Journal of Organometallic Chemistry, 76 (1974) 203—213

PREPARATION AND IMINOCARBONYLATION REACTIONS OF ORGANOALUMINIUM CHELATE COMPOUNDS CONTAINING P^V—NMe—Al BONDS

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(Received February 20th, 1974)

Summary

New organoaluminium compounds containing P^V—NMe—Al bonds, diethylaluminium dialkyl *N*-methylphosphoramidate, $(RO)_2P(O)NMeAlEt_2$, and tetraalkylphosphorodiamidic *N*-methylamide, $(R_2N)_2P(O)NMeAlEt_2$, were prepared. Cryoscopic measurements showed these compounds to be dimeric by intermolecular coordination. The introduction of bulky substituents on the phosphorus atom decreased the degree of association. The coordination of oxygen atom of P=O bonds to organoaluminium moiety was indicated by spectroscopic evidence.

In the reactions of $(RO)_2P(O)$—NMe—$AlEt_2$ with aromatic aldehydes or phenyl isocyanate, the corresponding imino compounds were obtained by an addition—elimination process.

Introduction

Some Group III organometallic chelate compounds of phosphinic acid derivatives have been studied [1—4]. In particular, organoaluminium, gallium and indium derivatives of alkyl (or aryl) phosphinic acids, $R_2P(O)$—O—MR'_2, were shown to exhibit strong intermolecular interaction between R'_2M (M = Al, Ga and In) moieties and the oxygen atom of phosphinyl group. However, little was known about the structural or chemical behavior of organoaluminium chelates of phosphoramidates $X_2P(O)$—NMe—$AlEt_2$.

It is well known that the specific affinity of phosphorus to oxygen atom is the driving force of Wittig type reactions. In this context, the dialkyl *N*-alkylphosphoramidate anion was recently reported to act as an iminocarbonylating agent [5, 6]. In pseudo-Wittig type reactions of organoaluminium compounds, a facile formation of stable Al—O bonds is considered to be the key step. For example, thiocarbonylation reactions with $(Et_2Al)_2S$ [7] and iminocarbonylation with Me_2Al—NMe—$SiMe_3$ [8] may be included in this category. Since both organoaluminium and organophosphorus groups show strong affinity to oxygen atoms, formation of a stable Al—O—P bond is expected in some addition—elimination reactions.

From the above point of view, we describe here the preparation of diethylaluminium derivatives of dialkyl *N*-methylphosphoramidates, $(RO)_2P(O)—NMe—AlEt_2$ (Ib—Vb), and tetraalkylphosphorodiamidic *N*-methylamides $(R_2N)_2$-$P(O)—NMe—AlEt_2$ (VIb, VIIb), together with the iminocarbonylation by means of diethylaluminium dialkyl *N*-methylphosphoramidates.

Results and discussion

Preparation of compounds $X_2P(O)—NMe—AlEt_2$ (X = RO and R_2N) (Ib—VIIb)

Dialkyl *N*-methylphosphoramidates (Ia—Va), obtained by the reaction of dialkyl hydrogen phosphites with CCl_4 and $MeNH_2$ [9], reacted with triethylaluminium to give the corresponding diethylaluminium derivatives (Ib—Vb) in 60—80% yield based on Et_3Al used (eqn. 1).

$$\underset{\text{(Ia—Va)}}{(RO)_2P(O)NHMe} + Et_3Al \xrightarrow[80^\circ C]{\text{benzene}} \underset{\text{(Ib—Vb)}}{(RO)_2P(O)NMeAlEt_2} + C_2H_6 \qquad (1)$$

