



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

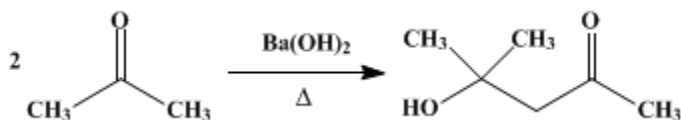
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.199 (1941); Vol. 1, p.45 (1921).

DIACETONE ALCOHOL

[2-Pentanone, 4-hydroxy-4-methyl-]



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1. Procedure

A 2-l. round-bottomed flask is fitted with a rubber stopper carrying a Soxhlet extractor (Note 1) which in turn is fitted with an efficient reflux condenser. In the flask are placed 1190 g. (1500 cc., 20.5 moles) of commercial acetone (Note 2) and a few pieces of porous plate to produce even boiling. Two of the usual paper thimbles are placed in the extractor, one above the other. The lower one is filled nearly full of barium hydroxide; the top one is filled about three-quarters full of the same substance (Note 3), and the remainder of the space is filled with glass wool.

The flask is heated on a steam bath or in an oil bath. The heat is so regulated that the acetone refluxes back into the extractor rather rapidly. As the reaction proceeds the boiling point of the mixture rises and more steam has to be turned on or the temperature of the oil bath has to be raised. The flask should finally be lowered as far as possible into the cone of the steam bath. The reaction is complete when the liquid no longer boils when heated as hot as possible on the steam bath. This usually requires ninety-five to one hundred and twenty hours (Note 4). The refluxing may be interrupted at any time for as long as desired. The liquid in the flask has now a specific gravity of about 0.91 (20°) which corresponds to about 80 per cent of diacetone alcohol (Note 5). The only loss of material is by volatilization of the acetone through the top of the condenser; this generally amounts to several per cent.

The crude diacetone alcohol is purified by distillation. The 2-l. round-bottomed flask is fitted with a three-bulbed Glinsky fractionating column and a well-cooled condenser. The flask is heated in an oil bath, the temperature of which is gradually raised to 125°. The temperature of the bath is held at this point until no more acetone distils over, the temperature at the top of the column registering about 70° when the process is complete. The recovered acetone, containing a few per cent of diacetone alcohol, amounts to about 200 g. and can be used to prepare more material. The residual liquid has a specific gravity of 0.928 (20°) and contains about 95 per cent of diacetone alcohol. It is transferred to a 2-l. Claisen flask and distilled under reduced pressure (Note 6). A little acetone first comes over and then the diacetone alcohol distils smoothly at 71–74°/23 mm. The yield is 850 g. (71 per cent of the theoretical amount based on the total acetone employed). The entire distillation requires about four hours.

2. Notes

1. Almost any form of a Soxhlet extractor and condenser will serve. It is advisable to use as much barium hydroxide as possible and to have the extractor empty as often and as completely as possible. The use of glass wool and care in filling the cups prevents any solid hydroxide from being carried down into the lower flask.

The use of tartaric acid in the flask has been recommended to neutralize any barium hydroxide that is carried down. This has been found unnecessary.

2. With some samples of commercial acetone containing considerable water, it has been found advisable to dry the acetone first with calcium chloride. This is usually not necessary.

3. If hydrated barium hydroxide $[\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}]$ is used in the thimbles this becomes dehydrated after one run; the anhydrous form is just as satisfactory and may be used over and over again.

4. The time of refluxing depends on the rapidity with which the liquid boils and on the way in which the Soxhlet extractor empties. Similarly, the point at which the liquid ceases to boil will vary somewhat with the way in which it is heated. The amount of diacetone alcohol produced will, thus, vary somewhat in similar experiments. Refluxing for forty to fifty hours produces about a 70 per cent mixture which is perfectly suitable for preparing the pure product, except that more [acetone](#) is recovered unchanged.
5. [Acetone](#) and diacetone alcohol are in equilibrium with each other. The speed of both reactions is greatly accelerated by the presence of a base. The equilibrium mixture contains only a few per cent of diacetone alcohol, but the dissociation of diacetone alcohol to [acetone](#) proceeds so slowly in the absence of [barium hydroxide](#) that it is possible to increase the concentration to 80 per cent by this procedure.
6. The final distillation of diacetone alcohol must be carried out under reduced pressure as otherwise some of the material decomposes into [acetone](#).

3. Discussion

Diacetone alcohol can be prepared from [acetone](#) by the action of alkali metal hydroxides,¹ [calcium hydroxide](#),² and [barium hydroxide](#).³ [Barium hydroxide](#) reacts more rapidly than [calcium hydroxide](#),³ and was accordingly used in the procedure described.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 1, 345](#)

References and Notes

1. Heintz, *Ann.* **169**, 114 (1873); Locquin, *Ann. chim.* (9) **19**, 32 (1923); Thomson, U. S. pat. 1,654,103 [*C. A.* **22**, 787 (1928)]; Ellis, U. S. pat. 1,701,473 [*C. A.* **23**, 1419 (1929)].
2. Hoffman, *Ger. pat.* 229,678 [*Frdl.* **10**, 998 (1910–12)]; U. S. pat. 1,082,424 [*C. A.* **8**, 788 (1914)]; Edmonds, U. S. pat. 1,550,792 [*C. A.* **20**, 51 (1926)].
3. Kyriakides, *J. Am. Soc.* **36**, 534 (1914).

Appendix

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

Diacetone alcohol

[calcium chloride](#) (10043-52-4)

[acetone](#) (67-64-1)

[tartaric acid](#) (87-69-4)

[barium hydroxide](#) (17194-00-2)

[2-Pentanone, 4-hydroxy-4-methyl-](#) (123-42-2)

[hydroxide](#) (14280-30-9)

[calcium hydroxide](#)

