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Formation of Phosphate Derivatives by the Reaction of Propyl and Allyl Halides with Phosphorus Trichloride and Oxygen

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In addition to phosphonyl dichlorides, a significant amount of phosphoryl dichlorides was obtained by the reaction of propyl and allyl halides with phosphorus trichloride in oxygen atmosphere. Formation of the P-O-C bond can be explained by a scheme involving a preferential reaction of the bridged intermediate radical with oxygen.

The reaction of hydrocarbons with phosphorus trichloride and oxygen provides a convenient route to alkylphosphonyl dichloride derivatives (P–C bond formation). Phosphoryl compounds occur only as minor products under high pressure of oxygen.[1] Boyce and Webb found that the reaction of 1,2-dichloroethylene with phosphorus trichloride–oxygen gives 1,2,2-trichloroethyl phosphate as the major product (*ca.* 40% yield) despite the fact that oxygen was used at atmospheric pressure.[2] No further investigations were made.

We have found that phosphoryl dichlorides are obtained from propyl and allyl halides in various yields under atmospheric pressure conditions of oxygen. The formation of phosphoryl dichloride was more remarkable in bromine-substituted hydrocarbon. The mechanism of the formation of phosphoryl dichloride will be discussed.

Results and Discussion

In a typical run, 0.1 mol of alkyl halide and 0.5 mol of phosphorus trichloride were placed in a 200 ml-cylindrical flask, fitted to a drying tube. Dried oxygen gas was bubbled into the mixture at a 50 ml/min rate for 3 hr. After the removal of phosphorus oxychloride and unreacted material at reduced pressure, the residue was distilled. The products were esterified with excess absolute ethanol, and analyzed by glc.

Chlorophosphonation of n-, *Isopropyl Chlorides, and the Same Bromides.* The yields and compositions of the products from these halides are given in Tables 1 and 3, respectively.

Table 1. Products from *n*- and isopropyl chlorides and the same bromides

Alkyl halide	Component (relative ratio %)
n-Propyl chloride	$CH_3CH_2CHClPO(OC_2H_5)_2$ (14)
	$CH_3CH[PO(OC_2H_5)_2]CH_2Cl$ (44)
	$CH_2[PO(OC_2H_5)_2]CH_2CH_2Cl$ (32)
	$CH_3CH[OPO(OC_2H_5)_2]CH_2Cl$ (10)
Isopropyl chloride	$CH_3CHClCH_2PO(OC_2H_5)_2$
n-Propyl bromide	$CH_3CH_2CHBrPO(OC_2H_5)_2$ (23)
	$CH_3CH[PO(OC_2H_5)_2]CH_2Br$ (34)
	$CH_3CH[OPO(OC_2H_5)_2]CH_2Br$ (7)
	$CH_3CHBrCH_2OPO(OC_2H_5)_2$ (7)
	$CH_2[PO(OC_2H_5)_2]CH_2CH_2Br$ (29)
Isopropyl bromide	$CH_3CH[PO(OC_2H_5)_2]CH_2Br$ (47)
	$CH_3CH[OPO(OC_2H_5)_2]CH_2Br$ (33)
	$CH_3CHBrCH_2OPO(OC_2H_5)_2$ (20)

n-Propyl chloride and bromide gave 10% and 14% of phosphate in composition, respectively. In the case of isopropyl bromide, the content of phosphate increased up to 53%.

The following facts suggest that the formation of a phosphoryl structure proceeds *via* a bridged intermediate radical. 1) In all the phosphoryl products, the P–O–C bonds are only at the *β*-position of halogen atom. 2) 1,2-Rearrangment of bromine atom occurs at the same time. 3) Phosphoryl dichloride production from the bromide is much greater than that from the chloride. It is well-known that bromine atom is more favorable in the formation of a symmetrical and stabilized bridged radical than chlorine atom.[3] 4) The phosphoryl dichloride production from the alkanes with other substituents (CN, COCl, Ph, and $OCOCH_3$) could not be observed under the same conditions.[4]

The bridged radical seems to be the more resonance-stabilized radical by means of delocalization of unpaired electron than the unbridged *β*-haloalkyl radical. The great reactivity of stable radical $Ph_3C\cdot$ with oxygen is well-known.[5] However, the stable radicals $(CH_3)_2\dot{C}CN$ and $Ph_3C\cdot$ were found to be unreactive toward phosphorus trichloride.[6] The bridged radical is therefore preferentially scavenged with oxygen to form the alkyl peroxide radical.

