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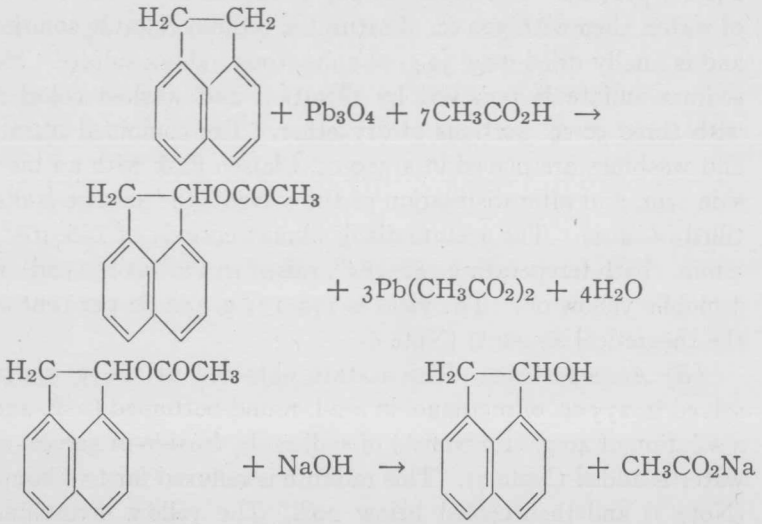


Submitted by JAMES CASON.
Checked by R. L. SHRINER and ELMER H. DOBRATZ.

1. Procedure

(*A*) *Acenaphthenol Acetate.*—In a 2-l. round-bottomed flask are placed 154 g. (1 mole) of acenaphthene (Note 1) and 1100 cc. of glacial acetic acid (Note 2). The flask is fitted with a tantalum or nichrome wire stirrer [1] and a thermometer extending below the surface of the liquid. The solution is stirred and heated to 60°, at which point the source of heat is removed and 820 g. of red lead (Note 3) is added in portions of about 50 g., each portion being added as soon as the color due to the previous portion has been discharged. During this operation, which requires thirty to forty minutes, the temperature is maintained at 60-70° (Note 4) by external cooling. The reaction is complete when a portion of the solution gives no test for lead tetraacetate (Note 5). The dark red syrupy solution (which may contain a few suspended particles of red lead and lead dioxide) is poured

[1] Hershberg, Ind. and Eng. Chem., Anal. Ed. 8, 313 (1936). Org. Syn. **17**, 31.

into 2 l. of water contained in a 4-l. separatory funnel. The acetate is extracted with a 350-cc. portion of ether and then with a 250-cc. portion. The total extract is washed first with 100 cc. of water, then with 300 cc. of saturated sodium chloride solution and is finally dried over 50 g. of anhydrous sodium sulfate. The sodium sulfate is removed by filtration and washed colorless with three 50-cc. portions of dry ether. The combined filtrate and washings are placed in a 500-cc. Claisen flask with an inset side arm, and after distillation of the solvent, the acetate is distilled *in vacuo*. The acetate distils almost entirely at 166–168°/5 mm. (bath temperature 180–185°, raised to 220° at the end) as a mobile yellow oil. The yield is 170–175 g. (80–82 per cent of the theoretical amount) (Note 6).

(*B*) *Acenaphthenol.*—The acetate obtained as above is dissolved in 275 cc. of methanol in a 2-l. round-bottomed flask, and a solution of 40 g. (1.2 equiv.) of sodium hydroxide in 400 cc. of water is added (Note 7). This mixture is refluxed for two hours (Note 7) and then cooled below 20°. The yellow crystalline acenaphthenol is collected on a filter and washed well with about 1.5 l. of water. The crude product is air-dried (138–143 g.) and then dissolved in 2 l. of boiling benzene. The solution is treated with 6-8 g. of decolorizing carbon (Note 8) and filtered through a heated funnel. The orange-red filtrate is concentrated to about 1 l., and the acenaphthenol is allowed to crystallize. After filtering with suction and washing with cold benzene (about 500 cc.) until the wash solvent is colorless, the acenaphthenol is obtained as practically colorless needles, m.p. 144.5–145.5° (corr.) (Note 9). It weighs 117–121 g. From the filtrate may be obtained an additional quantity of material which on one recrystallization gives only 3–5 g. of pure acenaphthenol. The total yield amounts to 120–126 g. (70–74 per cent of the theoretical amount based on the acenaphthene).

