# Addition of Phosphorus Tribromide to Olefins

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THE free-radical addition of phosphorus trichloride to simple olefins was reported briefly some time ago as leading to β-chloroalkylphosphonous dichlorides;[1] doubts have been expressed about the

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[1] M. S. Kharasch, E. V. Jensen, and W. H. Urry, *J. Amer. Chem. Soc.*, 1945, **67**, 1864; E. C. Ladd and J. R. Little, U.S.P. 2,510,699/1950.

nature of the product obtained in these reactions.[2] We have now shown that phosphorus tribromide can be added, under a variety of conditions, to simple olefins to give 1 : 1 adducts which are undoubtedly β-bromoalkylphosphonous dibromides. These compounds are potentially useful intermediates in the synthesis of phosphorus mustards, and heterocyclic compounds containing phosphorus.

The ultraviolet irradiation of a mixture of ethylene and phosphorus tribromide gave 14% of 2-bromoethylphosphonous dibromide, characterized by elemental analysis, by absence of a phosphoryl band in its infrared spectrum, and by oxidative hydrolysis to the known 2-bromoethylphosphonic acid.[3] The same phosphonous dibromide can be obtained in substantially better yield (40%) by a thermal addition reaction at 150° in the absence of any added initiator.

Ultraviolet irradiation of a mixture of refluxing propene and phosphorus tribromide gave 2-bromo-1-methylethylphosphonous dibromide, $\mathrm{MeCH(PBr_2)\cdot CH_2Br}$, containing a small amount of the isomeric 2-bromopropylphosphonous dibromide, $\mathrm{MeCHBr\cdot CH_2\cdot PBr_2}$. The thermal addition reaction with propene gave a mixture of these isomeric compounds containing 30% of the 2-bromo-isomer. The isomers were distinguished by their $^1$H nuclear magnetic resonance spectra at 60 Mc./sec. The major product of both reactions shows a quartet for the methyl group at $\delta = 2{\cdot}25$ p.p.m. (downfield from external $\mathrm{Me_4Si} = 0$), with $J_{\mathrm{Me-P}} = 17$ c./sec. and $J_{\mathrm{Me-CH}} = 7$ c./sec.; the minor product also shows a quartet, at $\delta = 2{\cdot}67$ p.p.m., with $J_{\mathrm{Me-CH}} = 7$ c./sec., but with $J_{\mathrm{Me-P}} = 1{\cdot}5$ c./sec. The small value of this last coupling constant indicates the remote position of the methyl group from the $\mathrm{PBr_2}$ group.

Addition of phosphorus tribromide to hept-1-ene, oct-1-ene, and cyclohexene can be initiated by ultraviolet radiation, or by peroxides or azo-compounds, and yields 1 : 1 adducts which seem to be mixtures of isomers, since they give two peaks on gas chromatography.

The free-radical nature of the additions reported is substantiated by the observation that addition does not occur at comparable temperatures if the initiators are lacking. The orientation of addition of the major product from propene is unusual, and suggests that both the bromine radical and the phosphorus dibromide radical may be involved in addition steps, and that the chain-transfer step may not be exclusively an abstraction from phosphorus tribromide. The following mechanism is in accord with other observations on the reactivity of phosphorus trihalides with olefins,[2] and accounts for the observed products:

$$\left.\begin{array}{l}
\mathrm{PBr_3} \xrightarrow{h\nu} \mathrm{Br\cdot} + \mathrm{\cdot PBr_2} \\
\mathrm{Br\cdot} + \mathrm{MeCH:CH_2} \rightarrow \mathrm{Me\dot{C}HCH_2Br} \\
\mathrm{Me\dot{C}HCH_2Br} + \mathrm{PBr_3} \rightleftharpoons \mathrm{MeCH(\dot{P}Br_3)CH_2Br} \\
\mathrm{MeCH(\dot{P}Br_3)CH_2Br} + \mathrm{MeCH:CH_2} \\
\qquad\qquad\qquad\downarrow \\
\mathrm{MeCH(PBr_2)CH_2Br} + \mathrm{Me\dot{C}HCH_2Br}
\end{array}\right\}\ \text{Major path}$$

$$\left.\begin{array}{l}
\mathrm{MeCH:CH_2} + \mathrm{\dot{P}Br_2} \rightarrow \mathrm{Me\dot{C}HCH_2PBr_2} \\
\mathrm{Me\dot{C}HCH_2PBr_2} + \mathrm{PBr_3} \\
\qquad\qquad\qquad\downarrow \\
\mathrm{MeCHBrCH_2PBr_2} + \mathrm{\dot{P}Br_2}
\end{array}\right\}\ \text{Minor path}$$

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[2] F. R. Mayo, L. J. Durham, and K. S. Griggs, *J. Amer. Chem. Soc.*, 1963, **85**, 3156.

[3] M. I. Kabachnik and P. A. Rossiiskaya, *Izvest. Akad. Nauk S.S.S.R. Otdel Khim. Nauk*, 1947, 389.