and the addition compound is decomposed by adding gradually 200 g. of ice, 100 cc. of water, and 100 cc. of concentrated hydro-

chloric acid (this is best done under a hood). The keto acid separates in the form of a stiff, grayish-white paste. The solvent is removed by steam distillation, in which operation it is advisable to use a very rapid flow of steam together with an efficient condensing system, such as that illustrated (Fig. 1). The condensing flask shown need be no more than 1 l. in capacity, and

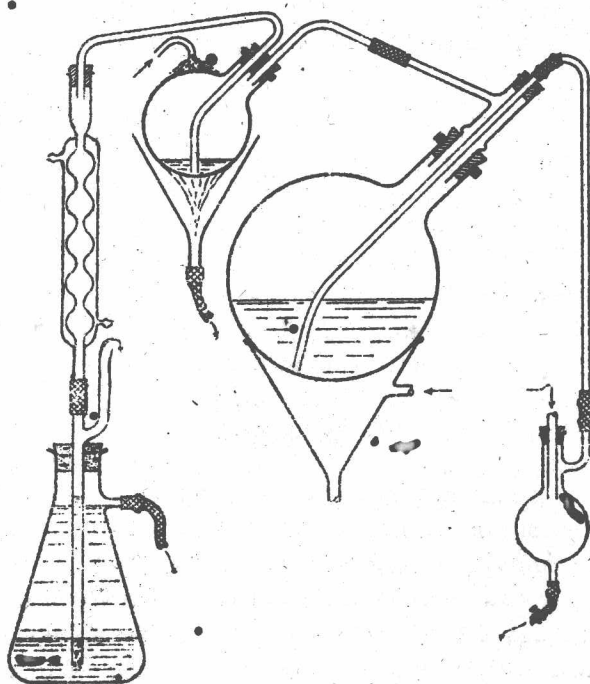


FIG. 1.

the exit tube should be centered at the bottom of this flask so that it can drain the contents completely. Some condensate ordinarily remains in the flask to serve as a vapor seal, a factor which adds greatly to the efficiency of condensation. For purposes of inspection, the flask can be emptied by diverting for a moment the stream of water to one side of the flask. The stoppers which are under pressure should be secured with wire. The distilling flask is heated to prevent too much condensation of steam (Note 3).

The bulk of the nitrobenzene comes over in about one and one-half hours, and the product then separates as a pasty mass which slowly disintegrates to a powder. During this process the elimination of nitrobenzene is very slow, but the steaming should be continued until only a few small lumps remain (four to five hours), although it is not necessary to remove every trace of solvent (Note 4). The mixture is cooled with tap water, the crude acid is filtered and returned to the flask, and 15 g. of sodium carbonate decahydrate is added, together with sufficient water to make the flask a little less than half full. The mixture is heated with shaking over a free flame until most of the solid has dissolved and the frothing has diminished. A few drops of capryl alcohol may be added to dissipate the froth. The dark brown solution is steam-distilled to eliminate the last traces of nitrobenzene (about one-half hour) and then filtered by suction from a very alight residue. One hundred grams of sodium chloride is dissolved in the hot solution (volume, about 1.5 l.), which is then allowed to cool without disturbance. The sodium salt of β -(3-acenaphthoyl)-propionic acid separates as colorless, fibrous needles, while the isomeric 1-acid largely remains in solution (Note 5). The product is collected on a large Büchner funnel and washed free of the dark mother liquor with half-saturated sodium chloride solution (about 150 cc.), the combined filtrates (A) being set aside. The sodium salt is crystallized once more from boiling water (1-1.5 l.) (Note 6), using Norite if required, and adding 50 g. of sodium chloride to the hot filtered solution. The mother liquor (B) is again saved. The purified salt is dissolved in 1200 cc. of hot water and the solution is acidified. The free acid separates as a white powder in a very pure condition. The yield of β -(3-acenaphthoyl)-propionic acid melting at 206-208° with decomposition is 133 g. (81 per cent of the theoretical amount) (Note 7).

2. Notes

1. By using a flask suitable for steam distillation, the loss in time and material attending a transfer is avoided.
2. Suitable material is supplied by Reilly Tar and Chemical

Corporation, New York, or Gesellschaft für Teerverwertung, Duisburg-Meiderich, Germany.

3. As compared with the apparatus shown in Fig. 24 (Org. Syn. Coll. Vol. 1, 467), this arrangement requires a much smaller flask and yet offers unlimited capacity. It also enables the operator to observe more closely the character of the distillate.