The subsequent process of the phosphoryl dichloride production can be explained by the mechanism represented by reactions (1)—(5).

$$R\cdot + O_2 \longrightarrow ROO\cdot \tag{1}$$

$$ROO\cdot + PCl_3 \longrightarrow RO\cdot + OPCl_3 \tag{2}$$ [6]

$$RO\cdot + PCl_3 \longrightarrow RO\dot{P}Cl_3 \tag{3}$$

$$ROPCl_3 + O_2 \longrightarrow ROPCl_3OO\cdot \tag{4}$$

$$ROPCl_3OO\cdot + PCl_3 \rightarrow ROPOCl_2 + OPCl_3 + Cl\cdot \tag{5}$$

In order to explain phosphate production from alkanes, Mayo, Durham, and Griggs suggested a heterolytic reaction (7) between phosphorus oxychloride and the alcohol produced by reaction (6).[1]

$$RO\cdot + RH \longrightarrow ROH + R\cdot \tag{6}$$

$$ROH + POCl_3 \longrightarrow ROPOCl_2 + HCl \tag{7}$$

The alkoxy radical appears to be the hydrogen-abstracting species. However, the isomer distributions of these reaction products differ from those of the reaction in which hydrogen abstraction by the alkoxy radical is operative, eliminating the possibility of mechanisms (6) and (7).[8]

Chlorophosphonation of Allyl Chloride and Bromide. Olefin also reacts with phosphorus trichloride–oxygen to give β-chloroalkylphosphonyl dichloride. The formation is explained by the following sequences of reactions.[9]

$$RCH{=}CHR' + Cl\cdot \rightarrow R\dot{C}HCHClR' \ \ (I) \tag{8}$$

$$R\dot{C}H\text{-}CHClR' + PCl_3 \rightarrow RCH(PCl_3\cdot)\text{-}CHClR' \tag{9}$$

$$RCH(PCl_3\cdot)\text{-}CHClR' + O_2 \rightarrow RCH(PCl_3OO\cdot)\text{-}CHClR' \tag{10}$$

$$RCH(PCl_3OO\cdot)\text{-}CHClR' + PCl_3 \rightarrow RCH(POCl_2)CHClR' + POCl_3 + Cl\cdot \tag{11}$$

In the case of allyl halide, the intermediate radical (I, R=CH_2X, R'=H) has two halogen atoms on both sides and the bridging effect thus seems to be more enhanced. The results obtained from allyl chloride and bromide are given in Table 2.

TABLE 2. PRODUCTS FROM ALLYL CHLORIDE AND ALLYL BROMIDE

Allyl halide	Component (relative ratio mol %)	
Allyl chloride	$CH_2ClCH[PO(OC_2H_5)_2]CH_2Cl$	(19)
	$CH_2ClCH[OPO(OC_2H_5)_2]CH_2Cl$	(79)
	$CH_2ClCHClCH_2OPO(OC_2H_5)_2$	(2)
Allyl bromide	$CH_2ClCH[PO(OC_2H_5)_2]CH_2Cl$	(3)
	$CH_2ClCH[OPO(OC_2H_5)_2]CH_2Cl$	(22)
	$CH_2ClCHClCH_2OPO(OC_2H_5)_2$	(1)
	$CH_2ClCH[OPO(OC_2H_5)_2]CH_2Br$	(25)
	$CH_2BrCH[OPO(OC_2H_5)_2]CH_2Br$	(49)
	$CH_2BrCHBrCH_2OPO(OC_2H_5)_2$	(trace)
	$CH_2ClCHBrCH_2OPO(OC_2H_5)_2$	(trace)
(and/or	$CH_2BrCHClCH_2OPO(OC_2H_5)_2$)	

