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THE REACTION OF TRIFLUOROMETHANESULPHONIC ANHYDRIDE WITH PHOSPHORYL COMPOUNDS

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Abstract - Hexamethylphosphortriamide and triphenylphosphine oxide react with trifluoromethanesulphonic anhydride to give diphosphonium salts.

Hexamethylphosphortriamide (HMPA) reacts exothermically with trifluoromethanesulphonic anhydride in CH_2Cl_2 at room temperature to give white crystals from ethanol, m.p. 230 °C (decomp.), yield 94%. The product was found to be a diphosphonium salt (2). (Found: C,26.84; H,5.59; N,13.38; P,9.38; S,9.63; M,643. $C_{14}H_{36}O_7N_6F_6P_2S_2$ requires C,26.25; H,5.67; N,13.12; P,9.67; S,10.01%, M,640.5). An X-ray crystallographic study[1] has shown that the N atoms in the salt are completely sp^2 hybridized and that the P-O-P angle is 180°.
The following reaction mechanism is proposed:

$$[(CH_3)_3N]_3PO + (CF_3SO_2)_2O \longrightarrow [(CH_3)_2N]_3\overset{+}{P}\text{-}OSO_2CF_3 \cdot CF_3SO_3^-$$

(1)

$$\xrightarrow{[(CH_3)_2N]_3PO} [(CH_3)_2N]_3\overset{+}{P}\text{-}O\text{-}\overset{+}{P}[N(CH_3)_2]_3 \cdot 2CF_3SO_3^-$$

(2)

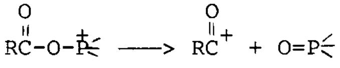
We believe that the first step in the reaction is the formation of the monophosphonium salt (1) which is rapidly attacked by the phosphoryl group of another molecule of HMPA. It is reasonable to assume that the monophosphonium salt (1) is very reactive since it contains two CF_3SO_3 groups with very low nucleophilicity. Consequently, we believe that the formation of a diphosphonium salt is a general feature when phosphine oxides react with trifluoromethanesulphonic anhydride. We therefore repeated the work reported by Hendrickson and Schwartzman[2] and found that the salt they postulated to be a monophosphonium salt, $(C_6H_5)_3\overset{+}{P}-OSO_2CF_3 \cdot CF_3SO_3^-$ in fact is a diphosphonium salt, $(C_6H_5)_3\overset{+}{P}-O-\overset{+}{P}(C_6H_5)_3 \cdot 2CF_3SO_3^-$. (Found:C,54.34; H,3.81; P,7.24; S,7.02; M,837. $C_{38}H_{30}O_7F_6P_2S_2$ requires C,54.41; H,3.61; P, 7.39; S,7.65%; M,838.7). For both salts, the molecular weight was determined by titration with aqueous sodium hydroxide. In contrast to the HMPA salt the triphenylphosphine oxide salt reacts very readily with water. The difference in reactivity may be ascribed to the greater tendency of an amino group to accept positive charge from a phosphorus atom than a phenyl group. Many of the reactions carried out by Hendrickson and Schwartzman can also be explained by the existence of a diphosphonium salt, e.g., the reaction with alcohols and acids:

$$ROH + \geqslant\overset{+}{P}-O-\overset{+}{P}\leqslant \cdot 2CF_3SO_3^- \longrightarrow R-O-\overset{+}{P}\leqslant \cdot CF_3SO_3^- + CF_3SO_3H\cdots\cdots O=P\leqslant$$

(3)

The monophosphonium salt (3) can act as an alkylation agent: $R-O-\overset{+}{P}\leqslant \longrightarrow R^+ + O=P\leqslant$

Similarly, acids should give an acylation agent:



$$R\overset{O}{\overset{\|}{C}}-O-\overset{+}{P}\leqslant \longrightarrow R\overset{O}{\overset{\|}{C}}{}^{+} + O=P\leqslant$$

References

1. A.Aaberg, T. Gramstad and S. Husebye, unpublished results.
2. J.B. Hendrickson and S.M. Schwartzman, Tetrahedron Lett., 277 (1975).

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