Phosphorimidates and Related Compounds

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Phosphorimidates and related compounds ($R^1R^2R^3P{:}NR^4$) have been prepared by Staudinger reactions between three-co-ordinate phosphorus nucleophiles and azides. I.r., mass, and n.m.r. spectral studies on the compounds are reported. Low-temperature ^1H n.m.r. studies suggest that the rotational barrier around the P:N bond in these compounds is below 8 kcal mol^{-1}. Thermal rearrangements of some methyl phosphorimidates to phosphoramidates [$>P(OMe){:}NMe \longrightarrow >P({:}O)NMe_2$] have been observed.

THE systems $\geqslant$P=C, $\geqslant$P=N, and $\geqslant$P=O form an isoelectronic series of which the representatives of the two end members, the phosphorus ylides and the phosphoryl compounds, have been more fully studied than the central group.[1] There is much potentially interesting chemistry in the P:N system including questions of structure and conformation, the nature of the phosphorus–nitrogen bond, and the reactions of the system. We describe here the preparations and some simple properties of phosphorimidates [$(R^1O)_3P{:}NR^2$] and related compounds.

EXPERIMENTAL

I.r. spectra were determined on Beckman IR-5 and IR-12 spectrophotometers, u.v. spectra on a Cary 14 instrument, ^1H n.m.r. spectra on Varian A-60 and HA-100 spectrometers, ^{31}P n.m.r. spectra on a Varian HA-100 spectrometer, and mass spectra on a Perkin-Elmer–Hitachi RMU-5 spectrometer (at 70 eV).

Materials.—The three co-ordinate phosphorus nucleophiles were either redistilled commercial materials (trialkyl phosphites; hexamethylphosphorous triamide) or were pre-

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[1] For reviews of phosphorus imides see A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966, ch. 6; P. A. T. Hoye in 'Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry, vol. VIII, Suppl. III, Phosphorus,' Wiley–Interscience, New York, 1971, pp. 1067—1081.

pared by conventional methods [2] from commercially available materials. Their purities were checked by ^{1}H n.m.r. examination.

Ethyl,[3] methyl,[3] and phenyl azides [4] were prepared by published procedures and their purities were checked by ^{1}H n.m.r. examination. Methyl azide, as prepared from dimethyl sulphate, was always contaminated with dimethyl ether (usually 30—40%). The ether did not appear to affect the course of reactions, so no attempt was made to separate it from the azide.

TABLE 1

Phosphorimidates and related compounds prepared

Phosphorus reagent	Azide	Conditions [a]	Product	% Yield	B.p. (°C) [mmHg]	Found (%) C	Found (%) H	Found (%) N	Required (%) C	Required (%) H	Required (%) N
$\mathrm{(MeO)_3P}$	$\mathrm{MeN_3}$	20; 20	$\mathrm{(MeO)_3P{:}NMe}$	80	27 [1·5]	31·25	7·65	9·40	31·4	7·85	9·15
$\mathrm{(MeO)_3P}$	$\mathrm{EtN_3}$	240; 20	$\mathrm{(MeO)_3P{:}NEt}$	90	36 [1·0]	36·0	8·40	8·35	35·9	8·37	8·37
$\mathrm{(EtO)_3P}$	$\mathrm{EtN_3}$	24; 20	$\mathrm{(EtO)_3P{:}NEt}$	90	44—46 [0·6]	46·65	9·80		45·9	9·56	
$\mathrm{(Me_2N)_3P}$	$\mathrm{EtN_3}$	3; 80	$\mathrm{(Me_2N)_3P{:}NEt}$	80	77 [2]	45·95	10·9	28·1	46·5	11·2	27·2
$\mathrm{PhP(OMe)_2}$	$\mathrm{MeN_3}$	2; 0	$\mathrm{PhP(OMe)_2{:}NMe}$	85	74 [0·3]	54·1	7·25		54·3	7·4	
$\mathrm{PhP(NMe_2)_2}$	$\mathrm{MeN_3}$	10; 20	$\mathrm{PhP(NMe_2)_2{:}NMe}$	90	95 [0·4]	58·8	9·00	18·5	58·6	8·90	18·7
$\mathrm{(Me_2N)_3P}$	$\mathrm{MeN_3}$	2; 100	$\mathrm{(Me_2N)_3P{:}NMe}$ [b]	85	64 [2]	43·2	10·7		43·75	10·9	
$\mathrm{(Me_2N)_3P}$	$\mathrm{PhN_3}$	2; 100	$\mathrm{(Me_2N)_3P{:}NPh}$ [b]	85	100 [0·5]	56·2	9·0		56·7	9·1	