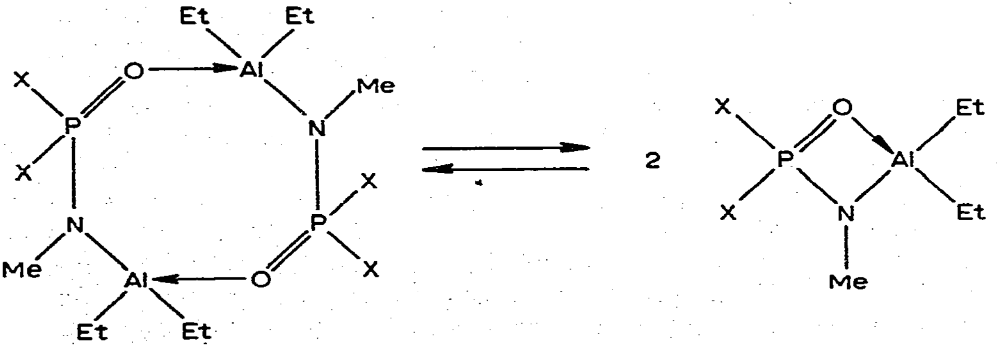
(I, R = Me; II, Et; III, i-Pr; IV, i-Bu; V, i-Am)

Tetraalkylphosphorodiamidic *N*-methylamide (VIa, VIIa) gave the corresponding aluminium compounds (VIb, VIIb) according to eqn. 2. Yields, b.p.'s and analyses of Ib—VIIb are summarized in Table 1.

$$\underset{\text{(VIa, VIIa)}}{(R_2N)_2P(O)NHMe} + Et_3Al \xrightarrow[80^\circ C]{\text{benzene}} \underset{\text{(VIb, VIIb)}}{(R_2N)_2P(O)NMeAlEt_2} + C_2H_6 \qquad (2)$$

(VI, R = Me; VII, Et)

These compounds (especially Ib—Vb) were thermally stable (up to ca. 200°) and distillable under reduced pressure. Cryoscopic molecular weight determinations showed that these compounds were dimeric in benzene by intermolecular coordination in the case of less bulky substituents (RO = MeO, EtO or Me_2N).



(3)

(X = RO and R_2N)

TABLE 1

PHYSICAL AND ANALYTICAL DATA OF THE COMPOUNDS $X_2P(O)NMeAlEt_2$

Compound	X	Yield (%)	B.p. (°C/mm)	Analysis found (calcd.) (%)			M.W. (calcd. as monomer)	Degree of association	Concentration (wt %)
				C	H	Al			
Ib	MeO	72	135—142 (0.28)	37.35	8.67	11.92	456 (223)	2.05	3.70
				(37.67)	(8.58)	(12.10)	381 (223)	1.71	2.66
IIb	EtO	78	140—145 (0.01)	43.17	9.27	10.90	405 (251)	1.62	2.76
				(43.03)	(9.23)	(10.74)			
IIIb	i-PrO	71	160—165 (0.25)	47.13	9.58	9.53	405 (279)	1.45	2.76
				(47.31)	(9.74)	(9.67)			
IVb	i-BuO	70	145—152 (0.13)	50.97	9.92	8.65	390 (307)	1.27	2.96
				(50.80)	(10.17)	(8.79)			
Vb	i-AmO	60	155—165 (0.5)	53.90	10.33	8.75	465 (335)	1.39	2.87
				(53.72)	(10.52)	(8.06)	415 (335)	1.24	1.55
VIb	Me_2N	60	110—120 (0.3)	43.53	10.01	11.26	474 (249)	1.91	3.61
				(43.37)	(10.11)	(10.84)			
VIIb	Et_2N	84	liquid	50.91	10.66	9.34	470 (305)	1.54	3.13
				(51.13)	(10.89)	(8.84)			

TABLE 2

DIFFERENCES IN ν(P=O) AND ν(P—N) BETWEEN $X_2P(O)NHMe$ (Ia—VIIa) AND $X_2P(O)NMeAlEt_2$ (Ib—VIIb) (cm^{-1})[a]

