

THE REACTION OF OLEFINS WITH  $\text{PBr}_3$  AND OXYGEN

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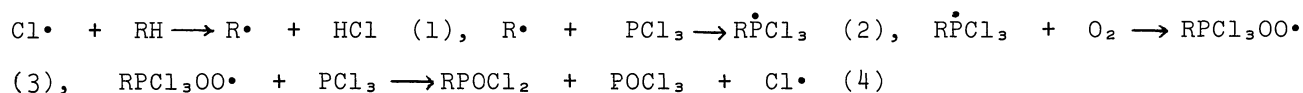
2-Bromoalkylphosphonic dibromides were obtained in good yield  
by the reaction of olefins with  $\text{PBr}_3$  and oxygen.

Since its discovery, the reaction of  $\text{PCl}_3$ , oxygen and saturated or unsaturated hydrocarbons (chlorophosponation) to give alkylphosphonic dichlorides and  $\text{POCl}_3$  has received much attention as a preparative method for alkylphosphonic dichlorides. There has been a considerable amount of work done to determine the experimental limitations of the reaction.<sup>1,2)</sup> But the reaction in which phosphorus tribromide was used in the place of  $\text{PCl}_3$  had not been yet reported.

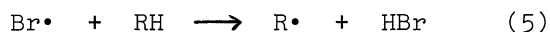
In the present paper, we report the reaction of hydrocarbon with  $\text{PBr}_3$  and oxygen. No phosphonation product could be obtained in the reaction of saturated hydrocarbon with  $\text{PBr}_3$  or a mixture of  $\text{PCl}_3$  and  $\text{PBr}_3$  (1:1) and oxygen. Phosphorus tribromide acts rather an inhibitor for chlorophosponation of saturated hydrocarbon. But in the reaction of olefins with  $\text{PBr}_3$  and oxygen, the phosphonation products could be obtained in good yield. The reaction was carried out with a mixture of cyclohexene (0.1 mol) and  $\text{PBr}_3$  (0.5 mol), cooled with an ice-salt bath ( $-20 - 0^\circ\text{C}$ ) and oxygen was bubbled into the mixture at flow rate of 50 ml/min for 3 hrs. The mixture was distilled at reduced pressure. The fraction boiling at  $130 - 132^\circ\text{C}/0.1$  mmHg (I) weighed 32.0 g (87 %). Found: C, 19.01; H, 2.52; P, 8.70; Br, 66.01%. Calcd for  $\text{C}_6\text{H}_{10}\text{POBr}_3$ : C, 19.59; H, 2.74; P, 8.42; Br, 64.90%. By the hydrolysis of I with water, free phosphonic acid (II) was obtained and recrystallized from ether, mp  $67 - 68^\circ\text{C}$ . II reacted with 5% aqueous solution of sodium hydroxide to give cyclohexene. This finding implied that II was 2-bromocyclohexylphosphonic acid.<sup>3)</sup> 2-Bromocyclohexylphosphonic dibromide (I) was esterified with ethanol-triethylamine to give diethyl 2-bromocyclohexylphosphonate (III), bp  $127 - 128^\circ\text{C}/0.1$  mmHg. Found: P, 10.21; Br, 27.21%; mol wt (cryoscopic in benzene) 297. Calcd for  $\text{C}_{10}\text{H}_{20}\text{PO}_3\text{Br}$ : P, 10.35; Br, 26.71%; mol wt 299.2. Mass spectrum did not show a molecular ion peak

but strong peaks at  $m/e$  219 (20%,  $M^+-Br$ ) and at  $m/e$  81 and 79 (base peak  $^{81}Br^+$  and 80%  $^{79}Br^+$ ). NMR spectrum showed a triplet at  $\delta$  1.35 (6H,  $OCH_2CH_3$ ,  $J_{H-H}$  7.0 Hz), a multiplet at 1.49 (9H,  $P-\overline{CH(CH_2)_4}CHBr$ ), an octet at 4.10 (4H,  $POCH_2CH_3$ ,  $J_{P-H}$  8.1 Hz), and a multiplet at 5.48 (1H,  $-CBrH-$ ). III was about 97% pure by glc (Ucon LB 550X, 3mX3mm $\phi$ , 140°C,  $N_2$  65ml/min). At a column temperature of 170°C, several peaks appeared in the region of the shorter retention time, presumably owing to the thermal decomposition of III. Any other phosphonation product could not be detected different from the case of chlorophosphonation of cyclohexene.<sup>3)</sup> The reaction of 1-hexene with  $PBr_3$  and oxygen gave 1-bromomethylpentylphosphonic dibromide (68%). Any other isomer could not be detected. The NMR spectrum of the diethyl ester showed a quartet for the methylene group ( $-CH_2Br$ ) at  $\delta$  3.39 with  $J_{BrCH_2-CH}$  7.0 Hz and  $J_{BrCH_2-P}$  17.0 Hz. Also, in the case of 1-octene, the similar result was obtained.

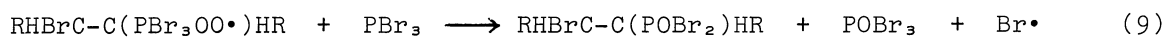
The mechanism of chlorophosphonation was represented by a sequence of the reactions (1) - (4), which involves the chlorine atom as a chain carrier.<sup>1)</sup>



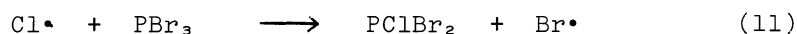
Chlorine atom attack on C-H bond is a strong exothermic process with low activation energy, whereas, in general, bromine atom attack is endothermic. Reaction (5) hardly occurs, particularly in liquid phase, at low temperature. Therefore,  $PBr_3$  is unreactive with saturated hydrocarbon in this reaction different from  $PCl_3$ .



But in the case of unsaturated hydrocarbon, radical chain reactions (6) - (9) may proceed, because bromine atom addition to olefinic double bond is exothermic.



The inhibiting action of  $PBr_3$  to chlorophosphonation of saturated hydrocarbon must involve the following step.<sup>4)</sup>



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