[a] Time (h) and temp. (°C) used for 0·05 mol of each reagent in diethyl ether (50 ml). [b] An intermediate is obtained in these reactions; see following paper.

TABLE 2

Representative i.r. spectra [a, b]

	$\mathrm{(MeO)_3P{:}NMe}$	$\mathrm{(MeO)_3P{:}NEt}$	$\mathrm{PhP(OMe)_2{:}NMe}$	$\mathrm{PhP(NMe_2)_2{:}NMe}$
CH str.	2985m, 2865m	2960m, 2865m	3077w, 2950m, 2840w	3080w, 3000w, 2898m, 2810w
C=C str.			1670—1590w	1680—1590w
CH def.	1454m, 1368m	1456m	1488sh, 1460sh	1477sh, 1453m
$\mathrm{C_6H_5{-}P}$			1445m	1440m
P:N str.	1307s	1333m	1300m	1282s
P–O–C	1060—1030vs	1060—1030vs	1064m, 1040—1030s	
$\mathrm{C_6H_5{-}P}$			993m	990—960s
P–O–C	839vs	825vs	826—813w	
$\mathrm{C_6H_5{-}}$			695	708s, 700sh

[a] Determined for 5% (v/v) solutions in $\mathrm{CCl_4}$. [b] Band positions in cm^{-1}.

Phosphorimidates.—The compounds were prepared by reactions between three-co-ordinate phosphorus nucleophiles and azides. Some typical preparations are described below. The reactions may be followed by observing the evolution of nitrogen.

Trimethyl N-*methylphosphorimidate*. Methyl azide (11·4 g, 0·20 mol) and dimethyl ether (4·2 g, 0·091 mol) were added to a mixture of trimethyl phosphite (12·4 g, 0·10 mol) and diethyl ether (15·0 mol) and the mixture was stirred at room temperature in a flask equipped with a condenser cooled in solid $\mathrm{CO_2}$ until nitrogen evolution ceased (20 h). The excess of azide and ether were removed *in vacuo* and the residue was distilled to yield the *phosphorimidate* (12·2 g, 0·080 mol, 80%), b.p. 25·0—25·5° at 0·8 mmHg. (Details of the characterization of this and other products are presented in the Tables and in the text below.)

Dimethyl N-*methylphenylphosphonimidate*. Methyl azide (6·0 g, 0·105 mol) and dimethyl ether (2·3 g, 0·05 mol) were added dropwise during 20 min to a stirred solution of dimethyl phenylphosphonite (15·0 g, 0·088 mol) in diethyl ether (50 ml) maintained at 0°. Reaction was rapid, and nitrogen evolution ceased after 1 h. The *product* had b.p. 70—74° at 0·3 mmHg (yield 14·9 g, 0·075 mol, 85%).

Thermal Rearrangements.—*Trimethyl* N-*methylphosphorimidate*. This compound (3·0 g; b.p. 27° at 1·5 mmHg) was sealed *in vacuo* and heated for 2 h at 120°. The liquid product was distilled (b.p. 100—101° at 35 mmHg) to yield dimethyl *NN*-dimethylphosphoramidate (2·9 g, 96%), identified by comparison of its i.r. and ^{1}H n.m.r. spectra with those of an authentic sample prepared by reaction between dimethylamine and dimethyl phosphorochloridate [2] [$\nu_{\mathrm{P:O}}$ 1265vs cm^{-1}; δ_{MeO} 3·64 ($J_{\mathrm{H,P}}$ 11·2 Hz), δ_{MeN} 2·61 ($J_{\mathrm{H,P}}$ 10·5 Hz)].

