Journal of Organometallic Chemistry, 108 (1976) 335—344

AMBIDENT NUCLEOPHILES

II *. REACTIONS OF PHOSPHORAMIDATES AND PHOSPHORIMIDATES WITH SOME HALIDES OF GROUP IV

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(Received October 23rd, 1975)

Summary

The *N,O* ambident nucleophile $(Me_2CHO)_2PONHCH_2Ph$ reacts with Me_3MX, but not with Ph_3MX (M = Si, Ge, Sn; X = halogen) to give N-bonded derivatives $(Me_2CHO)_2P(O)N(CH_2Ph)MR_3$: the sodium salt $[(Me_2CHO)_2PONCH_2Ph]^-Na^+$ reacts with Ph_3MX, also to give N-bonded products. The phosphorimidate $(EtO)_3PNCOPh$, although reacting readily with HCl to yield the quasi-Arbusov products $(EtO)_2P(O)NHCOPh$, does not react with MeI, EtI, Me_3SiCl or Me_3SnCl. IR and ^{31}P NMR data for a number of phosphoramidates and phosphorimidates are presented. Approaches to the synthesis of $(RO)_3PNCH_2Ph$ are outlined, and the energetics of the reactions $(RO)_2P(OM)NCH_2Ph \rightarrow (RO)_2P(O)N(CH_2Ph)M$ and $(RO)_3PNR' \rightarrow (RO)_2P(O)N(R')M$ are discussed.

Introduction

In Part I [1], we discussed the reactions of the *S,O* ambident nucleophile sodium *O,O*-diisopropylphosphorothioate with some molecular halides of Group IV: the halides of silicon, germanium and tin formed O-bonded isomers, which were shown by a simple thermochemical calculation to be the thermodynamically more stable isomers. Carbon halides, by contrast, sometimes yield the thermodynamically favoured S-bonded isomer and sometimes, presumably under kinetic control, the O-bonded isomer.

In this paper, the reactions of the *N,O* ambident nucleophiles *N*-benzyl-*O,O*-diisopropylphosphoramidate $((CH_3)_2CHO)_2PONHCH_2C_6H_5$, its sodium salt $[((CH_3)_2CHO)_2PONCH_2C_6H_5]^-Na^+$, and *N*-benzoyl-*O,O,O*-tri-ethylphosphorimidate $(C_2H_5O)_3PNCOC_6H_5$ towards some Group IV halides are reported. The only previous studies reported are of the reaction of the sodium salts $[(C_2H_5O)_2PONR]^-$

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* For Part I see ref. 1.

Na^+ with a range of substrates of general type X_2CO, including carbon dioxide, aldehydes, ketenes and isocyanates, in which the nucleophile reacts via nitrogen [2], and a report [3] of a single reaction between trimethylchlorosilane and $(C_2H_5O)_2P(O)NHCH_3$ in the presence of base, which yields the N-bonded isomer $(C_2H_5O)_2P(O)NCH_3Si(CH_3)_3$.

Results

Reactions of N-benzyl-O,O-diisopropylphosphoramidate and its sodium salt

In the presence of pyridine as hydrogen chloride acceptor, *N*-benzyl-*O*,*O*-diisopropylphosphoramidate reacts with trialkyl halides of silicon, germanium and tin to give good yields of the species $((CH_3)_2CHO)_2PON(CH_2C_6H_5)M(CH_3)_3$ (M = Si, Ge, Sn). These products were characterised by micro-analysis, and by their infrared, NMR, and mass spectra (see below). By contrast, the triaryl halides Ph_3MX did not react under similar conditions. However, the sodium salt $[((CH_3)_2CHO)_2PONCH_2C_6H_5]^-Na^+$ reacted smoothly with the triphenyls to give good yields of $((CH_3)_2CHO)_2PON(CH_2C_6H_5)M(C_6H_5)_3$. The failure of the triphenyl species to react with the neutral phosphoramidate is indicative that no anion is formed in the presence of pyridine, and may be influenced by steric factors.

The neutral phosphoramidate showed no reaction towards ethyl iodide, even on prolonged reflux. This is in marked contrast to the reaction of the thio analogues $(C_2H_5O)_2P(S)NHR$ which undergo alkyl exchange with 1-iodopropane to yield $(C_2H_5O)(CH_3CH_2CH_2S)P(O)NHR$ [4].