Compound	X	ν^A(P=O) of Ia—VIIa	ν^B(P=O) of Ib—VIIb	$\Delta\nu$(P=O) $=\nu^B$(P=O) $-$ ν^A(P=O)	ν^A(P—N) of Ia—VIIa	ν^B(P—N) of Ib—VIIb	$\Delta\nu$(P—N) $=\nu^B$(P—N) $-$ ν^A(P—N)
Ia, b	MeO	1260, 1243	1220, 1190	—40, —53	880	940	60
IIa, b	EtO	1254, 1235	1215, 1180	—39, —55	870	920	50
IIIa, b	i-PrO	1250, 1235	1215, 1175	—35, —60	895	933	38
IVa, b	i-BuO	1240, 1230	1215, 1185	—25, —45	890	940	50
Va, b	i-AmO	1250, 1235	1215, 1190	—35, —45	885	940	55
VIa, b	Me_2N	1215, 1190	1190, 1155	—25, —35	845	905	60
VIIa, b	Et_2N	1220, 1205	1200, 1170	—20, —35	850	895	45

[a] In 2% benzene solution.

TABLE 3

NMR SPECTRA OF $X_2P(O)NMeAlEt_2$ [a]

Compound	X	P—N—CH_3	J(PNCH) [b]	$AlCH_2$	$AlCH_2C\underline{H}_3$	J(HCCH)	P—O—R	P—N—R	J(P—H_β)
Ib	MeO	7.60	16.5 (12.0)	9.78	8.60	7.5	6.75 d		11.8
IIb	EtO	7.55	17.2 (12.0)	9.73	8.58	7.5	6.20 dq, 8.98 t		7.5
IIIb	i-PrO	7.45	17.2 (11.2)	9.74	8.54	8.3	5.45 m, 8.83 d		
IVb	i-BuO	7.43	17.2 (12.0)	9.71	8.53	7.5	6.25 dd, 7.80—8.50 m 9.18 d		6.0
Vb	i-AmO	7.40	17.3 (12.0)	9.68	8.50	7.5	5.96 dt, 8.30—8.90 m 9.12 d		6.8
VIb	Me_2N	7.78	17.5 (10.5)	9.78	8.55	7.5		7.65 d	11.3
VIIb	Et_2N	7.55	17.3 (12.0)	9.73	8.50	7.5		7.08 dq, 9.05 t	9.8

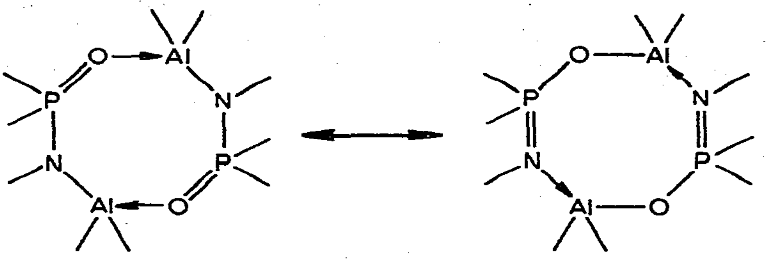
[a] Chemical shift τ in ppm, coupling constant J in Hz; 10 to 15% solutions in benzene were used. [b] The value in parentheses shows J(PNCH) of the parent compound (Ia—VIIa)

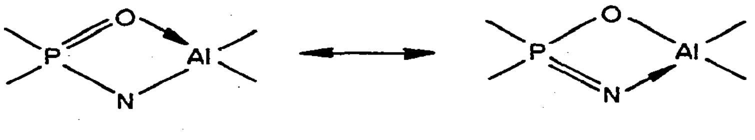
The introduction of bulky groups (RO = i-PrO, i-BuO, i-AmO or Et_2N) on the phosphorus atom decreased the degree of association. The steric effect of the substituent on phosphorus is explained in terms of the dissociative equilibrium between the intermolecularly coordinated dimer and the intramolecularly coordinated monomer (eqn. 3).

In this connection, the preparation of the di-tert-butyl *N*-methylphosphoramidate derivative, $(t\text{-}BuO)_2P(O)NMeAlEt_2$, failed. Evolution of excess ethane occurred (ca. 1.5 ~ 1.7 times the theoretical value).

