



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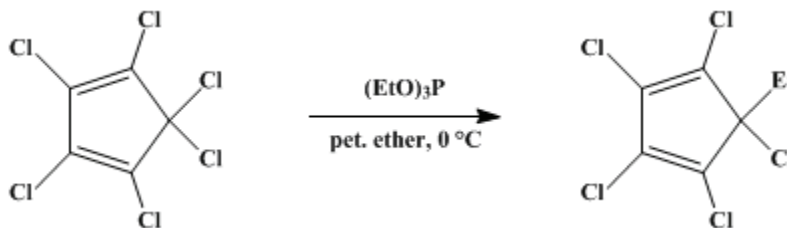
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.893 (1973); Vol. 43, p.90 (1963).*

## 1,2,3,4,5-PENTACHLORO-5-ETHYLCYCLOPENTADIENE

[Cyclopentadiene, 1,2,3,4,5-pentachloro-5-ethyl-]



Submitted by V. Mark, R. E. Wann, and H. C. Godt, Jr.<sup>1</sup>

Checked by William E. Parham, Wayland E. Noland, and G. Paul Richter.

### 1. Procedure

A solution of 183 g. (1.10 moles) of triethyl phosphite (Note 1) in 200 ml. of petroleum ether (b.p. 30–60°) is added to a 3-l., three-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, a dropping funnel, and an air condenser; the open end of the condenser is connected to a drying tube filled with calcium sulfate or calcium chloride. The flask is immersed in a freezing mixture of sodium chloride and ice, and the stirrer is started. When the temperature of the phosphite solution reaches 0°, a solution of 273 g. (1.00 mole) of hexachlorocyclopentadiene (Note 2) in 100 ml. of petroleum ether (b.p. 30–60°) is added through the dropping funnel at such a rate that the temperature remains between 0° and 10°. The addition requires about 4–6 hours. After the addition is complete, the freezing mixture is removed, and the brown, clear solution is allowed to warm up to room temperature.

The air condenser is replaced by an efficient water condenser set downward for steam distillation. One liter of water is added in one portion to the stirred reaction mixture, and stirring is continued for 30 minutes (Note 3). The dropping funnel is replaced by a steam-inlet tube reaching into the liquid, and steam is passed through the mixture until first the petroleum ether, then, separately, the ethylpentachlorocyclopentadiene is completely removed. The diene is separated from the steam distillate as a pale-yellow heavy oil. The aqueous phase of the steam distillate is extracted with petroleum ether, and the extract is combined with the diene and dried over calcium sulfate (Note 4). The petroleum ether is removed by evaporation on a steam bath or through a water aspirator at room temperature, leaving 245–257 g. (92–96%) of 1,2,3,4,5-pentachloro-5-ethylcyclopentadiene as a pale-yellow oil,  $n_D^{25}$  1.5387–1.5400. The diene can be distilled without appreciably lowering the yield; b.p. 51–53°/0.2 mm.;  $n_D^{25}$  1.5398.

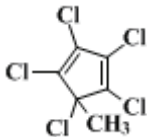
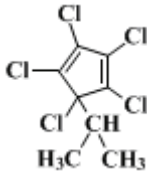
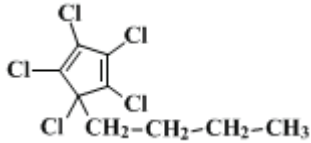
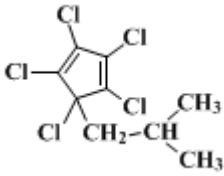
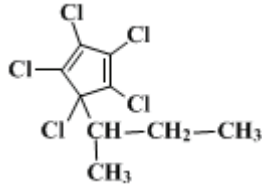
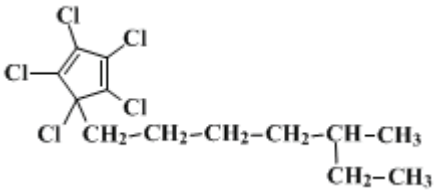
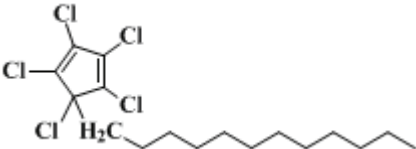
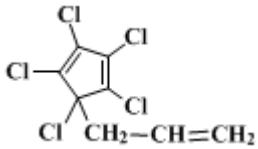
### 2. Notes

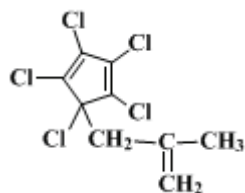
1. Triethyl phosphite can be obtained from Virginia Carolina Chemical Corp., Eastman Kodak Co., Aldrich Chemical Co., K and K Laboratories, and Matheson, Coleman and Bell. The presence of dialkyl hydrogen phosphite or trialkyl phosphate is not deleterious, but a correction for assay is required. Fractionation readily separates triethyl phosphite (b.p. 48–49°/11 mm.) from diethyl hydrogen phosphite (b.p. 72°/11 mm.) and triethyl phosphate (b.p. 90°/10 mm.). The presence of amines and amine hydrochlorides may seriously interfere with the alkylation, especially in the case of trimethyl phosphite (see Table I). The checkers redistilled triethyl phosphite obtained from Matheson, Coleman and Bell.