2. Notes

1. The "95 per cent acenaphthene" sold by Reilly Tar and Chemical Corporation melts at 92.5–93.5° (corr.) and is quite satisfactory for use in this reaction. A recrystallized sample of

this acenaphthene (m.p. 93–93.5) or acenaphthene from the Gesellschaft für Teerverwertung (m.p. 93–93.5) gives no better yield of pure acenaphthenol.

2. The glacial acetic acid should be purified by distillation from potassium permanganate. About 30–50 g. of potassium permanganate for each 1.5 l. of acetic acid should be used.

3. Mallinckrodt's Analytical Reagent red lead (assay 85–90 per cent) was used. Merck's and Baker's N.F. V red lead are also quite satisfactory. Previously prepared lead tetraacetate is in no way preferable to red lead for this oxidation.

4. If the oxidation is carried out at 50° the yield is unaffected, but several hours are required to complete the addition. At 40°, the reaction is very slow and the yield is lowered.

5. A drop of the reaction mixture is placed on a moist piece of starch-iodide paper. The development of a blue color shows the presence of lead tetraacetate.

6. The acenaphthenol acetate contains small amounts of acenaphthene and acenaphthenone but is pure enough for the next step.

7. The dark violet color appearing on addition of the alkali is probably due to the presence of acenaphthenone. Crystalline acenaphthenol begins to separate almost immediately after the alkali has been added. Care must be taken in heating to refluxing because when heated too rapidly the acenaphthenol crystallizes suddenly from solution and the heat evolved may blow part of it out through the condenser.

8. If the charcoal treatment is omitted, the acenaphthenol obtained is light yellow but practically pure.

9. Marquis [2] reported the melting point as 148°; von Braun and Bayer [3] reported it as 146°.

3. Methods of Preparation

Acenaphthenol has been prepared in poor yield by the oxidation of acenaphthene with lead dioxide; [2] and it is among

[2] Marquis, Compt. rend. **182**, 1227 (1926).

[3] von Braun and Bayer, Ber. **59**, 920 (1926).

the products obtained by hydrogenation of acenaphthene quinone.[3] The above procedure is essentially that described more briefly in the literature.[4]

ACETOACETANILIDE

$$CH_3COCH{=}C{=}O + C_6H_5NH_2 \rightarrow CH_3COCH_2CONHC_6H_5$$

Submitted by JONATHAN W. WILLIAMS and JOHN A. KRYNITSKY.
Checked by NATHAN L. DRAKE and JOSEPH LANN.

1. Procedure

IN a 500-cc. round-bottomed, three-necked flask fitted with a reflux condenser, dropping funnel, and a mercury-sealed stirrer (Note 1) is placed a solution of 46 g. (0.5 mole) of dry aniline in 125 cc. of pure dry benzene. Stirring is started, and a solution of 42 g. (0.5 mole) of ketene dimer (p. 64) in 75 cc. of pure dry benzene is added dropwise over a period of half an hour. The reaction mixture is then heated under reflux on the steam bath for one hour. After the major portion of the benzene has been removed by distillation from the steam bath, the remainder is removed under reduced pressure. The residue is dissolved in 500 cc. of hot 50 per cent aqueous alcohol from which the acetoacetanilide separates on cooling. The mixture is cooled to 0° before filtration. A second crop of crystals can be obtained by adding 250 cc. of water to the mother liquor and cooling again (Note 2). The total yield of product, m.p. 82–83.5°, is 65 g. (74 per cent of the theoretical amount). Further purification by recrystallization from 300 cc. of 50 per cent alcohol yields 55 g. of a product which melts at 84–85°.

2. Notes

1. A simpler seal (p. 40, Note 1) of rubber tubing lubricated by glycerol is satisfactory.

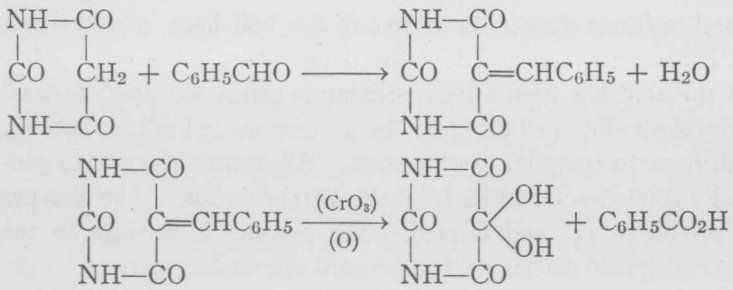
[4] Fieser and Cason, J. Am. Chem. Soc. **62**, 432 (1940).

2. If the second mother liquor is evaporated to about half of its original volume, a small third crop of very impure crystals may be obtained.

