CHEMISTRY LETTERS, pp. 599-600, 1973. Published by the Chemical Society of Japan

THE REACTION OF OLEFINS WITH PBr_3 AND OXYGEN

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2-Bromoalkylphosphonic dibromides were obtained in good yield by the reaction of olefins with PBr_3 and oxygen.

Since its discovery, the reaction of PCl_3, oxygen and saturated or unsaturated hydrocarbons (chlorophosphonation) to give alkylphosphonic dichlorides and $POCl_3$ 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.$^{1,2)}$ But the reaction in which phosphorus tribromide was used in the place of PCl_3 had not been yet reported.

In the present paper, we report the reaction of hydrocarbon with PBr_3 and oxygen. No phosphonation product could be obtained in the reaction of saturated hydrocarbon with PBr_3 or a mixture of PCl_3 and PBr_3 (1:1) and oxygen. Phosphorus tribromide acts rather an inhibitor for chlorophosphonation of saturated hydrocarbon. But in the reaction of olefins with 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 PBr_3 (0.5 mol), cooled with an ice-salt bath (-20 - 0°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°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 $C_6H_{10}POBr_3$: 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°C. II reacted with 5% aqueous solution of sodium hydroxide to give cyclohexene. This finding implied. that II was 2-bromocyclohexylphosphonic acid.$^{3)}$ 2-Bromocyclohexylphosphonic dibromide (I) was esterified with ethanol-triethylamine to give diethyl 2-bromocyclohexylphosphonate (III), bp 127 - 128°C/0.1 mmHg. Found: P, 10.21; Br, 27.21%; mol wt (cryoscopic in benzene) 297. Calcd for $C_{10}H_{20}PO_3Br$: 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 δ 1.35 (6H, $OCH_2C\underline{H}_3$, J_{H-H} 7.0 Hz), a multiplet at 1.49 (9H, $P\text{-}\overline{C\underline{H}(C\underline{H}_2)_4C}HBr$), an octet at 4.10 (4H, $POC\underline{H}_2CH_3$, J_{P-H} 8.1 Hz), and a multiplet at 5.48 (1H, -CBrH-). III was about 97% pure by glc (Ucon LB 550X, 3mX3mmϕ, 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.3) 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 δ 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.1)

$Cl\cdot + RH \longrightarrow R\cdot + HCl$ (1), $R\cdot + PCl_3 \longrightarrow R\dot{P}Cl_3$ (2), $R\dot{P}Cl_3 + O_2 \longrightarrow RPCl_3OO\cdot$ (3), $RPCl_3OO\cdot + PCl_3 \longrightarrow RPOCl_2 + POCl_3 + Cl\cdot$ (4)

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 occures, particularly in liquid phase, at low temperature. Therefore, PBr_3 is unreactive with saturated hydrocarbon in this reaction different from PCl_3.

$$Br\cdot + RH \longrightarrow R\cdot + HBr \qquad (5)$$

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

$Br\cdot + RHC{=}CHR \longrightarrow RHBrC\text{-}\dot{C}HR$ (6), $RHBrC\text{-}\dot{C}HR + PBr_3 \longrightarrow RHBrC\text{-}C(\dot{P}Br_3)HR$ (7)

$$RHBrC\text{-}C(\dot{P}Br_3)HR + O_2 \longrightarrow RHBrC\text{-}C(PBr_3OO\cdot)HR \qquad (8)$$

$$RHBrC\text{-}C(PBr_3OO\cdot)HR + PBr_3 \longrightarrow RHBrC\text{-}C(POBr_2)HR + POBr_3 + Br\cdot \qquad (9)$$

The inhibiting action of PBr_3 to chlorophosphonation of saturated hydrocarbon must involve the following step.4)

$$Cl\cdot + PBr_3 \longrightarrow PClBr_2 + Br\cdot \qquad (11)$$

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(Received March 13, 1973)