



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](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.

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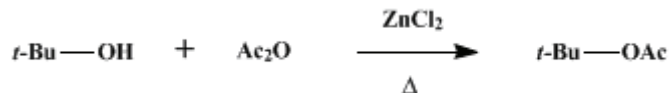
*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 3, p.141 (1955); Vol. 24, p.18 (1944).*

## ***tert*-BUTYL ACETATE**

[Acetic acid, *tert*-butyl ester]

### [I. ACETIC ANHYDRIDE METHOD]



Submitted by Robert H. Baker and Frederick G. Bordwell.

Checked by R. L. Shriner and Fred W. Neumann.

#### 1. Procedure

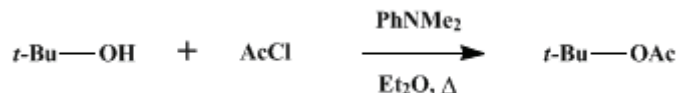
In a 1-l. flask equipped with a reflux condenser and drying tube are placed 200 ml. (2.1 moles) of *tert*-butyl alcohol (Note 1), 200 ml. (2.1 moles) of acetic anhydride, and 0.5 g. of anhydrous zinc chloride. After thorough shaking, the mixture is slowly heated to reflux temperature, maintained at gentle refluxing for 2 hours, and then cooled. The reflux condenser is replaced by a 20-cm. Vigreux column through which the mixture is distilled up to a temperature of 110°. The crude distillate, weighing 200–250 g., is washed with two 50-ml. portions of water, then with 50-ml. portions of 10% potassium carbonate until the ester layer is neutral to litmus; the product is finally dried over anhydrous potassium carbonate (about 20 g.).

After removal of the drying agent, the ester is fractionally distilled through an efficient fractionating column (Note 2). A fore-run of 21–37 g. is collected up to a temperature of 95°. The pure ester distils between 95° and 96° and amounts to 129–148 g. (53–60%) (Note 3).

#### 2. Notes

1. Eastman Kodak Company's best grade of *tert*-butyl alcohol and the practical grade of acetic anhydride are satisfactory. If these are not available, the alcohol should be dried over quicklime and distilled, and the acetic anhydride should be redistilled also.
2. The fractionating column may be a 16-plate Stedman column or a 30-cm. Carborundum-packed column.
3. The corrected boiling point of the ester is given as 97.9°.<sup>1</sup>

### [II. ACETYL CHLORIDE METHOD]



Submitted by C. R. Hauser, B. E. Hudson, B. Abramovitch, and J. C. Shivers.

Checked by R. L. Shriner and Fred W. Neumann.

#### 1. Procedure

In a 2-l. flask equipped with a reflux condenser, mercury-sealed stirrer, and a dropping funnel are placed 147 ml. (114 g., 1.5 moles) of *tert*-butyl alcohol (Note 1), 212 ml. (202 g., 1.67 moles) of dimethylaniline, and 200 ml. of dry ether. The solution is heated to refluxing, and 113 ml. (124 g., 1.58 moles) of acetyl chloride is run into the stirred solution at such a rate that moderate refluxing continues after the source of heat is removed. When approximately two-thirds of the acetyl chloride has been added, dimethylaniline hydrochloride begins to crystallize and the mixture refluxes very vigorously. An ice bath is applied immediately, and, after refluxing ceases, the remainder of the acetyl chloride is

added. Finally, the mixture is heated for 1 hour on a water bath. The mixture is cooled to room temperature, approximately 200 ml. of water is added, and stirring is continued until all the solid material dissolves. The ether layer is separated and extracted with 50-ml. portions of cold 10% sulfuric acid until the extract does not become cloudy when made alkaline with sodium hydroxide. After a final washing with 25 ml. of saturated sodium bicarbonate solution, the ether solution is dried by shaking it with 10 g. of anhydrous sodium sulfate. The solution is decanted and allowed to stand over 10 g. of Drierite overnight. The solution is filtered, and the ether is removed by distillation through a good fractionating column (Note 2). The residue is fractionally distilled, and 110–119 g. (63–68%) of *tert*-butyl acetate boiling at 95–98° is obtained (Note 2). Most of the ester boils at 97.0–97.5° (Note 3).

## 2. Notes

1. All reactants should be pure and anhydrous. The *tert*-butyl alcohol should be dried over quicklime and the dimethylaniline redistilled. Reagent grade acetyl chloride should be employed.