IR and NMR spectra of Ib—VIIb

As shown in Table 2, the stretching frequency of P=O bond in Ib—VIIb, showed values lower than in the original dialkyl *N*-methylphosphoramidates Ia—Va or in the tetraalkylphosphorodiamidic *N*-methylamides (VIa, VIIa) ($\Delta\nu$(P=O) ca. -20 to -60 cm^{-1}), which suggests the coordination of oxygen atom of P=O bonds to diethylaluminium group. The stretching frequency of the P—N bond (850 to 950 cm^{-1}) [10] shifted to higher values on introduction of the diethylaluminium moiety [$\Delta\nu$(P—N) ca. 40 to 60 cm^{-1}]. These two shifts of P=O (lower) and P—N (higher) stretching frequencies can be explained in terms of structure B or D, in which $(p\text{-}d)\pi$ bonding between phosphorus and nitrogen atoms is involved. When electronegative groups (RO or R_2N) are linked to the phosphorus atom, it is reported that the contraction of 3*d* orbitals increases their availability to $(p\text{—}d)\pi$ bonding [11].


(A) (B)


(C) (D)

The NMR spectroscopic results are summarized in Table 3. Changes of coupling constant, *J*(PNCH), by introduction of the diethylaluminium group, provide important information about the P—N bond. Dialkyl *N*-methylphosphoramidates or tetraalkylphosphorodiamidic *N*-methylamides $X_2P(O)NHMe$ (X = RO, R_2N) (Ia—VIIa) showed *J*(PNCH) values around 10 to 12 Hz. These values increased to 16 to 17 Hz for the organoaluminium homologs $X_2P(O)NMeAlEt_2$ (Ib—VIIb) as shown in Table 3. The increase of *J*(PNCH) by diethylaluminium group reflects the contribution of $(p\text{—}d)\pi$ interaction between phosphorus and

TABLE 4

REACTION PRODUCTS OF Ib, IIb WITH CARBONYL COMPOUNDS

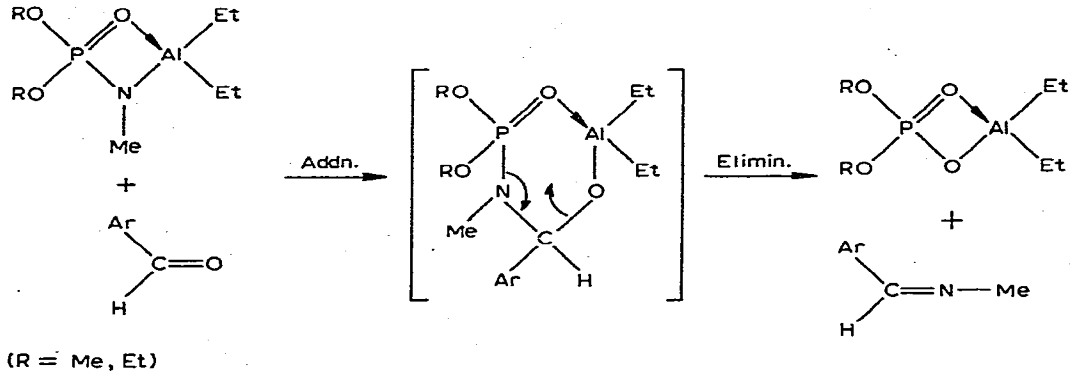
Carbonyl compounds	Products (% yield)	$[(MeO)_2P(O)NMeAlEt_2]_2$ (Ib)	$[(EtO)_2P(O)NMeAlEt_2]_2$ (IIb)
PhCH=O	PhCH=NMe	74	70
	$(RO)_2P(O)OAlEt_2$	98	86
p-$MeOC_6H_4CH$=O	p-$MeOC_6H_4CH$=NMe	70	71
	$(RO)_2P(O)OAlEt_2$	88	76
Ph—N=C=O [a]	Ph—N=C=N—Me	60	36
	Ph—NHCONH—Me	40	9
	$(RO)_2P(O)NMeCONHPh$	0	55
Ph_2C=O	Ph_2C=NMe		30

[a] Demetallated with dilute hydrochloric acid and yield was obtained by NMR analysis.

nitrogen atoms (cf. P^V=N—CH;J(PNCH) 20 to 30 Hz) [12, 13]. The change in coupling constants is also consistent with the strong interaction of oxygen with the aluminium atom.

