

1-Ethoxy-*p*-2-menthen-4-ol (9).—A mixture of 5 g of the ascaridole-triphenylphosphine reduction product and 12 ml of absolute ethanol was allowed to stand at room temperature for 3 days. The excess ethanol was removed under reduced pressure and the product was distilled: bp 81–84° (10 mm); nmr (CDCl₃) τ 4.25 (s, 2), 6.55 (q, 2, J = 7 Hz), 8.75 (s, 3), 8.85 (t, 3, J = 7 Hz), 7.8–8.6 (m, 5), 9.05 (d, 3, J = 6 Hz), 9.10 (d, 3, J = 6 Hz), and a one-proton singlet of concentration-dependent position.

Anal. Calcd for C₁₂H₂₂O₂: C, 72.67; H, 11.18. Found: C, 72.80; H, 10.98.

1-Methoxy-*p*-2-menthen-4-ol (10).—A mixture of 2 g of the ascaridole-triphenylphosphine reduction product and 5 ml of methanol was allowed to stand at room temperature for 3 days. The excess solvent was removed under reduced pressure and the product was distilled: nmr (neat) τ 4.30 (s, 2), 6.85 (s, 3), 7.8–8.6 (m, 5), 8.8 (s, 3), 9.08 (d, 3, J = 7 Hz), 9.13 (d, 3, J = 7 Hz), and a one-proton singlet of concentration-dependent position.

***p*-3-Menthene-1,2-diol (11).**—When the ascaridole-triphenylphosphine reduction product was hydrolyzed in 1% H₂SO₄ at 0° or in 1% HCl at 35°, a mixture of products resulted. The reaction mixture was neutralized with NaHCO₃ and extracted with ether. The ethereal solution was dried, concentrated by evaporation, and separated by column chromatography. One fraction from the chromatographic separation crystallized and was recrystallized from chloroform-petroleum ether B: mp 57–58° (lit.⁶ mp 57–58°); the infrared spectrum agreed with that reported in the literature;⁶ nmr τ 4.5 (m, 1), 5.8 (m, 1), 7.9–8.4 (m, 5), 8.8 (s, 3), 9.0 (d, 6, J = 6 Hz), and a two-proton singlet of concentration-dependent position.

Registry No.—1, 512-85-6; 2, 21473-34-7; 6, 562-74-3; 7, 21473-36-9; 8, 21473-37-0; 9, 21473-38-1; 10, 21473-39-2; triphenylphosphine, 603-35-0.

Acknowledgment.—We gratefully acknowledge the financial assistance of the Louis W. and Maud Hill Family Foundation.

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Phosphorus Pentachloride for the Replacement of Benzylic Hydrogen with Chlorine¹

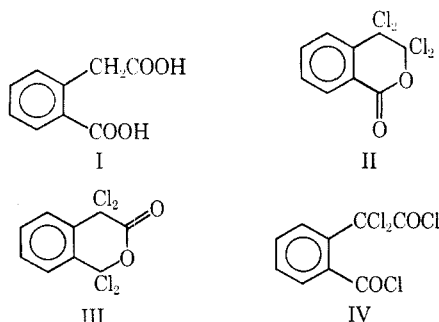
RAYMOND D. KIMBROUGH, JR. AND ROYCE N. BRAMLETT

Nuclear and Biological Sciences Division, Engineering Experiment Station, Georgia Institute of Technology, Atlanta, Georgia 30332

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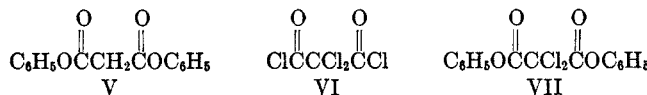
Phosphorus pentachloride has been widely used to replace the hydroxyl groups of alcohols and carboxylic acids to give alkyl chlorides and acyl chlorides, and to replace the carbonyl groups of aldehydes and ketones to give dichlorides.²