Reactions of N-benzoyl-O,O,O-triethylphosphorimidate

Although with hydrogen chloride, this phosphorimidate readily undergoes at room temperature the quasi-Arbusov reaction:

$$(C_2H_5O)_3P{=}NCOC_6H_5 + HCl \rightarrow (C_2H_5)_2P(O)NHCOC_6H_5 + C_2H_5Cl$$

it does not react with methyl or ethyl iodide, even on prolonged reflux in nitromethane. Similarly, treatment of the phosphorimidate with either trimethylchlorosilane or with trimethyltin chloride gave no reaction.

Infrared spectra

The infrared spectra of the new compounds prepared can be used to give information about the isomer formed. N-bonded isomers of type $(RO)_2P(O)N(CH_2$-

TABLE 1

DOUBLE-BOND STRETCHING FREQUENCIES IN PHOSPHORIMIDATES $(RO)_3PNR'$ AND PHOSPHORAMIDATES $(RO)_2P(O)NHR'$

R	R'	ν(P=N) (cm^{-1}) in $(RO)_3PNR'$	ν(P=O) (cm^{-1}) in $(RO)_2P(O)NHR'$
CH_3	COC_6H_5	1346	1239
CH_3	$COC_6H_3(NO_2)_2$-3,5	1335	1234
CH_3	$SO_2C_6H_4CH_3$-*p*	1354	1240
C_2H_5	COC_6H_5	1346	1238
C_2H_5	$COC_6H_3(NO_2)_2$-3,5	1336	1236
C_2H_5	$SO_2C_6H_4CH_3$-*p*	1368	1243

TABLE 2

DIAGNOSTIC P=O STRETCHING FREQUENCIES IN $(Me_2CHO)_2PON(CH_2C_6H_5)X$

X	H	$SiMe_3$	$GeMe_3$	$SnMe_3$	$SiPh_3$	$GePh_3$	$SnPh_3$
ν(P=O) (cm^{-1})	1231	1251	1237	1218	1239	1232	1235

Ph)X are expected to exhibit ν(P=O) in the range 1190—1275 cm^{-1} [5], while *O*-bonded isomers $(RO)_2P(OX)NCH_2Ph$ are expected to exhibit ν(P=N) in the range 1325—1400 cm^{-1} [6]. Table 1 records values of ν(P=N) and ν(P=O) for a number of phosphoramidates and phosphorimidates synthesised during this work: these are consistent with the above generalisation. In Table 2 are presented diagnostic ν(P=O) values for the parent *N*-benzyl-*O*,*O*-diisopropylphosphoramidate and its substituted derivatives $((CH_3)_2CHO)PON(CH_2Ph)MR_3$ (M = Si, Ge, Sn; R = CH_3, C_6H_5). No bands are observed for these compounds in the range 1325—1400 cm^{-1}, providing good evidence for the formation of the N-bonded isomers.

Mass spectra

All new compounds exhibited molecular ions, albeit sometimes very weak, in their mass spectra. Common features in the spectra were, apart from the prominent *m/e* 91 ($C_7H_7^+$) and its decomposition products, series of ions of *m/e* 187, 186, 185 ($C_7H_7NPO_3H_x^+$: x = 3,2,1) and 170, 169, 168 ($C_7H_7NPO_2H_x^+$: x = 2,1,0), and an intense ion having *m/e* 98 corresponding to $H_5NO_3P^+$ whose constitution is possibly monoprotonated phosphamic acid $H_2NP(OH)_3^+$ or $H_3NPO(OH)_2^+$. In the triphenyl species, $(M - C_6H_5)^+$ and $(M - 2 \times C_6H_5)^+$ are also prominent.

Very little could be deduced from the observed fragmentation patterns about the question of isomerism.

NMR spectra

All new compounds gave proton spectra whose integrals accorded with the constitutions postulated. The essential numerical data for the parent phosphoramidate and for its $(CH_3)_3M$ and $(C_6H_5)_3M$ derivatives are presented in Table 3.

As with a number of phosphorothioate derivatives [1] the isopropyl fragments in all these compounds have magnetically nonequivalent methyl groups, both in the proton and the ^{13}C spectra. Slow rotation about the C—O bond in the $Me_2CHOPXYZ$ fragment renders the two isopropyl methyl groups nonequivalent.

