The Ionic Reaction in the Chlorophosphonation of Alkylbenzenes

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The chlorophosphonation of toluene, *p*-xylene, ethylbenzene, and diphenylmethane gave methyldiphenylmethanes; 2,4′,5-trimethyldiphenylmethane and ethyl-1,1-diphenylethanes; and *p*-benzyltriphenylmethane respectively as the main products. Isopropylbenzene gave α-methylstyrene, 4-methyl-2,4-diphenylpentene-1, 4-methyl-2,4-diphenylpentene-2, and 1,1,3-trimethyl-3-phenylindane, in addition to the ordinary chlorophosphonated products. Those diphenylmethane derivatives may be formed by the electrophilic attack of the benzylic cations, presumably resulting from electron transfer from the benzylic radicals to phosphorus trichloride with the participation of the oxygen or oxy radical, upon toluene, *p*-xylene, ethylbenzene, or diphenylmethane. α-Methylstyrene may be formed by the elimination of a proton from the intermediate 1,1-dimethylbenzyl cation, resulting from isopropylbenzene in a manner similar to that above. Diphenylpentene and phenylindane derivatives may be formed by the acid-catalyzed dimerization of α-methylstyrene.

Jensen and Noller[1] reported that, on chlorophosphonation, toluene gave only a 12.8% yield of benzylphosphonic acid, ethylbenzene gave 11% of 2-phenylethylphosphonic acid, and diphenylmethane gave 2% of diphenylmethylphosphonic acid. Isbell and Wadsworth[2] reported that isopropylbenzene failed to react at all. Also, in our previous investigation of the chlorophosphonation of *n*-alkylbenzene,[3] it was found that the yield of the α-substituted product was abnormally lower than that to be anticipated from the inductive effect alone, in comparison with other isomers.

In the present paper, the chlorophosphonation of alkylbenzenes has been investigated in order to elucidate the reason for this anomalous behavior in the reactivity of the benzylic C–H bond of alkylbenzene.

Results and Discussion

The chlorophosphonation was performed on each alkylbenzene for 3 hr in the temperature range of −15—0 °C, with a 5-fold mole excess of phosphorus trichloride, by the control of the flow rate of oxygen gas. The products were isolated by vacuum distillation after the slipping of the phosphorus oxychloride and unreacted material. The isolated products were esterified with ethanol–triethylamine, followed by analysis with glc.

Toluene gave methyldiphenylmethanes (I) and diethyl benzylphosphonate (II) in the ratio of 50.0: 1.0; the isomer distribution of I was found by glc analysis to consist of 43.6% *o*-, 5.8% *m*-, and 50.6% *p*-isomers. This isomer distribution was similar to that of the benzylation of toluene with benzyl chloride catalyzed with aluminum trichloride in nitromethane.[4] *p*-Xylene gave 2,4′,5-trimethyldiphenylmethane (III) and diethyl *p*-methylbenzylphosphonate (IV) in the ratio of 3.2: 1.0. Ethylbenzene gave ethyl-1,1-diphenylethane (V), diethyl 1-, and diethyl 2-phenylethylphosphonate in the ratio of 12.5: 1.0: 2.0. The isomer distribution of V consisted of 6.6% *o*-, 2.1% *m*-, and 91.3% *p*-isomers. Styrene could not be detected. Diphenylmethane gave *p*-benzyltriphenylmethane (VI) and a trace amount of diphenylmethylphosphonic dichloride. Isopropylbenzene gave 1,1,3-trimethyl-3-phenylindane (VII) and diethyl 2-phenylpropylphosphonate as the main products in the ratio of 0.7: 1.0. Trace amounts of α-methylstyrene (VIII), 4-methyl-2,4-diphenylpentene-1 (IX), 4-methyl-2,4-diphenylpentene-2 (X), and diethyl 1-methyl-1-phenylethylphosphonate were also obtained.

