



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.

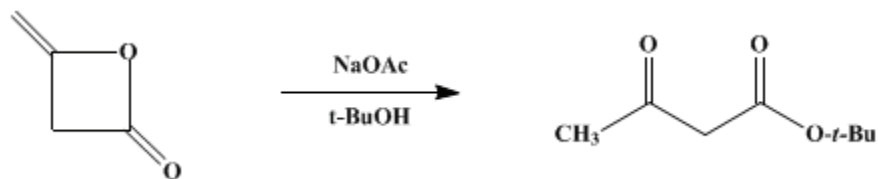
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.155 (1973); Vol. 42, p.28 (1962).

***t*-BUTYL ACETOACETATE**

[Acetoacetic acid, *tert*-butyl ester]



Submitted by Sven-Olov Lawesson, Susanne Gronwall, and Rune Sandberg¹.
Checked by William G. Dauben and Richard Ellis.

1. Procedure

Caution! This preparation should be conducted in a hood to avoid exposure to diketene, which is toxic and which may irritate mucous tissues such as those of the eyes; the use of safety goggles is recommended.

A 500-ml. three-necked flask is equipped with a sealed mechanical stirrer, a dropping funnel, and a two-armed addition tube, one arm of which bears a reflux condenser and the other arm of which is fitted with a thermometer. *t*-Butyl alcohol (79 g., 1.07 moles) (Note 1) is added to the flask and the thermometer arranged so that its bulb is immersed in the liquid but out of the path of the stirrer. The flask is heated by means of an electric mantle until the temperature of the liquid is 80–85°, and the mantle then is removed. Anhydrous sodium acetate (0.4 g., 4.8 mmoles) is added with stirring, and then 96 g. (1.14 moles) of diketene (Note 2) is added dropwise over a period of 2.5 hours. The temperature of the solution drops to 60–70° during the first 15 minutes and then increases slowly to 110–115°. When all the diketene is added, the reaction subsides and, after the resulting brown-black solution is stirred for an additional 30 minutes, the product is distilled immediately under reduced pressure through a short column. After a small fore-run, the yield of *t*-butyl acetoacetate, b.p. 85°/20 mm. (Note 3), n_D^{20} 1.4200–1.4203, is 127–135 g. (75–80%) (Note 4).

2. Notes

1. Eastman Kodak white label grade is used without further purification.
2. The submitters used material directly as supplied by Dr. Theodor Schuchardt and Co., Munich, Germany. The checkers used material directly as supplied by Aldrich Chemical Co., Milwaukee, Wisconsin.
3. The still residue is dehydroacetic acid.
4. In a run five times the size described, the submitters report that the reaction goes in the same manner and in 85–92% yield.

3. Discussion

t-Butyl acetoacetate has been prepared by self-condensation of *t*-butylacetate.^{2,3} The described procedure is based upon the method of Treibs and Hintermeier.⁴

The present preparation employs a method of considerable scope and is illustrative of a general method of preparing esters of acetoacetic acid; it gives much better yields, is considerably less laborious than other methods for the preparation of *t*-butyl acetoacetate, and appears to be the most convenient as starting materials are easily accessible. The title compound is of specific interest since the *t*-butoxy carbonyl group may be removed simply by heating the compound with catalytic amounts of *p*-toluenesulfonic acid. For instance, a new method has been developed for the preparation of acylloins by

introducing the benzoyloxy group into *t*-butyl acetoacetate, followed by *t*-butoxy carbonyl-elimination and hydrolysis.⁵ Using a similar technique and starting from *t*-butyl acetoacetate, levulinic esters,⁶ δ -ketonitriles,⁷ 1-methylcyclohexene-1-on-3,⁸ α,β -unsaturated ketones,⁹ and piperiton and related compounds¹⁰ have been prepared.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 179](#)

References and Notes

1. Present address: Department of Chemistry, University of Aarhus, 8000 Aarhus C, Denmark.
2. N. Fisher and S. M. McElvain, *J. Am. Chem. Soc.*, **56**, 1766 (1934).
3. W. B. Renfrow and G. D. Walker, *J. Am. Chem. Soc.*, **70**, 3957 (1948).
4. A. Treibs and K. Hintermeier, *Ber.*, **87**, 1163 (1954)
5. S.-O. Lawesson, S. Grönwall, and M. Andersson, *Arkiv Kemi*, **17**, 457 (1961).
6. S.-O. Lawesson, M. Dahlén, and C. Frisell, *Acta Chem. Scand.*, **16**, 1191 (1962).
7. G. Näslund, A. Senning, and S.-O. Lawesson, *Acta Chem. Scand.*, **16**, 1324 (1962).
8. G. Näslund, A. Senning, and S.-O. Lawesson, *Acta Chem. Scand.*, **16**, 1329 (1962).
9. S.-O. Lawesson, E. H. Larsen, G. Sundström, and H. J. Jakobsen, *Acta Chem. Scand.*, **17**, 2216 (1963).
10. S.-O. Lawesson, E. H. Larsen, H. J. Jakobsen, and C. Frisell, *Rec. Trav. Chim. Pays-Bas*, **83**, 464 (1964).

Appendix

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

[sodium acetate \(127-09-3\)](#)

[diketene \(674-82-8\)](#)

[Dehydroacetic acid \(520-45-6\)](#)

[t-butyl alcohol \(75-65-0\)](#)

[acetoacetic acid \(541-50-4\)](#)

[p-toluenesulfonic acid \(104-15-4\)](#)

[t-BUTYL ACETOACETATE,
Acetoacetic acid, tert-butyl ester \(1694-31-1\)](#)

[t-butylacetate](#)