Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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.

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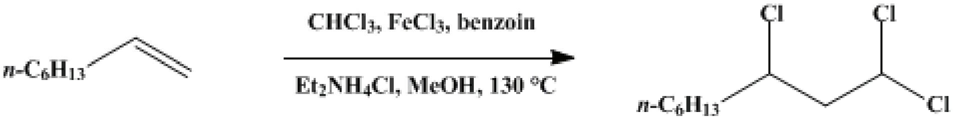
1,1,3-TRICHLORO-*n*-NONANE

[Nonane, 1,1,3-trichloro-]



Submitted by D. Vofsi and M. Asscher[1].
Checked by S. N. EGe and Peter Yates.

1. Procedure

A solution of 0.54 g. (2 mmoles) of ferric chloride hexahydrate and 0.33 g. (3 mmoles) of diethylammonium chloride (Note 1) in 5 g. of methanol is added to a solution of 11.2 g. (0.1 mole) of 1-octene (Note 2) and 0.42 g. (2 mmoles) of benzoin (Note 3) in 36 g. (0.3 mole) of chloroform (Note 4). The resulting homogeneous mixture is introduced into a Carius tube of about 100-ml. capacity. Air is displaced by dropping a few pieces of dry ice into the tube (Note 5). The tube is sealed (Note 6), heated to 130°, kept at that temperature for 15 hours, cooled to room temperature (Note 7), and opened. The contents of the tube are transferred to a separatory funnel, and the tube is rinsed with about 10 ml. of chloroform. The reaction mixture is washed with 40 ml. of water. The aqueous solution is extracted with 10 ml. of chloroform, and the extract is added to the original chloroform layer. Solvent is distilled at atmospheric pressure (bath temperature up to 130°). The distillation flask is allowed to cool, and distillation is continued at 25 mm. (bath temperature up to 120°) (Note 8). The flask is cooled again, and distillation is continued to dryness at 0.1 mm. (bath temperature up to 150°), giving crude 1,1,3-trichloro-*n*-nonane (19.4 g.) as a yellow oil, b.p. 60–85° (0.1 mm.), n^{25}D 1.4650. The purity of this product is 95% (Note 9), and the actual yield is 80%. Fractionation of this material through a 13-in. Vigreux column gives 15 g. (64%) of pure, colorless 1,1,3-trichloro-*n*-nonane, b.p. 61–62° (0.1 mm.), n^{25}D 1.4640 (Note 10) and (Note 11).

2. Notes

1. Pure diethylammonium chloride can be obtained from Fluka A. G., Buchs, S. G., Switzerland. If this salt is omitted, somewhat lower yields (about 75%) of adduct are obtained.
2. Phillips 1-octene of 99% minimum purity was used; however, it was freed of peroxide by percolating through acid-washed alumina.
3. Benzoin, Eastman Organic Chemicals, practical grade, can be used directly.
4. Reagent grade chloroform is used.
5. If air is not displaced before sealing, there is an induction period of about 1 hour.
6. The Carius tube has a short piece (about 4 in.) of heavy-walled tube (8-mm. external diameter) sealed to it. This greatly facilitates subsequent sealing and re-use of the tube. The solution is introduced by means of a funnel with a drawn-out stem.
7. On cooling, the contents of the tube separate into two layers.
8. Occasionally a few drops, consisting mainly of unconverted 1-octene, are collected. The receiver then must be changed before the distillation at 0.1 mm. is continued.
9. The purity was determined by gas chromatography (1.5-m. column packed with 25% silicone oil on Chromosorb W, at 180°, and a flow rate of 60 ml. of helium per minute). The yellow color, which is due to traces of benzil, may be removed by diluting the product with three times its volume of pentane, percolating the solution through a column of about 30 g. of acid-washed alumina, washing the alumina with 50 ml. of pentane, and distilling the pentane at atmospheric pressure. The residue, which is colorless, boils at 61–63° (0.1 mm.), n^{25}D 1.4643; the recovery is 95%.
10. The checkers distilled the reaction product directly through a 4-in. Vigreux column to obtain 15.4–15.8 g. (66–68%) of colorless product, b.p. 95–97° (2.5 mm.), n^{25}D 1.4632.
11. The submitters have found that the reaction may be carried out on a much larger scale in an

autoclave. The reaction must be run in a glass liner. As the hot reaction mixture is homogeneous, the autoclave may be heated while standing upright. The liner may be filled to three-quarters of its capacity.

