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.

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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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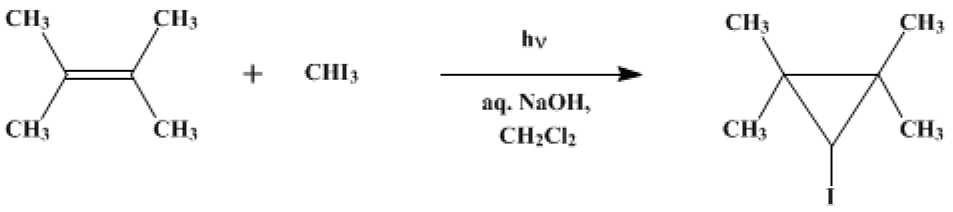
2,2,3,3-TETRAMETHYLIODOCYCLOPROPANE

[Cyclopropane, 3-iodo-1,1,2,2-tetramethyl]



$$I_2 + 2\ NaOH \longrightarrow NaI + NaOI + H_2O$$

Submitted by T. A. Marolewski and N. C. Yang[1].
Checked by T. Nakahira and K. B. Wiberg.

1. Procedure

Caution! The intense emission from the light source should be shielded from visibility in order not to damage the eyesight of the experimentalist.

Each of three 250-ml., round-bottomed Pyrex flasks is charged with 8.4 g. (0.10 mole) of 2,3-dimethyl-2-butene (Note 1), 175 ml. of dichloromethane, and 50 ml. of an aqueous 5 *M* sodium hydroxide solution. The flasks are kept rather full, making more efficient use of the incident light. A Teflon-covered magnetic stirring bar 2.5 cm. in length is added to each flask. Three 170 cm. by 90 cm. Pyrex crystallization dishes are partially filled with an ice–water mixture (Note 2), each dish is placed above a Mag-Mix magnetic stirrer, and each flask is immersed in the ice–water bath and held in place with a clamp. The three assemblies are arranged symmetrically around a Hanovia quartz immersion well (Note 3) cooled with running tap water, containing a Hanovia 450-watt, medium pressure, mercury lamp. The edge of each flask is placed approximately 1 cm. from the wall of the well. After 2.0 g. of iodoform is added to each flask, the mixtures are irradiated with stirring until the yellow color of the iodoform disappears. This process is continued until 39.4 g. (0.100 mole) of iodoform, equally distributed between the flasks, has been consumed (Note 4). After the reaction is complete, the reaction mixtures are combined and the organic layer is separated, washed once with water, and dried over anhydrous sodium sulfate. The solvent is removed with a rotary evaporator and a water pump. The residue is transferred to a 50-ml. flask, and 1.0 g. of sodium methoxide is added (Note 5). The mixture is distilled under reduced pressure in an apparatus with a 5-cm. Vigreux sidearm. The receiver is cooled in an ice–water bath and the first fraction, which boils at 45–48° (5 mm.), n_D^{25} 1.5087, is collected, yielding 14.0–15.0 g. (63–67%) of a clear distillate which should be stored in a refrigerator (Note 6) and (Note 7).

2. Notes

1. 2,3-Dimethyl-2-butene (99%) was purchased from the Chemical Samples Co.
2. At the beginning of irradiation, the mixture is mostly ice and contains just enough water to make efficient contact with the flask. The ratio of ice to water will vary during the course of irradiation, and ice is added to replace excess water from time to time.
3. Vycor or Pyrex wells are also satisfactory since the irradiation is carried out in Pyrex flasks.
4. The total period of irradiation was about 8 hours; however, this may vary with the equipment used.
5. The presence of sodium methoxide prevents decomposition of the product during the distillation.
6. The checkers also carried out the reaction using equimolar quantities of 2,3-dimethyl-2-butene and iodoform (0.1 mole each) and obtained 12.6–13.0 g. (56–58%) of the product. The submitters made the

same observation. They found that the yield increased slightly as the mole ratio of olefin to iodoform was increased from 1:1 to 3:1. Use of a larger excess of olefin resulted in no further increase in yield.

7. 1-Iodo-*cis,trans*-2,3-dimethylcyclopropane, b.p. 25–27° (8–10 mm.), n_{D}^{25} 1.5105, may be prepared in 56% yield from *trans*-2-butene (Matheson Gas Products) with this procedure. Both the 2,2,3,3-tetramethyliodocyclopropane and the 1-iodo-*cis,trans*-2,3-dimethylcyclopropane prepared by this procedure give only one peak on GC. The retention times are 272 and 114 seconds, respectively, on a 60-cm. 20% SE-30 on Chromosorb W column at a temperature of 81° and a helium flow rate of 41 ml. per minute.

3. Discussion

Bromo- and iodocyclopropanes cannot be prepared by the direct halogenation of cyclopropanes. Substituted chloro- and bromocyclopropanes have been synthesized by the photochemical decomposition of α-halodiazomethanes in the presence of olefins;[2] iodocyclopropanes have been prepared by the reaction of an olefin with iodoform and potassium *tert*-butoxide, followed by the reduction of the diiodocyclopropane formed with tri-*n*-butyltin hydride.[3] The method described employs a readily available light source and common laboratory equipment, and is relatively safe to carry out. The method can be modified for the preparation of cyclopropanes and halocyclopropanes as well, by using diiodomethane and halodiiodomethanes instead of iodoform.[4,5] If the olefin used gives two isomeric halocyclopropanes, the isomers are usually separable by chromatography.[4]

References and Notes

1. Department of Chemistry, University of Chicago, Chicago, Illinois 60637.
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3. J. P. Oliver and U. V. Rao, *J. Org. Chem.*, **31**, 2696 (1966).
4. N. C. Yang and T. A. Marolewski, *J. Am. Chem. Soc.*, **90**, 5644 (1968).
5. N. J. Pienta and P. J. Kropp, *J. Am. Chem. Soc.*, **100**, 655 (1978).

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

Bromo- and iodocyclopropanes

sodium hydroxide (1310-73-2)

sodium sulfate (7757-82-6)

sodium methoxide (124-41-4)

diiodomethane (75-11-6)

iodoform (75-47-8)

dichloromethane (75-09-2)

2,3-dimethyl-2-butene (563-79-1)

tri-n-butyltin hydride (688-73-3)

helium (7440-59-7)

2,2,3,3-Tetramethyliodocyclopropane,
Cyclopropane, 3-iodo-1,1,2,2-tetramethyl (39653-50-4)

diiodocyclopropane

potassium tert-butoxide (865-47-4)

trans-2-Butene (624-64-6)

1-Iodo-cis,trans-2,3-dimethylcyclopropane