In specific cases, phosphorus pentachloride is known to replace carbon-bound hydrogen. Homophthalic acid, I, with phosphorus pentachloride gives a series of

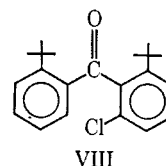


products including II, III, and IV, where replacement of carbon-bound hydrogen with chlorine has occurred.³

Phenyl malonate, V, and phosphorus pentachloride give a mixture of products including VI and VII where replacement of carbon-bound hydrogen by chlorine has occurred.⁴



Chlorination of hydrocarbons, specifically the chlorination of heptane to give heptyl chloride, with phosphorus pentachloride and peroxides has been reported.⁵ An aromatic hydrogen is replaced by heating 2,2'-di-*t*-butylbenzophenone and phosphorus pentachloride to 185°, giving VIII.⁶



In the present work, it has been found that benzylic hydrogen is replaced by chlorine when the material is heated with phosphorus pentachloride. The other products of the reaction are presumably phosphorus trichloride and hydrogen chloride.

The replacement of benzylic hydrogen may proceed by way of a free radical reaction pathway. The first step might be dissociation of the phosphorus pentachloride to phosphorus trichloride and chlorine, a reaction known to occur at elevated temperature.⁷ The chlorine would then react at the benzylic position in the familiar manner.⁸

Toluene was converted to benzyl chloride by refluxing with phosphorus pentachloride in almost quantitative yield. With excess phosphorus pentachloride, benzylidene chloride was obtained along with benzyl chloride and unreacted phosphorus pentachloride. Thus the replacement of successive benzylic hydrogen seems to be increasingly difficult.

When diphenylmethane was heated with 1 mol of phosphorus pentachloride, benzhydryl chloride was formed. Excess phosphorus pentachloride gave diphenylmethylene chloride. Triphenylmethane was converted to triphenylmethyl chloride in 93% yield by phosphorus pentachloride at 140–150°.

(1) This research was supported by Grant No. ES 00281 from the National Institutes of Health, U. S. Public Health Service.

(2) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1953, pp 91, 105, and 546.

(3) W. Davies and H. G. Poole, *J. Chem. Soc.*, 1816 (1928).

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(6) W. Theilacker and F. Boelsing, *ibid.*, **71**, 672 (1959).

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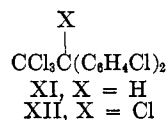
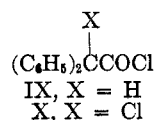
(8) D. J. Cram and G. S. Hammond, "Organic Chemistry," Second ed., McGraw-Hill Book Co. Inc., New York, N. Y., 1964, p 523.

TABLE I
 REACTIONS OF PHOSPHORUS PENTACHLORIDE

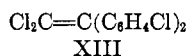
Starting material	Mol of PCl ₅ per mol of starting material	Conditions, °C, (hr)	Purification	Product	Yield, %	Mp or bp, °C (mm)	Lit. mp or bp, °C
Toluene	0.5	Reflux, 110 (40)	Distillation	Benzyl chloride ^a	97 ^b	68–70 (12)	179 ^c
Toluene	2	Sealed tube 140–150 (18)	Distillation	Benzylidene chloride ^a	38	105–107 (12)	214 ^c
Diphenylmethane	1	140–150 (18)	Distillation	Benzhydryl chloride ^a	78	160–162 (12)	161–162 ^d
Diphenylmethane	3	140–150 (18)	Distillation	Diphenylmethane chloride ^a	90	170–173 (12)	172 ^e
Triphenylmethane	2	140–150 (18)	Recrystallization, benzene–hexane ^f	Triphenylmethyl chloride ^a	93	111–113	113–114 ^f
Diphenylacetyl chloride ^g	2	140–150 (18)	Recrystallization, pentane	Diphenylchloroacetyl chloride ⁱ	85	49–51	50 ^j
1,1,1-Trichloro-2,2-bis(<i>p</i> -chlorophenyl)ethane (<i>p,p'</i> -DDT)	2	Sealed tube 180–200 (18)	Recrystallization, ethanol	1,1,1,2-Tetrachloro-2,2-bis-(<i>p</i> -chlorophenyl)-ethane ^g	88	90–92	90–91 ^g