2. Either a 30-cm. Carborundum-packed column or a 30-cm. Widmer column may be used. The pure ester was collected over a range of 94.5–95.5°.

3. The submitters report that the following *tert*-butyl esters have been prepared in a similar manner. Eastman Kodak Company chemicals were used.

(a) *tert*-Butyl propionate. From 221 ml. (171 g., 2.31 moles) of *tert*-butyl alcohol, 318 ml. (303 g., 2.5 moles) of dimethylaniline, and 206 ml. (220 g., 2.38 moles) of propionyl chloride, refluxed for 3 hours, there was obtained 184 g. (61.4%) of *tert*-butyl propionate, b.p. 117–118.5°; most of the product boiled at 118.0–118.5°.

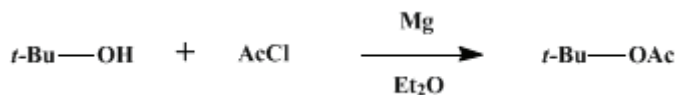
(b) *tert*-Butyl isobutyrate. From 94.5 ml. (73.4 g., 0.99 mole) of *tert*-butyl alcohol, 127 ml. (121 g., 1 mole) of dimethylaniline in 200 ml. of ether, and 105 ml. (108 g., 1 mole) of isobutyryl chloride in 50 ml. of ether, after standing for 15 hours at room temperature, the ether being distilled, and the residue heated for 5 hours on a water bath, there was obtained 102 g. (71%) of the ester boiling at 127–128.3°.

(c) *tert*-Butyl isovalerate. From 121.4 g. (1.64 moles) of *tert*-butyl alcohol, 198.5 g. (1.64 moles) of dimethylaniline, and 200.7 g. (1.66 moles) of isovaleryl chloride, after standing overnight, the ether being distilled, and the residue heated for 5 hours on a water bath, there was obtained 67.3 g. (26%) of *tert*-butyl isovalerate boiling at 154–157°.

(d) *tert*-Butyl cinnamate. The cinnamoyl chloride from 100 g. (0.675 mole) of cinnamic acid and 400 g. (3.37 moles) of thionyl chloride was treated with 64 ml. (49.5 g., 0.67 mole) of *tert*-butyl alcohol and 90 ml. (86.0 g., 0.71 mole) of dimethylaniline. The mixture was refluxed 12 hours and then allowed to stand 12 hours at room temperature. Distillation furnished 78.8 g. (58%) of *tert*-butyl cinnamate boiling at 144°/8 mm.

(e) *tert*-Butyl chloroacetate (submitted by Robert H. Baker). Thirty-five and four-tenths milliliters (0.4 mole) of *tert*-butyl alcohol was added over a period of 10 minutes to a mixture of 30.6 ml. (0.4 mole) of chloroacetyl chloride and 50 ml. (0.4 mole) of dimethylaniline, care being taken to keep the temperature below 30°. After standing 45 minutes at room temperature, the mixture was poured into water and worked up in the usual way. The ester was fractionated in a 6-in. Widmer column. The yield was 38 g. (63%) of ester which boiled at 48–49°/11 mm.;  $n_D^{20}$  1.4259–1.4260.

## [III. ACETYL CHLORIDE-MAGNESIUM METHOD]



Submitted by A. Spassow

Checked by W. E. Bachmann and J. Korman.

### 1. Procedure

In a 1-l. round-bottomed flask are placed 12 g. (0.5 gram atom) of magnesium powder, 37 g. (0.5 mole) of *tert*-butyl alcohol, and 100 g. of anhydrous ether (Note 1). The flask is fitted with an addition tube, one arm of which bears a reflux condenser and the other arm a dropping funnel. While the mixture

is being shaken by hand, a solution of 55 g. (0.7 mole) of [acetyl chloride](#) ([Note 2](#)) in 50 g. of anhydrous [ether](#) is added dropwise ([Note 3](#)). A lively reaction gradually ensues with evolution of [hydrogen](#), mixed with [ether](#) vapor and a little [hydrogen chloride](#) ([Note 4](#)). After all the [acetyl chloride](#) has been added, the reaction mixture is allowed to stand in a pan of cold water for 1 hour ([Note 5](#)). After another hour at room temperature the mixture is warmed in a water bath at 40–45° for 30 minutes in order to complete the reaction.

