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Addition of Phosphorus Trihalides to Olefins[1]

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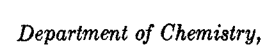
Phosphorus tribromide can be added to olefins to yield 1:1 adducts, with ultraviolet irradiation, peroxides, or heat as initiators. Asymmetrical olefins yield both isomers. Similar results are obtained with phosphorus trichloride.

The utility of free-radical addition reactions of compounds containing P–H bonds to olefins in the preparation of organophosphorus compounds is well recognized.[2] However, since the initial description of the free-radical addition of phosphorus trichloride to 1-octene,[3] little work has appeared on the potentially useful free-radical addition of P-halo compounds to olefins. A recent paper[4] describes the photochemical initiation of addition of phosphorus trichloride to olefins; 1:1 adducts were obtained with isobutylene and vinylcyclohexene.

An examination of bond energies[5] indicates that the addition of phosphorus tribromide or phosphorus trichloride to olefins should be an exothermic process. However, the lower bond strength of the P–Br bond ($\bar{E} = 62$ kcal/mole) as compared with the P–Cl bond ($\bar{E} = 76$ kcal/mole) should make phosphorus tribromide more easily dissociated into radicals, and a better chain-transfer agent, than phosphorus trichloride. Accordingly, the free-radical initiated addition of phosphorus tribromide to olefins was examined initially.



$$PX_3 + \text{>C=C<} \longrightarrow \text{-CX-C-PX}_2$$

$X = Cl, Br; \Delta H \sim -13$ kcals.

Three types of initiation were employed: ultraviolet light, peroxide, and thermal. All were effective in producing the desired adducts (see Table I). In the reaction between ethylene and phosphorus tribromide, thermal initiation was more effective than ultraviolet light, while for the longer chain olefins, ultraviolet light gave better yields, and a cleaner product, than did peroxide or thermal initiation.

The structure of the product from phosphorus tribromide and ethylene was established as 2-bromoethylphosphonous dibromide by its conversion, on being treated with aqueous hydrogen peroxide, to the known 2-bromoethylphosphonic acid.[6] The adduct from phosphorus tribromide and cyclohexene must be 2-bromocyclohexylphosphonous dibromide (probably a mixture of stereoisomers) but attempts to further characterize this compound by hydrolysis and oxidation to a phosphonic acid, or by reaction with amines to give a phosphonous diamide, invariably gave partially dehydrobrominated compounds, and it has not yet proved possible to obtain derivatives of the above kinds from this compound.

Similar difficulties were encountered with the phosphonous dibromides from 1-heptene and 1-octene, and again partial dehydrobromination occurred. The ^1H nuclear magnetic resonance (nmr) spectra of these compounds were extremely complex and not amenable to analysis. The compounds were, however, shown to be mixtures of both possible isomers (2-bromoalkyl-1-phosphonous dibromides and 1-bromoalkyl-2-phosphonous dibromides) by gas–liquid partition chromatographic analysis (see Experimental Section), and by ^{31}P nuclear magnetic resonance spectroscopy (see Table II).

The ^1H nmr spectrum of the product from propylene and phosphorus tribromide proved amenable to analysis and confirmed the presence of both 2-bromopropylphosphonous dibromide and 1-bromopropyl-2-phosphonous dibromide. The CH_3 region of the spectrum showed a relatively intense quartet at $\delta = 2.25$ ppm with $J_{\mathrm{CH_3CH}} = 7$ cps, and $J_{\mathrm{CH_3-C-P}} = 17$ cps; the assignment of the CH_3CP coupling constant was confirmed by a spin-decoupling experiment. The large value of this coupling constant indicates the proximity of the methyl group and the phosphorus atom and confirms the assignment of this quartet to $CH_3CH(PBr_2)CH_2Br$. In addition, a weaker quartet was observed at $\delta = 2.67$ ppm with $J_{\mathrm{CH_3CH}} = 7$ cps and $J_{\mathrm{CH_3CCP}} = 1.5$ cps. The small value of this last coupling constant indicates the relatively remote position of the methyl group from the phosphorus atom and the formulation of the compound giving rise to it as $CH_3CHBrCH_2PBr_2$.

The relative intensities of the two quartets varied according to the method of initiation of the reaction, confirming the fact that a mixture of products was being produced. Ultraviolet irradiation of a mixture of refluxing propylene in phosphorus tribromide gave almost pure $CH_3CH(PBr_2)CH_2Br$, containing only about 5% of the isomeric product. Thermal reaction at 150° gave 70% of $CH_3CH(PBr_2)CH_2Br$ and 30% of $CH_3CHBrCH_2PBr_2$.