4. If the flask fills up with condensed steam, it should be cooled, the contents filtered, and the product returned to the flask. The process of disintegration can be hastened by breaking up the lumps with a flattened stirring rod.

5. The small amount of isomeric 1-acid may be obtained from the mother liquors, A and B. The first of these on acidification gives a product which is dark and tarry, but which soon solidifies on being cooled and stirred. The material is dissolved in 1 l. of water containing 25-30 g. of sodium carbonate decahydrate, and the solution is boiled for one-half hour with Norite, filtered, cooled, and acidified. The product, which now solidifies at once and is lighter in color, is dried and combined with the material obtained by acidifying the second mother liquor, B (total amount, 23.9 g.). The crude mixture of acids is suspended in 170 cc. of cold methyl alcohol, 8.5 cc. of concentrated sulfuric acid is added, and the mixture is heated on the steam bath for about ten minutes, after which dissolution and esterification are complete. The dark product which crystallizes when the solution cools is largely the 1-ester, which is very much less soluble than the 3-ester. The 1-ester (13.1 g.) is washed free of acid; it crystallizes from ethyl alcohol with the use of decolorizing carbon in long needles melting at 126°; yield, 9 g. (Note 8). The ester is hydrolyzed by heating with 100 cc. of alcohol and 30 cc. of 25 per cent sodium hydroxide solution until dissolved; the solution is then diluted with water and acidified. The β -(1-acenaphthoyl)-propionic acid melts at 180° (crystallized from dilute alcohol, 181°) and weighs 8.4 g. (5 per cent) (Note 9).

6. If, owing to hydrolysis, the sodium salt fails to dissolve completely, alkali should be added as required.

7. The 3-acid crystallizes well from glacial acetic acid, alco-

hol, or xylene, but large volumes of solvent are required and there is no change in the melting point.

8. The 3-ester melts at 89° .

9. Ordinarily the mother liquors from the preparation and purification of 1-ester will be discarded, but a small additional quantity of the 3-acid may be obtained by concentrating these solutions, adding alkali to hydrolyze the ester, adding water, and acidifying. The precipitated material is purified by crystallizing the sodium salt twice, and from this 8 g. (5 per cent) of the pure 3-acid is obtained.

The ratio of 3-acid to 1-acid is dependent on the temperature, lower temperatures favoring the production of 3-acid. At -15° the yield of 3-acid is 87 per cent, and of 1-acid, 5 per cent. At room temperature there is some increase in the proportion of the 1-acid formed, but the product is very dark and difficult to work up, and the total yield is lower even though the aluminum chloride is added in nitrobenzene solution.

3. Methods of Preparation

This procedure is based upon a study¹ of the method outlined in the patent literature.² The procedure is a general one and may be used for the condensation of succinic anhydride with naphthalene and with the mono- and dimethylnaphthalenes, although in no other case are the purification and separation of isomers so easily accomplished. In this particular type of condensation, as well as in certain other types of Friedel-Crafts reactions, nitrobenzene is far superior to the solvents which are more frequently employed. This is partly because of its great solvent power and partly because it forms a molecular compound with aluminum chloride, and so decreases the activity of the catalyst in promoting side reactions.

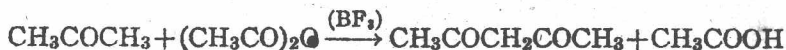
¹ Fieser, J. Am. Chem. Soc. 54, 4350 (1932).

² Fr. pat. 636,065 [Chem. Zentr. (1928), I, 2751]; Swiss pat. 131,959 [Chem. Zentr. (1930), I, 1539]; U. S. pat. 1,759,111 [Chem. Zentr. (1930), II, 806]; Ger. pat. 376,635 [Frdl. 14, 285 (1926)].

ACETYLACETONE

(Diacetylmethane; 2,4-Pentanedione)

(A) (Boron Trifluoride Method)



Submitted by C. E. DENOON, JR.

Checked by HOMER ADKINS and IVAN A. WOLFF.

