



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.

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.

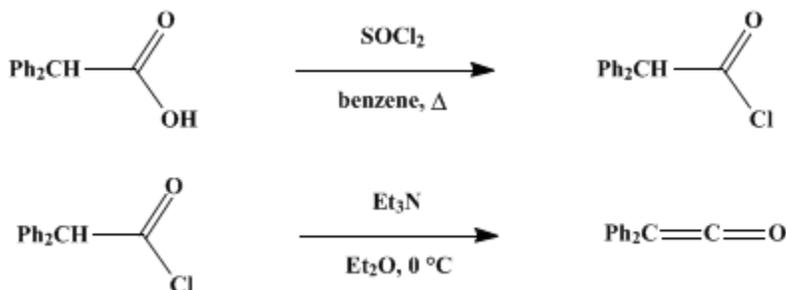
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.549 (1988); Vol. 52, p.36 (1972).

DIPHENYLKETENE

[Ethenone, diphenyl-]



Submitted by Edward C. Taylor¹, Alexander McKillop², and George H. Hawks.
 Checked by C. J. Michejda, D. D. von Riesen, R. W. Cornick, and Henry E. Baumgarten.

1. Procedure

Caution! Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

A. *Diphenylacetyl chloride.* A 500-ml., three-necked flask equipped with a dropping funnel and a reflux condenser carrying a calcium chloride drying tube is charged with 50.0 g. (0.236 mole) of diphenylacetic acid (Note 1) and 150 ml. of thiophene-free, anhydrous benzene. The mixture is heated under reflux, and 132 g. (80.1 ml., 1.11 mole) of thionyl chloride is added dropwise over 30 minutes. Refluxing is continued for 7 additional hours before the benzene and excess thionyl chloride are removed by distillation under reduced pressure. The pale yellow oil which remains contains a little thionyl chloride, best removed by adding 100 ml. of anhydrous benzene and again distilling under reduced pressure. The residue is dissolved in 150 ml. of refluxing, anhydrous hexane (Note 2). The hot solution is treated with charcoal and filtered, and the filtrate is chilled to 0° in a sealed flask. The product, which crystallizes as colorless plates (Note 3), is filtered, washed with a little cold hexane, dried at 25° under vacuum for 2 hours, and stored in a tightly stoppered bottle, giving 42–45 g. (77–84%) of product, m.p. 51–53°. Concentration of the hexane mother liquors to about 50 ml. followed by chilling to 0° and addition of a seed crystal gives an additional 2.5–4.0 g. (5–8%) of product of equal purity, for a total yield of 44.5–49 g. (82–94%) of diphenylacetyl chloride, m.p. 51–53° (Note 4).

B. *Diphenylketene.* A 500-ml., three-necked flask equipped with a magnetic stirring bar, a gas-inlet tube, a calcium chloride drying tube, and a dropping funnel is charged with a solution of 23.0 g. (0.0997 mole) of diphenylacetyl chloride in 200 ml. of anhydrous diethyl ether. The flask is cooled in an ice bath, dry nitrogen is passed through the system, and 10.1 g. (0.100 mole) of triethylamine is added dropwise over 30 minutes to the stirred solution; triethylamine hydrochloride precipitates as a colorless solid, and the ether becomes bright yellow in color. When addition of the triethylamine is complete, the flask is tightly stoppered and stored overnight at 0°. The hydrochloride is collected on a 9-cm., sintered glass funnel and washed with anhydrous ether until the washings are colorless. The ether is removed under reduced pressure; the residual red oil is transferred to a 50-ml., distilling flask fitted with a 10-cm. Vigreux column and distilled (Note 5), giving 10.2–10.8 g. (53–57%) of diphenylketene as an orange oil, b.p. 118–120° (1 mm.) (Note 6). It can be stored at 0° in a tightly stoppered bottle for several weeks without decomposition.

2. Notes

1. Superior grade diphenylacetic acid, m.p. 147–148° (Matheson, Coleman and Bell) was used without

further purification.

2. Commercial **hexane**, A. C. S. grade (Matheson, Coleman and Bell) was dried by distillation from **potassium hydroxide**.

3. **Diphenylacetyl chloride** crystallizes best when a seed crystal is added to the cold **hexane** solution. If, after several hours at 0°, crystallization has not commenced, scratching with a glass rod is sufficient to induce crystallization.

4. The checkers found it necessary to recrystallize the **diphenylacetyl chloride** twice to obtain the reported melting point.

5. Most of the **diphenylketene** distils cleanly at 118–119° (1 mm.) but strong heating is necessary for distillation of the final portion from the polymeric pot residue.

The checkers used a variety of different distillation setups. The best results were obtained when the oil being distilled filled the flask to about two-thirds its capacity, the Vigreux column was no longer than 10 cm. in length, the whole apparatus was kept as small as possible, and the distillation was conducted as rapidly as possible.

6. The submitters obtained yields of 73–84% on the scale described and yields of up to 70% on a scale twice that described. From IR analysis of the crude (undistilled) product the checkers concluded that this material represented a yield in excess of 80%. Thus, the critical step appears to be the distillation. The checkers have used the crude (undistilled) product for some applications, but this procedure has not been uniformly successful and is not recommended.

3. Discussion

Diphenylacetyl chloride has been obtained from the reaction of **diphenylacetic acid** with **phosphorus pentachloride**,³ **phosphorus oxychloride** and **phosphorus pentachloride**,⁴ or **thionyl chloride**.⁵ It has also been prepared by treatment of **diphenylketene** with **hydrogen chloride**.⁶ The methods of preparation of **diphenylketene** have been reviewed earlier in this series.⁷ To those cited should be added the debromination of **α-bromodiphenylacetyl bromide** with **triphenylphosphine**.⁸ The procedure above is a modification of that described by Staudinger.⁹

The present preparation consists of two very simple steps, uses relatively inexpensive starting materials, and does not involve hazardous or toxic chemicals or special apparatus. An important advantage is that the **diphenylketene**, until it is finally distilled, is never exposed to temperatures greater than 30–35°; hence polymerization is minimized (cf. ref. ⁶).

References and Notes

1. Department of Chemistry, Princeton University, Princeton, New Jersey 08540.
2. Present address: School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, United Kingdom.
3. F. Klingemann, *Justus Liebigs Ann. Chem.*, **275**, 50 (1893).
4. A. Bistrzycki and A. Landtwing, *Ber. Dtsch. Chem. Ges.*, **41**, 686 (1908).
5. W. A. Bonner and C. J. Collins, *J. Am. Chem. Soc.*, **75**, 5372 (1953).
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7. L. I. Smith and H. H. Hoehn, *Org. Synth.*, **Coll. Vol. 3**, 356 (1955).
8. S. D. Darling and R. L. Kidwell, *J. Org. Chem.*, **33**, 3974 (1968).
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Appendix

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

hydrogen chloride (7647-01-0)

Benzene (71-43-2)

ether,
diethyl ether (60-29-7)

phosphorus pentachloride (10026-13-8)

thionyl chloride (7719-09-7)

nitrogen (7727-37-9)

Phosphorus Oxychloride (21295-50-1)

potassium hydroxide (1310-58-3)

Diphenylacetic acid (117-34-0)

Triethylamine hydrochloride (554-68-7)

Diphenylacetyl chloride (1871-76-7)

Diphenylketene,
Ethenone, diphenyl- (525-06-4)

hexane (110-54-3)

triethylamine (121-44-8)

triphenylphosphine (603-35-0)

α -bromodiphenylacetyl bromide (17397-37-4)