Dimethyl N-*methylphenylphosphonimidate*. This compound (1·2 g) was sealed *in vacuo* and heated for 1·5 h at 120°. The liquid product (1·2 g) was *methyl* NN-*dimethylphenylphosphonamidate*, M^+ 199; $\nu_{\mathrm{P:O}}$ 1270vs cm^{-1}; δ_{MeN} 2·65 (6H, $J_{\mathrm{H,P}}$ 9·7 Hz), δ_{MeO} 3·68 (3H, $J_{\mathrm{H,P}}$ 11·2 Hz), δ_{Ph} 7·2—7·8 (6H, m).

RESULTS AND DISCUSSION

Phosphorimidates.—Reactions between trialkyl phosphites or phosphonites and azides proceed smoothly, with nitrogen evolution, to give phosphorimidates [equation (1)]. The more nucleophilic phosphonites react more

$$\mathrm{R^1P(OR^2)_2 + R^3N_3 \longrightarrow R^1P({:}NR^3)(OR^2)_2 + N_2} \quad (1)$$

rapidly with azides than do the phosphites. The compounds produced by these reactions are described in Table 1. They are all colourless liquids which can be distilled unchanged at low pressures. When heated at higher pressures they undergo rearrangement and elimination reactions which are discussed below.

I.r. Spectra.—The main i.r. bands of representative compounds prepared, together with some tentative assignments, are presented in Table 2. Recent studies

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[2] G. M. Kosolapoff and L. Maier, 'Organic Phosphorus Compounds,' Wiley–Interscience, New York, 1972, vol. 4.

[3] 'Rodd's Chemistry of Carbon Compounds,' ed. S. Coffey, Elsevier, Amsterdam, 1965, vol. 1, Part B, p. 163.

[4] L. F. Fieser and M. Fieser, 'Reagents for Organic Synthesis,' Wiley, New York, 1967, p. 829.

of trimethylphosphine *N*-methylimide [5] have shown that the P:N stretching vibration in this compound occurs as a very intense band at 1239 cm^{-1}. The present series of compounds all have strong or medium intensity bands in the range 1280—1330 cm^{-1} which have been tentatively assigned to P:N stretching, since the attachment of more electronegative *P*-substituents is expected to increase the band frequency over that observed in the phosphine imide, exactly as is seen for the isoelectronic P:O stretch.[6] Because most of the compounds have other bands in this spectral region, the assignment cannot be regarded as final. Other assignments can be made, as shown in Table 2, by analogy with literature assignments which are thoroughly documented.[6]

Since the P–N single bond vibration is usually assigned to a band in the 850—650 cm^{-1} range,[6] the P:N bond in phosphorimidates must have a substantially higher force stretching constant than a P–N single bond, and can be regarded as a multiple bond. The best description of the bond would seem to involve a σ framework of sp^3-hybridized phosphorus and sp^2-hybridized nitrogen, since phosphine imides are ' bent ' at nitrogen,[5] and a π framework involving some degree of interaction between the filled $2p$ orbital on nitrogen and a vacant d orbital on phosphorus. This bonding view will be enlarged upon when the n.m.r. spectra of the compounds are discussed.

Mass Spectra.—The mass spectra of the compounds were in agreement with postulated structures. The spectra were complex, with many fragment ions; the molecular ion was always observed, but was not the base peak. Two representative spectra are available in Supplementary Publication No. SUP 21157 (3 pp.) * (those of trimethyl and triethyl *N*-ethylphosphorimidate). The most significant ions that can be assigned in the spectrum of the trimethyl ester include *m/e* 167 (M^+), 166 (M — H), 152 (base peak, probably M — Me), and 138 (probably M — Et). In the spectrum of the triethyl ester the molecular ion peak at *m/e* 209 is of low intensity; the masses of the intense peaks of high *m/e* in the spectrum of this compound suggest that extensive rearrangement is accompanying fragmentation. For example, the peak at *m/e* 192 (M — 17) probably arises by loss of OH; that at *m/e* 165 (M — 44) may be due to the loss of EtNH. The base peak, *m/e* 138 (M — 71), perhaps indicates the loss of EtN:CHMe, though other possibilities can be suggested.

