Organic Syntheses

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.

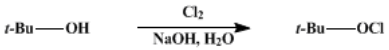
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.

Org. Synth. **1952**, *32*, 20
DOI: 10.15227/orgsyn.032.0020

tert-BUTYL HYPOCHLORITE



Submitted by H. M. Teeter and E. W. Bell[1].
Checked by Charles C. Price and T. C. Schwann.

1. Procedure

Caution! See the discussion in Org. Synth. 1973, Coll. Vol. 5, 183 with regard to potential hazards associated with the title compound.

Caution! This preparation should be carried out in a good hood. The product should be protected from strong light, over-heating, or exposure to rubber to avoid vigorous decomposition.

A solution of 80 g. (2 moles) (Note 1) of sodium hydroxide in about 500 ml. of water is prepared in a 2-l. three-necked round-bottomed flask equipped (Note 2) with a gas inlet tube reaching nearly to the bottom of the flask, a gas outlet tube, and a mechanical stirrer. The flask is placed in a water bath at 15–20° (Note 3), and, after the contents have cooled to this temperature, 74 g. (96 ml., 1 mole) of *tert*-butyl alcohol (Note 4) is added together with enough water (about 500 ml.) to form a homogeneous solution. With constant stirring, chlorine is passed into the mixture for 30 minutes at a rate of approximately 1 l. per minute (Note 5) and then for an additional 30 minutes at a rate of 0.5–0.6 l. per minute.

The upper oily layer is then separated with the aid of a separatory funnel (Note 6). It is washed with 50-ml. portions of 10% sodium carbonate solution until the washings are no longer acidic to Congo red. It is finally washed 4 times with an equal volume of water and dried over calcium chloride. The yield is 78–107 g. (72–99%) (Note 7); d_{20}^{20} 0.910; n_{D}^{20} 1.403. The product is best stored under an inert atmosphere (Note 8) in sealed bottles kept in the dark in a refrigerator (Note 9).

2. Notes

1. The submitters have successfully carried out this preparation in quantities up to 7 moles (519 g.) of *tert*-butyl alcohol using 2.25 hours for the addition of chlorine at each rate.
2. *tert*-Butyl hypochlorite reacts violently with rubber. The apparatus should therefore be assembled by means of ground-glass joints. Synthetic plastic tubing (Tygon) may be used instead of rubber tubing.
3. For 7-mole runs, a satisfactory bath consists of a 10-gal. earthenware jar fitted with a water inlet and an overflow device. The desired temperature is obtained by adjusting the rate of flow of tap water through the jar. The reaction can also be carried out successfully using an ice-water bath.
4. The *tert*-butyl alcohol was a commercial product obtained from the Shell Chemical Corporation, New York, New York.
5. Rates of flow are conveniently measured with the usual U-tube and capillary using one of the liquid Arochlors as the indicating fluid. The checkers did not use a flow meter but passed in chlorine rapidly at first and then slowly for 30 minutes after the initial rapid absorption.
6. In 7-mole runs carried out by the submitters, the bulk of the aqueous layer was removed conveniently by siphoning through the gas inlet tube.
7. This product, which is sufficiently pure for most purposes, contains about 2% free chlorine. It may be purified by distillation in an all-glass apparatus heated by a steam bath. The yield of pure product is 75–104 g. (69–96%); b.p. 77–78°/760 mm. Active chlorine assay indicates 97–98% purity for the crude product, 98–100% purity for the distilled material.
8. The inert atmosphere helps to minimize any tendency of vapors to ignite during sealing of the bottle. Filled bottles should be cooled in solid carbon dioxide before sealing.
9. When exposed to light, *tert*-butyl hypochlorite decomposes with formation of acetone and methyl chloride. When induced by radiation from an ultraviolet lamp, this decomposition proceeds rapidly enough to raise the temperature of the hypochlorite to the boiling point. The decomposition does not continue after irradiation is stopped. Customary room illumination does not induce the decomposition to a noticeable extent during ordinary handling of this material. However, a sealed glass bottle of hypochlorite should not be allowed to stand in light for a prolonged time as pressure sufficient to burst the bottle may be built up gradually.

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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. Organic Syntheses, Inc., its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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

3. Discussion

tert-Butyl hypochlorite has been prepared by the action of chlorine upon alkaline solutions of *tert*-butyl alcohol.[2,3,4,5] Solutions of *tert*-butyl hypochlorite have been prepared by shaking a solution of the alcohol in carbon tetrachloride,[6] fluorotrichloromethane (Freon 11), and other solvents[7] with aqueous hypochlorous acid. The procedure described is that of Teeter et al.[4]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 184
- Org. Syn. Coll. Vol. 5, 208
- Org. Syn. Coll. Vol. 5, 909
- Org. Syn. Coll. Vol. 6, 936
- Org. Syn. Coll. Vol. 5, 183

References and Notes

1. Northern Regional Research Laboratory, U. S. Department of Agriculture, Peoria, Illinois.
2. Chattaway and Backeberg, *J. Chem. Soc.*, **1923**, 2999.
3. Irwin and Hennion, *J. Am. Chem. Soc.*, **63**, 858 (1941).
4. Teeter, Bachmann, Bell, and Cowan, *Ind. Eng. Chem.*, **41**, 848 (1949).
5. Deanesly, U. S. pat. 1,938,175 [*C. A.*, **28**, 1053 (1934)].
6. Taylor, MacMullin, and Gammal, *J. Am. Chem. Soc.*, **47**, 395 (1925).
7. Fort and Denivelle, *Bull. soc. chim. France*, **1954**, 1109.

Appendix

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

calcium chloride (10043-52-4)

sodium hydroxide (1310-73-2)

sodium carbonate (497-19-8)

carbon tetrachloride (56-23-5)

carbon dioxide (124-38-9)

methyl chloride (74-87-3)

acetone (67-64-1)

chlorine (7782-50-5)

hypochlorous acid (7790-92-3)

fluorotrichloromethane (75-69-4)

tert-butyl alcohol (75-65-0)

tert-Butyl hypochlorite (507-40-4)