



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.

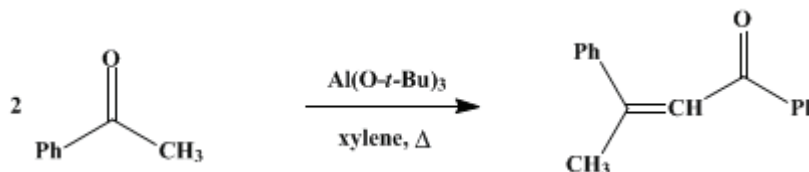
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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. 3, p.367 (1955); Vol. 21, p.39 (1941).

DYPNONE



Submitted by Winston Wayne and Homer Adkins.

Checked by Nathan L. Drake, Wm. H. Souder, Jr., and Ralph Mozingo.

1. Procedure

In a 1-l. round-bottomed three-necked flask, equipped with a thermometer, an efficient mechanical stirrer (Note 1), and a 35-cm. Vigreux column fitted to a condenser and receiver protected by a calcium chloride tube, are placed 345 g. (400 ml.) of dry *xylene*, 120 g. (117 ml., 1 mole) of dry *acetophenone*, and 135 g. (0.55 mole) of *aluminum tert-butoxide* (p. 48) (Note 2). The stirrer is started and the flask heated in an oil bath so that the temperature of the reaction mixture is held between 133° and 137°. *tert-Butyl alcohol* slowly distills at a temperature in the vapor of 80–85°. The distillation of the alcohol can be accomplished by maintaining the temperature of the heating bath between 150° and 155° for 2 hours after distillation has commenced (Note 3) and (Note 4).

The reaction mixture is cooled to 100°, and 40 ml. of water is added cautiously in small portions with continued stirring. As the water is added the mixture sets to a gel, and then, upon the addition of the remainder of the water and gentle tapping of the reaction flask, the stiff mass breaks up and boiling begins. Refluxing is continued by heating the oil bath for another 15 minutes to ensure the complete hydrolysis of the *aluminum tert-butoxide*.

After cooling, the reaction mixture is transferred in nearly equal portions to four centrifuge bottles and the *aluminum hydroxide* is centrifuged out (Note 5). The upper liquid layer is removed, and the *aluminum hydroxide* is worked up to a smooth paste, by means of a spatula, with a total of approximately 250 ml. of *ether* for the four portions. The *aluminum hydroxide* is again centrifuged out and the *ether* extract poured off. The centrifuging is repeated three more times so that approximately a liter of *ether* is used to separate the product from the *aluminum hydroxide* (Note 6).

Ether and *tert-butyl alcohol* are removed by distillation at atmospheric pressure without a column, and the *xylene* is removed by distillation through a 35-cm. Vigreux column at 25–50 mm. The residue is transferred to a smaller flask, and the *acetophenone* is first distilled at about 80°/10 mm., and finally the *dypnone* is distilled at 150–155°/1 mm. (Note 7) and (Note 8). The yield is 85–91 g. (77–82%) of a yellow liquid.

2. Notes

1. Instead of the customary mercury seal, a simple rubber tube seal suggested by Dr. L. P. Kyrides is recommended. The upper end of an 8-cm. length of 10-mm. glass tubing, projecting through a stopper, is fitted with a 2-cm. piece of 6-mm. rubber tubing so that it projects 5 mm. beyond the end of the glass tube. This projecting portion fits snugly to form a seal round an 8-mm. stirrer shaft running through the glass tubing. *Glycerol* is applied at the point of contact of glass and rubber to act as a lubricant and sealing medium. This type of seal can be conveniently used with reduced pressure down to 10 mm.
2. Slightly more than a mole of *aluminum tert-butoxide* is used for each mole of water split out as the alkoxide loses its effectiveness after the replacement of one alkoxy by an hydroxyl group.
3. The reaction may proceed so vigorously at first that the distillation temperature will rise to 100° or above. This is not detrimental and the temperature will soon fall.
4. As the reaction proceeds the color changes from yellow to deep orange and the mixture becomes viscous. After about 45 minutes the distillation temperature begins to fall and eventually reaches 70°

owing to the formation of **butylene** from the **aluminum tert-butoxide** which decomposes slightly at this temperature.

