



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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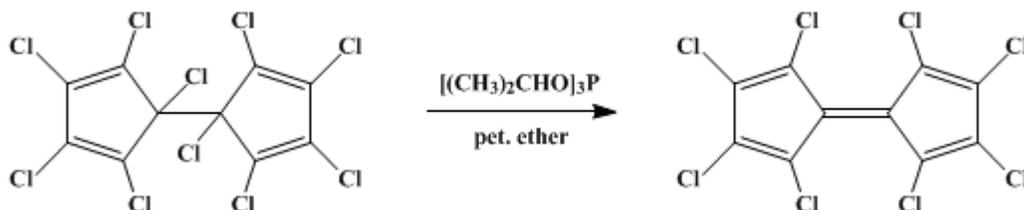
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.901 (1973); Vol. 46, p.93 (1966).

PERCHLOROFULVALENE

[Bicyclopentadienyliene, octachloro-]



Submitted by V. Mark¹

Checked by M. Rosenberger and Peter Yates.

1. Procedure

A slurry of 47.5 g. (0.100 mole) of [decachlorobi-2,4-cyclopentadienyl](#) ([Note 1](#)) in 200 ml. of petroleum ether (b.p. 30–60°) is prepared in a 1-l., three-necked, round-bottomed flask equipped with a Hershberg stirrer, thermometer, dropping funnel, and air condenser fitted with a drying tube. The reaction flask is immersed in a water bath at 20–24° and the stirrer is started. A solution of 25.2 g. (0.121 mole) of [triisopropyl phosphite](#) ([Note 2](#)) in 25 ml. of petroleum ether (b.p. 30–60°) is added from the dropping funnel at such a rate that the temperature of the mildly exothermic reaction remains between 20° and 25°. During the addition, which requires 50–80 minutes, the light yellow slurry of the starting material is converted to a dark blue slurry of [perchlorofulvalene](#).

After the addition is completed, the reaction mixture is stirred for an additional period of 20 minutes. The crystalline product is filtered rapidly by suction through a sintered-glass funnel ([Note 3](#)) and rapidly washed with three 20-ml. portions of petroleum ether (b.p. 30–60°). After the last washing, the [perchlorofulvalene](#) is allowed to dry at room temperature. The yield of the dark bluish-violet, uniform crystals is 26–29 g. (65–72%). The chlorocarbon is of a high purity, as indicated by infrared and ultraviolet spectroscopy ([Note 4](#)); it can be recrystallized from [benzene](#), [cyclohexane](#), [hexane](#), [carbon tetrachloride](#), or [methylene chloride](#) without appreciable lowering of the yield.

2. Notes

1. [Decachlorobi-2,4-cyclopentadienyl](#) [bis-(pentachlorocyclopentadienyl)], m.p. 123–124°, can be obtained from Columbia Organic Chemicals Co., Inc., and Aldrich Chemical Co., Inc. The checkers used purified material, m.p. 124–126°, obtained by recrystallization of commercial material from [hexane](#). They found that without prior purification of the commercial starting materials or correction for assay (cf. ([Note 2](#))) the yield was reduced to 50%. The checked runs were carried out under [nitrogen](#), but it was not determined whether this influenced the yield.

2. [Triisopropyl phosphite](#) can be obtained from Virginia Carolina Chemical Corporation, Eastman Organic Chemicals, Aldrich Chemical Company, Matheson Coleman and Bell, and K and K Laboratories. The presence of [diisopropyl hydrogen phosphite](#) or [triisopropyl phosphate](#) is not deleterious, but a correction for the assay is required. Fractionation readily separates [triisopropyl phosphite](#), b.p. 60–61° (10 mm.), from [diisopropyl hydrogen phosphite](#), b.p. 70–71° (10 mm.), and [triisopropyl phosphate](#), b.p. 95–96° (10 mm.). The checkers used a fraction, b.p. 85–88° (33 mm.) (cf. ([Note 1](#))).

Alternatively, [triethyl phosphite](#) (available from the suppliers given above) can be substituted, in equivalent amount, for [triisopropyl phosphite](#); the yield of [perchlorofulvalene](#) is 55–60%. The use of [trimethyl phosphite](#) gives lower yields (45–48%) and a less pure product.