^1H N.m.r. Spectra.—These spectra are presented in Table 3. The values of $^3J_{HCOP}$ are unexceptional and are very like those observed [7] in other four-co-ordinate phosphorus compounds [*cf.* $^3J_{HCOP}$ in $(MeO)_3P{:}O$ = 11·0 Hz; in $(MeO)_3P{:}NMe$ = 11·6 Hz]. Similarly the values of $^3J_{HCOP}$, where nitrogen is formally singly bonded to phosphorus, also parallel those reported earlier [7] [$^3J_{HCNP}$ in $(Me_2N)_3P{:}NMe$ = 9·5 Hz; and in $(Me_2N)_3P{:}O$ = 9·5 Hz also]. However, the observed $^3J_{HCN:P}$ values are substantially larger than this, ranging, in the P:NMe compounds examined, from 23 to 26 Hz. It seems most reasonable to assign this increase primarily to the change in the nature of the PN bond. In singly bonded PN compounds like $(Me_2N)_3{:}PO$ the PN bond is best viewed as a bond between sp^3-hybridized phosphorus and sp^3-hybridized nitrogen. However in the multiple bonded imides, as pointed out above, the best view of the multiple PN bond is of sp^3-hybridized phosphorus bonded to sp^2-hybridized nitrogen. There is thus an increase of s character in the orbital used by nitrogen in bonding, and this is, in turn, reflected in an increase in $J_{HCN:P}$.

In these phosphorus imides the barrier to rotation about the formal P:N ' double ' bond is apparently low. If rotation about this bond could be slowed, then *P*-substituents which are otherwise equivalent on the n.m.r. time-scale would become diastereotopic. How-

TABLE 3

^{1}H N.m.r. spectra [a]

	$(CH_3O)_3P{:}N\text{-}CH_3$		$(CH_3O)_3P{:}N\text{-}CH_2\text{–}CH_3$			$(CH_3\text{–}CH_2O)_3P{:}N\text{–}CH_2\text{–}CH_3$			
δ	3·65	2·78	3·54	3·26	1·19	1·27	4·02	3·12	1·11
$J_{H,P}$	11·6	24·0	11·4	22·4	1·6	0·8	7·7	23·6	1·3
Solvent	Neat liq.		Neat liq.			CDCl$_3$			
T_L(solvent) [b]	−130°($CH_2{:}CHCl$)								

	$[(CH_3)_2N]_3P{:}N\text{-}CH_3$		$[(CH_3)_2N]_3P{:}N\text{–}CH_2\text{–}CH_3$			$PhP[N(CH_3)_2]_2{:}N\text{–}CH_3$	
δ	2·50	2·70	2·52	3·32	1·29	2·65	3·37
$J_{H,P}$	9·5	23·3	10·0	18·2	2·5	10·2	23·8
Solvent	CDCl$_3$		C_6H_6			CDCl$_3$	
T_L(solvent) [b]	−100°($CFCl_3$)					−125° (Me_2O)	

	$PhP(OCH_3)_2{:}N\text{-}CH_3$	
δ	3·51	2·89
$J_{H,P}$	12·3	25·7
Solvent	CCl_3F	
T_L(solvent) [b]	−110°($CFCl_3$)	

[a] Solutions were 10% v/v; δ values (Me_4Si internal standard); J in Hz. [b] Lowest temperature attained with reasonable resolution; see text.

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* For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue (items less than 10 pp. are supplied as full size copies).

[5] J. Bragin, S. Chan, E. Mazzola, and H. Goldwhite, *J. Phys. Chem.*, 1973, **77**, 1506.

[6] D. E. C. Corbridge, *Topics Phosphorus Chem.*, 1967, **6**, 235; R. A. Nyquist and W. J. Potts in 'Analytical Chemistry of Phosphorus Compounds,' ed. M. Halmann, Wiley–Interscience, New York, 1972, p. 189.