5. Ordinary undried **ether** is used in balancing the centrifuge bottles, in removing any **aluminum hydroxide** and product remaining in the flask, and in the subsequent extraction of the **aluminum hydroxide**.

6. This method eliminates the washing and drying of the customary extraction. procedure. The small amount of water present distils off with the solvent. The extraction should be done carefully and thoroughly. If it has been carried out properly the **aluminum hydroxide** will be white or faintly yellow and at least 95% of the original **acetophenone** can be accounted for after the final distillation.

7. The **acetophenone** and **dyponone** are easily separated in any of the common types of fractionating columns. The column should be short (12–18 cm.) and electrically heated because of the high boiling point of the product. An undistillable residue of 5–10 g. remains.

8. The boiling point varies greatly with the rate of distillation and the amount of ebullition.

3. Discussion

Dyponone has been prepared by the action of **sodium ethoxide**,¹ **aluminum bromide**,² **phosphorus pentachloride**,³ **aluminum triphenyl**,⁴ **zinc diethyl**,⁵ **calcium hydroxide**,⁶ anhydrous **hydrogen chloride**,^{5,7} anhydrous **hydrogen bromide**,⁸ **aluminum chloride**,⁴ **aluminum tert-butoxide**,⁹ and **hydrogen fluoride**¹⁰ on **acetophenone**. It has been obtained by the action of **aniline hydrochloride** on acetophenone anil followed by treatment with **hydrochloric acid**.¹¹ The preparation of **aluminum tert-butoxide** has been described.^{9,12,13} The procedure described is a modification of that by Adkins and Cox.⁹

This preparation is referenced from:

- **Org. Syn. Coll. Vol. 3, 188**
- **Org. Syn. Coll. Vol. 3, 387**
- **Org. Syn. Coll. Vol. 4, 291**
- **Org. Syn. Coll. Vol. 4, 427**
- **Org. Syn. Coll. Vol. 4, 881**

References and Notes

1. Eijkman, *Chem. Weekblad*, **1**, 349 (1904).
 2. Konowalow and Finogjew, *J. Russ. Phys. Chem. Soc.*, **34**, 944 (1902) [*Chem. Zentr.*, **74**, I, 521 (1903)].
 3. Taylor, *J. Chem. Soc.*, **1937**, 304.
 4. Calloway and Green, *J. Am. Chem. Soc.*, **59**, 809 (1937).
 5. Henrich and Wirth, *Monatsh.*, **25**, 423 (1904).
 6. Porlezza and Gatti, *Gazz. chim. ital.*, **56**, 265 (1926).
 7. Delacre, *Bull. classe sci. Acad. roy. Belg.*, (3) **20**, 467 (1898); Colonge, *Bull. soc. chim. France*, (4) **49**, 426 (1931); Kohler, *Am. Chem. J.*, **31**, 642 (1904).
 8. Müller and Spinosa-Stöckel, *Österr. Chem. Ztg.*, **49**, 130 (1948).
 9. Adkins and Cox, *J. Am. Chem. Soc.*, **60**, 1151 (1938).
 10. Simons and Ramler, *J. Am. Chem. Soc.*, **65**, 1390 (1943).
 11. Reddelien, *Ber.*, **46**, 2712 (1913).
 12. Oppenauer, *Rec. trav. chim.*, **56**, 137 (1937).
 13. *Org. Syntheses Coll. Vol. 3, 48* (1954).
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Appendix

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

aluminum triphenyl

zinc diethyl

acetophenone anil

hydrogen chloride,
hydrochloric acid (7647-01-0)

ether (60-29-7)

phosphorus pentachloride (10026-13-8)

glycerol (56-81-5)

hydrogen bromide (10035-10-6)

aniline hydrochloride (142-04-1)

hydrogen fluoride (7664-39-3)

Acetophenone (98-86-2)

aluminum chloride (3495-54-3)

sodium ethoxide (141-52-6)

calcium hydroxide

xylene (106-42-3)

aluminum bromide

aluminum hydroxide

butylene

tert-butyl alcohol (75-65-0)

ALUMINUM tert-BUTOXIDE

Dyprone (495-45-4)