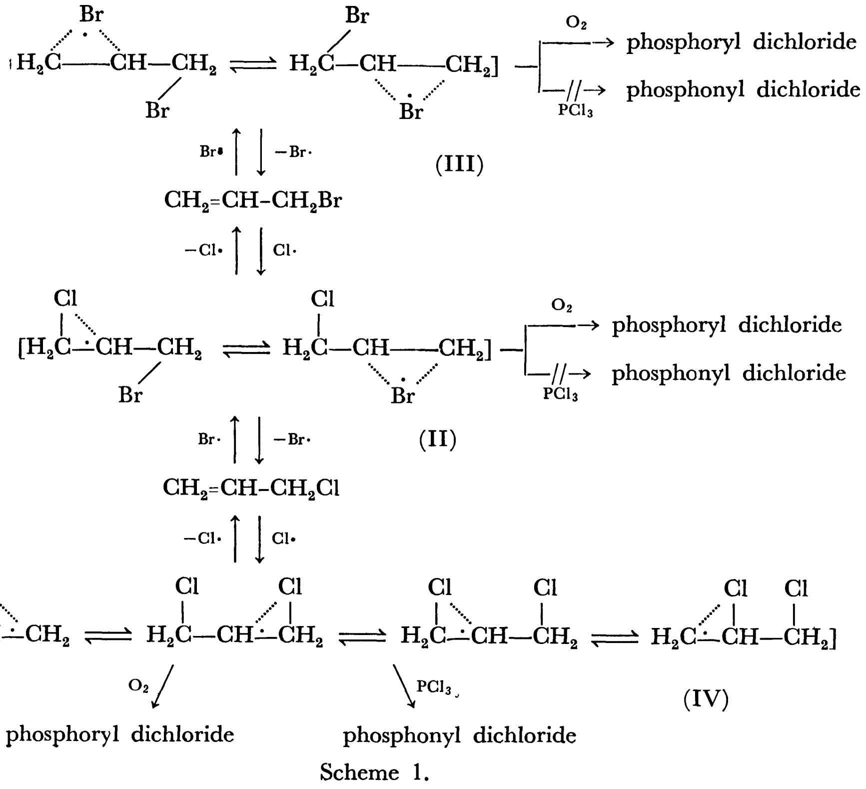
In the case of allyl bromide, the content of phosphate in the product exceeds 97%, halogen exchange occurring at the same time. The formations are illustrated by Scheme 1.

The addition of chlorine atom to the double bond of allyl bromide gives 1-chloromethyl-2-bromoethyl radical (II), which reacts only with oxygen to give phosphate. On the other hand, elimination of bromine atom from II gives allyl chloride. The resulting bromine atom reacts with allyl bromide to give 1-bromomethyl-2-bromoethyl radical (III), which is the most resonance-stabilized radical by bridging with either of bromine atom in both sides. III also reacts with oxygen to give the phosphate. Addition of chlorine atom to allyl chloride gives 1-chloromethyl-2-chloroethyl radical (IV), which is best described as an unsymmetrically bridged radical.[4] IV seems to be less resonance-stabilized than radicals II or III. It therefore reacts not only with oxygen but also phosphorus trichloride to give both phosphoryl and phosphonyl dichlorides.

Experimental

All the boiling points are uncorrected. NMR spectra were obtained at 100 MHz on a JNM-100 spectrometer with TMS as an internal reference in CCl_4 solution. The mass spectra were obtained on a Hitachi RMU-6 or RMU-7 spectrometer with a direct inlet. GC-MS were obtained on a Hitachi RMS-4 spectrometer.

Glc analyses were carried out with a Shimadzu GC-3AF on a 3 m×3 mmφ column packed with 5% Ucon LB 550X on Shimalite W. Preparative work was carried out with a



Scheme 1.

Hitachi 023 on a 1 m×12 mmϕ column with the same packing.

All the reagents were prepared by purifying commercial products. Vacuum distillation was carried out under nitrogen.

General Procedure of Chlorophosphonation. Oxygen was bubbled for 3 hr into a mixture of phosphorus trichloride (1.0 mol) and halide (0.2 mol) cooled in a bath at −15—0 °C at such a rate (50 ml/min) that the temperature of the mixture did not rise above 0 °C. After removal of a large portion of unreacted material and phosphorus oxychloride, the residue was vacuum-distilled yielding a colorless liquid. The yields and boiling points of the products from *n*-, isopropyl chlorides, *n*-, isopropyl bromides, allyl chloride, and allyl bromide are given in Table 3.

TABLE 3. YIELDS IN THE CHLOROPHOSPHONATION OF THE HALIDES

Halide	Yield (g)	Bp °C/mmHg
n-Propyl chloride	7.5	55—83 /1
Isopropyl chloride	5.7	58—78 /1
n-Propyl bromide	4.0	85—123/7
Isopropyl bromide	2.1	65—75 /1
Allyl chloride	35.0	68—84 /0.5
Allyl bromide	34.8	70—95 /0.5

Ethanolysis of the Reaction Products. The above reaction product (2.0 g) was stirred and cooled at−5 °C and a stream of dry nitrogen was passed through it. Absolute ethanol (20 ml) was then added dropwise for 2 hr. The mixture was stirred at 0—5 °C for 3 hr and then at room temperature overnight. Glc analysis of residue after removal of ethanol *in vacuo* was carried out.

