



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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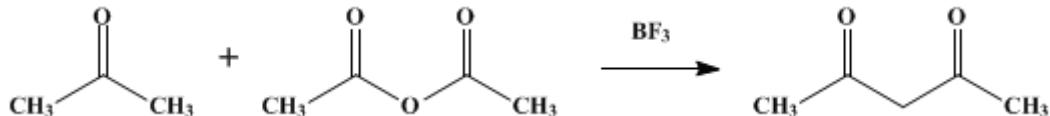
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.16 (1955); Vol. 20, p.6 (1940).

ACETYLACETONE

[Diacetyl methane; 2,4-pentanedione]

[I. 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 5 hours (2 bubbles per second). The reaction mixture is poured into a solution of 800 g. of hydrated sodium acetate in 1.6 l. of water contained in a 5-l. flask. The mixture is then steam-distilled and the distillate collected in the following portions: 1 l., 500 ml., 500 ml., 400 ml.

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 1.4 l. of the hot copper acetate solution to the first fraction of the acetylacetone, 700 ml. to the second, 500 ml. to the third, and 400 ml. to the fourth fraction. After standing for 3 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 ml. of 20% sulfuric acid and 800 ml. of ether, and the ether layer is removed. The aqueous layer is extracted with 400 ml. and then 200 ml. of ether. The combined extracts are dried with 250 g. of anhydrous sodium sulfate, and the ether is 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% based on acetone).

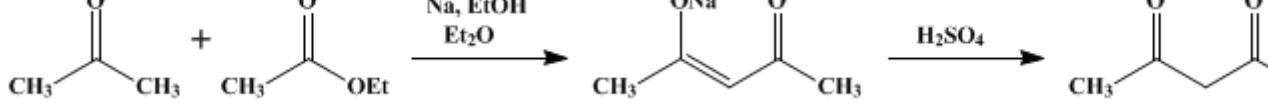
2. Notes

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.

[II. 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 ml. 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 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-ml. 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. Syntheses*, 17, 31), and a 250-ml. dropping funnel. The condenser and dropping funnel are protected by drying tubes containing absorbent cotton (Note 4). One hundred and thirty-eight grams (175 ml., 3 moles) of anhydrous ethanol is placed in the dropping funnel, and the stirrer is started. The alcohol is dropped in over a period of 2–3 hours with gentle refluxing. The reaction mixture is refluxed with stirring for 6 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 ml., 3 moles) of acetone (Note 1, p. 17) is dropped in over a period of 15–20 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 1 hour; the stirrer is then stopped and the contents of the flask are allowed to stand at room temperature for 12 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-ml. portions of ether, and the ether extract is 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 diketone is extracted from the solution with four 300-ml. portions of ether. The combined ether extracts are dried for 24 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 is extracted with 100 ml. of anhydrous ether. This extract is added to the ether solution, and the ether is distilled by means of a steam bath. The residue is transferred to a 500-ml. 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 1 hour and, after the carbonate has been removed, is redistilled through the Widmer column. The portion boiling at 134–136° is collected; it amounts to 115–136 g. (38–45% based on 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% sodium hydroxide solution for 2 hours, thoroughly washed with dilute acetic acid, and dried.
3. Commercial anhydrous ethyl ether and ethanol are satisfactory. If these are unavailable, the ether should be purified as for use in the Grignard reaction and the ethanol as described in *Org. Syntheses Coll. Vol. 1*, 249 (1941).
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 3 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 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 2 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. Discussion

Acetylacetone has been prepared by the reaction of acetyl chloride with aluminum chloride, followed by hydrolysis;³ by the condensation of acetone with ethyl acetate in the presence of sodium,⁴ sodium amide,^{5,6} sodium ethoxide,^{5,7,8} and alkali or alkaline-earth hydrides;⁹ by the reaction of acetone and acetic anhydride in the presence of boron trifluoride;¹⁰ by the pyrolysis of isopropenyl acetate;^{11,12,13} by the reaction of ethyl acetoacetate and acetic anhydride in the presence of magnesium at 140°;¹¹ from methyl or ethyl diacetylacetate by treatment with acids;¹⁴ and by the dehydrogenation of 4-pentanol-2-one in the presence of Raney nickel.¹⁵

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 251
- Org. Syn. Coll. Vol. 3, 829

References and Notes

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Appendix

**Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)**

copper salt of acetylacetone

condenser

Hershberg stirrer

methyl or ethyl diacetylacetate

ethanol (64-17-5)

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

ethyl acetate (141-78-6)

ether,
ethyl ether (60-29-7)

acetic anhydride (108-24-7)

sodium acetate (127-09-3)

sodium hydroxide (1310-73-2)

acetyl chloride (75-36-5)

magnesium (7439-95-4)

carbonate (3812-32-6)

sodium sulfate (7757-82-6)

sodium bisulfite (7631-90-5)

calcium sulfate (7778-18-9)

Raney nickel (7440-02-0)

acetone (67-64-1)

aluminum chloride (3495-54-3)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

copper acetate (142-71-2)

xylene (106-42-3)

Ethyl acetoacetate (141-97-9)

boron trifluoride (7637-07-2)

Acetylacetone,
Diacetyl methane,
2,4-pentanedione (123-54-6)

maleic anhydride (108-31-6)

isopropenyl acetate (108-22-5)

4-pentanol-2-one

phosphorus pentoxide (1314-56-3)

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