3. Methods of Preparation

Acetoacetanilide has been prepared by the reaction of aniline with ethyl acetoacetate [1, 2, 3] and by the reaction of ketene dimer with aniline.[4]

ALLOXAN MONOHYDRATE



Submitted by JOHN H. SPEER and THOMAS C. DABOVICH.
Checked by W. E. BACHMANN and R. O. EDGERTON.

1. Procedure

(*A*) *Benzalbarbituric Acid.*—A mixture of 128 g. (1 mole) of barbituric acid (Org. Syn. **18**, 8) and 1250 cc. of water in a 2-l. three-necked, round-bottomed flask equipped with an efficient stirrer and a reflux condenser is heated on a steam bath to effect solution (Note 1). When the acid has dissolved, 115 g. (110 cc., 1.08 moles) of benzaldehyde is added while heating and stirring are continued. The solution rapidly fills with the insoluble

[1] Knorr, Ann. **236**, 69 (1886).
[2] Roos, Ber. **21**, 624 (1888).
[3] Knorr and Reuter, ibid. **27** 1169 (1894).
[4] (*a*) Chick and Wilsmore, J. Chem. Soc. **1908**, 946; (*b*) Boese, Ind. Eng. Chem. **32**, 16 (1940).

benzalbarbituric acid. The mixture is heated for one hour on the steam bath to complete the reaction, and then filtered by suction (Note 2). The filter cake is washed with several portions of hot water and dried at 100°. The yield is 190–205 g. (88–95 per cent of the theoretical amount) of product possessing a very pale-yellow color. The substance melts at 254–256° and needs no further purification.

(*B*) *Alloxan Monohydrate.*—A mixture of 730 cc. of acetic acid, 95 cc. of water, and 162 g. (1.62 moles) of chromium trioxide (Note 3) is placed in a 2-l. three-necked, round-bottomed flask fitted with a stirrer and a thermometer, the stirrer is started, and the mixture is warmed to 50°. To the solution 180 g. (0.83 mole) of benzalbarbituric acid is added in small portions during the course of one-half hour, a cold water bath being used to maintain the temperature at 50–60°. After all the acid has been added, stirring is continued and the temperature maintained at 50–60° by a warm water bath for another half-hour to complete the reaction. Alloxan monohydrate generally starts to crystallize from the warm solution. The mixture is cooled to 15° and filtered. The product is washed on the filter with cold glacial acetic acid until the washings are no longer green, and then dried by washing with ether. The yield is 105–112 g. (79–84 per cent of the theoretical amount) of yellow crystals which melt at about 254° (Note 4) with decomposition and are sufficiently pure for most purposes.

In order to obtain practically colorless alloxan monohydrate (Note 5), 25 g. of the yellow crystals is dissolved in 37 cc. of hot water, the solution is boiled with Norite, and the hot solution is filtered into a 500-cc. round-bottomed flask. About 15–20 cc. of water is removed by distillation under reduced pressure on a water bath. The colorless crystalline residue is dissolved in the minimal volume of hot water, the solution is cooled somewhat, and to it is added 250 cc. of glacial acetic acid. After the mixture has been kept cold (5–10°) for four to six hours, the alloxan monohydrate is filtered. The yield is 20–21 g. (80–84 per cent recovery) (Note 6) of practically colorless crystals which melt at about 254° (Note 7) with decomposition.

2. Notes

1. The submitters report that a single attempt to use the aqueous-alcoholic solution of barbituric acid obtained in Org. Syn. **18**, 8, before recrystallization of the product gave an excellent yield of an apparently isomeric product unsuited for the preparation of alloxan.

2. This filtration may be done hot or cold at the convenience of the operator.

3. The technical grade (flakes) was found quite satisfactory.

4. This value is obtained in a Pyrex capillary tube; the solid remains yellow until about 254° when it suddenly decomposes to a red melt with vigorous evolution of gas. When a soft-glass capillary tube is used, the solid assumes a red color at about 180–200° and melts between 240° and 250°.

5. By recrystallization of the yellow product from glacial acetic acid (12 cc. per g.), using Norite, the checkers invariably obtained yellow crystals (75–80 per cent recovery) instead of the practically colorless crystals reported by the submitters. By adding a volume of water equal to the weight of crystals to the hot acetic acid solution, the checkers obtained a pale-yellow product.

6. This represents the first crop of crystals.

7. This value is obtained in a Pyrex capillary tube. The colorless solid begins to turn yellow at about 180° and melts at about 254° (occasionally 258–260°) to a red liquid with vigorous evolution of gas.