Analysis. The products were identified by comparison of their retention times with those of authentic samples prepared by the methods described below. The other products were identified by elemental analysis, NMR, and mass spectra after being fractionated by preparative glc.

Authentic Sample. Diethyl 3-chloropropylphosphonate (bp 78—80 °C/1 mmHg)[10] and diethyl 3-bromopropylphosphonate (bp 94—95 °C/2 mmHg)[10] were prepared by Arbuzov reactions of 3-chloropropyl bromide and trimethylene dibromide with triethyl phosphite respectively. Diethyl 1-chloropropylphosphonate (bp 53—54 °C/0.1 mmHg)[4] was prepared by chlorination of diethyl 1-hydroxypropylphosphonate with thionyl chloride. Diethyl 2-chloropropylphosphonate(bp 77—79 °C/1 mmHg)[10] was prepared by the ethanolysis of 2-chloropropylphosphonyl dichloride, obtained by the reaction of propylene with phosphorus pentachloride.[10] Diethyl 2-bromopropyl phosphate (bp 95—97 °C/2 mmHg, Found: C, 30.41; H, 5.88%. Calcd for $C_7H_{16}O_4PBr$: C, 30.56; H, 5.86%), diethyl 2,3-dichloropropyl phosphate (bp 123—125 °C/4 mmHg).[10] Diethyl 1-chloromethyl-2-chloroethyl phosphate (bp 112—114 °C/2 mmHg)[10] were prepared from the corresponding alcohols and diethyl phosphorochloridate.[10] Diethyl 2,3-dibromopropyl phosphate (bp 122—123 °C/10^{-3} mmHg, Found: C, 23.61; H, 4.30%. Calcd for $C_7H_{15}O_4PBr_2$:C, 23.75; H, 4.27%.) were prepared by the addition of bromine to diethyl allyl phosphate.[11]

