



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.

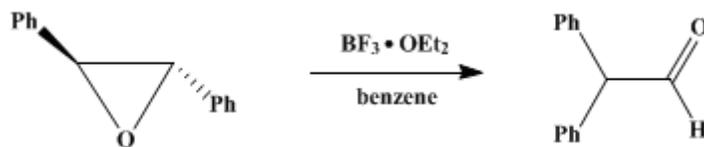
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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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## DIPHENYLACETALDEHYDE

### [Acetaldehyde, diphenyl-]



Submitted by Donald J. Reif and Herbert O. House<sup>1</sup>.

Checked by M. S. Newman and W. H. Powell.

### 1. Procedure

In a 1-l. separatory funnel is placed a solution of 39.2 g. (0.2 mole) of *trans*-stilbene oxide (Note 1) in 450 ml. of reagent benzene. To the solution is added 13.2 ml. (0.1 mole) of boron trifluoride etherate (Note 2). The solution is swirled, allowed to stand for 1 minute (Note 3), and then washed with two 300-ml. portions of water. The organic layer is separated, and the benzene is removed by distillation (Note 4). The residual crude aldehyde is purified by distillation under reduced pressure. The product, collected at 115–117°/0.6 mm., amounts to 29–32 g. (74–82%),  $n_D^{25}$  1.5875–1.5877 (Note 5).

### 2. Notes

1. The *trans*-stilbene oxide (p.860) should be free of *trans*-stilbene, since the stilbene, if present, is not altered by the reaction conditions and will contaminate the final product.
2. A practical grade of boron trifluoride etherate, purchased from Eastman Kodak Company, was redistilled before use. The pure etherate boils at 126°.
3. Longer reaction times result in a marked decrease in the yield of diphenylacetaldehyde.
4. The submitters found that distillation of the benzene solution is necessary to obtain an anhydrous product. If the benzene solution is dried over magnesium sulfate and the benzene removed under reduced pressure, the diphenylacetaldehyde is contaminated with water.
5. The product obtained by this procedure, when treated with 2,4-dinitrophenylhydrazine,<sup>2</sup> produced the 2,4-dinitrophenylhydrazone of diphenylacetaldehyde, m.p. 146.8–147.8°, in 94% yield.

### 3. Discussion

Diphenylacetaldehyde has been prepared by the isomerization of 1,2-dihydroxy-1,2-diphenylethane either thermally<sup>3</sup> or in the presence of sulfuric acid,<sup>4,5,6</sup> oxalic acid,<sup>7</sup> or acetic anhydride.<sup>8</sup> The aldehyde has also been produced by the reaction of 2,2-diphenyl-2-hydroxyethyl ether with sulfuric acid<sup>6,7</sup> or oxalic acid;<sup>7,9</sup> by the reaction of hydrochloric acid with 2-amino-1,1-diphenylethanol;<sup>10</sup> by the reaction of hydrobromic<sup>11</sup> or hydrochloric<sup>12</sup> acid with 2-diethylamino-1,1-diphenylethanol; by the hydrolysis of  $\beta,\beta$ -diphenylvinyl ethyl ether;<sup>13</sup> by the thermal rearrangement of deoxybenzoin;<sup>14</sup> by the hydrolysis and decarboxylation of the glycidic ester obtained from ethyl chloroacetate and benzophenone;<sup>15</sup> by passing a mixture of diphenylacetic and formic acid over thorium oxide on pumice at 450°;<sup>16</sup> and by the hydrolysis of diphenylacetaldehyde enol methyl ether (obtained from benzophenone and methoxymethylenetriphenylphosphorane).<sup>17</sup>

Diphenylacetaldehyde also has been prepared by the isomerization of *trans*-stilbene oxide in the presence of sodium bisulfite<sup>18</sup> or lithium diethylamide,<sup>19</sup> or by the isomerization of either *cis*- or *trans*-stilbene oxide in the presence of boron trifluoride etherate.<sup>2</sup> The procedure chosen illustrates the ready isomerization of substituted ethylene oxides to carbonyl compounds. The procedure is applicable to substituted epoxides in which one of the carbon atoms of the oxirane ring is bonded either to two other carbon atoms or to an aromatic nucleus or a carbon-carbon double bond.