TABLE 1. EFFECT OF SOLVENT ON THE ISOMER DISTRIBUTIONS AND YIELDS OF DIMERS OF VIII

Solvent	Yield (%)	Products (mol%)		
		IX	X	VII
PCl_3	20.8[a]	89.8	9.9	0.3
$POCl_3$	54.1[a]	29.2	68.6	2.2
PCl_3+POCl_3	38.3[a]	31.4	68.2	0.4
$POCl_3+H_3PO_4$	quant.[b]	trace	trace	100

a) Isolated yield. b) By glc.

The dimerization of VIII might give VII, IX, and X with an acid-catalyzed reaction.[5] The isomer distributions of VII, IX, and X obtained by the dimerization of VIII and with the participation of phosphorus trichloride, phosphorus oxychloride, a mixture of phosphorus trichloride and phosphorus oxychloride, or phosphorus oxychloride containing a small amount of phosphoric acid are given in Table 1. The phosphorus trichloride-catalyzed dimerization of VIII gave IX predominantly, while phosphorus oxychloride gave X as the major product and IX as a minor product. On the other hand, when a small amount of protic acid was added to phosphorus oxychloride, VIII dimerized to give VII only. The isomer distribution of the dimers obtained in the chlorophosphonation of isopropyl benzene was similar to that obtained in the last case. This similarity suggests that the dimerization of VIII which occurs during the chlorophosphonation is catalyzed effectively with protic acid, resulting from the hydrolysis of phosphorus trichloride or phosphorus oxychloride with the moisture in the reaction mixtures.

Mechanism. Mayo, Durham, and Griggs[6] have presented good evidence for the following sequence in the chlorophosphonation of cyclohexane:

$$RH + Cl\cdot \longrightarrow R\cdot + HCl \quad (1)$$

$$R\cdot + PCl_3 \longrightarrow \dot{R}PCl_3 \quad (2)$$

$$\dot{R}PCl_3 + O_2 \longrightarrow RPCl_3OO\cdot \quad (3)$$

$$RPCl_3OO\cdot + PCl_3 \longrightarrow RPOCl_2 + POCl_3 + Cl\cdot \quad (4)$$

$$RPCl_3OO\cdot + PCl_3 \longrightarrow R\cdot + 2POCl_3 \quad (5)$$

However, the formation of I, III, V, VI, and VIII can not be explained only in terms of the radical substitution or disproportionation of R· in reaction (1) or (5), because the isomer distribution of I or V implies that they are formed *via* the electrophilic attack of the benzylic cation on the aromatic nucleus.

The addition of a small amount of iodine, a radical scavenger, to the reaction mixture of toluene and phosphorus trichloride inhibited the formation of both I and II. Moreover, by the reaction of toluene with di-*t*-butyl peroxide at 110 °C, in the presence of an equivalent amount of phosphorus trichloride, I and II were given in the ratio of 5.0: 1.0 without any bibenzyl. These facts, therefore, suggest that the benzyl radical is involved as an intermediate in the process of the formation of I.

A possible mechanism to account for the formation of I can be proposed. The benzyl chloride formed by

