



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.

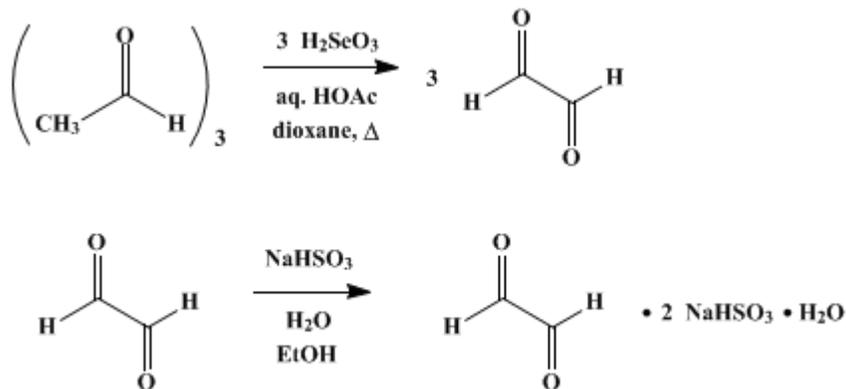
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.438 (1955); Vol. 24, p.61 (1944).

GLYOXAL BISULFITE



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1. Procedure

In a 2-l. round-bottomed flask, attached to an efficient reflux condenser (Note 1) and set in a hot water bath, are placed 222 g. (1.72 moles) of selenious acid (Note 2), 270 ml. of paraldehyde (Note 3), 540 ml. of dioxane, and 40 ml. of 50% acetic acid (Note 4), and the mixture is refluxed for 6 hours (Note 5). The solution is then decanted from the inorganic material (Note 6), which is washed with two 150-ml. portions of water. The combined solutions are steam-distilled through a still head (p. 65) until the paraldehyde and dioxane have been removed; this requires about 3.5 hours (Note 7). The mixture is decanted from a little selenium (Note 6), and to the solution, without filtration, is added a slight excess of 25% lead acetate solution (Note 8) and (Note 9). The lead selenite is removed by filtration, and the filtrate is saturated with hydrogen sulfide in a hood (Note 8). Then 20 g. of Norit is added; the whole is warmed to 40° in a hood and filtered with suction. The water-clear solution is concentrated on a hot water bath under reduced pressure to about 150 ml. in the usual apparatus (Note 10).

This concentrate is added to a previously prepared and filtered solution of sodium bisulfite in 40% ethanol (Note 11) contained in a 4-l. beaker provided with a mechanical stirrer (Note 12). The mixture is stirred for 3 hours, and the addition product then is filtered with suction on an 18-cm. Büchner funnel and washed, first with two 150-ml. portions of ethanol and then with 150 ml. of ether. The yield of air-dried product is 350–360 g. (72–74%, based on the selenious acid used) (Note 13).

2. Notes

1. The loss of large quantities of acetaldehyde is avoided by use of a spiral condenser, with sufficient heating so that a vapor lock is formed—the entrapped liquid should fill about two-thirds of the spiral. In cold weather, the tap water is usually cold enough so that any efficient long condenser, or two in series, is sufficient.
2. The selenious acid does not need to be freshly prepared. A larger amount does not increase the yield. The submitters specified selenium dioxide as the oxidizing agent, but the checkers prepared their material by evaporating an aqueous solution to dryness on the water bath. They, therefore, have considered the oxidizing agent to be selenious acid and have calculated the yield on this basis. If this product is in reality selenium dioxide, then the yield is 62–64%, and 222 g. is 2.0 moles.
3. This amount of paraldehyde represents a considerable excess over the theoretical but was found to be most satisfactory.
4. Acetic acid appears to function both as an accelerator for the oxidation and an inhibitor of the rearrangement to glycolic acid.
5. This is regulated by the temperature of the water bath, 65–80° being the required range.
6. This material, impure selenium, may be reoxidized,¹ and then it is suitable for a subsequent

preparation. About 130 g. is recovered at this point, and 8–10 g. after the concentration.

7. Alternatively, direct distillation may be employed; this requires only 2.5 hours but demands more attention. The volume is reduced to 200–300 ml., and then 800 ml. of water is added.

8. A test sample is filtered, and the clear filtrate is treated with more of the reagent to determine the end point.

9. [Lead acetate](#) is more satisfactory than [sulfur dioxide](#) for the removal of [selenious acid](#), provided that the solution is kept cool and a large excess is avoided.

10. This volume of solution is most easily handled. Should [glyoxal](#) itself be desired, the solution may be evaporated to dryness in a desiccator. The product thus obtained is identical with that sold as "polyglyoxal."

11. The solution is prepared by dissolving 312 g. of technical [sodium bisulfite](#) in 2.1 l. of warm (about 40°) water, and adding 1.4 l. of 95% [ethanol](#).

12. Alternatively, this may be done in a flask, which is shaken by hand frequently to prevent formation of a solid cake. The use of a stirrer results in a granular product. The mother liquor retains about 7 g. of [glyoxal bisulfite](#) per liter.

13. This product is pure enough for most purposes. It can be recrystallized by dissolving it in water and adding enough alcohol to make a 40% solution. The recovery is 90–92%.

3. Discussion

[Glyoxal](#) has been obtained by several methods, only a few of which are of preparative value. The most feasible are the oxidation of [acetaldehyde](#) by nitric^{2,3,4} or selenious⁵ acid; the hydrolysis of [dichlorodioxane](#);⁶ and the hydrolysis of the product resulting from the action of fuming [sulfuric acid](#) upon tetrahaloethanes.⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 824](#)

References and Notes

1. [Org. Syntheses Coll. Vol. 2, 510, Note 2 \(1943\)](#).
2. Lubawin, *Ber.*, **8**, 768 (1875).
3. Wyss, *Ber.*, **10**, 1366 (1877).
4. Behrend and Kölln, *Ann.*, **416**, 230 (1918).
5. Riley, Morley, and Friend, *J. Chem. Soc.*, **1932**, 1881.
6. Butler and Cretcher, *J. Am. Chem. Soc.*, **54**, 2988 (1932).
7. Ott, Ger. pat. 362,743 [*C. A.*, **18**, 991 (1924)].

Appendix

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

[ethanol](#) (64-17-5)

[acetaldehyde](#) (75-07-0)

[sulfuric acid](#) (7664-93-9)

[acetic acid](#) (64-19-7)

ether (60-29-7)

glyoxal (107-22-2)

hydrogen sulfide (7783-06-4)

sulfur dioxide (7446-09-5)

sodium bisulfite (7631-90-5)

Norit (7782-42-5)

selenium dioxide (7446-08-4)

lead acetate

dioxane (5703-46-8)

selenium

glycolic acid (79-14-1)

selenious acid (7783-00-8)

Glyoxal bisulfite (18381-20-9)

dichlorodioxane

lead selenite

paraldehyde (123-53-7)