Similarly in all species containing $(CH_3)_3M$ or $(C_6H_5)_3M$ groups the two protons in the methylene group of the benzyl fragment are magnetically non-equivalent, although in the parent compound these are equivalent. The CH_2 resonance in the ^{13}C spectra of all these compounds is a singlet. The simplest rationalisation is in terms of the inversion rate of the nitrogen atom. If this inversion is slow enough the two CH_2 protons can be rendered non-equivalent, but if fast enough on the NMR time scale these protons can be rendered dynamically equivalent. It is reasonable to suggest that substitution of H by R_3M can slow down the inversion.

The closeness of the phosphorus chemical shifts in the R_3M derivatives to that in the parent compound are good evidence for a similar *N*-bonded constitution.

TABLE 3

NMR DATA FOR $(Me_2CHO)_2PON(CH_2C_6H_5)X$

X	Proton shift [a]					Phosphorus shift [b]
	$(C\underline{H}_3)_2CH$	$(CH_3)_2C\underline{H}$	$C\underline{H}_2$	$C_6\underline{H}_5$	$C\underline{H}_3M$	$\underline{P}$
H	1.28 1.33	4.64	4.09	7.31	—	−7.34
$SiMe_3$	1.27 1.32	4.59	4.04 4.15	7.3	0.11	−5.92
$GeMe_3$	1.26 1.32	4.62	4.07 4.16	7.4	0.52	−6.01
$SnMe_3$	1.26 1.31	4.57	3.99 4.08	7.3	0.67	−5.40
$SiPh_3$	1.29 1.35	4.68	4.08 4.18	7.3—7.6	—	−6.81
$GePh_3$	1.29 1.34	4.66	4.07 4.18	7.2—7.6	—	−6.86
$SnPh_3$	1.29 1.35	4.68	4.08 4.18	7.4	—	−6.88

[a] Proton shifts δ in ppm from Me_4Si. [b] Phosphorus shifts δ in ppm from 85% H_3PO_4.

However it is important to compare phosphorus shifts in similar $(RO)_2P(O)NXR'$ and $(RO)_3PNR'$ species. There are essentially no phosphorus shift data recorded for phosphorimidates: consequently we have prepared a number of $(RO)_3PNR'$ species by means of the reaction between $R'N_3$ and $(RO)_3P$ [7]; conversion to the quasi-Arbusov products $(RO)_2P(O)NHR'$ was then effected by reaction with HCl [8]. Phosphorus shifts for these species are presented in Table 4. For the *N*-acyl derivatives the shift in $(RO)_3PNR'$ is some 17 ppm to low field of that in $(RO)_2P(O)NHR'$: however this shift is only some 3—4 ppm in the *N*-sulphonyl species. Since the compounds of interest are *N*-benzyl, not *N*-benzoyl, derivatives, we sought means of preparing species $(RO)_3PNCH_2C_6H_5$ without recourse to the highly dangerous benzyl azide.

TABLE 4

NMR COMPARISON OF $(RO)_3PNR'$ AND $(RO)_2P(O)NHR'$

R	R′	δ(P) [a] in $(RO)_3PNR'$	δ(P) in $(RO)_2P(O)NHR'$
CH_3	C_6H_5CO	−18.24	−1.02
C_2H_5	C_6H_5CO	−14.08	+2.32
C_6H_5	C_6H_5CO	+2.02	n.s.
CH_3	$3,5\text{-}(O_2N)_2C_6H_3CO$	−18.05	+0.51
C_2H_5	$3,5\text{-}(O_2N)_2C_6H_3CO$	−13.95	+3.61
CH_3	$p\text{-}CH_3C_6H_4SO_2$	−0.87	+3.33
C_2H_5	$p\text{-}CH_3C_6H_4SO_2$	+3.35	+6.13
C_6H_5	$p\text{-}CH_3C_6H_4SO_2$	+21.69	n.s.
$C_6H_5CH_2$	$p\text{-}CH_3C_6H_4SO_2$	+3.69	n.s.

[a] Phosphorus shift in ppm from 85% H_3PO_4.

Approaches to compounds $(RO)_3PNCH_2C_6H_5$

Two routes were attempted: one from dibenzylhexachlorodiazadiphosphetidine $(Cl_3PNCH_2C_6H_5)_2$, and the other from $(RO)_3PNCOC_6H_5$. When $(Cl_3PNCH_2C_6H_5)_2$, prepared by reaction of phosphorus(V) chloride with benzylammonium chloride [9], was treated with isopropanol, the sole product was $(Me_2CHO)_2P(O)NHCH_2Ph$, possibly resulting from the quasi-Arbusov reaction of HCl with $(Me_2CHO)_3PNCH_2Ph$. However, in the presence of pyridine as hydrogen chloride acceptor, reaction with isopropanol again gave $(Me_2CHO)_2P(O)NHCH_2Ph$ but this time some of the benzyl groups were oxidised to benzaldehyde, possibly via the Schiff base $(Me_2CHO)_2P(O)N{=}CHPh$. Nor was any $(Me_2CHO)_3PNCH_2C_6H_5$ isolated from the reaction of $NaOCHMe_2$ with $(Cl_3PNCH_2C_6H_5)_2$; all isopropyl groups in the reaction mixture showing no coupling to phosphorus.

