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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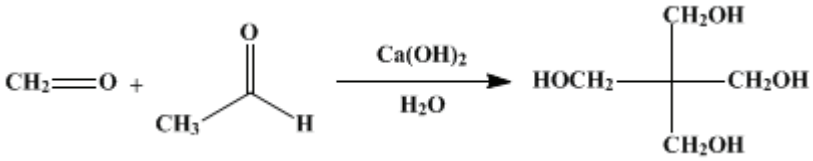
Organic Syntheses, Coll. Vol. 1, p.425 (1941); Vol. 4, p.53 (1925).

PENTAERYTHRITOL



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1. Procedure

To a suspension of 800 g. of paraformaldehyde (corresponding to 26.7 moles of formaldehyde) (Note 1) in 5.5 l. of water containing 210 g. (4.77 moles) of acetaldehyde there is added 180 g. (3.22 moles) of powdered quicklime in small portions with vigorous mechanical stirring (Note 2). The rate of addition is so adjusted that the temperature rises to 50° in thirty minutes, and during the subsequent additions the temperature of the mixture is not allowed to exceed 55°. The mixture takes on a slightly yellow color. After the addition is complete, stirring is continued for three hours, the mixture is filtered by gravity, and the yellow filtrate is acidified with just enough dilute hydrochloric acid to give an acid reaction to litmus. Subsequent to the addition of 30 g. of Norite and stirring for five minutes, the solution is again filtered.

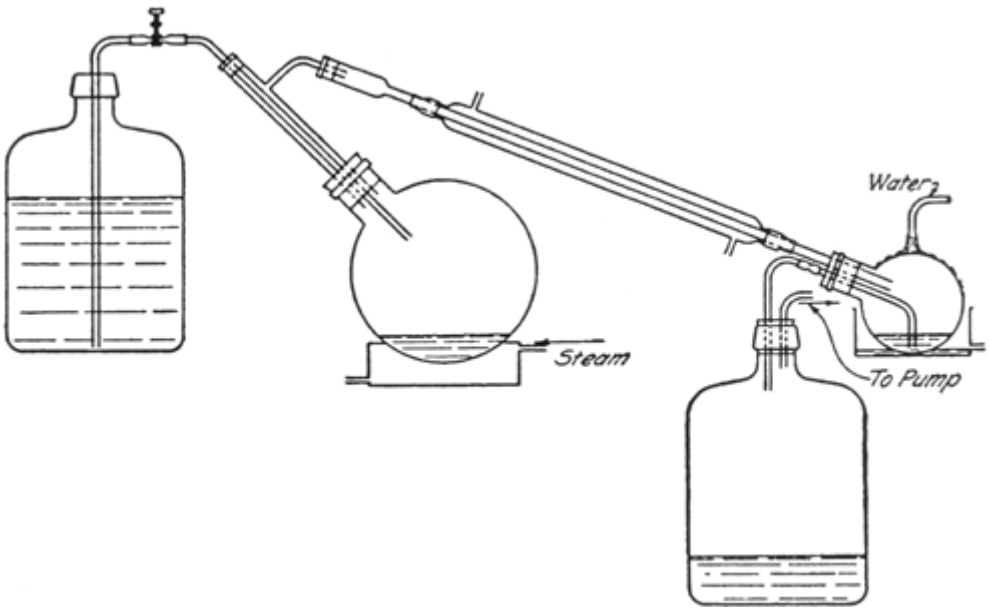
The filtrate, which should be colorless, is concentrated on the steam bath under reduced pressure (Fig. 23) (Note 3) until crystalline material begins to separate. The liquor, amounting to approximately 3 l., is heated on the steam bath at atmospheric pressure and filtered with suction while hot, any crystals remaining on the filter being washed through by aspiration of wet steam. The filtrate is allowed to stand in the refrigerator overnight and the first crop of crystals filtered off. This weighs approximately 300 g. and melts at about 237° (corr.). The mother liquor is concentrated to approximately 2 l. and a second crop obtained as above; this weighs 60–70 g. and melts at 242° (corr.). A third crop of 50–60 g. melting at 249° (corr.) is obtained by concentrating the mother liquor to 1.2 l. The mother liquor is finally concentrated to a sirup, when a fourth crop weighing about 10 g. and melting at 248° (corr.) is obtained.