$$R\cdot + O_2 \longrightarrow ROO\cdot \quad (6)$$

$$ROO\cdot + PCl_3 \longrightarrow RO\cdot + POCl_3 \quad (7)$$

$$RO\cdot + RH \longrightarrow ROH + R\cdot \quad (8)$$

$$ROH + PCl_3(POCl_3) \longrightarrow RCl + HP(O)Cl_2 \quad (9)$$

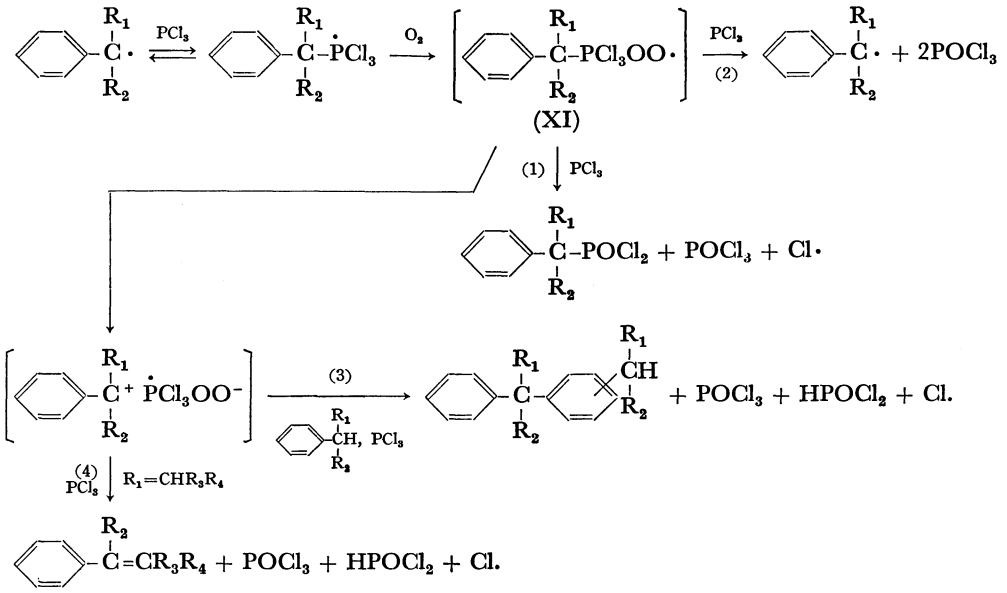
the sequence of radical reactions (6)—(8) and a successive ionic reaction (9),[6] may react with toluene by means of the catalytic action of phosphorus trichloride or phosphorus oxychloride as a Lewis acid, thus giving I. However, this possibility can be eliminated on the basis of the following two facts: benzyl chloride could not be detected in the reaction mixture and, after a mixture of benzyl chloride and toluene with phosphorus trichloride or phosphorus oxychloride had been allowed to stand for at least 24 hr at room temperature, no I could be detected in the mixture.

The UV-irradiation of a mixture of benzyl chloride and toluene with phosphorus trichloride under degassed conditions gave neither bibenzyl nor I, but small amounts of unidentified products, although the irradiation of the same mixture without phosphorus trichloride gave bibenzyl in an appreciable yield, indicating the formation of the benzyl radical. These findings suggest that the presence of oxygen or an oxy radical is also required for the formation of I.

When the temperature of the chlorophosphonation of toluene was raised from —15—0 °C to 65—75 °C, the combined yield of I and II was reduced to one-third. This negative temperature effect is not incompatible with the idea that a thermally unstable phosphoranyl intermediate radical may be present in this process.[20]

The formation of I from toluene, like the formation of III, V, VI, and VIII from the other alkylbenzenes, can be explained by the following scheme, Scheme 1.

The intermediate peroxide radical (XI) may react with phosphorus trichloride to give alkylphosphonic dichloride, phosphorus oxychloride, and atomic chlorine (Path 1) or the alkyl radical and two mol of phosphorus oxychloride (Path 2), as presented by Mayo *et al.*[6] Competing with these reactions, however, the radicals of a low ionization potential, such as the benzyl radical,[7] may transfer an electron to the phosphorus trichloride–oxygen complex, thus resulting in the benzylic cation or the ionic complex $[C_6H_5\overset{+}{C}R_1R_2\dot{P}Cl_3\text{-}OO^-]$. A subsequent ionic reaction of the benzylic cation with the alkylbenzenes may give I, III, V, or VI. Isopropylbenzene gave VIII and its dimers, IX, X, and VII, but not isopropyl-2,2-diphenylpropane, which would be derived from the electrophilic attack of the 1,1-dimethylbenzyl cation on isopropylbenzene. The formation of VIII may be explained by the elimination of a proton from the methyl groups of the 1,1-dimethylbenzyl cation. The dimerization of VIII gives IX, X, and VII by means of the catalytic action of phosphorus trichloride and phosphorus oxychloride con-



