



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.

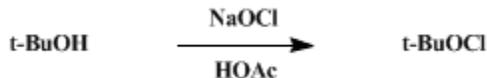
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.184 (1973); Vol. 49, p.9 (1969).

***t*-BUTYL HYPOCHLORITE**



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Checked by Lois A. Ablin and Henry E. Baumgarten.

1. Procedure

Caution! This preparation should be carried out in a hood to avoid exposure to the hypochlorite produced. To avoid vigorous decomposition the product should be handled only in dim light and should not be heated above its boiling point or be exposed to rubber.

In a 1-l. Erlenmeyer or round-bottomed flask equipped with a mechanical stirrer is placed 500 ml. of a commercial household bleach solution (Note 1). The flask is placed in a pail of ice and rapidly stirred until the temperature drops below 10°. At this point the lights in the vicinity of the apparatus should be turned off (Note 2). A solution of *t*-butyl alcohol (37 ml., 0.39 mole) and glacial acetic acid (24.5 ml., 0.43 mole) (Note 3) is added in a single portion to the rapidly stirred bleach solution, and stirring is continued for about 3 minutes (Note 4).

The entire reaction mixture is poured into a 1-l. separatory funnel. The lower aqueous layer (Note 5) is discarded, and the oily yellow organic layer is washed first with a 50-ml. portion of 10% aqueous sodium carbonate and then with 50 ml. of water. The product is dried over 1 g. of calcium chloride and filtered. The yield of *t*-butyl hypochlorite, 99–100% pure, is 29.6–34 g. (70–80%) (Note 1), (Note 6). The product can be stored conveniently in a freezer or refrigerator over calcium chloride in amber glass bottles (Note 7).

2. Notes

- Both the submitters and checkers used the commercial household bleach solution, Clorox (Proctor and Gamble Co.). This solution is stated to be 5.25% sodium hypochlorite (NaOCl). The submitters found it to be 0.75–0.80M by iodometric titration for total oxidant (assumed to be NaOCl). Thus 500 ml. of this solution would contain 0.375–0.400 mole of NaOCl. The checkers found that as little as 440 ml. of fresh Purex (Purex Corp., Ltd., stated to be 6% sodium hypochlorite) gave the stated yield. However, samples from different bottles from one case of "Purex" gave consistently lower yields, 57–70%. Probably the lower yield was due to a lowering of the hypochlorite concentration on standing. The submitters and checkers recommend either discarding bleach solution over 6 months old or checking the titer before use. Presumably other household bleaches will give comparable results with possible small variations in yield.
- Whereas the inorganic hypochlorite is rather stable to photodecomposition, *t*-butyl hypochlorite is much more readily decomposed. It is not necessary to work in a totally darkened room, but the incidence of strong light should be avoided—both for reasons of safety and to ensure that hypochlorite of high purity will be isolated.
- The *t*-butyl alcohol was a commercial product obtained from Matheson Coleman and Bell, and the glacial acetic acid a commercial product obtained from Union Carbide.
- The submitters have carried out runs using up to 4 l. of the commercial bleach solution (3 moles)—as the largest scale conveniently run in the laboratory—and found no change in the reaction behaviour.
- The checkers observed that the aqueous layer was colorless when Clorox was used and was yellow when Purex was used.
- The purity of the hypochlorite may be determined by iodometric titration. This titration is run conveniently by weighing out a small portion of the hypochlorite (<0.5 g.) in a 4-ml. vial and then dropping the vial and its contents into an iodine flask containing 20 ml. of glacial acetic acid, 10 l. of

water, and 3 g. of [potassium iodide](#). The titration is then conducted in the usual fashion.
7. The product isolated by this procedure is sufficiently pure for almost any purpose. It was found that distillation did not change the product purity and often led to product of lower purity.