The solid reaction product is cooled in ice water and decomposed by addition of an ice-cold solution of 20 g. of [potassium carbonate](#) in 250 ml. of water, cooling being continued throughout ([Note 6](#)). The mixture is extracted three times with 35-ml. portions of [ether](#); the [ether](#) extract is dried over [calcium chloride](#) and then distilled ([Note 7](#)). The ester is obtained from the fraction boiling at 85–98° by fractional distillation by means of a good column ([Note 8](#)). The purified ester boils at 95–97°/740 mm. and weighs 37–45 g. (45–55%).

## 2. Notes

1. The [tert-butyl alcohol](#) must be completely anhydrous. It was dried over [sodium](#) and distilled from [sodium](#) just before use. The [ether](#) was likewise dried over [sodium](#).
2. The [acetyl chloride](#) was distilled before use.
3. The addition of the [acetyl chloride](#) requires about 15 minutes. After the addition of about two-thirds of the acid chloride, the reaction mixture rapidly becomes semisolid.
4. The course of the esterification is best followed by the evolution of the [hydrogen](#), the [hydrogen](#) being led by means of a tube from the top of the condenser through a wash bottle containing a small amount of water. A moderate rate of reaction is obtained throughout by judicious immersion of the reaction flask in a pan of cold water.
5. After 30 minutes the reaction becomes more lively and the mixture more fluid.
6. The [potassium carbonate](#) solution is added all at once. The [carbon dioxide](#) which is evolved does not interfere with the extraction of the ester.
7. Since the ester is quite volatile, the [ether](#) is distilled through a 60-cm. Vigreux column. The distillation is interrupted at 40°, and a 40-cm. column is employed. A fraction boiling up to 85° and one boiling from 85° to 98° are collected. The first fraction, which contains considerable amounts of the ester, is redistilled, and the portion boiling above 85° is added to the second fraction. The fraction boiling from 85° to 98° weighs 43–48 g.
8. A 40-cm. Vigreux or Widmer column is used for this distillation. The fore-run is redistilled from the same flask.

## 3. Discussion

[tert-Butyl acetate](#) has been prepared from the alcohol and [acetyl chloride](#) in the presence of [pyridine](#),<sup>1</sup> [dimethylaniline](#),<sup>2</sup> or [magnesium](#). [Acetic anhydride](#) has been used with [zinc chloride](#),<sup>2</sup> a small amount of [zinc dust](#),<sup>2</sup> or anhydrous [sodium acetate](#).<sup>3</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 171](#)
- [Org. Syn. Coll. Vol. 5, 586](#)
- [Org. Syn. Coll. Vol. 6, 259](#)

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## References and Notes

1. Bryant and Smith, *J. Am. Chem. Soc.*, **58**, 1016 (1936).
  2. Norris and Rigby, *J. Am. Chem. Soc.*, **54**, 2097 (1932).
  3. Tronow and Ssibgatullin, *Ber.*, **62**, 2850 (1929).
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

Drierite

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

hydrogen chloride (7647-01-0)

ether (60-29-7)

acetic anhydride (108-24-7)

sodium acetate (127-09-3)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

acetyl chloride (75-36-5)

thionyl chloride (7719-09-7)

sodium bicarbonate (144-55-8)

magnesium,  
magnesium powder (7439-95-4)

sodium sulfate (7757-82-6)

carbon dioxide (124-38-9)

pyridine (110-86-1)

zinc (7440-66-6)

sodium (13966-32-0)

zinc chloride (7646-85-7)

chloroacetyl chloride (79-04-9)

dimethylaniline (121-69-7)

cinnamic acid (621-82-9)

isobutyryl chloride (79-30-1)  
propionyl chloride (79-03-8)  
dimethylaniline hydrochloride (5882-44-0)  
isovaleryl chloride (108-12-3)  
cinnamoyl chloride  
tert-butyl alcohol (75-65-0)  
tert-Butyl acetate,  
Acetic acid, tert-butyl ester (540-88-5)  
tert-Butyl propionate (20487-40-5)  
tert-Butyl isobutyrate (16889-72-8)  
tert-Butyl isovalerate (16792-03-3)  
tert-Butyl cinnamate (14990-09-1)  
tert-Butyl chloroacetate (107-59-5)