Scheme 1.

taining a small amount of acid. Ethylbenzene gave only V without the elimination of a proton from the 1-methylbenzyl cation. The difference in their behavior may result from differences in the stabilities or electrophilicities of their intermediate cations. Thus, Path 4 may be favorable for the more stable and less electrophilic 1,1-dimethylbenzyl cation, whilst the competing Path 3 may be favorable for the less stable and more electrophilic 1-methylbenzyl cation.

The mechanism proposed involves an intermediate complex, which then undergoes an ionic process to give the products. The formation of such similar complexes has been postulated for the reaction of benzoyl peroxide with tertiary amines or tertiary phosphine,[8] and for the inhibitation of the polymerization of acrylonitrile, vinyl chloride, or butyl acrylate with dimethylaniline.[9]

Recently, the formation of diphenylmethane derivatives by the thermal decomposition of benzoyl peroxide in toluene in the presence of boron trifluoride has also been reported.[10] In this case, a similar mechanism may be applied.

Experimental

All the boiling points are uncorrected. The NMR spectra were obtained at 100 MHz on a JNM-TS-100 spectrometer, with TMS as the internal reference. The mass spectra were obtained on a Hitachi RMU-6 or RMU-7 spectrometer with a direct inlet. The GC–MS were obtained on a Hitachi RMS-4 spectrometer. The gas-chromatographic analyses were done using a Shimadzu GC-3AF on a 3 m×3 mmϕ column packed with 5% Ucon LB 550X on Shimalite W, Mixed Nitrate on C-22,[11] or 10% Benton 34 on Neopack 1A. The preparative work was done using a Hitachi 023 on a 1 m×12 mmϕ column packed with 10% Benton 34 on Neopack 1A.

All the reagents used in this study were commercially available and were purified in all cases except that of di-*t*-butyl peroxide by distillation until found to be at least 99% pure by glc.

General Procedure of Chlorophosphonation. A mixture of alkylbenzene (0.2 mol) and phosphorus trichloride (1.0 mol) was placed in a reaction vessel equipped with a gas inlet and an outlet tube protected from moisture by a drying tube. Dry oxygen was bubbled into the mixture at a flow rate of 100 ml/min and at a temperature of −15—0 °C for 3 hr. After the removal of a large portion of the unreacted material and the phosphorus oxychloride, the residue was distilled *in vacuo*. The yields and boiling points of the products are given in Table 2.

Table 2. Yields of products in the chlorophosphonation of alkylbenzenes

Starting Material	Yield (g)	Bp °C/mmHg
Toluene	4.8	80—113/0.8
p-Xylene	7.8	96—121/1.0
Ethylbenzene	4.5	66— 86/0.1
Diphenylmethane	4.6	180/0.1
Isopropylbenzene	4.5	80—119/0.2

Analysis. The products were treated with ethanol–triethylamine, followed by distillation *in vacuo*, except for the products obtained from the reaction of diphenylmethane. The distillates were identified by a comparison of their retention times in glc with those of authentic samples, prepared by the methods to be described below. The products obtained from the reaction of diphenylmethane were identified with the data from the NMR and mass spectra of each component as follows; *p*-benzyltriphenylmethane; NMR(CCl_4): δ 3.85 (s, 2H, methylene), 5.40 (s, 1H, methine), 6.94 and 7.06 (19H, phenyl), MS: *m/e* 334 (M^+). Diphenylmethylphosphonic dichloride; NMR(CCl_4): δ 4.73 (d, 1H, J_{PCH} 20.0 Hz, methine), 7.30 (m, 10H, phenyl), MS: *m/e* 167 (M^+-121). Also, the two products, IX and X, obtained from the reaction of isopropylbenzene were identified with the data from the NMR on each component fractionated by a preparative glc and GC–MS as follows; 4-methyl-2,4-diphenylpentene-1 (IX); NMR(CCl_4): δ 1.20 (s, 6H, methyl), 2.80 (s, 2H, methylene), 4.75 (d, 1H, J 2.0 Hz, vinyl), 5.10 (d, 1H, J 2.0 Hz, vinyl), 7.16 (10H, phenyl), GC–MS: *m/e* 236 (M^+). 4-Methyl-2,4-diphenylpentene-2 (X); NMR(CCl_4): δ 1.21 (d, 3H, J 5.0 Hz, methyl), 1.44 (s, 6H, methyl), 6.00 (qui, 1H, J 5.0 Hz, vinyl), 7.13 (m, 10H, phenyl), GC–MS: *m/e* 236 (M^+).