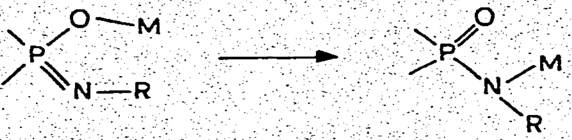
An attempt was made to convert $(EtO)_3PNCOC_6H_5$ to $(EtO)_3PNCH_2C_6H_5$ by the method of Borch [10], using triethyl-oxonium tetrafluoroborate followed by reduction with sodium borohydride. The product isolated was $(EtO)_2P(O)NHCOC_6H_5$ rather than the *N*-benzyl phosphorimidate: it is possible that the reaction proceeds via $(EtO)_3PNC(OEt)C_6H_5^+BF_4^-$ which with borohydride is converted, with loss of ethane, to $(EtO)_2P(O)NC(OEt)C_6H_5$, which is hydrolysed to the observed product during the work-up. This product is in marked contrast to the result of a similar reduction procedure applied to $Ph_3PNCOPh$: in this example the amido function is reduced but with concurrent cleavage of the P—N bond, giving ultimately triphenylphosphine and the benzylammonium cation. Benzylamine was found not to react with either $Ph_3PNCOPh$ or $(EtO)_3PNCOPh$.

Discussion

On the basis of their infrared and ^{31}P NMR spectra, the products from the reactions of *N*-benzyl-*O*,*O*-diisopropylphosphoramidate or its sodium salt with halides of silicon, germanium and tin are to be regarded as N-bonded phosphoramidates, rather than O-bonded phosphorimidates.

Energetics

The enthalpy changes for the processes of eq. 1 are readily estimated from



(1)

bond energy terms (eq. 2).

$$\Delta H = +B(\text{M—O}) + B(\text{P—O}) + B(\text{P=N}) - B(\text{M—N}) - B(\text{P=O}) - B(\text{P—N}), \qquad (2)$$

Calculations for M = H, C, Si, Ge, and Sn are set out in Table 5.

Values for *B*(Sn—N) have been reported [14] as 418 kJ in bis(tributylstannyl)-carbodiimide, $(Bu_3SnN)_2C$ and 427 kJ in tributylstannylisocynanate, Bu_3SnNCO: these values were derived from combustion calorimetry employing a value for *B*(C=N) of 469 kJ, derived from the Russian edition of Cottrell: substituting the value of *B*(C=N) cited in the original edition [15], 615 kJ, the values of

TABLE 5

BOND ENERGY TERMS (kJ) AND ENTHALPY CHANGES (kJ mol^{-1}) FOR REACTION 1

M	$+B(M—O)$	$+ B(P—O)$	$+ B(P=N)$	$— B(M—N)$	$— B(P=O)$	$— B(P—N)$	$= \Delta H$
H	+458 [a]	+368 [b]	+459 [c]	—389 [a]	—620 [b]	—347 [f]	—71
C	+358 [b]	+368	+459	—305 [a]	—620	—347	—87
Si	+445 [b]	+368	+459	—335 [a]	—620	—347	—30
Ge	+356 [b]	+368	+459	—255 [d]	—620	—347	—39
Sn	+376 [b]	+368	+459	—276 [e]	—620	—347	—40

[a] Ref. 11. [b] Ref. 1. [c] Ref. 12. [d] Calculated from Pauling's geometric-mean equation. [e] See text. [f] Ref. 13.

$B(Sn—N)$ become 272 and 281 kJ respectively, very close to the estimate, 261 kJ, derived using Pauling's geometric-mean equation. A mean value of 276 kJ is employed here.

From the data in Table 5, and treating the entropy term as before [1] it is concluded that the N-bonded phosphoramidate, which is observed when M = H, Si, Ge, or Sn is the thermodynamically stable isomer.