Although the mechanism of the thermal addition reaction may be disputable, the ultraviolet light

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[1] This investigation was supported by Public Health Service Research Grant CA 07182 from the National Cancer Institute. For a preliminary account of the phosphorus tribromide additions, see B. Fontal and H. Goldwhite, *Chem. Commun.*, 111 (1965).

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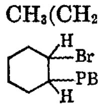
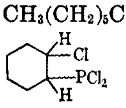
TABLE I

ADDITION OF PHOSPHORUS TRIBROMIDE TO OLEFINS

Olefin	Initiator	% yield of 1:1 adduct	Bp, °C (mm)	Calcd, %				Found, %			
				C	H	Br	P	C	H	Br	P
C_2H_4	Ultraviolet light	14	100 (0.5)	8.03	1.3	80.2		8.2	1.0	80.4	
C_2H_4	Heat	44	60–62 (0.01)			80.2				79.8	
C_3H_6	Ultraviolet light	9	84 (0.5)	11.5	1.9	76.7	9.9	11.8	1.8	77.0	9.2
C_3H_6	Heat	34	79 (0.5)			76.7				76.5	
Cyclohexene	Ultraviolet light	38	114 (10)	20.4	2.8	67.0	8.8	21.2	3.4	65.2	8.6
Cyclohexene	(*t*-BuO)$_2$	34	115 (10)			67.0	8.8			66.0	8.6
1-Heptene	Ultraviolet light	40	115–120 (0.5)	22.8	3.8	65.0	8.4	23.2	4.2	65.5	8.6
1-Heptene	(*t*-BuO)$_2$	17	120 (0.5)			65.0	8.4			64.0	9.0
1-Heptene	Heat	17	115–120 (0.5)			65.0				64.2	

TABLE II

^{31}P CHEMICAL SHIFTS[a] FOR SOME PHOSPHONOUS DIHALIDES

Bromides		Chlorides	
Compound	Chemical shift	Compound	Chemical shift
$CH_3CH(PBr)_2CH_2Br$	−189[b] (4)	$CH_3(CH_2)_4CH(PCl_2)CH_2Cl$	−189 (4)
$CH_3CHBrCH_2PBr_2$	−183[b] (1)	$CH_3(CH_2)_4CHClCH_2PCl_2$	−191 (1)
$CH_3(CH_2)_4CHPBr_2CH_2Br$	−191[c] (3)	$CH_3(CH_2)_5CH(PCl_2)CH_2Cl$	−185 (4)
$CH_3(CH_2)_4CHBrCH_2PBr_2$	−178[c] (2)	$CH_3(CH_2)_5CHClCH_2PCl_2$	−191 (1)
	−185 (1)		−187 (5)
	−202 (1)		−199 (6)

[a] Chemical shifts are in parts per million from external 85% H_3PO_4. A negative sign indicates a downfield shift. Relative intensities of peaks are in parenthesis. [b] Assigned by relative intensities; mixture composition was known from ^1H nmr (see text). [c] Assigned by analogy with the propylphosphonous dibromides.

initiated reactions are clearly free radical in nature since no products are obtained if there is no irradiation. The structure of the major product from propylene is unusual for a free-radical addition reaction since addition of such compounds as methanethiol, trichlorosilane, hydrogen bromide, and 2-cyanoethylphosphine (*cf.* ref 2) has been shown to give almost exclusive terminal addition to this olefin. However, phosphorus tribromide may be functioning in this reaction not only as a chain-transfer agent but also as a radical scavenger. Work on the reaction between alkanes, phosphorus trichloride, and oxygen has shown that phosphorus trichloride is an excellent radical scavenger,[7] and the following mechanism is suggested as an extension of this idea to the free-radical addition of phosphorus tribromide to olefins.