Authentic Samples. The following diethyl alkylphosphonates were prepared by the Arbuzov reaction of alkyl bromides with triethyl phosphite,[12] or by the Michaelis-Becker reaction of alkyl bromides with diethyl sodium phosphite;[12] diethyl benzylphosphonate[13] (II bp 121—122 °C/3 mmHg), diethyl *p*-methylbenzylphosphonate[14] (IV bp 134—135 °C/3 mmHg), diethyl 1-phenylethylphosphonate[13] (bp 120—121 °C/0.7 mmHg), diethyl 2-phenylethylphosphonate[13] (bp 154—156 °C/6 mmHg), and diethyl 2-phenylpropylphosphonate (bp 120—122 °C/0.5 mmHg). Diethyl 1-methyl-1-phenylethylphosphonate[15] was prepared by the reaction of diethyl 1-lithio-1-phenylethylphosphonate with methyl iodide (bp 92—93 °C/0.1 mmHg). The diphenylmethane derivatives were prepared by the Friedel-Crafts reaction of alkylbenzenes with their corresponding α-chloro derivatives.[4] *m*- And *p*-isopropyl-2,2-diphenylpropane[16] were prepared by the Friedel-Crafts reaction of 2,2-diphenylpropane[17] with isopropyl alcohol (bp 96—99 °C/0.1 mmHg). 1,1,3-Trimethyl-3-phenylindane (VII) was prepared by the dimerization reaction of α-methylstyrene in the presence of sulfuric acid.

The Chlorophosphonation of Toluene in the Presence of Iodine. Three grams of iodine were added to a mixture of toluene (0.2 mol) and phosphorus trichloride (1.0 mol). The chlorophosphonation was then performed in the same manner as in the general procedure. Glc analysis showed no detectable amount of a product.

The Thermal Decomposition of Di-t-butyl Peroxide[18] in a Mixture of Toluene and Phosphorus Trichloride. A mixture of phosphorus trichloride (0.3 mol), toluene (0.3 mol), and di-*t*-butyl peroxide (1.0 mol) was refluxed for 5 hr. After the removal of a large portion of the unreacted material, the residue was treated with a solution of ethanol–triethylamine. Glc analysis showed I and II in the ratio of 5.0: 1.0; the isomer distribution of the former consisted of 45.1% *o*-, 5.9% *m*-, and 49.0% *p*-isomers. When a mixture of toluene and di-*t*-butyl peroxide was refluxed in the absence of phosphorus trichloride, only bibenzyl was obtained.

The Reaction of Benzyl Chloride and Toluene in the Presence of Phosphorus Trichloride or Phosphorus Oxychloride. A mixture of benzyl chloride (0.1 mol), toluene (0.1 mol), and phosphorus trichloride (1.0 mol) or phosphorus oxychloride (1.0 mol) was stirred under a nitrogen atmosphere at room temperature for 4.5 hr. Glc analysis showed no detectable amount of a product.