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

ever, even at the lowest temperatures achievable experimentally (see Table 3), ranging down to −130° for solutions of $(MeO)_3P{:}NMe$ in vinyl chloride, the potentially diastereotopic methyl groups were not observed to become non-equivalent. The most reasonable explanation for this is that the barrier to rotation about the $P{:}N$ bond is quite low, probably below 29 kJ mol^{-1} (7 kcal mol^{-1}). Similar observations have been made [5] for trimethylphosphine *N*-methylimide. It is interesting that rotational barriers about formal multiple PN bonds in these four-co-ordinate phosphorus compounds are *lower* than rotational barriers about formal single PN bonds in three-co-ordinate phosphorus compounds like chloro(dimethylamino)(methyl)phosphine. It has been argued [8] that the PN bond in these latter compounds has some multiple-bond character, and it may be that the highly unsymmetrical substitution of the three-co-ordinate compounds produces a ligand field lifting of the degeneracy of the phosphorus *d* orbitals which is highly dependent on the rotational disposition of the PN bond. The four-co-ordinate compounds studied here have *P*-substituents of less widely different character, and perhaps the ligand-field effects in these compounds do not lead to such a marked dependence of energy on the rotational geometry of the PN bond.

^{31}P *N.m.r. Spectra.*—^{31}P Chemical shifts are reported in Table 4; the two phosphorimidates derived from trimethyl phosphite have chemical shifts very close to that of external H_3PO_4. Introduction of a phenyl group shifts the resonance about 16 p.p.m. downfield, and the compounds derived from phosphorus imides have resonances at even lower field.

TABLE 4

^{31}P N.m.r. chemical shifts

Compound	δ [a]	Compound	δ [b]
$(MeO)_3P{:}NEt$	−0·1	$(MeO)_3P{:}O$	−2·5
$(MeO)_3P{:}NMe$	−1·1		
$PhP(OMe)_2{:}NMe$	−16·7	$PhP(OMe)_2{:}O$	−21·4
$PhP(NMe_2)_2{:}NMe$	−29·3	$PhP(NMe_2)_2{:}O$	−28·1
$(Me_2N)_3P{:}NMe$	−32·6	$(Me_2N)_3P{:}O$	−23·4

[a] Present work; all values are in p.p.m. (downfield negative) from external H_3PO_4 (85%), for neat liquid samples. [b] From V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 227.

As the comparison values show in Table 4, there is a general parallelism between ^{31}P chemical shifts in the phosphorimidate and the isoelectronic phosphoryl series; indeed, even the numerical values for analogous compounds are generally close. It seems that at least in terms of electron density at the phosphorus nucleus the isoelectronic analogy between $\geqslant P{:}O$ and $\geqslant P{:}NR$ is meaningful, and that the bonding descriptions of these two groups must be similar.

Thermal Rearrangements.—During an attempted high-pressure distillation of trimethyl *N*-methylphosphorimidate the compound rearranged to dimethyl *NN*-dimethylphosphoramidate [equation (2)]. The product

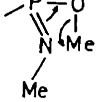
$$(MeO)_3P{:}NMe \longrightarrow (MeO)_2P({:}O)NMe_2 \qquad (2)$$

was identical with an authentic sample prepared from dimethyl phosphorochloridate and dimethylamine. The rearrangement occurred smoothly and quantitatively in 2 h at 100°.

A similar rearrangement of dimethyl *N*-methylphenylphosphonimidate occurred in 1 h at 140°. However, thermal treatment of *N*-ethyl imides gave intractable products; apparently an elimination reaction occurs in the more complex cases. Thermal rearrangements of dialkyl allyl phenylphosphorimidates to phosphoramidates have been previously reported [9] [equation (3)].

$$(R^1O)_2P({:}NPh)O{\cdot}CHR^2{\cdot}CH{:}CHR^3 \longrightarrow (R^1O)_2P({:}O)NPh(CHR^3{\cdot}CH{:}CHR^2) \qquad (3)$$

In this transformation of allyl esters the rearrangement of the allyl group strongly suggests the involvement of a cyclic transition state. If a similar intramolecular mechanism applies to the reactions observed here, the transition state must be four-membered [see (A)].



(A)

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[8] S. DiStefano and H. Goldwhite, *Org. Magnetic Resonance*, 1974, **6**, 1.

[9] A. N. Pudovik, I. M. Aladzheva, V. G. Kotova, and A. F. Zinkovskii, *J. Gen. Chem.* (*U.S.S.R.*), 1969, **39**, 1498.