$$PBr_3 \xrightarrow{h\nu} Br\cdot + PBr_2\cdot$$

$$\text{main reaction path} \left\{ \begin{array}{l} Br\cdot + CH_3CH{=}CH_2 \longrightarrow CH_3\dot{C}HCH_2Br \\ CH_3\dot{C}HCH_2Br + PBr_3 \rightleftharpoons CH_3\dot{C}H(PBr_3)CH_2Br \\ CH_3CH(\dot{P}Br_3)CH_2Br + CH_3CHC{=}H_2 \longrightarrow \\ \qquad\qquad CH_3CH(PBr_2)CH_2Br + CH_3\dot{C}HCH_2Br \end{array} \right.$$

$$\text{minor path} \left\{ \begin{array}{l} \cdot PBr_2 + CH_3CH{=}CH_2 \longrightarrow CH_3\dot{C}HCH_2PBr_2 \\ CH_3\dot{C}HCH_2PBr_2 + PBr_3 \longrightarrow \\ \qquad\qquad CH_3CHBrCH_2PBr_2 + \cdot PBr_2 \end{array} \right.$$

Alternatively, a bridged-radical intermediate[4] could account for the observed products.

In view of the successful results achieved with phosphorus tribromide, analogous reactions were attempted with phosphorus trichloride. With this halide thermal initiation was unsuccessful. Benzoyl peroxide gave low yields of adducts and initiation by ultraviolet light proved to be most successful (see Table III), as has been observed independently by Little and Hartman.[4] Fair yields of 1:1 adducts, shown to be mixtures of both possible products by gas chromatography and by ^{31}P nmr spectroscopy, were obtained with 1-heptene, 1-octene, and cyclohexene. Under comparable conditions ethylene was unreactive.

The observed ^{31}P chemical shifts for the adducts all lie within the range of −178 to −205 ppm from external 85% H_3PO_4. This confirms their formulation as RPX_2 compounds rather than $RPOX_2$. Chemical shifts reported[8] for phosphonous halides, RPX_2 (X = Cl, R = alkyl) have been in the range of −158 ($R = ClCH_2$, X = Cl) to −196 ppm ($R = C_2H_5$, X = Cl), whereas those for phosphonyl halides have ranged from −10 to −53 ppm.

Experimental Section

Materials.—Olefins, phosphorus halides, and peroxides were commercially available materials. The olefins and halides were distilled under nitrogen before being used. Ethylene and propylene were handled in a conventional vacuum system. Products were routinely handled in nitrogen-filled glove bags.

Nmr Spectra.—^1H spectra were determined on a Varian A-60 spectrometer fitted with a Nuclear Magnetic Resonance Specialities heteronuclear decoupler. ^{31}P spectra were determined on a Varian V-4300B spectrometer with a probe operating at 24.3 Mc/sec.

Gas Chromatography.—Chromatography was carried out on an F & M Model 720 chromatograph using helium as carrier gas and a 2 ft × 0.25 in. column with silicone rubber stationary phase; 1-μl samples of the mixtures were injected. The retention volumes observed and oven temperatures are shown in Table IV.

Reaction of Ethylene with Phosphorus Tribromide. A. Photochemical Initiation.—Phosphorus tribromide (5.0 ml) was placed in a 250-ml silica tube which was evacuated; 47.6 mmoles

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(7) F. R. Mayo, L. J. Durham, and K. S. Griggs, *J. Am. Chem. Soc.*, **85**, 3156 (1963).

(8) E. Fluck, "Die Kernmagnetische Resonanz und ihre Anwendung in der Anorganischen Chemie," Springer-Verlag, Berlin, 1963, pp 256–260.

TABLE III

ADDITIONS OF PHOSPHORUS TRICHLORIDE TO OLEFINS

Olefin	Initiator	% yield of 1:1 adduct	Bp, °C (mm)	Found, % C	Found, % H	Found, % Cl	Calcd, % C	Calcd, % H	Calcd, % Cl
Ethylene	Ultraviolet light	0	...						
1-Heptene	$(PhCOO)_2$	6	94–95 (1)	36.4	6.12	44.8	35.7	5.95	45.5
1-Octene	$(PhCOO)_2$	3	110–112 (2)	40.0	6.98	42.0	38.5	6.42	43.0
1-Octene	Ultraviolet light	9	113–115 (2)			42.1			43.0
Cyclohexene	$(PhCOO)_2$	10	135 (12)	33.5	4.99	47.7	32.8	4.56	48.5
Cyclohexene	Ultraviolet light	16	98–100 (1)			47.9			48.5

TABLE IV

Adduct	Oven temp, °C	Retention volume (cc of He) of Major component	Retention volume (cc of He) of Minor component
C_2H_4–PBr_3	160	105	
C_3H_6–PBr_3/ultraviolet	193	50 (brd, unresolved)	
Cyclohexene–PBr_3/ultraviolet	193	48 (peaks of similar area)	114
1-Heptene–PBr_3/ultraviolet	193	54	138
Cyclohexene–PCl_3/ultraviolet	193	66 (brd, unresolved)	
1-Octene–PCl_3/ultraviolet	193	81	54

of ethylene was condensed into the tube which was then irradiated 6 in. from a 250-w 'Uviarc' medium-pressure mercury arc lamp for 45.5 hr. Unreacted ethylene (37.8 mmoles) was removed and the residual liquid was combined with that from another similar tube and distilled to give recovered PBr_3, bp 70–79°, (25 mm), and 2-bromoethylphosphonous dibromide, bp 100–102° (0.5 mm), 4.4 g.