Photochemical Reaction of Benzyl Chloride in Toluene.[19] A mixture of toluene (4 g) and benzyl chloride (3 g) in a

Pyrex tube was irradiated with a high-pressure mercury arc at room temperature for 24 hr. The formation of bibenzyl alone was observed by glc. When phosphorus trichloride (7 g) was added to the mixture, and it was then irradiated in the same manner as above, neither bibenzyl nor I could be detected.

Dimerization Reaction of α-Methylstyrene. *a)*: A mixture of VIII (12 g) and phosphorus trichloride (13.7 g) was allowed to stand for 40 hr, protected from atmospheric moisture by a drying tube. After the removal of the VIII and the phosphorus trichloride by means of an aspirator, dimers were obtained by vacuum distillation (yield, 2.5 g; bp 86—98 °C/0.2 mmHg).

b): Phosphorus oxychloride (15 g) was used in place of phosphorus trichloride, and the reaction was carried out in a manner similar to that in *a)* (yield, 6.5 g; bp 84—98 °C/0.2 mmHg).

c): A mixture of phosphorus trichloride (7 g) and phosphorus oxychloride (7.5 g) was used in place of phosphorus trichloride, and the reaction was carried out in a manner similar to that in *a)* (yield, 4.5 g; bp 89—103 °C/0.5 mmHg).

d): A mixture of VIII (2 g), phosphorus oxychloride (60 g), and phosphoric acid (2 g) was allowed to stand for 15 hr. After the distillation of the phosphorus oxychloride, the solution was washed with water and extracted with ether. Glc analysis showed only VII.

References

1) W. L. Jensen and C. R. Noller, *J. Amer. Chem. Soc.*, **71**, 2384 (1949).
2) A. F. Isbell and F. T. Wadsworth, *ibid.*, **78**, 6042 (1956).
3) Y. Okamoto and H. Sakurai, *J. Japan Oil Chemists' Soc.*, **20**, 573 (1971).
4) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, **84**, 1688 (1962).
5) A. Švob, DJ. Deur-Šiftar, and V. Jarm, *J. Chromatog.*, **38**, 326 (1968).
6) F. R. Mayo, L. J. Durham, and K. S. Griggs, *J. Amer. Chem. Soc.*, **85**, 3156 (1963).
7) "Handbook of Chemistry and Physics," 54th ed. by R. C. Weast, Published by The Chemical Rubber Co., Cleaveland. Ohio, E-73 (1973).
8) M. Imoto, "Yukihanno no Riron," II, Kyoritutosyo, Tokyo (1961) p. 451.
9) M. Imoto, *ibid.*, II, p. 498.
10) G. A. Razuvaev, N. A. Kartshova, and L. S. Bogvslaskaya, *Zh. Organ. Khim.*, **2**, 1372 (1966).
11) W. W. Hanneman, C. F. Spencer, and J. F. Johnson, *Anal. Chem.*, **32**, 1386 (1960).
12) G. M. Kosolapoff, "Organic Reaction," Vol. 6, John Wiley & Sons, Inc, New York. London, (1960) p. 273.
13) F. Kagan, R. D. Birknmeyer, and R. E. Strube, *J. Amer. Chem. Soc.*, **81**, 3026 (1959).
14) B. P. Lugovkin and B. A. Arubzov, *Dok. Akad. Nauk S S S R*, **59**, 1301 (1959).
15) Y. Okamoto and H. Sakurai, *J. Japan Oil Chemists' Soc.*, **20**, 821 (1972).
16) E. I. Dupont de Nemours & Co., Brit. 753384 (1956).
17) A. Schneider, U. S. 2742512 (1956).
18) E. H. Farmer and C. G. Moor, *J. Chem. Soc.*, **16**, 131 (1951).
19) G. Porter and F. J. Wright, *Trans. Farady. Soc.*, **51**, 1469 (1955), G. Porter and E. Starchan, *ibid.*, **54**, 1595 (1958).
20) J. I. G. Cadogan, "Advances in Free-radical Chemistry," Vol. 2, (1967), p. 203.