3. Methods of Preparation

Alloxan monohydrate has been prepared by the oxidation of uric acid with chlorine,[1,2] or potassium chlorate and hydrochloric acid;[3] by the oxidation of alloxantin,[4] xanthine,[5] uramil,[4] and

[1] McElvain, J. Am. Chem. Soc. **57**, 1303 (1935).

[2] Biltz and Heyn, Ann. **413**, 60 (1917).

[3] Fischer and Helferich, "Anleitung zur Darstellung organischer Präparate," 10th Ed., p. 66, Braunschweig, 1922.

[4] Wöhler and Liebig, Ann. **26**, 256 (1838).

[5] Fischer, ibid. **215**, 310 (1882).

thiouramil;[6] and by the hydrolysis of dibromobarbituric acid.[7] The method here described is originally due to Biilmann and Berg.[8]

ALUMINUM *tert.*-BUTOXIDE

$$3(CH_3)_3COH + Al \rightarrow Al[OC(CH_3)_3]_3 + 3(H)$$

Submitted by WINSTON WAYNE and HOMER ADKINS.
Checked by NATHAN L. DRAKE, WM. H. SOUDER, JR., and RALPH MOZINGO.

1. Procedure

IN a 2-l. round-bottomed flask, bearing a reflux condenser protected by a calcium chloride tube, are placed 64 g. (2.37 gram atoms) of aluminum shavings, 200 g. (254 cc., 2.7 moles) of dry *tert.*-butyl alcohol, and 5 to 10 g. of aluminum *tert.*-butoxide (Note 1). After the mixture is heated to boiling on a steam bath, approximately 0.4 g. of mercuric chloride is added followed by vigorous shaking (Note 2). As the heating is continued the color of the reaction mixture gradually changes from clear to milky to black, and hydrogen is evolved. When the mixture has become black, the heating is interrupted.

After the reaction has been allowed to proceed for an hour without heating, an additional 244 g. (309 cc., 3.3 moles) of dry *tert.*-butyl alcohol (total quantity, 6 moles) and 200 cc. of dry benzene are added. The reaction will again set in upon gentle heating and will continue vigorously without further heating. After about two hours the reaction subsides and the mixture is refluxed for about ten hours.

The benzene and unchanged *tert.*-butyl alcohol are removed by distillation from the steam bath, the final traces being removed under 10–30 mm. pressure. A liter of *dry* ether is added, and the solid aluminum *tert.*-butoxide is dissolved by refluxing for a short

[6] Fischer and Ach, Ann. **288**, 160 (1895).
[7] Baeyer, ibid. **127**, 230 (1863); **130**, 131 (1864).
[8] Biilmann and Berg, Ber. **63B**, 2201 (1930).

period. After cooling, 35 cc. of *undried* ether is added, followed immediately by vigorous shaking (Note 3). After standing for two hours the solution is centrifuged for thirty minutes to remove unused aluminum, aluminum hydroxide, and mercury (Note 4).

The solvent is removed by distillation from the steam bath, the final traces under 10–30 mm. pressure. The flask is allowed to cool with a calcium chloride tube attached, and the product crushed with a spatula and transferred to bottles sealed against moisture. The yield is 394–418 g. (80–85 per cent of the theoretical amount) of a white or slightly gray solid.

2. Notes

1. Commercial *tert.*-butyl alcohol dried over calcium oxide is suitable for this preparation. Aluminum isopropoxide or ethoxide [1, 2] may be used in place of the aluminum *tert.*-butoxide to remove traces of water. The grade of metal known as "fast cutting rods" has proved most satisfactory. The checkers used turnings made from aluminum cast from melted-down kitchen utensils. Aluminum *tert.*-butoxide has also been prepared successfully in another laboratory from commercially pure aluminum (2S) and from rods of the alloy 17ST (communication from L. F. Fieser). The checkers were able to obtain considerably higher yields of the butoxide from pure aluminum than from a copper-bearing alloy.

2. The use of larger amounts of mercuric chloride increases the difficulty of getting the final product free from color. This difficulty may be avoided by previously amalgamating the aluminum.[3, 4] The mixture is shaken to distribute the mercuric chloride and thus aid in an even amalgamation of the aluminum.

3. The small amount of water introduced with the undried ether forms aluminum hydroxide which aids in the precipitation

[1] Tischtschenko, J. Russ. Phys. Chem. Soc. **31**, 694 (1899) [Chem. Zentr. **71**, I, 10 (1900)].