^a The infrared spectrum was identical with that of the authentic material. ^b This yield was based on unrecovered toluene. Based on phosphorus pentachloride, it was 42%. ^c N. H. Lange, "Handbook of Chemistry," 7th ed, Handbook Publishers, Inc., Sandusky, Ohio, 1949. ^d H. Gilman and J. E. Kirby, *J. Amer. Chem. Soc.*, **48**, 1735 (1926). ^e L. Gattermann and H. Schulze, *Ber.*, **29**, 2944 (1896). ^f L. Gattermann and H. Wieland, "Die Praxis des organischen Chemikers," 39th ed, Walter de Gruyter & Co., Berlin, 1959, p 298. ^g The melting point of this material was not depressed by mixture with the authentic material. ^h H. Staudinger, *Ber.*, **44**, 1619 (1911). ⁱ The identity of this material was established by conversion into ethyl diphenylchloroacetate, mp 42–44° (lit.⁹ mp 43–44°), by solution in ethanol, and by conversion into mandelic acid, mp and mmp 117–118°, by reflux in potassium carbonate solution. ^j H. Bickel, *Ber.*, **22**, 1539 (1889).

Diphenylacetyl chloride, IX, heated with excess phosphorus pentachloride gave diphenylchloroacetyl chloride, X, in 85% yield.



When 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane, the insecticide *p,p'*-DDT, XI, was heated with phosphorus pentachloride at 180–200° for 18 hr, an 88% yield of 1,1,1,2-tetrachloro-2,2-bis(*p*-chlorophenyl)-ethane, XII, was obtained. The preparation of XII is usually from XI in two steps, the dehydrochlorination of XI with base to give 1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethylene, XIII, followed by the addition of chlorine to the ethylenic double bond of XIII to give XII.⁹



To test the possibility that XIII might be an intermediate in our conversion of XI to XII with phosphorus pentachloride, XIII was heated with phosphorus pentachloride. An almost quantitative yield of XII was obtained. Hence all that can be said is that XIII may be an intermediate in this reaction. The use of phosphorus pentachloride for the addition of chlorine to an ethylenic double bond is known.¹⁰ The chlorination of the other compounds in Table I cannot involve such an olefinic intermediate.

The several compounds mentioned above in which benzylic hydrogen is replaced by chlorine on heating

with phosphorus pentachloride suggest that this is a general reaction.

Experimental Section

Replacement of Benzylic Hydrogen with Chlorine Using Phosphorus Pentachloride.—A reaction typical of those outlined in Table I is described for the preparation of XII. A mixture of 5.0 g (0.013 mol) of XI and 7.2 g (0.026 mol) of phosphorus pentachloride was sealed in a 40-ml glass tube and heated at 180–200° for 18 hr. The cooled reaction mixture was added to ice water and stirred until the excess phosphorus pentachloride and the phosphorus trichloride were decomposed. The insoluble material was taken up in ether and the ether layer was dried with magnesium sulfate and evaporated. The residue was recrystallized from ethanol: yield 4.5 g (88%); mp 90–92° (lit.⁹ mp 91–92°).

Registry No.—Phosphorus pentachloride, 10026-13-8; toluene, 108-88-3; diphenylmethane, 101-81-5; triphenylmethane, 519-73-3; IX, 1871-76-7; XI, 50-29-3.

The Platinum-Catalyzed Air Oxidation of Hindered Phenols

EUGENE F. LUTZ AND PAUL H. WILLIAMS

Shell Development Company, Emeryville, California

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Although the platinum-catalyzed air oxidation of aliphatic alcohols has been widely studied, only minor attention has been devoted to hydroxy aromatics.¹

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