It is of interest also to consider the enthalpy changes (eq. 4) accompanying the reaction 3.

$$(RO)_3PNCOPh + MX \rightarrow (RO)_2P(O)N(COPh)X + RX \qquad (3)$$

$$\Delta H = +B(C—O) + B(P—O) + B(P{=}N) + B(M—X) - B(C—X) - B(P{=}O) - B(P—N) - B(M—N) \qquad (4)$$

Calculations are set out in Table 6: these indicate that for all the M considered, this reaction is thermodynamically feasible. We observed that it readily occurs when M = H, but not when M = Si, Sn or C. This latter observation is in contrast to the work of Kabachnik and Gilyarov [16], who found that $(EtO)_3PNPh$ readily underwent quasi-Arbusov reaction with CH_3I, C_2H_5I and CH_3COCl, to yield $(EtO)_2P(O)NMePh$, $(EtO)_2P(O)NEtPh$, and $(EtO)_2P(O)N(COMe)Ph$. It is possible that the failure of Group IV halides to react with this phosphorimidate represents a rare example of kinetic control of reaction at silicon or tin.

Related systems

N,O ambident nucleophiles similar to phosphoramidates are carboxylic acid amides, hydroxylamine H_2NOH and the isocyanate anion NCO^-.

Monosilylation of acetamide is reported to yield the N-bonded isomer [17,18], whereas both isomers (*N,O* and *N,N*) of the bis-silyl $CH_3CON(SiMe_3)_2$ are known

TABLE 6

BOND ENERGY TERMS (kJ) AND ENTHALPY CHANGES (kJ mol^{-1}) FOR THE REACTION 3

M	X	$+B(C—O)$	$+ B(P—O)$	$+ B(P=N)$	$+ B(M—X)$	$— B(C—X)$	$— B(P=O)$	$— B(P—N)$	$— B(M—N) =$	ΔH
H	Cl	+358 [a]	+368 [b]	+459 [c]	+441 [a]	—330 [a]	—620 [b]	—347 [d]	—389 [a]	—60
C	I	+358	+368	+459	+239 [a]	—239 [a]	—620	—347	—305 [a]	—87
Si	Cl	+358	+368	+459	+402 [a]	—330 [a]	—620	—347	—335 [a]	—45
Ge	Br	+358	+368	+459	+280 [a]	—272 [a]	—620	—347	—225 [e]	—29
Sn	Cl	+358	+368	+459	+314 [a]	—330 [a]	—620	—347	—276 [f]	—74

[a] Ref. 11. [b] Ref. 1. [c] Ref. 12. [d] Ref. 13. [e] Calculated from Pauling's geometric-mean equation. [f] See text.

[19,20]. Monosilylation of hydroxylamine yields the O-bonded isomer H_2NO-SiR_3 [21], while only the N-bonded isocyanates R_3SiNCO are known, there being no report of species R_3SiOCN [22]. For germanium and tin, the NCO derivatives are N-bonded [22]: there appear to be no reports of Ge or Sn derivatives of carboxylic acid amides or of hydroxylamines: we intend to investigate these systems and report in forthcoming communications.

Experimental

Materials were as previously described [1]. NMR spectra were recorded using Varian Associates instruments: HA-100 (^1H and ^{31}P), XL-100 (^{31}P) and CFT-20 (^{13}C).

N-Benzyl-*O,O*-diisopropylphosphoramidate was prepared by reaction [13] of diisopropyl hydrogen phosphite [24] with benzylamine in carbon tetrachloride solution: after washing with 5 *M* HCl and water, and removal of the solvent, recrystallisation from chloroform yielded the product as white crystals, m.p. 57—58°C. Found: C, 57.8; H, 8.0; N, 5.2. $C_{13}H_{22}NO_3P$ calcd.: C, 57.6; H, 8.2; N, 5.2%. Conversion to the sodium salt was effected with sodium hydride in tetrahydrofuran [2].

Reactions of N-benzyl-O,O-diisopropylphosphoramidate

(a) With ethyl iodide. The phosphoramidate (2.71 g, 10×10^{-3} mol) and ethyl iodide (15.6 g, 0.1 mol) were refluxed in nitromethane (150 ml) during 20 h. After removal of the solvent and of excess ethyl iodide, the phosphoramidate was recovered unchanged.