Iminocarbonylation reactions of $(RO)_2P(O)NMeAlEt_2$ with aromatic aldehydes and ketone

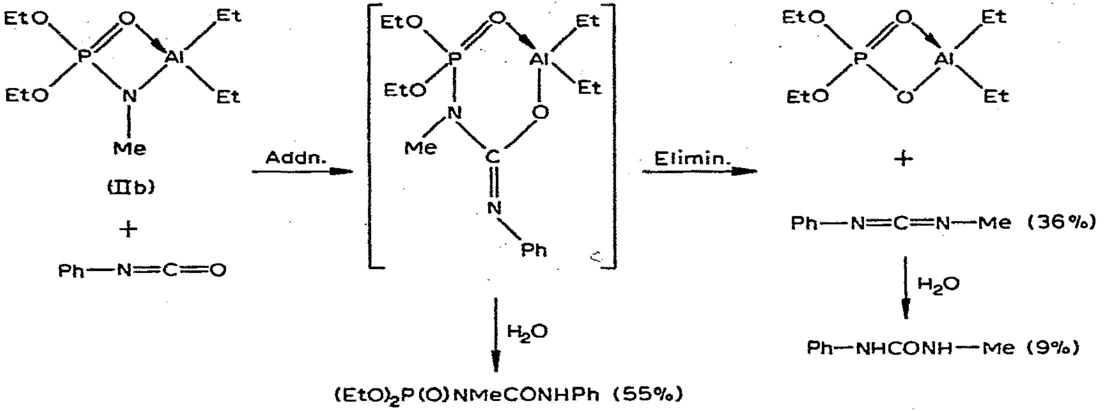
When diethylaluminium dimethyl (and diethyl) N-methylphosphoramidate (Ib and IIb), reacted with aromatic aldehydes, the corresponding N-arylidenemethylamines were obtained in 70 to 80% yield along with diethylaluminium dialkyl phosphate (80 to 90% yield) (eqn. 4) as summarized in Table 4. The reaction between IIb and benzophenone was extremely slow even at 80°, probably due to a steric effect.



(4)

Reactions of $X_2P(O)NMeAlEt_2$ [X = MeO (Ib), EtO (IIb) and Me_2N (VIb) with phenyl isocyanate

Phenyl isocyanate showed remarkable differences in reactivity which depended upon the degree of association of the starting aluminium compound. The reaction of dimeric compounds $(RO)_2P(O)NMeAlEt_2$ (Ib, IIb) (R = Me, Et), with phenyl isocyanate did not proceed at room temperature. On heating up to 80°, a subsequent elimination reaction occurred immediately. In the case of IIb, three products were present: methylphenylcarbodiimide (36%; elimination product), *N*-methyl-*N'*-phenylurea (9%; hydrolysis product of carbodiimide) and $(EtO)_2P(O)NMeCONHPh$ (55%; hydrolysis product of the corresponding 1/1 insertion intermediate) (see Table 4). The presence of both elimination (methylphenylcarbodiimide and its urea derivative) and insertion products [$(EtO)_2P(O)$-NMeCONHPh] indicates the addition—elimination process shown in eqn. 5.



(5)

The hydrolysis product of the 1/1 insertion product is consistent with the conclusion that the Al—N bond of IIb was cleaved exclusively.

The addition reaction of phenyl isocyanate with IIIb or IVb (R = i-Pr or i-Bu) took place at room temperature more readily than with Ib or IIb. It is reasonable to conclude that the active species of the addition reaction should be monomeric, because the content of monomeric species in IIIb or IVb is larger than that in Ib or IIb as shown in Table 1. Therefore the dissociation to the monomeric form is required for Ib (R = Me) or IIb (R = Et) prior to insertion.

The reactivity of VIb to Ph—N=C=O at room temperature was quite low compared with those of Ib—IVb. The addition process took place slowly even at 80°. Hydrolysis of the reaction mixture gave only the 1/1 insertion product, $(Me_2N)_2P(O)NMeCONHPh$ and no elimination products.