This preparation is referenced from:

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## References and Notes

1. Massachusetts Institute of Technology, Cambridge, Massachusetts.
  2. House, *J. Am. Chem. Soc.*, **77**, 3070 (1955).
  3. Ramart-Lucas and Salmon-Legagneur, *Compt. rend.*, **186**, 1848 (1928).
  4. Henze and Leslie, *J. Org. Chem.*, **15**, 901 (1950).
  5. Tiffeneau, *Compt. rend.*, **142**, 1537 (1906); *Ann. chim. (Paris)*, [8] **10**, 322 (1906).
  6. Stoermer, *Ber.*, **39**, 2288 (1906).
  7. Danilov and Venus-Danilova, *Ber.*, **59B**, 1032 (1926).
  8. Tiffeneau, *Compt. rend.*, **150**, 1181 (1910).
  9. Behal and Sommelet, *Bull. soc. chim. France*, [3] **31**, 300 (1904).
  10. Thomas and Bettzieche, *Z. physiol. Chem.*, **140**, 261 (1924).
  11. Sou, *Bull. fac. sci. univ. franco-chinoise Peiping*, **1935**, No. 5, 1 [*C. A.*, **30**, 4463 (1936)].
  12. Bersch, Meyer, and Hubner, *Pharm. Zentralhalle*, **96**, 381 (1957) [*C. A.*, **52**, 13684 (1958)].
  13. Buttenberg, *Ann.*, **279**, 324 (1894).
  14. Brueur and Zincke, *Ann.*, **198**, 141 (1879).
  15. Ecary, *Ann. chim. (Paris)*, [12] **3**, 445 (1948).
  16. Haarmann & Reimer, Chemische Fabrik zu Holzminden G.m.b.H., Ger. pat. 825,085 [*C. A.*, **49**, 11713 (1955)].
  17. Wittig and Knauss, *Angew. Chem.*, **71**, 127 (1959).
  18. Klages and Kessler, *Ber.*, **39**, 1753 (1906).
  19. Cope, Trumbull, and Trumbull, *J. Am. Chem. Soc.*, **80**, 2844 (1958).
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## Appendix

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

2,4-dinitrophenylhydrazone

2,2-diphenyl-2-hydroxyethyl ether

deoxybenzion

diphenylacetic and formic acid

pumice

diphenylacetaldehyde enol methyl ether

Diphenylacetaldehyde

cis- or trans-stilbene oxide

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

[hydrochloric acid \(7647-01-0\)](#)

Benzene (71-43-2)  
acetic anhydride (108-24-7)  
Oxalic acid (144-62-7)  
sodium bisulfite (7631-90-5)  
thorium oxide  
carbon (7782-42-5)  
Benzophenone (119-61-9)  
oxirane (75-21-8)  
ethylene (9002-88-4)  
Ethyl chloroacetate (105-39-5)  
2,4-Dinitrophenylhydrazine (119-26-6)  
magnesium sulfate (7487-88-9)  
stilbene  
Diphenylacetaldehyde,  
Acetaldehyde, diphenyl- (947-91-1)  
boron trifluoride etherate,  
boron trifluoride etherate (109-63-7)  
1,2-dihydroxy-1,2-diphenylethane (52340-78-0)  
2-amino-1,1-diphenylethanol  
2-diethylamino-1,1-diphenylethanol  
 $\beta,\beta$ -diphenylvinyl ethyl ether  
methoxymethylenetriphenylphosphorane  
lithium diethylamide  
carbon-carbon  
trans-Stilbene oxide (1439-07-2)  
trans-Stilbene (103-30-0)