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Reactions of Aminophosphines with Isothiocyanates. Dipolar Ionic Products

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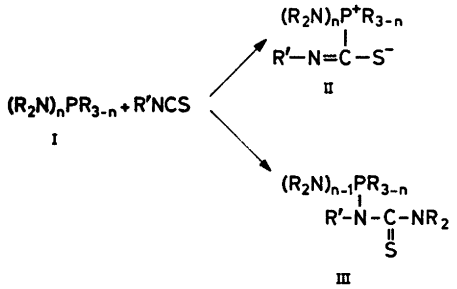
The reactions of three methyl substituted aminophosphines with methyl- and phenylisothiocyanate have been studied. The products are shown by ^1H and ^{31}P NMR spectroscopy to be dipolar ions, and analogous to those formed by trialkylphosphines. The dipolar ionic compounds derived from trimethylphosphine and methiodides of all dipolar ionic compounds have been prepared for comparison.

Aminophosphines (I) have been claimed by Oertel *et al.*[1] to react with isothiocyanates to give insertion products (III). They were formulated as insertion products because they (i) gave thioureas on hydrolysis and (ii) displayed an IR band at 1490 cm^{-1} "characteristic of thioureas". The alternative structure II, which is analogous to that of the known trialkylphosphine isothiocyanate adducts,[2,3] was not considered. We have reinvestigated the reaction and present evidence that product structure corresponds to II.



The investigation has been limited to the reaction of I, R = CH_3, $n = 1,2,3$ with methyl- and phenylisothiocyanate. A crystalline precipitate was generally formed upon mixing the aminophosphine and the isothiocyanate in ether or pentane at −20 °C. Ethyl- and isopropylisothiocyanate react similarly, but no compound could be isolated from *tert*-butylisothiocyanate. Also, we were unable to isolate any reaction product when the aminophosphine was *P*-phenyl substituted. Yields, melting points, and microanalyses of the compounds prepared and their methiodides IV are given in Table 1. Two of the compounds (IIa and IIb) are, judging from their melting points, identical to products obtained by Oertel *et al.* and described as insertion compounds.[1]

Assignment of structure. The adducts are assigned structure II on the basis of their ^1H and ^{31}P NMR spectra (Table 2): (i) Each compound, regardless of the number of amino groups, displays only one $(CH_3)_2N$ doublet with a rather large coupling constant (9.3 − 10.8 Hz). Since this is a coupling to phosphorus,* its magnitude and the fact that all R_2N groups are equivalent indicate that no R_2N group is separated from phosphorus by insertion of RNCS in a P−N bond. (ii) Dissociation to I and isothiocyanate is evident for several of the adducts as observed from their ^1H NMR spectra in $CDCl_3$. This is most unlikely for compounds with structure III. (iii) The ^{31}P chemical shifts are in the range expected for phosphonium compounds (general chemical shift range for phosphonium compounds containing R_2N groups −65 to −25 ppm).[4] The chemical shifts

* All couplings in Table 2 are shown by ^{31}P decoupling to be P···H couplings.

Table 1. Reaction products of aminophosphines with isothiocyanates. Dipolar ionic compounds and their methiodides.

No.	Compound	Yield, %	M.p., °C	Analyses (C, H, N, S)
IIa	$(Me_2N)_3P^+$ $MeNCS^-$	65 [a]	66 – 67 [b]	Found: 40.68, 8.99, 24.00, 13.65 Calc.: 40.70, 8.91, 23.75, 13.54
IVa	$(Me_2N)_3P^+$ I^- $MeNCSMe$	90 [a]	70 – 72	Found: 28.49, 6.04, 14.94, 8.40 Calc.: 28.60, 6.35, 14.85, 8.47
IIb	$(Me_2N)_3P^+$ $PhNCS^-$	90	70 – 70.5 [c]	Found: 52.19, 7.74, 18.76, 10.66 Calc.: 52.20, 7.75, 18.75, 10.72
IVb	$(Me_2N)_3P^+$ I^- $PhNCSMe$	85 [a]	111 – 112	Found: 37.60, 5.97, 12.74, 7.27 Calc.: 38.18, 5.92, 12.73, 7.29
IIc	$(Me_2N)_2P^+Me$ $MeNCS^-$	25	56.5 – 58 [d]	Found: 40.33, 8.95, 20.19, 15.40 Calc.: 40.56, 8.75, 20.27, 15.47
IVc	$(Me_2N)_2P^+Me$ I^- $MeNCSMe$	65 [a]	88.5 – 89	Found: 27.40, 5.95, 12.10, 8.92 Calc.: 27.51, 6.06, 12.03, 9.18
IId	$(Me_2N)_2P^+Me$ $PhNCS^-$	90	58 – 59	Found: 53.39, 7.47, 15.60, 11.81 Calc.: 53.51, 7.48, 15.60, 11.91
IVd	$(Me_2N)_2P^+Me$ I^- $PhNCSMe$	60 [a]	102 – 103.5	Found: 37.95, 5.64, 10.43, 7.53 Calc.: 37.96, 5.64, 10.22, 7.80
IIe	$Me_2NP^+Me_2$ $MeNCS^-$	65	87.5 – 88	Found: 40.08, 8.42, 15.70, 17.79 Calc.: 40.40, 8.44, 15.73, 18.00
IVe	$Me_2NP^+Me_2$ I^- $MeNCSMe$	70 [e]	118 – 118.5	Found: 25.85, 5.66, 8.75, 9.86 Calc.: 26.10, 5.64, 8.71, 9.95
IIf	$Me_2NP^+Me_2$ $PhNCS^-$	70 [e]	98 – 99	Found: 55.38, 7.22, 11.90, 13.16 Calc.: 55.00, 7.13, 11.68, 13.37
IVf	$Me_2NP^+Me_2$ I^- $PhNCSMe$	50 [f]	145 – 146	Found: 37.55, 5.38, 7.26, 8.33 Calc.: 37.70, 5.24, 7.33, 8.39
IIg	P^+Me_3 $MeNCS^-$	90	136 – 138	Found: 39.95, 8.13, 9.47, [g] Calc.: 40.25, 8.11, 9.39, 21.49
IVg	P^+Me_3 I^- $MeNCSMe$	80 [f]	160 – 161	Found. 24.84, 5.14, 4.84, 10.92 Calc.: 24.75, 5.19, 4.81, 11.01