For the formation of P—O—Al bond at the elimination stage, the $(RO)_2$-P(O) group is more effective than $(R_2N)_2P(O)$ group. This suggests that the acidic character of the phosphorus atom plays an important role in the elimination step, because the acidity of the phosphorus atom in the former is larger than that of the latter.

Experimental

General remarks

Dialkyl *N*-methylphosphoramidates, $(RO)_2P(O)NHMe$, and tetraalkylphosphorodiamidic *N*-methylamides, $(R_2N)_2P(O)NHMe$, were prepared by known methods [9, 14]. The physical data of these new compounds are summarized in Table 5. Commercial Et_3Al (Ethyl Corp.) was used without further purification. Hydrocarbon solvents were thoroughly dried over sodium wire. All reactions and measurements of physical constants of the products were carried out under dry nitrogen or argon. Molecular weights in benzene solution were

TABLE 5

PHYSICAL AND ANALYTICAL DATA OF $X_2P(O)NHMe$

Compound	X	Yield (%)	B.p. (°C/mm)	Analysis found (calcd.) (%)		
				C	H	N
Ia	MeO	73	89–91/0.5	25.92 (25.91)	7.07 (7.25)	10.24 (10.07)
IIa	EtO	74	81–83/0.03	Known compound [a]		
IIIa	i-PrO	82	78–82/0.08	43.80 (43.09)	9.10 (9.29)	6.65 (7.18)
IVa	i-BuO	85	115–118/0.25	48.73 (48.42)	9.59 (9.93)	6.30 (6.27)
Va	i-AmO	97	114–117/0.23	52.98 (52.57)	10.19 (10.43)	5.39 (5.57)
VIa	Me_2N	68	125–128/3	Known compound [b]		
VIIa	Et_2N	30	125–130/0.35	48.70 (48.85)	10.71 (10.93)	19.36 (18.99)

[a] Lit. [19] b.p. 130/15. [b] Lit. [20] b.p. 137–143/3.

determined cryoscopically. Infrared spectra were recorded with a Japan Spectroscopic Co. Model IR-S and NMR spectra were recorded with a Japan Electron Optics Co. Model C-60HL using TMS as an internal standard. Elemental analyses of organoaluminium compounds were carried out by Alfred Bernhardt Microanal. Lab. in West Germany.

Preparation of diethylaluminium dialkyl N-methylphosphoramidates (Ib—Vb) and tetraalkylphosphorodiamidic N-methylamides (VIb, VIIb)

The preparation of diethylaluminium dimethyl *N*-methylphosphoramidate (Ib) is described as an example; IIb—VIIb were prepared analogously. Dimethyl *N*-methylphosphoramidate (Ia)(2.44 g, 17.5 mmol) in 20 ml of benzene was added dropwise to Et_3Al (1.99 g, 17.5 mmol) in 20 ml benzene at room temperature. During the addition of Ia evolution of gas was observed. The reaction mixture was heated up to 80° and refluxed for 1 h. After the gas evolution had ceased completely, the solvent was removed, and the product was distilled under reduced pressure to give liquid Ib, b.p. 135—142°/0.28 mm. Yield 2.81 g (72%) based on Et_3Al used. See Tables 1—3 for data.

Reaction of Ib with aldehydes

Benzaldehyde. Benzaldehyde (0.416 g, 3.92 mmol) in 10 ml of benzene was added dropwise to Ib (0.871 g, 3.92 mmol) in 10 ml of benzene at room temperature. After 15 h both absorption bands at 1700 cm^{-1} [ν(C=O)] and 940 cm^{-1} [ν(P—N)] had not vanished. The reaction mixture was heated to reflux. The two above-mentioned absorption bands completely disappeared, and the appearance of new band at 1650 cm^{-1} [ν(C=N)] was noted. Removal of the solvent and distillation under reduced pressure gave *N*-benzylidenemethylamine, b.p. 75—80°/20 mm (lit. b.p. 60°/8 mm) [15], 0.35 g (yield 74%) and a residue, 0.81 g (yield 98%) of diethylaluminium dimethyl phosphate [$(MeO)_2P(O)—O—AlEt_2$]. *N*-benzylidenemethylamine showed the same infrared and NMR spectra as the authentic compound [16].