The combined product, weighing 410-420 g., is recrystallized from an equal weight of hot water containing 10 cc. of concentrated hydrochloric acid. The color is removed by the addition of 5 g. of Norite. By suitably concentrating the mother liquors, second, third, and fourth crops may be obtained, all of which appear to be of the same purity as the first crop. The total yield is 360–370 g. (55-57 per cent of the theoretical amount) of a product melting at 258–260° (corr.) and containing negligible amounts of calcium (Note 4). The final residue, amounting to 20–30 g., leaves a considerable quantity of ash on ignition.

2. Notes

1. Since commercial paraformaldehyde contains varying amounts of moisture, the latter must be determined and the amount taken must be based on the actual paraformaldehyde content.
2. The reaction may conveniently be carried out in a crock covered to minimize losses by evaporation.
3. The apparatus shown in Fig. 23 has been found convenient for such evaporations under reduced pressure. The distillation is started with 3.5–4 l. in the 12-l. flask, and the level of liquid is maintained by controlling the rate of addition by means of a screw clamp. A 2-l. flask has been found satisfactory for the condensing intermediate receiver, provided that the outside is completely wetted by the cold water.

Fig. 23.



It has been recommended that some paraffin wax be added to prevent severe frothing during evaporation.

4. The product should give only a slight opalescence when a concentrated solution is treated with ammonium oxalate.

It has been shown[1] that pentaerythritol prepared as above always contains an appreciable proportion of dipentaerythrityl ether, m.p. 221°, which cannot be removed by recrystallization from hot water but forms a more soluble tetranitrate. Pure pentaerythritol, prepared from the purified tetranitrate, is stated to melt at 260°.

3. Discussion

Pentaerythritol can be prepared by condensing acetaldehyde with formaldehyde in aqueous solution by means of calcium hydroxide or barium hydroxide.[2] The patents covering this process are too numerous to review. The procedure described has proved rather more convenient than that previously published in this series.[3] Paraformaldehyde is stated[4] to give a better yield than formalin.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 49
- Org. Syn. Coll. Vol. 2, 135
- Org. Syn. Coll. Vol. 2, 476
- Org. Syn. Coll. Vol. 2, 545

References and Notes

1. Friedrich and Brün, Ber. **63**, 2681 (1930).
2. Tollens and Wigand, Ann. **265**, 316 (1891); Rave and Tollens, Ann. **276**, 58 (1893); Stettbacher, Z. ges. Schiess-Sprengstoffw. **2**, 182 (1916) [C. A. **11**, 2543 (1917)]; Rheinisch-Westfälische Sprengstoff-A. G., Ger. pat. 298,932 [Frdl. **13**, 86 (1923)]; Ger. pat. 390,622 [Frdl. **14**, 167 (1926)]; Burke, U. S. pat. 1,716,110 [C. A. **23**, 3717 (1929)]; Friedrich and Brün, Ber. **63**, 2681 (1930); Backer and Schurink, Rec. trav. chim. **50**, 923 (1931); Corbellini and Langini, Giorn. chim. ind. applicata **15**, 53 (1933) [C. A. **27**, 4256 (1933)].
3. Chemical Laboratory, Picatinny Arsenal, Org. Syn. **4**, 53 (1925); Aaronson, U. S. pat. 1,678,623 [C. A. **22**, 3418 (1928)].

4. Radulescu and Tanasescu, Bull. soc. sci. Cluj **1**, 528 (1923) [C. A. **19**, 494 (1925)].

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

quicklime

tetranitrate

acetaldehyde (75-07-0)

hydrochloric acid (7647-01-0)

formaldehyde,
formalin (50-00-0)

Norite (7782-42-5)

calcium (7440-70-2)

barium hydroxide (17194-00-2)

calcium hydroxide

Pentaerythritol (115-77-5)

ammonium oxalate (1113-38-8)

dipentaerythrityl ether

paraformaldehyde (30525-89-4)