1. Procedure

ONE HUNDRED AND SIXTEEN grams (2 moles) of acetone (Note 1) and 510 g. (5 moles) of reagent grade acetic anhydride are placed in a 2-l. three-necked flask and cooled in an ice-salt bath. One neck of the flask is stoppered, the second neck contains a tube for admitting boron trifluoride, and the third neck contains an outlet tube leading to an alkali trap to catch any unabsorbed boron trifluoride. Commercial grade boron trifluoride (Note 2) is passed through a Kjeldahl bulb, to prevent the reaction mixture from sucking back into the cylinder, and is then bubbled into the reaction mixture at such a rate that 500 g. is absorbed in about five hours (2 bubbles per second). The reaction mixture is poured into a solution of 800 g. of hydrated sodium acetate in 1600 cc. of water contained in a 5-l. flask. The mixture is then steam-distilled and the distillate collected in the following portions: 1000 cc., 500 cc., 500 cc., 400 cc.

A solution of reagent grade hydrated copper acetate is made by dissolving 240 g. of the salt in 3 l. of water at about 85° and filtering from any basic acetate. The copper salt of acetylacetone is then precipitated by adding 1400 cc. of the hot copper acetate solution to the first fraction of the acetylacetone, 700 cc. to the second, 500 cc. to the third, and 400 cc. to the fourth fraction. After standing for three hours, or better overnight, in a refrigerator the salt is filtered, washed once with water, and sucked dry. The salt is shaken in a separatory funnel with 800 cc. of 20 per cent sulfuric acid and 800 cc. of ether, and the ether

layer is removed. The aqueous layer is extracted with 400 cc. and then 200 cc. of ether. The combined extracts are dried with 250 g. of anhydrous sodium sulfate and the ether removed by distillation. The residue is distilled through a Widmer column (Note 3) and yields 160–170 g. of acetylacetone boiling at 134–136° (80–85 per cent of the theoretical amount based on the acetone).

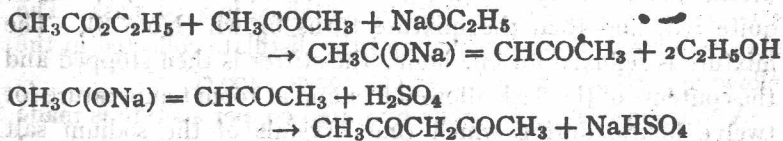
2. Notes

1. Acetone is preferably dried over anhydrous potassium carbonate or anhydrous calcium sulfate, followed by phosphorus pentoxide if a very dry product is required. Calcium chloride is commonly used (100–150 g. per liter), but this is less satisfactory since it combines chemically with acetone.¹ For this preparation the checkers used acetone that had been dried over calcium chloride, followed by distillation from phosphorus pentoxide.

2. Boron trifluoride may be purchased in cylinders from Harshaw Chemical Company, Cleveland, Ohio.

3. The Widmer column used contained a spiral 15 cm. in length, 13 mm. in diameter, with 15 turns of the helix.

(B) (Sodium Ethoxide Method)



Submitted by HOMER ADKINS and JAMES L. RAINEY

Checked by R. L. SHRINER and NEIL S. MOON.

1. Procedure

SIXTY-NINE grams (3 gram atoms) of sodium, from which all the oxide coating has been cut away, and 400 cc. of dry xylene (Note 1) are placed in a 1-l. round-bottomed flask and heated until the sodium is melted. The flask is closed with a rubber

¹ Bagster, J. Chem. Soc. (1917), 494.

stopper (Note 2) and the sodium is finely powdered by vigorous shaking. The contents of the flask are transferred to a 3-l. three-necked flask, and the xylene decanted. The sodium is washed with two 100-cc. portions of anhydrous ether (Note 3) by decantation. One liter of anhydrous ether is added, and the flask is placed on a steam bath and fitted with a condenser, Hershberg stirrer (Org. Syn. 17, 31), and a 250-cc. dropping funnel. The condenser and dropping funnel are protected by drying tubes containing absorbent cotton (Note 4). One hundred and thirty-eight grams (175 cc., 3 moles) of anhydrous ethyl alcohol is placed in the dropping funnel, and the stirrer is started. The alcohol is dropped in over a period of two to three hours with gentle refluxing. The reaction mixture is refluxed with stirring for six hours (Note 5) after the addition of the alcohol. The stirrer is stopped, the condenser turned downward, and the ether distilled as completely as possible from the steam bath (Note 6).

