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.

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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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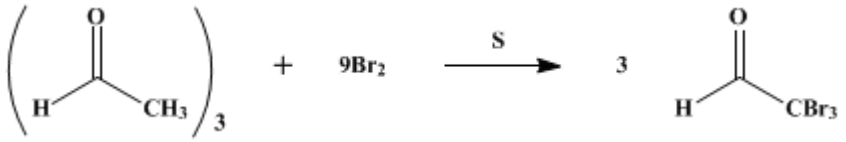
BROMAL



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1. Procedure

In a 2-l. three-necked, round-bottomed flask, fitted with a liquid-sealed mechanical stirrer, a dropping funnel, and an efficient reflux condenser, are placed 720 g. (230 cc., 4.5 moles) of bromine (Note 1) and 1.5 g. of sulfur (Note 2). A glass tube is connected to the top of the condenser to carry the evolved hydrogen bromide to a gas trap. Sixty-nine grams (69 cc., 0.52 mole) of dry paraldehyde (Note 1) is added slowly, with stirring, over a period of about four hours. The reaction proceeds under its own heat during the addition of the paraldehyde; subsequently the mixture is heated externally for two hours at 60–80°. The solution is distilled and a fraction collected over the range 155–175° (Note 3).

On redistillation under reduced pressure there is obtained 220–240 g. (52–57 per cent of the theoretical amount) of reddish yellow bromal, boiling at 59–62°/9 mm., or 71–74°/18 mm.

2. Notes

1. The bromine is dried by shaking with concentrated sulfuric acid; the paraldehyde is dried over calcium chloride.
2. The use of sulfur as a catalyst increases the yield 5–10 per cent and causes no trouble in the purification.
3. The fore-run amounts to 90–180 g. and consists mostly of bromine, bromoacetaldehyde, and dibromoacetaldehyde. An additional quantity of bromal may be obtained by treating this material with a small amount of bromine, heating for two hours at 60–80°, and distilling as before.

3. Discussion

Bromal has been prepared by brominating a solution of paraldehyde in ethyl acetate,[1] by passing bromine vapor through absolute alcohol,[2] and by treatment of chloral with a metallic bromide.[3]

References and Notes

1. Pinner, Ann. **179**, 67 (1875).
2. Schäffer, Ber. **4**, 366 (1871).
3. Müller, U. S. pat. 2,057,964 [C. A. **31**, 112 (1937)].

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

metallic bromide

alcohol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

ethyl acetate (141-78-6)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

sulfur (7704-34-9)

Bromal (115-17-3)

dibromoacetaldehyde

chloral (75-87-6)

bromoacetaldehyde (17157-48-1)

paraldehyde (123-53-7)