B. Thermal Initiation (Carried out by D. G. Rowsell).—Phosphorus tribromide (100 ml, 285 g, 1.1 moles) was added to an autoclave (500-ml capacity) which was then evacuated and cooled to −196°. Ethylene (0.5 mole) was condensed in and the autoclave was heated at 140–150° for 20 hr. Unreacted ethylene (0.2 mole) was transferred into the vacuum system and the brown viscous residue remaining in the autoclave was distilled under reduced pressure. The first fraction, bp 35–37° (0.1 mm), was identified as phosphorus tribormide (50 ml, 145 g, 0.55 mole). The second fraction was 2-bromoethylphosphonous dibromide (65 g, 0.22 mole, 44%), bp, 60–62° (0.01 mm). A small amount of unidentified brown solid residue remained in the distillation flask.

Oxidative Hydrolysis of 2-Bromoethylphosphonous Dibromide.—The dibromide (0.37 g) was dropped into 2 ml of water, and the suspension was gently warmed; 5 ml of 30% hydrogen peroxide was slowly added to the resulting solution which was then heated to reflux for 15 min. Evaporation of the water then gave an oil which crystallized to yield the hygroscopic 2-bromoethylphosphonic acid, mp 83–85° (lit.[6] mp 86–87°). *Anal.* Calcd for $BrC_2H_4PO_3H_2$: equiv wt, 94.3. Found: equiv wt, 93.0.

Reaction of Propylene with Phosphorus Tribromide. A. Photochemial Initiation.—In a 250-ml silica flask, carrying a cold-finger condenser cooled with solid CO_2, and filled with nitrogen at 1 atm, was placed 100 g, 0.36 mole, of PBr_3; 0.20 mole of propylene was condensed into the flask which was then irradiated with a 250-w medium-pressure mercury arc lamp for 9.5 hr. Unreacted propylene (0.12 mole) was removed and the residue was distilled to give phosphorus tribromide and a mixture of bromopropylphosphonous dibromides (2.1 g, 9%), bp 84° (0.5 mm). A semisolid residue was left. A control reaction omitting only the irradiation gave a quantitative recovery of the starting materials.

B. Thermal Initiation.—Phosphorus tribromide (25 ml) was placed in a 150-ml stainless steel bomb which was then evacuated; 0.10 mole of propylene was condensed into the bomb which was then heated at 130° for 23 hr. Unreacted propylene (0.015 mole) was removed and the residual liquid was distilled to give recovered phosphorus tribromide (18 ml) and bromopropylphosphonous dibromide (8.9 g, 34%), bp 79° (0.5 mm).

Reactions of Higher Olefins with Phosphorus Trihalides.—The procedures followed were of the same general nature and can be summarized as follows (see Tables I and III for yields, etc.).

A. Photochemical Initiation.—A silica tube of 50-ml capacity containing a mixture of 0.3 mole of phosphorus trihalide and 0.15 mole of olefin was evacuated and sealed. The tube was then irradiated 9 in. from a 250-w mercury arc lamp for 18 hr. It was then cooled and opened, and its contents distilled.

B. Thermal Initiation.—The bomb described above for propylene was used; a mixture of 0.12 mole of olefin and 0.24 mole of phosphorus trihalide was placed in it and heated at 150° for 18 hr. The liquid product was then distilled.

C. Peroxide Initiation.—In the phosphorus trichloride reactions benzoyl peroxide was used as initiator; with phosphorus tribromide, di-*t*-butyl peroxide was used. To a mixture of 0.1 mole of olefin and 0.2 mole of phosphorus halide, 1 mmole of peroxide was added. The mixture was refluxed under nitrogen and at 90-min intervals three further portions of 1 mmole of peroxide were added. The mixture was refluxed for a further 15 hr and distilled initially at 1 atm and then under reduced pressure.

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