New Type of Phosphorus Compound By Autocondensation of Hexamethylphosphoric Triamide

By C. ANSELMI, B. MACCHIA,* F. MACCHIA, and L. MONTI

(*Istituti di Chimica organica e Chimica farmaceutica, Università di Pisa, 56100 Pisa, Italy*)

Summary Hexamethylphosphoric triamide reacts with alkyl iodides to produce a salt of a new type for which the structure $(Me_2N)_3P{\cdot}O{\cdot}P(O)(NMe_2)_2\ I^-$ has been established.

IN connection with our studies on the reactions of epoxides in dipolar aprotic solvents,[1] we were interested in the nucleophilic properties of hexamethylphosphoric triamide (hmpt).

Hmpt has been reported to be methylated by dimethyl sulphate[2] to salts of type (**1**). However when hmpt (5 g) was refluxed for 6 days with methyl iodide (24 g), tetramethylammonium iodide (1·5 g) precipitated, and dilution with ether of the filtrate gave a hygroscopic iodide which was converted into the tetraphenylborate (4·85 g), m.p. 142—143° (from ethyl acetate) which analysed correctly for $C_{10}H_{30}N_5O_2P_2,Ph_4B$. The same compound was obtained when ethyl iodide was used, but the initial precipitate was diethyldimethylammonium iodide, identified from its picrate, m.p. 291°, and its n.m.r. spectrum.[3]

$$(Me_2N)_3\overset{+}{P}OMe\ X^-$$

(**1**)

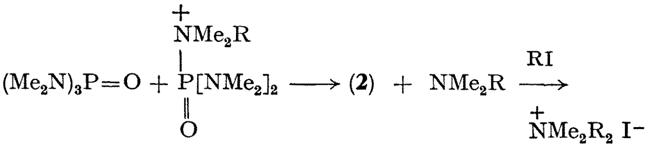
Structure (**2**) ($X = Ph_4B$) was attributed to the new salt on the basis of elemental analysis and n.m.r. evidence. The ^1H n.m.r. spectrum† showed, beside Ph signals, only two doublets at δ 2·53 (12H, *J* 10·7 Hz) and 2·37 (18H, *J* 10·8 Hz) p.p.m. indicating the presence of two groups of respectively two and three equivalent methyls exhibiting a PNCH type of coupling with phosphorus.[2,4] The ^{31}P n.m.r. spectrum confirmed the presence of two non-equivalent phosphorus atoms as unresolved signals respectively at -27 and $-10{\cdot}2$ p.p.m.

$$(Me_2N)_3\overset{+}{P}{\cdot}O{\cdot}P(O)(NMe_2)_2\ X^-$$

(**2**)

No evidence was found for the formation of the cation of (**1**) as a side-product; or as an intermediate during the reaction of hmpt with methyl iodide in $CHCl_3$, CH_2Cl_2, without solvent at room temperature, or at reflux for times of up to 10 days. The reaction was easily followed by n.m.r. and the bands characteristic for the cation of (**2**) became visible after refluxing for 7 h, while the OMe doublet of the cation of (**1**) δ *ca.* 4·00 p.p.m. (*J* 11 Hz) was not observed. On the other hand in the reaction of hmpt with dimethyl sulphate in CH_2Cl_2 or without solvent the OMe doublet of the cation of (**1**) readily appeared, but the signals of the cation of (**2**) did not, even after long reaction times; the product was isolated as the tetraphenylborate salt, $(Me_2N_3)\overset{+}{P}OMePh_4B^-$, m.p. 198–201°.

These experiments indicate that methyl iodide and dimethyl sulphate behave differently towards hmpt. The former reagent does not attack the oxygen atom, but probably one of the amino-groups, thus activating the molecule for nucleophilic attack by a second molecule of hmpt with formation of the cation of (**2**) and displacement of tertiary amine, possibly through a pentaco-ordinated trigonal bipyramidal transition state.[5]



$$(Me_2N)_3P{=}O + \overset{\overset{+}{N}Me_2R}{\underset{\underset{O}{\|}}{\overset{|}{P}}}[NMe_2]_2 \longrightarrow (2) + NMe_2R \xrightarrow{RI} \overset{+}{N}Me_2R_2\ I^-$$

An alternative mechanism involving alkylation on oxygen, followed by O to N migration of the alkyl group, as in the reaction of DMSO with MeI,[6] seems to be ruled out in our case, both because the presence of the ion (**1**) could not be detected in the methyl iodide reaction, and because (**1**) did not rearrange to (**2**) in the reaction medium even in the presence of methyl or sodium iodide.

An analogy for the different behaviour of methyl iodide and dimethyl sulphate can be found in the alkylation of ambident nucleophiles such as enolate anions which undergo preferential *C*-methylation with the former and *O*-alkylation with the latter reagent.[7]

---

† ^1H spectra were taken in $CDCl_3$ on a JEOL C60HL spectrometer, with Me_4Si as internal standard. The ^{31}P spectrum was taken in $CDCl_3$ with a Perkin-Elmer R-10, with P_4O_6 as external standard; chemical shifts are expressed in p.p.m. from 85% H_3PO_4.

We thank C.N.R. for financial support and Dr. G. Mavel for the ^{31}P n.m.r. spectrum.

(*Received, April 6th,* 1971; *Com.* 516.)

[1] G. Berti, B. Macchia, and F. Macchia, *Tetrahedron Letters*, 1965, 3421; P. L. Barili, G. Berti, B. Macchia, F. Macchia, L. Monti, and D. Tei, *Chimica e Industria*, 1969, **51**, 1391; C. Anselmi, P. L. Barili, G. Berti, B. Macchia, F. Macchia, and L. Monti, *ibid.*, 1970, **52**, 506.

[2] A. Schmidpeter and H. Brecht, *Z. Naturforsch.*, 1969, **24b**, 179.

[3] E. F. Mooney and P. H. Winson, *Ann. Rev. N.M.R. Spectroscopy*, 1969, **2**, 236.

[4] G. Mavel, *Progr. N.M.R. Spectroscopy*, 1966, **1**, 251.

[5] F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70.

[6] S. G. Smith and S. Winstein, *Tetrahedron*, 1958, **3**, 317.

[7] R. G. Pearson and J. Songstad, *J. Org. Chem.*, 1967, **32**, 2899.