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.

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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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Organic Syntheses, Coll. Vol. 1, p.15 (1941); Vol. 6, p.1 (1926).

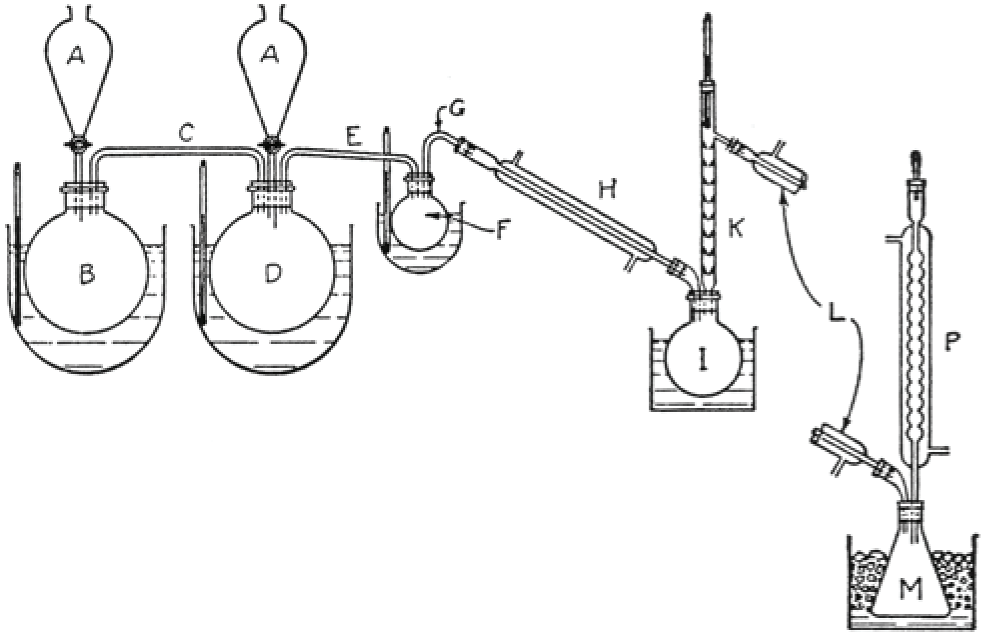
ACROLEIN

Submitted by Homer Adkins and W. H. Hartung.
Checked by Frank C. Whitmore and M. L. Wolfrom.

1. Procedure

The apparatus is assembled according to Fig. 1. B and D are 5-l. round-bottomed flasks, immersed to about two-thirds of their height in deep oil baths heated by large burners. Each bath is provided with a thermometer reaching to the level of the bottom of the flask. Flask B is fitted with a specially treated two-holed cork stopper (Note 1), in one hole of which is fitted a 500-cc. separatory funnel A and in the other a delivery tube C of 12-mm. diameter. The tubes must not extend more than 3 mm. below the stopper. Flask D is fitted with a three-holed cork stopper connected with a separatory funnel, the delivery tube from B, and the delivery tube E of 12-mm. tubing leading to flask F. F is a 500-cc. round-bottomed flask immersed to two-thirds of its height in an oil bath heated by a Bunsen burner and provided with a thermometer.

Fig. 1.



Flask F is provided with a two-holed cork stopper connected with tube E, and with tube G which connects with the first condenser H and may be of smaller bore than tubes C and E. H is a condenser with a 30-cm. water jacket. H is connected with I by means of an adapter. I is a 1-l. round-bottomed flask supported in a pan which is at first filled with ice and later used as a water bath. Flask I is fitted with a two-holed cork stopper carrying the adapter connected with condenser H and a Vigreux column K of 2-cm. diameter and a length of 30 cm. to the side arm. Flask I and condenser H are covered with black cloth (Note 2). The side arm of K is connected with a 90-cm. water-jacketed condenser L which leads into M through an adapter. M is a 750-cc. Erlenmeyer flask immersed in an ice bath. Flask M is provided with a two-holed stopper connected with the adapter from L and an upright bulb condenser that is provided with a tube leading through a window or to a hood.