The condenser is again arranged for refluxing, and 1.2 l. of ethyl acetate (Note 7) is added to the warm sodium ethoxide through the separatory funnel as rapidly as possible. The stirrer is started immediately, and 174 g. (220 cc., 3 moles) of acetone (Note 1, p. 7) is dropped in over a period of fifteen to twenty minutes, refluxing being maintained by heating if necessary. Addition of the acetone must be started as soon as the ethyl acetate has been added. During the addition the solution becomes quite red, and then the mixture turns brown (Note 8). The mixture is refluxed for one hour; the stirrer is then stopped and the contents of the flask allowed to stand at room temperature for twelve hours, during which time crystals of the sodium salt separate.

The liquid layer is decanted into a 5-l. flask and the sodium salt of the diketone is dissolved and washed into the flask with 2.5 l. of ice water. After the salt is dissolved, the ester layer is separated as soon as possible (Note 9). The water layer is extracted twice with 300-cc. portions of ether and the ether extract discarded. To the water solution is added ice-cold dilute sulfuric acid (150 g. of concentrated sulfuric acid and 400 g. of cracked ice) until the solution is just acid to litmus. The dike-

tone is extracted from the solution with four 300-cc. portions of ether. The combined ether extracts are dried for twenty-four hours over 60 g. of anhydrous sodium sulfate in the icebox. The ether solution is decanted into a 2-l. round-bottomed flask and the sodium sulfate extracted with 100 cc. of anhydrous ether. This extract is added to the ether solution and the ether distilled by means of a steam bath. The residue is transferred to a 500-cc. flask, rinsing with a little ether, and distilled through a Widmer column, the portion boiling between 130° and 139° being collected. This fraction is dried over 5 g. of anhydrous potassium carbonate for one hour and, after removing the carbonate, redistilled through the Widmer column. The portion boiling at 134 – 136° is collected and amounts to 115–136 g. (38–45 per cent of the theoretical amount based on the acetone).

2. Notes

1. The xylene is dried by distillation from sodium.
2. Rubber stoppers should be used throughout, including the drying of reagents, as corks contain some moisture. The stoppers should be boiled in 10 per cent sodium hydroxide solution for two hours, thoroughly washed with dilute acetic acid, and dried.
3. Commercial anhydrous ethyl ether and ethyl alcohol are satisfactory. If these are unavailable, the ether should be purified as for use in the Grignard reaction and the alcohol as described in *Org. Syn. Coll. Vol. 1*, 244.
4. Absorbent cotton is an excellent drying agent and more convenient for drying tubes than anhydrous calcium chloride.² It is possible to keep maleic anhydride in a flask closed only by a plug of absorbent cotton, for three weeks without appreciable change in the titration value (F. P. Pingert, private communication).
5. The period of heating varies somewhat with the size of the powdered sodium. Almost all the sodium should be used up before removal of the ether. However, a few small pieces do no harm.
6. The success of the reaction depends upon the quality of the sodium ethoxide used. The product at this point should be white

² Obermiller and Goertz, *Z. physik. Chem.* **109**, 162 (1924).

and very finely divided. All moisture must be excluded during its preparation in order to avoid the formation of sodium hydroxide, which markedly lowers the yield.

7. The ethyl acetate is allowed to stand over calcium chloride for two days, with occasional shaking. The calcium chloride is removed by filtration, and the ester is allowed to stand over phosphorus pentoxide several hours. It is then distilled directly from the phosphorus pentoxide.

8. After about half of the acetone has been added, the mixture usually sets to a solid mass. The stirrer is turned by hand and the addition of acetone continued. In a few minutes the mass can again be stirred.

9. The ethyl acetate layer is washed with water, sodium bisulfite solution, saturated calcium chloride solution, and again with water. It is further purified as in Note 6, giving 316-400 g. of recovered ester. The amount of recovered ester depends somewhat upon the length of time the two layers are allowed to remain in contact before separating.

3. Methods of Preparation

Acetylacetone has been prepared by the reaction of acetyl chloride with aluminum chloride followed by hydrolysis,³ and by the condensation of acetone with ethyl acetate under the influence of sodium,⁴ sodamide,⁵ and sodium ethoxide,^{5,6,7} and by the reaction of acetone and acetic anhydride in the presence of boron trifluoride.⁸

³ Combes, *Ann. chim. phys.* (6) **12**, 207 (1887).

⁴ Claisen, *Ann.* **277**, 168 (1893).

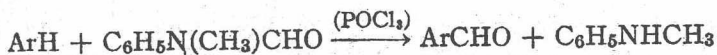
⁵ Claisen, *Ber.* **38**, 695 (1905).

