Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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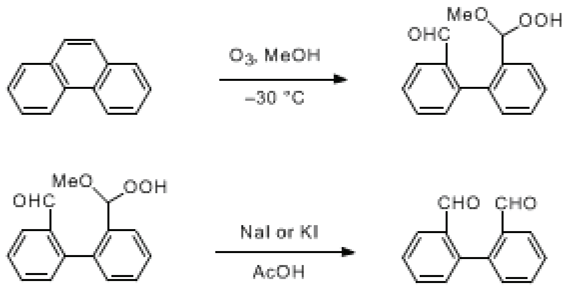
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.041.0041

Organic Syntheses, Coll. Vol. 5, p.489 (1973); Vol. 41, p.41 (1961).

DIPHENALDEHYDE

[Biphenyl, 2,2'-diformyl-]



Submitted by Philip S. Bailey and Ronald E. Erickson[1].
Checked by Marjorie C. Caserio and John D. Roberts.

1. Procedure

Caution! Ozone is extremely toxic and can react explosively with certain oxidizable substances. Ozone also reacts with some compounds to form explosive and shock-sensitive products. Ozone should only be handled by individuals trained in its proper and safe use and all operations should be carried out in a well-ventilated fume hood behind a protective safety shield. [Note added September 2009].

A finely divided suspension (Note 1) and (Note 2) of 10.0 g. (0.056 mole) of phenanthrene (Note 3) in 200 ml. of dry methanol (Note 4) is placed in a standard ozonolysis vessel (Note 5). The reaction mixture is cooled in a Dewar flask by an acetone-Dry Ice mixture to about −30° (Note 6) and (Note 7), and ozone (Note 8) is passed through at a rate of about 20 l. per hour (Note 9) until all the phenanthrene has reacted (Note 10).

To the cooled reaction mixture are added 25–30 g. (roughly 1.5 times the theoretical 0.112 mole) of sodium or potassium iodide and 30 ml. of glacial acetic acid (Note 11). After the addition, the reaction mixture is allowed to stand at room temperature for 30 minutes to 1 hour. The released iodine is reduced with 10% sodium thiosulfate solution, after which the reaction mixture is placed immediately under an air blast (Note 12). As the methanol evaporates, the product begins to crystallize (Note 13). The crystallization should be well advanced by the time most of the methanol has evaporated. Water is then added, and the solid is removed by filtration and dried. The yield of crude product, softening at about 54° and melting at 59–62°, is 9.2–11.4 g. (78–96%). The crude product may be recrystallized by dissolving it in the minimal amount (40–50 ml.) of dry ether and slowly adding about 150 ml. of ligroin (Note 14). Small crystals separate halfway through the addition, and crystallization is completed by cooling the mixture in an acetone-Dry Ice bath. An 80–90% recovery of pale yellow crystals melting at 62–63° is obtained. A second recrystallization from 70% aqueous ethanol gives nearly colorless crystals melting at 62.5–63.5° (Note 15).

2. Notes

1. This is produced by dissolving the phenanthrene in the refluxing solvent and cooling rapidly.

2. The finely divided suspension is necessary in order for the phenanthrene to go into solution and react readily during the ozonolysis.

3. Eastman white label 599, m.p. 99–100°, was used.

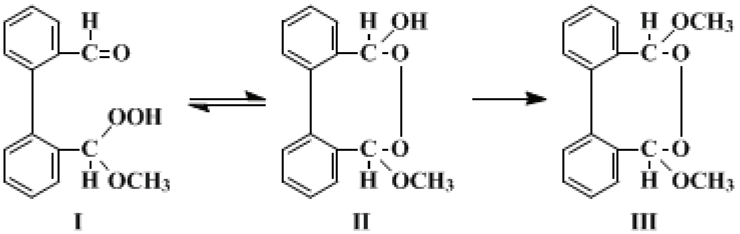
4. Commercial methanol reagent containing 0.1% or less of water is satisfactory.

5. The usual long, cylindrical, gas-absorption-type vessel with an inlet tube extending to near the bottom is satisfactory.[2] The total volume of the vessel should be at least twice that of the reaction solution. More elaborate reaction vessels equipped with a stirrer[3] are very useful in reactions such as this in which the reactant is suspended in the solvent. However, the commercially available vessels of this type are not large enough for the reaction mixture described here.

6. The temperature of the reaction mixture should not be allowed to rise above −20°, because at higher temperatures ozone tends to react with the solvent and the reactions shown below also occur. Compound III is not readily reduced to the dialdehyde.

7. Compound II may precipitate during ozonolysis at −30° or below. This is in no way detrimental.

8. A Welsbach T23 ozonator was used by the submitters. Oxygen dried by a Pittsburg Laboratory-Lectrodryer to a dew point of −60° was passed through the ozonator, which was set to produce a 5–6% by weight concentration of ozone.[4] Following the ozonation flask were a potassium iodide trap and a wet-test meter.[4] The checkers used a simple ozonator capable of producing 3.8% by weight of ozone at a flow rate of 20 l. per hour from oxygen dried by passage through a 30-cm. column of silica gel.



9. The rate should be sufficiently great to cause considerable agitation of the suspended phenanthrene. As the reaction proceeds, the reaction vessel should be shaken frequently in order to maintain good contact between the phenanthrene and ozone. For smaller runs a reaction vessel that includes a stirrer is advantageous (Note 5).

The checkers found it convenient to use leads of Tygon tubing of sufficient length to allow the reaction flask to be withdrawn at intervals from the Dewar flask and shaken manually.

