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.

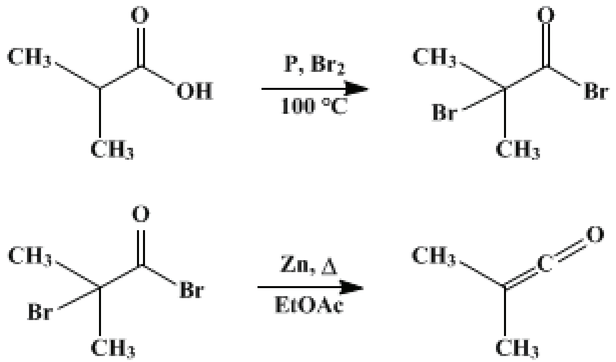
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.033.0029

Organic Syntheses, Coll. Vol. 4, p.348 (1963); Vol. 33, p.29 (1953).

DIMETHYLKETENE

[Ketene, dimethyl-]



Submitted by C. W. Smith and D. G. Norton[1].
Checked by T. L. Cairns and J. C. Sauer.

1. Procedure

A. *α-Bromoisobutyryl bromide.* To a mixture of 250 g. (2.85 moles) of isobutyric acid and 35 g. (0.28 mole) of red phosphorus in a 1-l. three-necked flask, fitted by ground-glass joints to a dropping funnel, mechanical stirrer, and reflux condenser, is added, dropwise with stirring, 880 g. (5.5 moles) of bromine. After the addition is complete, the solution is warmed to 100° over a period of 6 hours. The unreacted bromine and hydrogen bromide are removed under reduced pressure (30 mm.). The α-bromoisobutyryl bromide is decanted from the phosphorous acid and fractionated through a short helices-packed column. After a considerable fore-cut, the main fraction, 493–540 g. (75–83%), is collected at 91–98° (100 mm.).

B. *Dimethylketene* (Note 1). The apparatus for this preparation consists of a 500-ml. flask equipped with an inlet tube for nitrogen and a dropping funnel and fitted to a 6-in. modified Claisen still head leading to a tared spiral inlet trap having stop-cocks on the inlet and exit sides and cooled in Dry Ice-acetone (Note 2). This trap is connected to a vacuum line, and the reaction is carried out at 300 mm. pressure. After 40 g. (0.61 g. atom) of zinc turnings and 300 ml. of ethyl acetate have been placed in the flask and the system has been flushed with nitrogen (free of oxygen and moisture) and heated to incipient boiling, 111 g. (0.48 mole) of α-bromoisobutyryl bromide is added dropwise at such a rate that the ethyl acetate boils gently. A slow stream of nitrogen is continued throughout the reaction. Dimethylketene distils along with ethyl acetate and is obtained in 46–54% yield as a 9–10% solution in ethyl acetate (15–18 g. of dimethylketene in 190–200 ml. of ethyl acetate) (Note 3).

2. Notes

1. This ketene reacts rapidly with oxygen to form an explosive peroxide. Drops of solution allowed to evaporate in air may detonate. Washing with water is an efficient means of decontamination.
2. If simple traps are used, it is necessary to use two in series to condense all the dimethylketene and ethyl acetate.
3. The concentration of dimethylketene is determined by titration of an aliquot at ice temperatures with 0.1*N* sodium hydroxide using phenolphthalein indicator. Under these conditions, blank determinations indicate that ethyl acetate is not hydrolyzed.

The identity of the dimethylketene may be determined (and an approximate check made on the concentration) by adding 35 g. of dimethylketene solution to 15 g. of aniline in 75 ml. of ether. After 2–3 minutes, the ether solution is washed with dilute hydrochloric acid, dilute potassium carbonate, then water, and the ether is evaporated. Isobutyroanilide, m.p. 102–103° (103–104° after one recrystallization, no melting-point depression in mixture with an authentic sample), is obtained in about

90% yield based on the concentration of dimethylketene indicated by titration.

3. Discussion

The preparation of ketenes has been discussed by Hanford and Sauer in *Organic Reactions*.[2] Dimethylketene has been prepared by the treatment of α-bromoisobutyryl bromide with zinc,[3] and by the pyrolysis of isobutyrylphthalimide,[4] dimethylmalonic anhydride,[5] or α-carbomethoxy-α, β-dimethyl-β-butyrolactone.[6] Dimethylketene dimer has been prepared by heating isobutyryl chloride with a tertiary amine. Pyrolysis of the dimer yields dimethylketene.[7]

α-Bromoisobutyryl bromide has been prepared in a two-step process involving the bromination of isobutyric acid to α-bromoisobutyric acid followed by treatment with phosphorus tribromide.[8] A one-step process utilizing the Hell-Volhard-Zelinsky reaction[9] is more satisfactory.

References and Notes

1. Shell Development Company, Emeryville, California.
2. Hanford and Sauer, in Adams, *Organic Reactions*, Vol. 3, p. 108, John Wiley & Sons, 1946.
3. Staudinger and Klever, *Ber.*, **39**, 968 (1906).
4. Hurd and Dull, *J. Am. Chem. Soc.*, **54**, 2432 (1932).
5. Staudinger, *Helv. Chim. Acta*, **8**, 306 (1925).
6. Ott, *Ann.*, **401**, 159 (1913).
7. See reference 2, p. 136.
8. Taufen and Murray, *J. Am. Chem. Soc.*, **67**, 754 (1945).
9. Volhard, *Ann.*, **242**, 161 (1887).

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

red phosphorus

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

ethyl acetate (141-78-6)

ether (60-29-7)

aniline (62-53-3)

sodium hydroxide (1310-73-2)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

oxygen (7782-44-7)

phosphorus tribromide (7789-60-8)

nitrogen (7727-37-9)

zinc,
zinc turnings (7440-66-6)

phenolphthalein (77-09-8)

isobutyryl chloride (79-30-1)

phosphorous acid (13598-36-2)

isobutyric acid (79-31-2)

Dimethylketene,
Ketene, dimethyl- (598-26-5)

α-bromoisobutyryl bromide (20769-85-1)

Isobutyroanilide (4406-41-1)

isobutyrylphthalimide

dimethylmalonic anhydride

α-carbomethoxy-α, β-dimethyl-β-butyrolactone

α-bromoisobutyric acid (2052-01-9)