⁶ Claisen and Ehrhardt, *ibid.* **22**, 1010 (1889).

⁷ Sprague, Beckham, and Adkins, *J. Am. Chem. Soc.* **56**, 2665 (1934).

⁸ Meerwein and Vossen, *J. prakt. Chem.* **141**, 149 (1934).

9-ANTHRALDEHYDE; 2-ETHOXY-1-NAPHTHALDEHYDE



Submitted by (A) L. F. FIESER, J. L. HARTWELL, and J. E. JONES;

(B) J. H. WOOD and R. W. BOST.

Checked by C. F. H. ALLEN and J. VAN ALLAN.

1. Procedure

(A) *9-Anthraldehyde*.—In a 2-l. round-bottomed flask fitted with a mechanical stirrer and reflux condenser are placed 35 g. (32 cc., 0.26 mole) of methylformanilide (p. 66), 35 g. (21 cc., 0.23 mole) of phosphorus oxychloride, 20 cc. of *o*-dichlorobenzene, and 22.5 g. (0.13 mole) of anthracene (Note 1). This is heated on the steam bath, with stirring, to 90–95° over a period of twenty minutes; the anthracene dissolves during this time to give a deep red solution, and hydrogen chloride is evolved (Note 2). The heating is continued for one hour (Note 3), after which a solution of 140 g. of crystalline sodium acetate in 250 cc. of water (Note 4) is added to the cooled mixture, and the *o*-dichlorobenzene and most of the methylaniline are rapidly distilled with steam (fifteen to twenty minutes). The residual reddish oil solidifies on cooling. The solid residue is broken up, and, after decanting the aqueous liquor through a Büchner funnel, it is washed by decantation with two 100-cc. portions of 6 *N* hydrochloric acid to remove amine, and then thoroughly with water (1000–1200 cc.). The crude solid (22–24 g., m. p. 97–101°) is recrystallized from 50 cc. of hot glacial acetic acid; when cold, the bright yellow aldehyde is filtered by suction and washed on the filter with 30 cc. of methanol (Note 5). The yield is 20–22 g. (77–84 per cent of the theoretical amount) and the melting point is 104.5–105° (Note 6).

(B) *2-Ethoxy-1-naphthaldehyde*.—A mixture of 45 g. (0.33 mole) of methylformanilide (p. 66), 51 g. (0.33 mole) of phosphorus oxychloride, and 43 g. (0.25 mole) of β -naphthyl ethyl ether in a 500-cc. round-bottomed flask provided with an air con-

denser (Note 2) is heated on a steam bath for six hours. The hot mixture is then poured in a thin stream into 700 cc. of cold water with very vigorous stirring, to avoid the formation of large lumps (Note 7); the aldehyde separates in a granular condition. It is filtered by suction and washed thoroughly, using 1 l. of water. Without drying, the crude aldehyde is dissolved in 450 cc. of alcohol and decolorized by the addition of 4 g. of Norite, boiling for fifteen minutes, and filtering hot (Note 8), using a double filter paper. The filtrate is cooled and the product is collected on a filter and washed with 40 cc. of cold alcohol; it crystallizes in pale yellow needles, m.p. 111-112°. The yield is 37-42 g. (74-84 per cent of the theoretical amount).

2. Notes

1. The yield and purity of the anthraldehyde depend on the quality of the hydrocarbon. The figures given are attained only if the anthracene melts at 213° or higher. With anthracene, m.p. 208-210°, the yield is 19-20 g., m.p. 103-104° (Note 6).

2. The reaction may be carried on in a hood, or a gas trap (Org. Syn. 14, 2) may be used.

3. When run on a fourfold scale, the time of heating should be extended to two hours. Prolonged heating leads to the formation of tars.

4. Sodium acetate appears to decompose a product of the condensation of methylaniline with phosphorus oxyhalides; substances other than the aldehyde are largely retained in the sodium acetate solution.

5. A brighter-colored product is secured by this wash.

6. The aldehyde also exists in a low-melting form, m.p. 98.5-99.5°, and occasionally this form is obtained from the reaction. It is less stable than the high-melting form, into which it is easily converted by seeding.

7. Care must be exercised to prevent the reaction product from lumping upon being poured into water. If this happens, decomposition by the water is slow and subsequent purification is more difficult. Any lumps which are formed should be broken

up and the reaction mixture should then be permitted to stand overnight in contact with the water. The flask in which the reaction is carried out is also filled with water to decompose the product adhering to the walls. This is purified with the rest.