10. Unreacted ozone starts passing through to the potassium iodide trap toward the end of the reaction. However, it is best to continue the reaction until all the suspended phenanthrene has disappeared. This usually requires a total of 1.1–1.3 mole-equivalents of ozone. Unless all the phenanthrene has reacted, difficulty is encountered in the crystallization and/or recrystallization of the dialdehyde.

11. The reduction may be carried out in the ozonolysis flask, or the reaction mixture may be transferred first to an Erlenmeyer flask or beaker. The iodide and acetic acid should be added simultaneously. The reaction of peroxides with iodide ion is exothermic. The temperature of the reaction mixture should be kept below −20° while the sodium iodide and acetic acid are added, after which it may be allowed to rise slowly to room temperature.

12. It seems to be detrimental to the crystallization and recrystallization of the product to postpone the evaporation of the reaction mixture, probably because the product becomes contaminated with sulfur if the reduced reaction mixture is allowed to stand.

13. Sometimes difficulty is encountered in starting the crystallization, since the product may separate as a yellow oil. It is helpful to induce crystallization by rubbing the sides of the vessel with a stirring rod and seeding the solution with any crystals that form on the sides of the vessel during the evaporation.

14. The ligroin used was Skellysolve B.

15. About 30 ml. of warm absolute ethanol readily dissolves 8–9 g. of product. Addition of 15 ml. of water and cooling effect crystallization with about 90% recovery of product.

3. Discussion

Previously, diphenaldehyde has been made by the Ullman coupling of *o*-iodobenzaldehyde,[5,6] by bromination of *o,o′*-bitolyl and hydrolysis of the resulting tetrabromo compound,[7] and by lithium aluminium hydride reduction of the N-methylanilide of diphenic acid.[8] These methods involve more steps and give poorer yields than ozonolysis of phenanthrene.

The present method is based on the earlier described ozonolysis of phenanthrene in methanol.[9] The reduction of the peroxidic reaction mixture with trimethyl phosphite to give diphenaldehyde, isolated as the di-*p*-nitrophenylhydrazone, in quantitative yield has been described recently.[10] The disadvantage of this method is that the dialdehyde cannot be isolated in the free state in high yield. Diphenaldehyde has also been obtained by sodium iodide reduction of peroxidic products from ozonolysis of phenanthrene in solvents that do not react[2] with the zwitterion intermediate.[11,12] The yields are inferior to those obtained by the present method. The aldehyde has been obtained in 91% yield using dimethyl sulfide as the reducing agent.[13] An 81% yield of diphenaldehyde has been obtained from the ozonolsis in acqueous *t*-butyl alcohol followed by distillation of the solvent at pH 7.5.[14] Hydrogen peroxide is a by-product.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 493
- Org. Syn. Coll. Vol. 6, 43

- Org. Syn. Coll. Vol. 7, 168

References and Notes

1. Department of Chemistry, University of Texas, Austin, Tex.
2. P. S. Bailey, *Chem. Revs.*, **58**, 985 (1958).
3. A. Maggiolo, *Organic Ozone Reactions and Techniques*, The Welsbach Corp., Ozone Porcesses Division, Philadelphia, Pa., Third Revision, 1956, pp. 21–22.
4. *Basic Manual of Applications and Laboratory Ozonization Techniques*, The Welsbach Corp., Ozone Processes Division, Philadelphia, Pa., First Revision, pp. 18–25.
5. F. Mayer, *Ber.*, **44**, 2304 (1911); **45**, 1107 (1912).
6. W. S. Rapson and R. G Shuttleworth, *J. Chem. Soc.*, 489 (1941).
7. J. Kenner and E. G. Turner, *J. Chem. Soc.*, **99**, 2112 (1911).
8. F. Weygand, G. Eberhardt, H. Linden, F. Schafer, and I. Eigen, *Angew. Chem.*, **65**, 525 (1953).
9. P. S. Bailey, *J. Am. Chem. Soc.*, **78**, 3811 (1956).
10. W. S. Knowles and Q. E. Thompson, *J. Org. Chem.*, **25**, 1031 (1960).
11. P. S. Bailey and S. B. Mainthia, *J. Org. Chem.*, **23**, 1089 (1958).
12. W. J. Schmitt, E. J. Moriconi, and W. F. O'Connor, *J. Am. Chem. Soc.*, **77**, 5640 (1955).
13. J. J. Pappas, W. P. Keaveney, E. Gancher, and M. Berger, *Tetrahedron Lett.*, 4273 (1966).
14. M. B. Sturrock, E. L. Cline, and K. R. Robinson, *J. Org. Chem.*, **28**, 2340 (1963).

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

ligroin

Diphenaldehyde

N-methylanilide of diphenic acid

di-p-nitrophenylhydrazone

ethanol (64-17-5)

acetic acid (64-19-7)

methanol (67-56-1)

ether (60-29-7)

oxygen (7782-44-7)

potassium iodide (7681-11-0)

sodium thiosulfate (7772-98-7)

sulfur (7704-34-9)

iodine (7553-56-2)

sodium (13966-32-0)

hydrogen peroxide (7722-84-1)

sodium iodide (7681-82-5)

ozone (10028-15-6)

iodide (20461-54-5)

dimethyl sulfide (75-18-3)

phenanthrene (85-01-8)

lithium aluminium hydride (16853-85-3)

t-butyl alcohol (75-65-0)

trimethyl phosphite (121-45-9)

Biphenyl, 2,2'-diformyl- (1210-05-5)

o-iodobenzaldehyde (26260-02-6)

o,o'-bitolyl (612-75-9)