(b) With trimethyltin chloride. A solution of trimethyltin chloride (1.0 g, 5×10^{-3} mol), the phosphoramidate (1.35 g, 5×10^{-3} mol) and pyridine (1.1 g, 15×10^{-3} mol) in nitromethane (50 ml) was refluxed for 12 h. Filtration and removal of the solvent yielded *N*-benzyl-*N*-trimethylstannyl-*O,O*-diisopropylphosphoramidate as a pale yellow oil (1.92 g, 4.4×10^{-3} mol; 88%). Found: C, 44.2; H, 6.7; N, 3.2. $C_{16}H_{30}NO_3PSn$ calcd.: C, 44.1; H, 6.9; N, 3.2%.

(c) With trimethylchlorosilane. Trimethylchlorosilane (0.55 g, 5×10^{-3} mol), the phosphoramidate (1.35 g, 5×10^{-3} mol) and pyridine (1.1 g, 15×10^{-3} mol) were refluxed for 10 h in nitromethane (50 ml). Work-up as above yielded *N*-benzyl-*N*-trimethylsilyl-*O,O*-diisopropylphosphoramidate (1.34 g, 3.9×10^{-3} mol; 79%). Found: C, 55.8; H, 9.1; N, 4.2. $C_{16}H_{30}NO_3PSi$ calcd.: C, 56.0; H, 8.8; N, 4.1%.

(d) With trimethylbromogermane. The phosphoramidate (1.35 g; 5×10^{-3} mol) was refluxed for 10 h with trimethylbromogermane (1.0 g, 5×10^{-3} mol), and pyridine (1.1 g, 15×10^{-3} mol) in nitromethane (50 ml) to yield, after work-up, *N*-benzyl-*N*-trimethylgermyl-*O,O*-diisopropylphosphoramidate (1.38 g, 3.5×10^{-3} mol; 71%). Found: C, 49.4; H, 7.6; N, 3.7%. $C_{16}H_{30}GeNO_3P$ calcd.: C, 49.5; H, 7.8; N, 3.6%.

(e) With triphenyltin chloride. A mixture of phosphoramidate 2.7 g, 10×10^{-3} mol), triphenyltin chloride (3.8 g, 10×10^{-3} mol) and pyridine (0.8 g, 10×10^{-3} mol) in nitromethane was refluxed for 10 h. After removal of volatile components, NMR and mass spectrometry revealed only starting materials. Reaction in 50 : 50 v : v benzene : carbon tetrachloride likewise yielded only starting materials.

(f) With triphenylchlorosilane and triphenylbromogermane. Equimolar mixtures were refluxed as in *(e)*; after removal of the solvent, spectroscopic examination revealed only starting materials.

Reactions of sodium N-benzyl-O,O-diisopropylphosphoramidate

(a) With triphenylchlorosilane. The sodium salt (2.93 g, 10^{-2} mol) and triphenylchlorosilane (2.94 g, 10^{-2} mol) were mixed together in 1,2-dimethoxyethane (150 ml) and heated to 80°C for 0.5 h. The mixture was cooled, centrifuged and then filtered. The solvent was then removed to yield a light brown solid, recrystallisation of which from benzene yielded the product (2.12 g, 4.0×10^{-3} mol; 40%). Found: C, 69.7; H, 7.1; N, 2.6. $C_{31}H_{36}NO_3PSi$ calcd.: C, 70.3; H, 6.9; N, 2.7%.

(b) With triphenylbromogermane. The sodium salt (2.94 g, 10^{-2} mol) and the germane (3.80 g, 10^{-2} mol) were heated together in dimethoxyethane (150 ml) for 1 h at 70°C. Work-up as in (a), followed by recrystallisation from toluene yielded the product (3.56 g, 6.2×10^{-3} mol; 62%). Found: C, 65.2; H, 6.4; N, 2.5. $C_{31}H_{36}GeNO_3P$ calcd.: C, 64.8; H, 6.3; N, 2.4%.

(c) With triphenyltin chloride. The chloride (3.84 g, 10^{-2} mol) and the sodium salt (2.94 g, 10^{-2} mol) were heated together in dimethoxyethane (180 ml) for 0.5 h at 70°C. Work-up as above, followed by recrystallisation from toluene yielded the product (3.41 g, 5.5×10^{-3} mol; 55%). Found: C, 61.2; H, 5.5; N, 2.4. $C_{31}H_{36}NO_3PSn$ calcd.: C, 60.0; H, 5.9; N, 2.3%.

Reactions of N-benzoyltriethylphosphorimidate

(a) With ethyl iodide. The phosphorimidate (2.8 g, 10^{-2} mol) and ethyl iodide (31 g, 0.2 mol) were refluxed together for 10 h. After removal of the excess ethyl iodide, the phosphorimidate was recovered unchanged.

