



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](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.

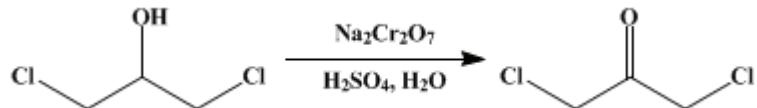
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 1, p.211 (1941); Vol. 2, p.13 (1922).*

## **$\alpha,\gamma$ -DICHLOROACETONE**

### [2-Propanone, 1,3-dichloro-]



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### 1. Procedure

In a 2-l. flask are placed 375 g. (1.3 moles) of commercial sodium dichromate (Note 1), 225 cc. of water, and 300 g. (2.3 moles) of glycerol  $\alpha,\gamma$ -dichlorohydrin (p. 292) (b.p. 68–75°/14 mm.). The flask is set in a water bath and equipped with a thermometer and a mechanical stirrer (Note 2). The contents are vigorously stirred, and 450 g. (245 cc.) of concentrated sulfuric acid, diluted with 115 g. of water, are introduced during the course of seven to eight hours. It is convenient to add the acid at ten-minute intervals. The temperature is kept between 20° and 25° during the entire reaction; this is accomplished by adding a little ice to the water bath from time to time. The stirring is continued for sixteen to seventeen hours after all the acid has been added; as there is very little heat evolved during this part of the reaction, the water bath may be allowed to come to room temperature (Note 3).

Sufficient water (300–800 cc.) is now added to the mixture to dissolve the pasty chromium salts (Note 4). The mass of crystals is then rapidly filtered on a Büchner funnel and sucked as dry as possible. The crystals are then transferred to a small laboratory centrifuge and centrifuged for several minutes. The crystals are washed in the centrifuge with about 15–25 cc. of ice water, then with 10–15 cc. of cold petroleum ether, and finally centrifuged until as dry as possible (Note 5). The crude dichloroacetone is dried in a vacuum desiccator over sulfuric acid overnight. It weighs about 220 g.

The crude product is best purified by distillation from a 250-cc. distilling flask fitted with an air condenser. A very small fraction (10–15 g.) of low-boiling material is obtained, and the dichloroacetone (170–175°) is then collected. It solidifies in the receiver to a white crystalline mass which weighs 200–220 g. (68–75 per cent of the theoretical amount). A few grams more may be obtained by chilling the low-boiling fraction and filtering off the water.

### 2. Notes

1. Commercial sodium dichromate is hygroscopic and contains varying amounts of water. The 375 g. required in these directions is equivalent to 319 g. of anhydrous material.
2. Great caution should be exercised in working with dichloroacetone, as it is extremely lachrymatory and blisters the skin.
3. The total time required for the oxidation is twenty-four hours. It is convenient to start the reaction in the morning. In this way the last part of the reaction, which requires no attention, will be accomplished during the night. The regulation of the temperature is necessary, as the reaction proceeds very slowly below 20°; on the other hand, the dichloroacetone itself is oxidized at a somewhat higher temperature than 25°.
4. In transferring the crystals from the reaction flask to the Büchner funnel it is necessary to use a certain amount of water to dissolve the pasty chromium salts which are otherwise quite impossible to filter. The amount necessary varies greatly in different runs, according to the manner in which the chromium salts separate. The amount of this water is kept low in order to dissolve as little of the product as possible. Nevertheless, 10–15 g. of dichloroacetone are thus dissolved; this material, together with a little unchanged dichlorohydrin, may be recovered by a long procedure involving extraction with ether and sodium bisulfite. This is not profitable, however.
5. It is not necessary to wash the crystals in the centrifuge until they are white. A small amount of

chromic salt will not interfere with the subsequent purification.

### 3. Discussion

$\alpha,\gamma$ -Dichloroacetone can be prepared by the direct chlorination of acetone;<sup>1</sup> by the oxidation of glycerol  $\alpha,\gamma$ -dichlorohydrin;<sup>2</sup> by the action of hypochlorous acid on 2,3-dichloropropene;<sup>3</sup> and by the action of sulfur monochloride on epichlorohydrin.<sup>4</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 292

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### References and Notes

1. Fittig, Jahresber. 345 (1859); Barbaglia, Ber. **7**, 467 (1874); Bischoff, Ber. **8**, 1330, 1438 (1875); Fritsch, Ber. **26**, 598 (1893); Ann. **279**, 315 (1894); Posner and Ronde, Ber. **42**, 3233 (1909).
2. Glutz and Fischer, Jahresber. 531 (1871); J. prakt. Chem. (2) **4**, 52 (1871); Markownikov, Ber. **6**, 1210 (1873); Ann. **208**, 355 (1881); Hoermann, Ber. **13**, 1706 (1880); Grimaux and Adam, Bull. soc. chim. (2) **36**, 19 (1881); Clöez, Ann. chim. phys. (6) **9**, 145 (1886); Erlenbach, Ann. **269**, 46 (1892); Posner and Rohde, Ber. **42**, 3233 (1909).
3. Henry, Compt. rend. **94**, 1428 (1882).
4. Malinovskii, J. Gen. Chem. (U.S.S.R.) **9**, 832 (1939) [C. A. **34**, 375 (1940)].

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

petroleum ether

Glycerol  $\alpha,\gamma$ -dichlorohydrin

chromium salts

dichlorohydrin

chromic salt

sulfuric acid (7664-93-9)

ether (60-29-7)

Epichlorohydrin (106-89-8)

sodium bisulfite (7631-90-5)

acetone (67-64-1)

sodium dichromate (7789-12-0)

hypochlorous acid (7790-92-3)

*α,γ*-Dichloroacetone,  
2-Propanone, 1,3-dichloro- (534-07-6)

dichloroacetone (513-88-2)

2,3-dichloropropene (78-88-6)

sulfur monochloride

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