[2] Young, Hartung, and Crossley, J. Am. Chem. Soc. **58**, 100 (1936).

[3] Wislicenus and Kaufman, Ber. **28**, 1325 (1895).

[4] Adkins, J. Am. Chem. Soc. **44**, 2175 (1922).

of the black suspended material. Shaking is essential to obtain the hydroxide formation throughout the solution.

4. The centrifuging may be carried out in 250-cc. stoppered bottles at 2000 r.p.m. After centrifuging, the solution should be colorless or light tan. If it is still dark in color another 25-cc. portion of undried ether should be added and the centrifuging repeated.

3. Methods of Preparation

Aluminum *tert.*-butoxide can be prepared by refluxing dry *tert.*-butyl alcohol with amalgamated aluminum [1, 5, 6] or aluminum plus mercuric chloride.[6] The method described is that of Adkins and Cox.[6] The preparation of amalgamated aluminum has been described.[3, 4] Aluminum isopropoxide can be prepared from dry isopropyl alcohol and aluminum,[1, 2] the method being essentially that described for aluminum ethoxide (Org. Syn. **15**, 82).

o-AMINOBENZYL ALCOHOL

$$o\text{-}NH_2C_6H_4CO_2H + 4H \rightarrow o\text{-}NH_2C_6H_4CH_2OH + H_2O$$

Submitted by GEORGE H. COLEMAN and HERBERT L. JOHNSON.
Checked by REYNOLD C. FUSON and E. A. CLEVELAND.

1. Procedure

THE reduction is carried out in four cells of the type shown in Fig. 1. Each cell consists of a 1-l. beaker (B), a porous cup (P), a mechanical stirrer, and sheet lead electrodes (E_1 and E_2) each having a total surface area of 100 sq. cm. (Note 1). In the cathode space of each cell are placed 25 g. (0.18 mole) of anthranilic acid (Note 2) and 400 cc. of 15 per cent sulfuric acid. In each porous cup is placed 200 cc. of 15 per cent sulfuric acid. The cells are connected in series as shown in Fig. 1 with an ammeter (A) and suitable resistance (R) (Note 3) also in the circuit.

[5] Oppenauer, Rec. trav. chim. **56**, 137 (1937).
[6] Adkins and Cox, J. Am. Chem. Soc. **60**, 1151 (1938).

The stirrers are started, the current (110 volt D.C.) turned on, and the resistance so adjusted that the ammeter records 10–12 amperes. The temperature of the solution in the cells is maintained at 20–30° by surrounding them with a bath of cool water (Note 4). The reduction is complete after 60–70 ampere-hours. This fact is indicated by the increased evolution of hydrogen and the complete solution of the anthranilic acid.

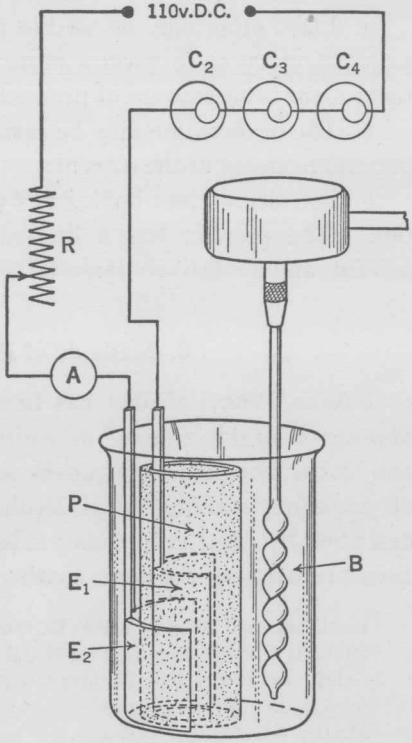


FIG. 1

The cathode liquid is removed from the cells and neutralized with solid ammonium carbonate or concentrated aqueous ammonia. The solution is filtered to remove any resinous material, then saturated with ammonium sulfate and extracted with five 80-cc. portions of chloroform (Note 5). The chloroform solution is dried with 20 g. of anhydrous sodium or magnesium sulfate, filtered, and the chloroform removed by evaporation on a steam bath (Note 6). The yield of *o*-aminobenzyl alcohol obtained from the four cells is 62–70 g. (69–78 per cent of the theoretical amount).

This product has a light brown color and melts at 75–80°. After one recrystallization from petroleum ether the melting point is 80–81° (Note 7).

2. Notes

1. Ordinary sheet lead of 99.9 per cent purity is satisfactory.
2. The anthranilic acid melted at 143–144°.