3. The use of a large-size (500-ml.), coarse-grade, sintered-glass funnel permits rapid filtration and the washing of the filter cake directly in the funnel. Rapid removal of the co-product, [diisopropyl phosphorochloridate](#), (C₃H₇O)₂P(O)Cl, from [perchlorofulvalene](#) is necessary in order to prevent its

hydrolysis to petroleum ether-insoluble products.

4. Since [perchlorofulvalene](#) does not melt below its decomposition point around 200°, infrared and ultraviolet spectroscopic analyses provide the most satisfactory method of checking the purity of the product. The characteristic infrared maxima of perchlorofulvalene occur at 6.55, 7.56, 7.97, 8.10, 8.63, 10.37, 13.03, 14.24, and 14.53 μ , and the ultraviolet and visible maxima at 386 $m\mu$ (ϵ 35,800) and 590 $m\mu$ (ϵ 505). The absence of [decachlorobi-2,4-cyclopentadienyl](#) in the product is indicated by the absence of its characteristic bands at 6.27, 12.35, and 14.83 μ .

3. Discussion

The present procedure is that described by the submitter.² [Perchlorofulvalene](#) has also been obtained by the dechlorination of [decachlorobi-2,4-cyclopentadienyl](#) catalytically at 500° and 0.1 mm. in 57% yield,³ or by a mixture of [iron](#) and [ferric chloride](#) in warm [tetrahydrofuran](#) in 14% yield⁴ or by [stannous chloride](#) in refluxing [acetone](#) in 36% yield.^{5 6}

4. Merits of the Preparation

[Perchlorofulvalene](#) and the more recently prepared [perbromofulvalene](#)⁷ are the only stable compounds known at present in which the fulvalene system alone represents all the unsaturation. The current listing of a compound as "[perchlorofulvalene](#)" in various chemical catalogs is based on earlier work shown to be in error;² this compound has been shown to be a C₁₅Cl₁₂ chlorocarbon with a trindane skeleton.²

[Perchlorofulvalene](#) is a highly reactive chlorocarbon which undergoes a variety of reactions, including dimerization and oligomerization⁸ and other addition reactions, including chlorination,⁶ (2+4)-cycloadditions,⁸ and reaction with nucleophiles.⁸ It has a unique structure⁹ which reflects a compromise between steric hindrance and conjugation. More recently its dipole moment¹⁰ and nqr spectrum¹¹ have been determined.

References and Notes

1. General Electric, Plastics Department, Mt. Vernon, Indiana 47620.
2. V. Mark, *Tetrahedron Lett.*, 333 (1961); V. Mark, U.S. Patent 3,328,472 (1967).
3. A. E. Ginsberg, P. Raatz, and F. Korte, *Tetrahedron Lett.*, 779 (1962).
4. R. R. Hindersinn, U.S. Patent 3,475,502 (1969).
5. D.C.F. Law, Ph.D. Thesis, The University of Wisconsin, 1966;
6. R. M. Smith and R. West, *J. Org. Chem.*, **35**, 2681 (1970).
7. P. T. Kwitowski and R. West, *J. Am. Chem. Soc.*, **88**, 4541 (1966); R. West and P. T. Kwitowski, *J. Am. Chem. Soc.*, **90**, 4697 (1968).
8. V. Mark, unpublished results.
9. P. J. Wheatley, *J. Chem. Soc.*, 4936 (1961).
10. I. Agranat, H. W. Feilchenfeld, and R. J. Loewenstein, *Chem. Comm.*, 1154 (1970).
11. I. Agranat, D. Gill, M. Hayek, and R. J. Loewenstein, *J. Chem. Phys.*, **51**, 2756 (1969).

Appendix

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

petroleum ether

[Benzene](#) (71-43-2)

iron (7439-89-6)
carbon tetrachloride (56-23-5)
nitrogen (7727-37-9)
stannous chloride
cyclohexane (110-82-7)
acetone (67-64-1)
ferric chloride (7705-08-0)
methylene chloride (75-09-2)
Tetrahydrofuran (109-99-9)
hexane (110-54-3)
triisopropyl phosphite (116-17-6)
Triethyl phosphite (122-52-1)
diisopropyl hydrogen phosphite
trimethyl phosphite (121-45-9)
Perchlorofulvalene,
Bicyclopentadienylidene, octachloro- (6298-65-3)
decachlorobi-2,4-cyclopentadienyl
triisopropyl phosphate
diisopropyl phosphorochloridate
perbromofulvalene