Table 1. Continued.

IIh	P^+Me_3		85	90.5–92	Found: 56.90, 6.78, 6.71, 15.21
	PhNCS$^-$				Calc.: 56.84, 6.67, 6.63, 15.18
IVh	P^+Me_3	I^-	60 [f]	138–138.5	Found: 37.58, 4.86, 3.97, 8.66
	PhNCSMe				Calc.: 37.41, 4.85, 3.97, 9.08

[a] Dissolved in acetone and reprecipitated with ether. Lit. values[1] for the claimed insertion products: [b] 66, [c] 70, [d] oil, b.p. 120–122/0.15 mmHg. [e] Recrystallized from acetone. [f] Recrystallized from 2-propanol. [g] Exploded.

Table 2. ^1H and ^{31}P NMR data [a] for aminophosphines, dipolar ionic products with isothiocyanates, and their methiodides.

Compound	$\delta(^1H)$ CH_3NP	CH_3P	CH_3NC	CH_3S	J_{PNCH}	J_{PCH}	J_{PCNCH}	J_{PCSCH}	$\delta(^{31}P)$
Ia	2.48				9.1				−123.0
IIa	2.86		3.44		9.3		4.8		−31.7
IVa	2.95		3.72	2.73	10.1		4.4	1.7	−34.6
IIb	2.82				9.3				−32.0
IVb	3.05			2.14	10.2			1.8	−34.1
Ic	2.65	1.23			9.2	7.1			−86.3
IIc	2.82	2.02	3.42		9.9	12.6	4.4		−43.3
IVc	2.94	2.55	3.70	2.76	10.6	12.9	4.0	1.2	−50.5
IId	2.80	2.02			9.9	12.6			−44.5
IVd	3.01	2.54		2.23	10.5	13.3		1.3	−51.7
Ie	2.54	1.08			10.3	4.8			−39.6
IIe	2.83	1.99	3.41		10.8	12.5	4.2		−36.4
IVe	2.94	2.53	3.72	2.71	10.8	13.2	3.7	1.3	−53.4
IIf	2.88	2.05			10.7	12.5			−37.6
IVf	2.99	2.63		2.16	10.7	13.6		1.2	−53.8
Ig		1.02				1.7			61.2
IIg		1.96	3.40			13.4	4.4		−6.2
IVg		2.51	3.77	2.68		14.2	3.8	1.5	−29.4
IIh		1.87				13.3			−8.4
IVh		2.59		2.15		14.2		1.4	−30.4

[a] 1–5 % solutions in $CDCl_3$ at *ca.* 35 °C. Chemical shifts in ppm, $\delta(^1H)$ from TMS, $\delta(^{31}P)$ from external 85 % H_3PO_4, coupling constants J in Hz.

of III are expected to be much closer to those of I. (iv) The coupling constants J_{PCH} in the products are larger than those in I in agreement with the formulation of the compounds as phosphonium compounds.[5] (v) The ^1H chemical shifts are close to those found for similar phosphonium compounds [6] and agree with a deshielding of the protons by P^+, relative to the protons of I.

Methylation of the compounds II results in a further NMR deshielding of all protons and phosphorus in accord with a reduced electron density in the methiodides IV (Table 2). Apart from the deshielding and the doublet (due to coupling to phosphorus) from the S-CH_3 group the spectra of II and IV are very much alike, as expected for compounds with similar structures.