(b) With methyl iodide. Methyl iodide (20 g, 0.14 mol) and the phosphorimidate (2.8 g, 10^{-2} mol) were dissolved in nitromethane (30 ml), and the solution was refluxed during 6 h. Removal of the volatiles gave a quantitative recovery of the phosphorimidate.

(c) With trimethyltin chloride. The phosphorimidate (1.42 g, 5×10^{-3} mol) and the halide (1.00 g, 5×10^{-3} mol) were dissolved in nitromethane (100 ml). After 6 h reflux, the solvent was removed: spectroscopic examination of the residue revealed only unchanged starting materials.

(d) With trimethylchlorosilane. The ester (2.85 g, 10^{-2} mol) and the silane (1.10 g, 10^{-2} mol) were refluxed for 5 h in nitromethane (80 ml). After removal of the volatiles, the product remaining was identified as the phosphorimidate, contaminated with a small proportion of *N*-benzoyl-*O*,*O*-diethylphosphoramidate.

Preparation of compounds $(RO)_3PNR'$

These were prepared by reaction [7] of the azide $R'N_3$ [25] with the phosphite $(RO)_3P$ in benzene solution. All showed molecular ions in their mass spectra. Among compounds so prepared were:

(i) $(CH_3O)_3PNCOC_6H_5$. $\delta(C_6\underline{H}_5)$ 8.50, 7.90, 7.26; $\delta(C\underline{H}_3)$ 3.59 ppm. $\nu(C{=}O)$ 1608; $\nu(P{=}N)$ 1346 cm^{-1}.

(ii) $(CH_3O)_3PNCOC_6H_3(NO_2)_2$-3,5. $\delta(C_6\underline{H}_3)$ 9.02, 8.66; $\delta(C\underline{H}_3)$ 3.63 ppm. $\nu(C{=}O)$ 1628; $\nu(P{=}N)$ 1335 cm^{-1}.

(iii) $(CH_3O)_3PNSO_2C_6H_4CH_3$-*p*. $\delta(C_6\underline{H}_4)$ 8.01, 7.03; $\delta(C\underline{H}_3O)$ 3.57; $\delta(C\underline{H}_3C)$ 2.13 ppm. $\nu(P{=}N)$ 1354 cm^{-1}.

(iv) $(C_2H_5O)_3PNCOC_6H_5$. $\delta(C_6\underline{H}_5)$ 8.50, 7.85, 7.30; $\delta(C\underline{H}_2)$ 4.10; $\delta(C\underline{H}_3)$ 1.14 ppm. $\nu(C{=}O)$ 1610; $\nu(P{=}N)$ 1346 cm^{-1}.

(v) $(C_2H_5O)_3PNCOC_6H_3(NO_2)_2$-3,5. $\delta(C_6\underline{H}_3)$ 9.10, 8.65; $\delta(C\underline{H}_2)$ 4.10; $\delta(C\underline{H}_3)$ 1.22 ppm. $\nu(C{=}O)$ 1626; $\nu(P{=}N)$ 1336 cm^{-1}.

(vi) $(C_2H_5O)_3PNSO_2C_6H_4CH_3$-*p*. $\delta(C_6\underline{H}_4)$ 8.05, 6.97; $\delta(C\underline{H}_2)$ 4.03; $\delta(C\underline{H}_3Ar)$ 2.10; $\delta(C\underline{H}_3CH_2)$ 1.07 ppm. $\nu(P{=}N)$ 1368 cm^{-1}.

(vii) $(C_6H_5O)_3PNCOC_6H_5$. $\delta(C_6\underline{H}_5CO)$ 9.35, 7.93; $\delta(C_6\underline{H}_5O)$ 7.10—7.25 ppm.

(viii) $(C_6H_5O)_3PNSO_2C_6H_4CH_3$-*p*. $\delta(C_6\underline{H}_4)$ 7.45, 6.84; $\delta(C_6\underline{H}_5)$ 7.20—7.30; $\delta(C\underline{H}_3)$ 2.27 ppm.

(ix) $(C_6H_5CH_2O)_3PNSO_2C_6H_4CH_3$-*p*. $\delta(C_6\underline{H}_4)$ 7.70, 6.83; $\delta(C_6\underline{H}_5)$ 7.05—7.25; $\delta(C\underline{H}_2)$ 4.87; $\delta(C\underline{H}_3)$ 2.35 ppm.