8. A heated funnel is desirable. Some of the product usually crystallizes during the filtration.

3. Methods of Preparation

This aldehyde synthesis is applicable to compounds of the aromatic series having a labile hydrogen atom (phenyl ethers,¹ naphthols,² dialkylanilines,^{3,4} naphthostyryl,² anthrones²) and to certain hydrocarbons of requisite reactivity (anthracene,^{5,6} 1,2-benzanthracene,⁶ 3,4-benzpyrene,^{3,7} pyrene,⁸ styrene,⁹ and α , α -diarylethylenes⁹). With polynuclear hydrocarbons the best results are secured by the use of a solvent such as *o*-dichlorobenzene. 9-Anthraldehyde has also been prepared by the action of hydrogen cyanide and aluminum chloride on anthracene in chlorobenzene.¹⁰

With liquid or low-melting ethers no solvent is required. 2-Ethoxy-1-naphthaldehyde has also been prepared by ethylation of the hydroxy compound,¹¹ and from β -naphthyl ethyl ether by the Gattermann reaction.¹²

¹ Wood and Bost, J. Am. Chem. Soc. **59**, 1722 (1937).

² Ger. pat. 514,415 [Frdl. 17¹, 564 (1932)].

³ Vilsmeier and Haak, Ber. **60**, 119 (1927).

⁴ Ger. pat. 547,108 [Frdl. 18², 2973 (1933)].

⁵ Ger. pat. 519,444 [Frdl. 17¹, 565 (1932)].

⁶ Fieser and Hartwell, J. Am. Chem. Soc. **60**, 2556 (1938).

⁷ Fieser and Hershberg, *ibid.* **60**, 2547 (1938).

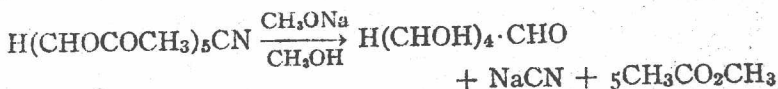
⁸ Vollmann, Becker, Corell, and Streeck, Ann. **581**, 1 (1937).

⁹ Brit. pat. 504,125 [C. A. **33**, 7313 (1939)].

¹⁰ Hinkel, Ayling, and Beynon, J. Chem. Soc. (1936), 344.

¹¹ Bartsch, Ber. **36**, 1975 (1903).

¹² Gattermann, Ann. **357**, 367 (1907).

d-ARABINOSE

Submitted by GÉZA BRAUN.

• Checked by H. T. CLARKE and S. M. NAGY.

1. Procedure

A SOLUTION of 100 g. (0.26 mole) of pentaacetyl glucononitrile (p. 74) in 150 cc. of chloroform in a 1-l. Erlenmeyer flask is chilled to -12° . A chilled (-12°) solution of 16 g. (0.7 gram atom) of sodium in 250 cc. of anhydrous methyl alcohol is added with continual shaking and chilling to the chloroform solution of the nitrile. The mixture soon solidifies to a pale yellow, gelatinous mass. After ten minutes at -12° this is broken up with a heavy glass rod and dissolved in 600 cc. of a suspension of ice in water. The resulting solution is acidified with an ice-cold mixture of 33 g. (18 cc., 0.32 mole) of 95 per cent sulfuric acid, 5 cc. of acetic acid, and 45 g. of ice. The aqueous layer is separated, washed once with 50 cc. of chloroform, and evaporated without delay (Note 1) under reduced pressure. The residual heavy syrup is dissolved in 300 cc. of water and again evaporated as completely as possible under reduced pressure, in order to remove residual hydrogen cyanide (Note 2). The highly viscous residue, which contains some crystals of sodium sulfate, is dissolved in 500 cc. of hot methyl alcohol. After about ten minutes the sodium sulfate is filtered with suction and washed with two 25-cc. portions of methyl alcohol. The filtrate is concentrated under reduced pressure at 40° to a heavy syrup which is poured while warm into a 200-cc. Erlenmeyer flask. The distilling flask is rinsed twice with 20-cc. portions of hot ethyl alcohol, and this rinse is added to the filtrate. The resulting alcohol solution soon begins to deposit crystals of arabinose; it is stirred by hand during the crystallization and gradually diluted with more alcohol until 100 cc. in all has been added during the course