



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.

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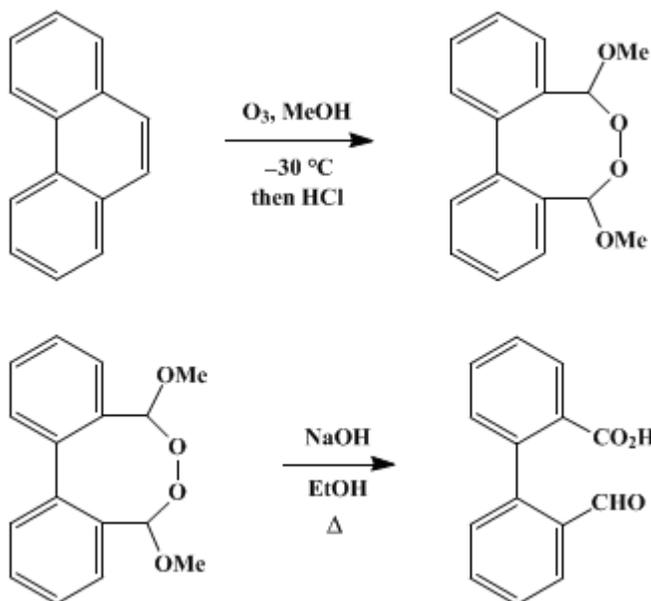
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.493 (1973); Vol. 41, p.46 (1961).*

## DIPHENALDEHYDIC ACID

### [2-Biphenylcarboxylic acid, 2'-formyl-]



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### 1. Procedure

A. *3,8-Dimethoxy-4,5,6,7-dibenzo-1,2-dioxacyclooctane*. The ozonolysis of 10 g. (0.0562 mole) of phenanthrene in dry methanol is carried out as described in the diphenaldehyde preparation (p. 489). The reaction mixture is not reduced, however, but is acidified with 1–3 drops of concentrated hydrochloric acid (Note 1) and allowed to stand at room temperature for an hour and then in the refrigerator for several hours or overnight. Suction filtration yields 11.5–12.5 g. (75–82%) of crystals melting at  $178$ – $181^\circ$ . Trituration with methyl ethyl ketone gives a 90–95% recovery of colorless crystals melting at  $180$ – $181^\circ$  (Note 2).

B. *Diphenaldehydic acid*. A mixture of 10 g. (0.0368 mole) of 3,8-dimethoxy-4,5,6,7-dibenzo-1,2-dioxacyclooctane, 50 ml. of 10% sodium hydroxide solution, and 200 ml. of 95% ethyl alcohol is heated under reflux for 15 minutes, during which time the solid dissolves (Note 3). The solution is cooled, acidified with concentrated hydrochloric acid, and diluted to the cloud point with water. Crystallization is induced by rubbing the side of the vessel with a stirring rod (Note 4). More water is then added slowly until crystallization is complete. Filtration yields 6.7–7.3 g. (81–88%) of colorless to yellowish crystals melting at  $130$ – $132^\circ$ . Recrystallization from 100 ml. of 1:1 methanol-water gives an 80–95% recovery of diphenaldehydic acid melting at  $134$ – $135^\circ$  (Note 5), (Note 6), and (Note 7).

### 2. Notes

1. The acid catalyzes formation of the dimethoxy compound from the initial ozonolysis products (see Note 6 of the diphenaldehyde preparation, p. 490). Compound I forms only slowly in the absence of the hydrochloric acid.
2. The trituration is carried out at room temperature, but the mixture is cooled before filtering. The product can be recrystallized from methyl ethyl ketone, but this requires large volumes of the solvent and is unnecessary.
3. After solution has occurred, 1 ml. of the solution is acidified and tested with sodium or potassium

iodide. If no iodine is released, the reaction is complete.

4. If the solution resists crystallization, it can be evaporated one-half or two-thirds of its volume and cooled further. The checkers found that, if product was allowed to oil out and solidify, the subsequent purification was rendered more difficult.

5. Often recrystallization is unnecessary since the first crystalline product melts at 134–135°. The yields then are 81–84%.

6. If sodium hydroxide is omitted in this preparation and the reaction mixture is refluxed until it no longer gives a positive peroxide test with iodide ion (Note 3) (about 2 hours), the product is the methyl ester of diphenaldehydic acid in 91–98% yield (m.p. 50–51°).<sup>2</sup>

7. If, in the reaction mixture described, twice the volume of 10% sodium hydroxide solution and 25 ml. of 30% hydrogen peroxide are employed and the reaction mixture is refluxed until it no longer gives a positive peroxide test with iodide ion (about 30 minutes to 1 hour), the product is diphenic acid (m.p. 220–223°) in 73–85% yield.

### 3. Discussion

The method here described is based on the reported ozonolysis of phenanthrene in methanol, followed by conversion of the initial ozonolysis product to diphenaldehyde (p. 489), diphenaldehydic acid, methyl diphenaldehydate (Note 6), and diphenic acid (Note 7).<sup>2</sup> Diphenaldehydic acid has previously been made in low yields by oxidative decomposition of the monohydrazide of diphenic acid.<sup>3,4</sup> The presently described method is far superior, not only in yield, but also in simplicity.

Diphenic acid has been prepared by the reduction of diazotized anthranilic acid with cuprous ion,<sup>5</sup> Ullman coupling of potassium *o*-bromobenzoate,<sup>6</sup> and oxidation of phenanthrene or phenanthrenequinone with various oxidizing agents.<sup>7</sup> The latter methods have been reviewed recently.<sup>7</sup> The ozonolysis method has also been carried out in solvents<sup>8</sup> that do not react with the zwitterion intermediate.<sup>9</sup>

Of the various routes to diphenic acid, the present method and the peracetic acid oxidation of phenanthrene<sup>7</sup> seem to be the simplest. The yields are equally good.

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### References and Notes

1. Department of Chemistry, University of Texas, Austin, Tex.
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### Appendix

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

Diphenic acid

Diphenaldehyde

Diphenaldehydic acid

methyl ester of diphenaldehydic acid

methyl diphenaldehydate

ethyl alcohol (64-17-5)

hydrochloric acid (7647-01-0)

methanol (67-56-1)

sodium hydroxide (1310-73-2)

potassium iodide (7681-11-0)

iodine (7553-56-2)

sodium (13966-32-0)

hydrogen peroxide (7722-84-1)

Anthranilic Acid (118-92-3)

phenanthrenequinone (84-11-7)

methyl ethyl ketone (78-93-3)

phenanthrene (85-01-8)

peracetic acid (79-21-0)

potassium o-bromobenzoate

3,8-Dimethoxy-4,5,6,7-dibenzo-1,2-dioxacyclooctane (6623-54-7)

2-Biphenylcarboxylic acid, 2'-formyl- (6720-26-9)