3. Discussion

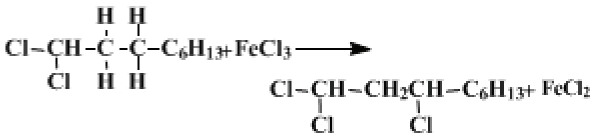
The method described, which is the only one available for the direct preparation of 1,1,3-trichloroalkanes, is applicable to aliphatic olefins and gives good yields, especially with terminal olefins.[2] With styrene or butadiene, yields are much lower.

4. Merits of the Preparation

1,1,3-Trichloroalkanes are potential starting materials for the preparation of unsaturated aldehydes.[3]

A similar method[2] can be used for the addition of carbon tetrachloride to nonpolymerizable olefins (*e.g.*, 1-octene, 2-octene, 1-butene, 2-butene); pure adducts are obtained in yields of over 90% if the components are allowed to react at 100° for 6 hours. Adducts of carbon tetrachloride with vinylic monomers (styrene, butadiene, acrylonitrile, methyl acrylate, etc.) can be prepared in good yields by substituting cupric chloride dihydrate in acetonitrile for ferric chloride hexahydrate and benzoin.

In ordinary homolytic reactions (as distinguished from the reaction described here), chloroform adds to the double bond in the sense H-CCl_3.[4] Bromodichloromethane adds in the sense Br-$CHCl_2$,[3] similar to the orientation of chloroform additions in the present method (Cl-$CHCl_2$). The present method has the advantage of giving high yields while using cheap reagents, and it is thought to proceed as shown in the following equations.



$$Cl{-}\underset{\displaystyle Cl}{CH}{-}\overset{\displaystyle H}{\underset{\displaystyle H}{\dot{C}}}{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}C_6H_{13}+FeCl_3 \longrightarrow Cl{-}\underset{\displaystyle Cl}{CH}{-}CH_2\underset{\displaystyle Cl}{CH}{-}C_6H_{13}+FeCl_2$$

Carbon tetrachloride can be substituted for chloroform in this reaction when the cupric chloride modification described above is used.

References and Notes

1. Plastics Research Laboratory, Polymer Department, The Weizmann Institute of Science, Rehovoth, Israel.
2. M. Asscher and D. Vofsi, *Chem. Ind. (London)*, 209 (1962); *J. Chem. Soc.*, **1963**, 1887, 3921; **1964**, 4962.
3. M. S. Kharasch, B. M. Kuderna, and W. Urry, *J. Org. Chem.*, **13**, 895 (1948).
4. M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Am. Chem. Soc.*, **69**, 1100 (1947).

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

alumina

methanol (67-56-1)

acetonitrile (75-05-8)

chloroform (67-66-3)

carbon tetrachloride (56-23-5)

Benzil (134-81-6)

Benzoin (119-53-9)

1-butene (106-98-9)

cupric chloride (7758-89-6)

Pentane (109-66-0)

styrene (100-42-5)

methyl acrylate (96-33-3)

butadiene (106-99-0)

ferric chloride hexahydrate (10025-77-1)

acrylonitrile (107-13-1)

helium (7440-59-7)

Nonane, 1,1,3-trichloro-,
1,1,3-TRICHLORO-n-NONANE (10575-86-7)

diethylammonium chloride

1-octene (111-66-0)

cupric chloride dihydrate (10125-13-0)

Bromodichloromethane (75-27-4)

2-butene

2-octene (13389-42-9)