p-Anisaldehyde. In an analogous manner, reaction of Ib, (0.645 g, 2.90 mmol) in 10 ml benzene and *p*-anisaldehyde (0.395 g, 2.90 mmol) in 10 ml of benzene gave by distillation under reduced pressure *N-p*-methoxybenzylidenemethylamine, b.p. 63—65°/0.08 mm, 0.30 g (yield 70%). Spectroscopic and physical data of the isolated product were identical with those of an authentic sample. A residue, 0.538 g (yield 88% as diethylaluminium dimethyl phosphate), was also obtained.

Reaction of Ib with phenyl isocyanate

Phenyl isocyanate (0.338 g, 2.83 mmol) in 10 ml of benzene was added dropwise to Ib, (0.629 g, 2.83 mmol) in 10 ml of benzene at room temperature. After 16 h, both absorption bands at 2260 cm^{-1} [ν(NCO)] and 940 cm^{-1} [ν(PN)] remained. The reaction mixture was heated to 80° and refluxed for 6 h. Both of the above two absorption bands disappeared completely and new bands at 2130 cm^{-1} [ν(NCN)], characteristic of *N*-methyl-*N'*-phenylcarbodiimide, 1695 and 1650 cm^{-1} appeared. After hydrolysis of the mixture with dilute hydrochloric acid the product was extracted with benzene. The benzene solution was dried with anhydrous Na_2SO_4; removal of the solvent gave 0.511 g of an oil. NMR analysis of this oil showed the presence of *N*-methyl-*N'*-phenylcarbodiimide (60%) and

PhNHCONHMe (40%). The authentic sample of carbodiimide was prepared according to ref. 17.

Reaction of IIb with aldehydes and ketones

Benzaldehyde. When a mixture of benzaldehyde (0.250 g, 2.32 mmol) and IIb, (0.584 g, 2.32 mmol) in 20 ml of benzene was kept at room temperature for 24 h and heated at reflux for 12 h, absorption bands at 1700 cm^{-1} [ν(C=O)] and 920 cm^{-1} [ν(PN)] disappeared, and a new absorption band at 1650 cm^{-1} [ν(C=N)] appeared. The products were PhCH=NMe (0.19 g, 70%) and (EtO)$_2$P(O)—O—AlEt$_2$ (0.51 g, 92%).

p-Anisaldehyde. In an analogous manner a mixture of IIb, (0.871 g, 3.50 mmol) and *p*-anisaldehyde (0.476 g, 3.50 mmol) in 20 ml of benzene was kept at room temperature for 17 h and then refluxed for 4 h. The products were *p*-MeOC$_6$H$_4$CH=NMe (0.34 g, 71%) and (EtO)$_2$P(O)—O—AlEt$_2$ (0.54 g, 76%).

Benzophenone. A mixture of IIb, (0.664 g, 2.64 mmol) and benzophenone (0.482 g, 2.64 mmol) in 20 ml of benzene was heated at reflux for 5 days. During the heating, the intensity of ν(C=O) (1680 cm^{-1}) band of the ketone decreased slightly and that the 1640 cm^{-1} [ν(C=N)] band increased gradually. However, the reaction did not go to completion. The corresponding imino compound, (C$_6$H$_5$)$_2$C=NMe, was obtained in 30% yield on the basis of NMR. NMR (CCl$_4$): τ 6.93 s (NCH$_3$), 2.38—3.28 ppm (m, phenyl).