TABLE I SYNTHESIS OF 5-ALKYLPENTACHLOROCYCLOPENTADIENES,  $\text{RC}_5\text{Cl}_5$

| $\text{R}^a$ | Temperature, °C. <sup>b</sup> | B.P., °C./mm. | $n_D^{25}$ | %Yield |
|--------------|-------------------------------|---------------|------------|--------|
|--------------|-------------------------------|---------------|------------|--------|

Methyl

|   |       |             |        |    |
|---|-------|-------------|--------|----|
|  <p>Isopropyl</p>        | 20–22 | 45–47/0.3   | 1.5465 | 89 |
|  <p>Butyl</p>            | 2–5   | 67–68/0.4   | 1.5397 | 95 |
|  <p>Isobutyl</p>         | 5–10  | 72–74/0.3   | 1.5270 | 84 |
|  <p><i>sec</i>-Butyl</p> | 5–10  | 73–75/0.4   | 1.5254 | 72 |
|  <p>2-Ethylhexyl</p>   | 20–25 | 90–92/0.7   | 1.5370 | 89 |
|  <p>Dodecyl</p>        | 5–10  | 105–107/0.3 | 1.5172 | 90 |
|  <p>Allyl</p>          | 5–10  | 130–135/0.2 | 1.5043 | 78 |
|  <p>Methallyl</p>      | 20–22 | 63–65/0.5   | 1.5450 | 75 |



25-40      80-83/0.5    1.5385    80

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*a* All the trialkyl phosphites required for the preparations listed are available from the suppliers mentioned in (Note 1).

*b* Temperature range during the addition period.

2. A commercial product obtained from Matheson, Coleman and Bell was used.

3. Water hydrolyzes diethyl phosphorochloridate [chlorodiethoxyphosphorus (V) oxide] readily but does not affect the diene. Alternatively, the reaction mixture can be processed by fractionation. Evaporation of the petroleum ether and fractionation of the residue through a 25-cm. × 2.2-cm. column of glass helices yields 170 g. (98.5%) of diethyl phosphorochloridate, b.p. 34-36°/0.2 mm.,  $n_D^{25}$  1.4210-1.4250 (the refractive index indicates that it contains 5-10% of the title compound), and 240-255 g. (90-96%) of 1,2,3,4,5-pentachloro-5-ethylcyclopentadiene, b.p. 51-53°/0.2 mm.,  $n_D^{25}$  1.5398. The reaction mixture can also be processed by chromatography. The crude reaction mixture is poured on a 90-cm. × 4.5-cm. column of alumina (e.g., Fisher "adsorption grade") and eluted with about 2 l. of technical-grade pentane. This yields a pale-yellow solution that is free of diethyl phosphorochloridate. Evaporation of the pentane gives 240-255 g. (90-96%) of 1,2,3,4,5-pentachloro-5-ethylcyclopentadiene.

4. Calcium chloride or sodium sulfate can also be used.

### 3. Discussion

1,2,3,4,5-Pentachloro-5-ethylcyclopentadiene has been prepared only by the present procedure.<sup>2</sup>

### 4. Merits of the Preparation

5-Alkyl-1,2,3,4,5-pentachlorocyclopentadienes are a novel class of compounds.<sup>2</sup> The alkylation of hexachlorocyclopentadiene by trialkyl phosphites is a synthetic procedure of considerable scope (Table I) and represents a new method of forming carbon-to-carbon bonds. The products, 5-alkylpentachlorocyclopentadienes, show the manifold reactions of the parent chlorocarbon and undergo a variety of substitution and addition reactions, including Diels-Alder reactions.

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### References and Notes

1. Monsanto Chemical Co., Agricultural Chemicals Division, St. Louis, Missouri.
2. V. Mark, *Tetrahedron Lett.*, 296 (1961).

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### Appendix

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

petroleum ether

calcium chloride (10043-52-4)

sodium chloride (7647-14-5)

allyl (1981-80-2)

sodium sulfate (7757-82-6)

calcium sulfate (7778-18-9)

methyl (2229-07-4)

Pentane (109-66-0)

butyl (2492-36-6)

isopropyl (2025-55-0)

2-ethylhexyl

Dodecyl

isobutyl (4630-45-9)

methallyl (15157-95-6)

Triethyl phosphite (122-52-1)

diethyl hydrogen phosphite (762-04-9)

hexachlorocyclopentadiene

trimethyl phosphite (121-45-9)

1,2,3,4,5-Pentachloro-5-ethylcyclopentadiene,  
Cyclopentadiene, 1,2,3,4,5-pentachloro-5-ethyl-,  
ethylpentachlorocyclopentadiene (16177-48-3)

triethyl phosphate (78-40-0)

diethyl phosphorochloridate (814-49-3)

chlorodiethoxyphosphorus (V) oxide

sec-butyl (2348-55-2)