Before the final assembling of the apparatus, the flasks are charged as follows: One kilo of freshly fused and finely powdered acid potassium sulfate, 200 g. of powdered potassium sulfate, and 300 g. (238 cc.) of dry glycerol (Note 3) are thoroughly mixed in each of flasks B and D. In each of flasks I and M is placed about 1 g. of hydroquinone to act as a stabilizer for the acrolein.[1]

The apparatus is assembled as indicated and the oil baths under B and D are heated to about 190–200° (Note 4), and the oil bath under F to about 110–120°. The bath under I is filled with ice. The volatile products are collected in I which is kept carefully protected from light. When the reaction is well started 300 g. of dry glycerol is placed in each separatory funnel, and added drop by drop during the heating. After the first violent reaction has abated (about one hour) the baths under B and D are raised to 215–230° and maintained there until no more volatile product comes over (a total time of heating of about four and one-half hours). After B and D have been heated about four hours the ice under I is replaced by water which is heated to 75–80° to distil the acrolein into flask M, which is packed in ice. Near the end of the distillation the water under I is heated to boiling.

The product in M is treated with small amounts of solid sodium bicarbonate to neutralize any acid present. The cold liquid is filtered through a small filter into a 1500-cc. distilling flask containing about 1 g. of hydroquinone. It is then distilled into a tared dark bottle containing about 1 g. of hydroquinone. The yield of product boiling at 52.5–55.5° (Note 5) obtained from 1200 g. (13 moles) of dry glycerol is 240–350 g. (33–48 per cent of the theoretical amount).

2. Notes

1. The corks used in the apparatus are made tight and heat-resistant by treatment with sodium silicate solution. After being properly fitted and bored they are placed in the silicate solution contained in a bottle that is connected with a suction pump. The solution is forced into the pores of the corks by alternately making and breaking the reduced pressure and shaking the solution vigorously. After the excess of solution has been wiped off, the corks are put in place while still wet. After this the outside of each cork is given an extra coat of the silicate solution. When corks treated in this way were used no odor of acrolein was noted in the laboratory.
Acrolein has pronounced lachrymatory properties and is also highly toxic.
2. The exclusion of light slows up the polymerization of the acrolein. If the condensers are not protected from light a solid polymer collects in them.
3. The glycerol is dried by heating slowly in an open dish in a hood until the temperature of the liquid is 170°. A sand bath is used and the heating requires about three hours. "Dynamite glycerine," 96–98 per cent, may be used instead of the dried glycerol.
4. The heating must not be too rapid nor too high at first as there is danger of frothing followed by a clogging of the apparatus.
5. Pure acrolein boils at 52.5°/760 mm.[2]

3. Discussion

Acrolein can be prepared by heating glycerol with magnesium or alkali sulfates under various conditions,[3] by heating glycerol with a "bleaching earth" catalyst,[4] from glycerol with iron and lithium phosphates as catalysts,[5] from epichlorohydrin by heating with water and an inorganic acid,[6] and from propylene with aqueous sulfuric acid and mercuric sulfate.[7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 166
- Org. Syn. Coll. Vol. 1, 506
- Org. Syn. Coll. Vol. 2, 137
- Org. Syn. Coll. Vol. 3, 502

References and Notes

1. Moureu, Compt. rend. **170**, 26 (1920).
2. Moureu, Boutaric and Dufraisse, J. chim. phys. **18**, 333 (1921).
3. Wohl and Mylo, Ber. **45**, 2046 (1912); Witzemann, J. Am. Chem. Soc. **36**, 1766 (1914); Moureu and Lepape, Compt. rend. **169**, 885 (1919); Ann. chim. (9) **15**, 176 (1921); Evans and Haas, J. Am. Chem. Soc. **48**, 2703 (1926).
4. Freund, U. S. pat. 1,672,378 [C. A. **22**, 2571 (1928)].
5. Schering-Kahlbaum A.-G., Fr. pat. 695,931 [C. A. **25**, 2740 (1931)].
6. Shell Development Company, U. S. pat. 2,106,347 [C. A. **32**, 2542 (1938)].
7. E. I. du Pont de Nemours and Co., U. S. pat. 2,197,258 [C. A. **34**, 5468 (1940)].

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

acid potassium sulfate

Dynamite glycerine

alkali sulfates

lithium phosphates

sulfuric acid (7664-93-9)

Acrolein (107-02-8)

potassium sulfate (37222-66-5)

glycerol (56-81-5)

hydroquinone (123-31-9)

sodium bicarbonate (144-55-8)

sodium silicate

silicate (15593-90-5)

magnesium (7439-95-4)

iron (7439-89-6)

Epichlorohydrin (106-89-8)

propylene (115-07-1)