The following products were identified by means of the data of NMR, mass spectra and elementary analysis. Diethyl 1-methyl-2-chloroethylphosphonate; NMR: δ 1.05 (d, 3H, J_{HH} 7.0 Hz, $CH-C\underline{H}_3$), 1.35(t, 6H, J_{HH} 7.5 Hz, $CH_2-C\underline{H}_3$), 1.5—2.0(m, 1H, $-C\underline{H}-CH_3$), 3.65(d, 2H, J_{HH} 5.0 Hz, $-C\underline{H}_2Cl$), and 4.10(q-d, 4H, J_{POCH} 7.4 Hz, $-OCH_2-$). Found: C, 39.08; H, 7.48%. Calcd for $C_7H_{16}O_3PCl$: C, 39.17; H, 7.51%. Diethyl 1-methyl-2-chloroethyl phosphate;[11] NMR: δ 1.40(d, 3H, J_{HH} 7.2 Hz, $-CH-C\underline{H}_3$), 1.44(t, 6H, J_{HH} 7.5 Hz, $CH_2C\underline{H}_3$), 3.54(d, 2H, J_{HH} 7.2, CH_2Cl), 4.05(q-d, 4H, J_{POCH} 7.5 Hz, $-OCH_2-$), and 4.3—4.6 (m, 1H, $OCH-CH_3$). Diethyl 1-bromopropylphosphonate; NMR δ 1.12(t, 3H, J_{HH} 7.0 Hz, $CH-C\underline{H}_3$) 1.34(t, 6H, J_{HH} 7.0 Hz, $OCH_2-C\underline{H}_3$), 2.00(m, 2H, $C\underline{H}_2-CH$), 3.62(d-t, 1H, J_{HH} 10 Hz, J_{PCH} 5.0 Hz, $C\underline{H}Br-P$), and 4.12(qui, 4H, J_{POCH} 7.0 Hz, $-C\underline{H}_2-CH_3$). Found: C, 32.64; H, 6.18%. Calcd for $C_7H_{16}O_3PBr$: C; 32.45; H, 6.23%. Diethyl 1-methyl-2-bromoethylphosphonate; NMR δ 1.30(d-d, 3H, J_{HH} 7.0 Hz, J_{PCCH} 15 Hz, $CH-C\underline{H}_3$), 1.33(t, 6H, J_{HH} 7.0 Hz, $-CH_2C\underline{H}_3$), 2.04(m, 1H, $P-C\underline{H}-$), 3.20(t-d, 1H, J_{HH} 5.0 Hz, $J_{H_aH_b}$ 11.0 Hz, J_{PCCH} 11.0 Hz, $-C\underline{H}_aH_bBr$), 3.76(t-d, 1H, J_{HH} 5.0 Hz, J_{PCCH} 11.0 Hz, $-CH_a\underline{H}_bBr$), and 4.06 (qui, 4H, J_{POCH} 0.7 Hz, $-OC\underline{H}_2-$). Found: C, 32.40; H, 6.33%. Calcd for $C_7H_{16}O_3PBr$: C, 32.45; H, 6.23%. Diethyl 1-methyl-2-bromoethyl phosphate; NMR δ 1.41(t, 6H, J_{HH} 7.0 Hz, $-CH_2C\underline{H}_3$) 1.44(d, 3H, J_{HH} 7.0 Hz, $-CH-C\underline{H}_3$), 3.46 (d, 2H, J_{HH} 5.0 Hz, $C\underline{H}_2Br$), and 4.06(q-d, 4H, J_{POCH} 7.4 Hz, $-OC\underline{H}_2-$), Found: C, 29.87; H, 5.80%. Calcd for $C_7H_{16}O_4PBr$: C, 30.56; H, 5.86%. Diethyl 1-chloromethyl-2-chloroethylphosphonate; NMR δ 1.36(t, 6H, J_{HH} 7.0 Hz, $CH_2C\underline{H}_3$), 2.48(m, 1H, $P-C\underline{H}-$), 3.90(d-d, 4H, J_{HH} 5.0 Hz, J_{PCCH} 14.5 Hz, $-C\underline{H}_2Cl$), and 4.08(qui, 4H, J_{POCH} 7.0 Hz, $-C\underline{H}_2-$). Found: C, 34.21; H, 6.12%. Calcd for $C_7H_{15}O_3PCl_2$: C, 33.75: H, 6.07%. Diethyl 1-chloromethyl-2-chloroethyl phosphate;[10] NMR δ 1.36(t, 6H, J_{HH} 7.0 Hz, $-CH_2C\underline{H}_3$), 3.78(d, 4H, J_{HH} 4.0 Hz, $-C\underline{H}_2Cl$), 4.08(qui, 4H, J_{POCH} 7.0 Hz, $-OC\underline{H}_2-$), and 4.60(m, 1H, $P-OC\underline{H}-$). Diethyl 1-chloromethyl-2-bromoethyl phosphate; NMR δ 1.36(t, 6H, J_{HH} 7.0 Hz, $CH_2C\underline{H}_3$), 3.62(d, 2H, J_{HH} 5.0 Hz, $-C\underline{H}_2Br$), 3.78(d, 2H, J_{HH} 5.0 Hz, $-C\underline{H}_2Cl$), 4.08 (qui, 4H, J_{POCH} 7.0 Hz, $-OC\underline{H}_2-$), and 4.20(m, 1H, $-OC\underline{H}-$). Found: C, 27.04; H, 4.90%. Calcd for $C_7H_{15}O_4PBrCl$: C, 27.16; H, 4.88%. Diethyl 1-bromomethyl-2-bromoethyl phosphate; NMR δ 1.36(t, 6H, J_{HH} 7.0 Hz, $CH_2C\underline{H}_3$), 3.63(d, 4H, J_{HH} 5.0 Hz, $-C\underline{H}_2Br$), 4.08(qui, 4H, J_{POCH} 7.0 Hz, $-OC\underline{H}_2-$), and 4.48(m, 1H, $OC\underline{H}-$). Found: C, 23.65; H, 4.21%. Calcd for $C_7H_{15}O_4PBr_2$: C, 23.75; H, 4.27%.

A strong ion peak of *m/e* 99($P(OH)_4^+$) was observed in the mass spectra of all the phosphate components, not of the phosphonate components. Diethyl 1(2)-bromo-2(1)-chloropropyl phosphate was identified by comparison of its relative retention time in glc. The mass spectrum of this fraction showed no molecular ion peak but strong peaks at *m/e* 229 and 231 (M^+–Br) and at *m/e* 81 and 79 ($^{81}Br^+$ and $^{79}Br^+$). A significant amount of allyl chloride was detected in the chlorophosphonation of allyl bromide.

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