3. Discussion

t-Butyl hypochlorite has been prepared by treatment of an alkaline solution of *t*-butyl alcohol with [chlorine](#),^{3,4,5,6,7} and a recent warning^{8,9} cautions against allowing the temperature to rise above 20° during this reaction. *t*-Butyl hypochlorite has been prepared in solution by shaking a solution of the alcohol in [carbon tetrachloride](#),¹⁰ [fluorotrichloromethane](#) (Freon 11), and other solvents¹¹ with aqueous [hypochlorous acid](#). It has also been prepared by the action of [chlorine](#) on an aqueous *t*-butyl alcohol suspension of [calcium carbonate](#),¹² and by the action of [chlorine monoxide](#) on a [carbon tetrachloride](#) solution of the alcohol.¹³

The procedure described here has previously been reported by Mintz¹⁴ and was adapted from work by Geneste and Kergomard,¹⁵ Kergomard,¹⁶ Sumner,¹⁷ and Clark.¹⁸ It eliminates the dangers in working with a compressed gas ([chlorine](#)) and the danger from explosion due to poor temperature control during the addition of [chlorine](#).^{3,8,9} The availability and low cost of the commercial bleach solution (NaOCl), the simplicity of the equipment needed, the short time involved, and the high purity of the *t*-butyl hypochlorite produced confer additional merit on this preparation. The submitters have also prepared [benzyl dimethylcarbinyl hypochlorite](#), [cumyl hypochlorite](#), and [isopropyl hypochlorite](#) by this procedure. The checkers have used essentially the same procedure (with twice as much [sodium hypochlorite](#) solution and [acetic acid](#)) to prepare [N,N-dichloro-*t*-butylamine](#).

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 208](#)
- [Org. Syn. Coll. Vol. 5, 909](#)
- [Org. Syn. Coll. Vol. 6, 581](#)
- [Org. Syn. Coll. Vol. 6, 601](#)

References and Notes

1. E. C. Britton Research Laboratory, The Dow Chemical Company, Midland, Michigan 48640.
 2. Department of Chemistry, Columbia University, New York 10027.
 3. [H. Teeter and E. Bell, *Org. Syntheses, Coll. Vol. 4, 125 \(1963\)*](#).
 4. F. Chattaway and O. Backeberg, *J. Chem. Soc.*, 2999 (1923).
 5. R. Deanesly, U. S. Patent 1,938,175 [*Chem. Abstr.*, **28**, 1053 (1934)].
 6. C. Irwin and G. Hennion, *J. Am. Chem. Soc.*, **63**, 858 (1941).
 7. H. Teeter, R. Bachmann, E. Bell, and J. Cowan, *Ind. Eng. Chem.*, **41**, 849 (1949).
 8. *Org. Syntheses*, **44** (1964); sheet to be inserted in *Org. Syntheses, Coll. Vol. 4, 125 (1963)*.
 9. C. P. C. Bradshaw and A. Nechvatal. *Proc. Chem. Soc.*, 213 (1963).
 10. M. Taylor, R. MacMullin, and C. Gammal, *J. Am. Chem. Soc.*, **47**, 395 (1925).
 11. R. Fort and L. Denivelle, *Bull. Soc. Chim. France*, 1109 (1954).
 12. W. Hanby and H. Rydon, *J. Chem. Soc.*, 114 (1946).
 13. M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1105 (1954).
 14. M. J. Mintz, Ph.D. Thesis, Columbia University, 1965, p. 66.
 15. J. Geneste and A. Kergomard, *Bull. Soc. Chim. France*, 470 (1963).
 16. A. Kergomard, *Bull. Soc. Chim. France*, 2360 (1961).
 17. G. Sumner, Ph.D. Thesis, Massachusetts Institute of Technology, 1934.
 18. B. F. Clark Jr., *Chem. News*, **143**, 265 (1931).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

calcium chloride (10043-52-4)

acetic acid (64-19-7)

sodium carbonate (497-19-8)

carbon tetrachloride (56-23-5)

potassium iodide (7681-11-0)

calcium carbonate (471-34-1)

chlorine (7782-50-5)

hypochlorous acid (7790-92-3)

sodium hypochlorite,
NaOCl (7681-52-9)

fluorotrichloromethane (75-69-4)

t-butyl alcohol (75-65-0)

chlorine monoxide

N,N-dichloro-t-butylamine

t-BUTYL HYPOCHLORITE (507-40-4)

benzyl dimethylcarbinyl hypochlorite

cumyl hypochlorite

isopropyl hypochlorite