Preparation of compounds $(RO)_2P(O)NHR'$

These compounds were prepared by passing dry HCl gas through a benzene solution of $(RO)_3PNR'$ for 4 h [8]. Compounds so prepared were:

(i) $(CH_3O)_2PONHCOC_6H_5$. $\nu(C{=}O)$ 1679; $\nu(P{=}O)$ 1239 cm^{-1}. Found: C, 47.1; H, 5.4; N, 6.3. $C_9H_{12}NO_4P$ calcd.: C, 47.2; H, 5.3; N, 6.1%.

(ii) $(CH_3O)_2PONHCOC_6H_3(NO_2)_2$-3,5. $\nu(C{=}O)$ 1699; $\nu(P{=}O)$ 1234 cm^{-1}; Found: C, 33.8; H, 3.2; N, 12.8. $C_9H_{10}N_3O_8P$ calcd.: C, 33.9; H, 3.2; N, 13.2%.

(iii) $(CH_3O)_2PONHSO_2C_6H_4CH_3$-*p*. $\nu(P{=}O)$ 1240 cm^{-1}. Found: C, 38.4; H, 5.2; N, 5.1. $C_9H_{14}NO_5PS$ calcd.: C, 38.7; H, 5.1; N, 5.0%.

(iv) $(C_2H_5O)_2PONHCOC_6H_5$. $\nu(C{=}O)$ 1685; $\nu(P{=}O)$ 1238 cm^{-1}. Found: C, 51.9; H, 6.6; N, 5.2. $C_{11}H_{16}NO_4P$ calcd.: C, 51.4; H, 6.3; N, 5.5%.

(v) $(C_2H_5O)_2PONHCOC_6H_3(NO_2)_2$-3,5. $\nu(C{=}O)$ 1701; $\nu(P{=}O)$ 1236 cm^{-1}. Found: C, 37.8; H, 4.2; N, 12.0. $C_{11}H_{14}N_3O_8P$ calcd.: C, 38.0; H, 4.1; N, 12.1%

(vi) $(C_2H_5O)_2PONHSO_2C_6H_4CH_3$-*p*. $\nu(P{=}O)$ 1243 cm^{-1}. Found: C, 42.7; H, 5.9; N, 4.4%. $C_{11}H_{18}NO_5PS$ calcd.: C, 43.0; H, 5.9; N, 4.6%.

Reactions of dibenzylhexachlorodiazadiphosphetidine $(C_6H_5CH_2NPCl_3)_2$ *[9]*

(a) The phosphazene (7.0 g, 14.5 × 10^{-3} mol) was dissolved in carbon tetrachloride (150 ml) and propan-2-ol (5.3 g, 8.8 × 10^{-2} mol) was added dropwise with stirring over 2 h. The mixture was then refluxed for 4 h. Removal of solvent followed by recrystallisation from chloroform gave *N*-benzyl-*O*,*O*-diisopropylphosphoramidate (6.9 g, 24.7 × 10^{-3} mol; 85%), identical with a sample prepared from diisopropyl hydrogen phosphite.

(b) To a solution of the phosphazene (3.3 g, 6.8 × 10^{-3} mol) in carbon tetrachloride (100 ml) was added dropwise over 0.5 h a solution of propan-2-ol (2.5 g, 41.7 × 10^{-3} mol) and pyridine (3.3 g, 42.3 × 10^{-3} mol) in the same solvent (50 ml). The mixture was stirred for 1 h, and the pyridinium chloride was filtered off. After removal of the solvent were isolated *N*-benzyl-*O*,*O*-diisopropylphosphoramidate (2.7 g, 10^{-2} mol; 73%), and benzaldehyde (0.3 g, 2.8 × 10^{-3} mol), identified as its 2,4-dinitrophenylhydrazone (m.p. 236°C; lit. [26] 237°C).

(c) To a solution of sodium isopropoxide (4.95 g, 6 × 10^{-2} mol) in ether (300 ml) was added portionwise $(Cl_3PNCH_2C_6H_5)_2$ (4.8 g, 10^{-2} mol). The mixture was refluxed for 4 h, and then cooled poured into cold ether (400 ml) and then stirred for 1 h: it was then filtered twice, and the solvent removed. The residue was extracted with benzene, which was subsequently evaporated. NMR examination of the resulting pale yellow oil showed that none of the isopropyl groups present was coupled to phosphorus.

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