Preparation of authentic diethylaluminium diethyl phosphate

Diethyl phosphate [18] (1.60 g, 10.3 mmol) in 20 ml of benzene was added to Et$_3$Al (1.17 g, 10.3 mmol) in 20 ml of benzene. During the addition of the phosphate, evolution of gas was observed. The reaction mixture was heated to 80°. After gas evolution ceased completely, removal of the solvent and distillation under reduced pressure gave diethylaluminium diethyl phosphate, 1.95 g (yield 80% based on Et$_3$Al used), b.p. 108—114°/0.35 mm. (Found: Al, 10.15; active ethyl groups 1.84. C$_8$H$_{20}$O$_4$ Pal calcd.: Al, 11.32%; active ethyl groups 2.00 per mol.) NMR (benzene): τ 9.75 q (AlCH$_2$, 4H, *J* 7.5 Hz), 9.03 t (P—O—CH$_2$—C$\underline{H}_3$, 6H, *J* 6.8 Hz), 8.51 t (AlCH$_2$C$\underline{H}_3$, 6H, *J* 7.5 Hz), 6.17 dq ppm (P—O—C$\underline{H}_2$—CH$_3$, 4H, *J*(POCH) 7.8 Hz, *J* (HCCH) 6.8 Hz). IR (benzene: ν(P=O) 1280 s and 1262 s, ν(P—O—C) 1020—1045 vs cm^{-1}.

Reaction of IIb with phenyl isocyanate

An equimolar mixture of IIb, (0.578 g, 2.30 mmol) and phenyl isocyanate, (0.275 g, 2.30 mmol) in 20 ml of benzene was kept at room temperature for 1 day. However, no reaction occurred. The mixture was heated to 80° and refluxed for 6 h. Both absorption bands at 2260 cm^{-1} [ν(NCO)] and 920 cm^{-1} [ν(P—N)] disappeared completely, while new bands at 2130 cm^{-1} [ν(N=C=N)], 1690 cm^{-1} and 1650 cm^{-1} appeared. Hydrolysis of the mixture gave an oil, 0.455 g, which contained three components, *N*-methyl-*N'*-phenylcarbodiimide (36%), PhNHCONHMe (9%) and the 1/1 insertion product (EtO)$_2$P(O)NMeCONHPh (55%). (EtO)$_2$P(O)NMeCONHPh; NMR (CCl$_4$): τ 8.65 t (P—O—CH$_2$C$\underline{H}_3$, *J* 6.8 Hz), 7.05 d (P—N—CH$_3$, *J*(PNCH) 6.8 Hz), 5.88 dq (P—O—C$\underline{H}_2$CH$_3$, *J*(POCH) 7.5, *J*(HCCH) 6.8 Hz), 2.38—3.32 (phenyl), —0.10 s ppm (P—N$\underline{H}$—Me). IR (CCl$_4$): 3230 m [ν(NH)], 1700 s [ν(C=O)], 1276 s [ν(P=O)], 1014 s [ν(P—O—C)], 873 m cm^{-1} [ν(P—N)].

Reaction of VIb with phenyl isocyanate

An equimolar mixture of VIb, (1.21 g, 4.85 mmol) and phenyl isocyanate (0.578 g, 4.85 mmol) in 20 ml of benzene was kept at room temperature for 60 h. No reaction occurred. Heating at reflux for 17 h caused the disappearance of ν(NCO) (2260 cm^{-1}) and appearance of bands at 1630 cm^{-1} and 1660 cm^{-1}. Hydrolysis of the mixture as before gave an oil, *N*-tetramethylphosphorodiamidic-*N*-methyl-*N'*-phenylurea, $(Me_2N)_2P(O)NMeCONHPh$, in 73% yield. IR (benzene): 3160 m [ν(NH)], 1690 vs [ν(C=O)], 1260 vs [ν(P=O)] and 985 vs, 970 vs cm^{-1} [ν(P—O—C)]. NMR (CCl_4): τ 7.38 d [P—N$(CH_3)_2$, 12H, *J*(PNCH) 9.8 Hz), 7.21 d (P—N—CH_3, *J*(PNCH) 7.5 Hz, 3H), 2.45—3.32 m (phenyl, 5H) and —0.62 s (CON$\underline{H}$Ph, 1H). (Found: C, 50.56; H, 6.68; N, 19.75. $C_{12}H_{21}N_4O_2P$ calcd.: C, 50.70; H, 7.45; N, 19.71%.)

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