For comparison we have included the analogous compounds (II, $n=0$) derived from trimethylphosphine (I, $n=0$) in the investigation. The NMR spectra of these (Table 2) are very similar to those of the compounds described above. Since tertiary phosphines are not able to give insertion compounds analogous to III, but are known to give dipolar ionic compounds

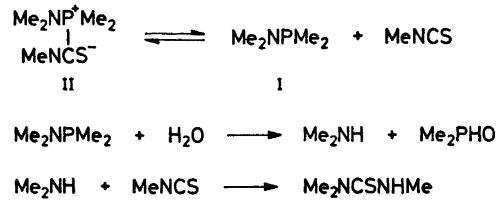
with isothiocyanates,[2,3] this similarity of the NMR spectra support the evidence given above for the dipolar ions structure of the aminophosphine adducts.

Compounds II and IV are expected to exist as mixtures of *E* and *Z* isomers due to restricted rotation about the C=N bond.

IVZ IVE

However, we were in no case able to observe more than one set of ^{1}H NMR signals at temperatures down to −50 °C in $CDCl_3$. These results indicate that II and IV exist mainly as one of the *E*−*Z* isomers, and we suggest that to be the *Z* isomer for the following reasons. (i) The rather large J_{PCNCH} coupling constant in I and IV (R′=CH_3) indicate a *trans* configuration for P^+ and CH_3 about the C=N bond. (ii) The *Z* isomer is probably the most stable isomer for both steric ($-P^+$ is larger than S^- and probably also SCH_3) and electronic reasons (the lonepair of nitrogen being closer to $-P^+$).

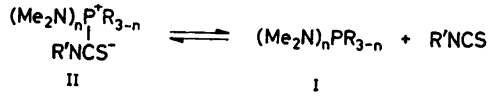
Properties of adducts II. The compounds are colourless to yellow solids which are easily hydrolysed by moist air. The hydrolysis products are thioureas, as found by Oertel *et al.*,[1] and various phosphorus acids. These hydrolysis products are explained by the fact that II is reversibly dissociated to I and isothiocyanate. Hydrolysis of I, a fast process, gives Me_2NH which subsequently combines with the isothiocyanate to give a thiourea, *e.g.*



The dissociation of II to I and isothiocyanate is perceptible from the smell of the solid II, and in most cases is also observable by ^{1}H NMR in $CDCl_3$ solution (Table 3). The values in Table 3 show that dissociation occurs more readily in the order of R′: Me < Ph < Bu^t. This variation is probably due to increasing steric hindrance in II with larger R′. The steric hindrance is expected to be largest for $(Me_2N)_3P$ and smallest for PMe_3, in accordance with the values which show a larger variation with R′ in the former case. An increase in the dissociation of II is also seen with decreasing number of amino groups (decreasing *n*). This variation shows that dimethylamino groups stabilize II relative to I + R′NCS, probably by stabilizing the phosphonium centre by $p\pi$-$d\pi$ overlap.[6] The values in the last column show that substituting a Me group on phosphorus for a Ph group strongly increases the dissociation of II. This is expected from the well-known reduced nucleophilicity of tertiary phosphines when phenyl groups are introduced.[7]

The compounds II are thermally rather un-

Table 3. Degree of dissociation of II to I and R′NCS [100 × mol I/(mol I + mol II) at equilibrium, starting solutions 2.0×10^{-1} M of II in $CDCl_3$, *t ca.* 35 °C, calculated from ^{1}H NMR integral values].



R′NCS	I $(Me_2N)_3P$	$(Me_2N)_2PMe$	Me_2NPMe_2	PMe_3	$(Me_2N)_2PPh$
MeNCS	< 1	< 1	3	27	*ca.* 97 [a]
PhNCS	25	16	17	33	*ca.* 98 [a]
Bu^{t}NCS	> 95 [a]				

[a] 2.0×10^{-1} M in aminophosphine and isothiocyanate.

stable. Although stable for several months at −20 °C, they decompose within a few days at room temperature. From the ^{1}H NMR spectra of the decomposing compounds in $CDCl_3$ it seems that II is first transformed into two new compounds. These subsequently decompose, and the presence of at least three new compounds is established by ^{31}P decoupling experiments. Likewise we obtained mixtures upon attempts to distil the compounds following Oertel *et al.* who isolated some of their products by distillation. One of the compounds in the mixtures may have the structure III, but it seems unlikely that the products obtained by Oertel *et al.* in any case were pure III. The thermal decomposition of II is under further investigation in our laboratories.

The IR spectra of II showed a strong band at 1475−1515 cm^{-1} (KBr). This band is assigned (mainly) to a C=N stretching vibration because a band is found in the same range in the IR spectra of IIg and IIh, and because the band is shifted to higher wavenumbers in the methiodides IV. Although thioamides and thioureas have a band in the same region (the B-band [8]), it is nevertheless not solely characteristic of thioureas, as implied by Oertel *et al.*

EXPERIMENTAL

Microanalyses were carried out at the Microanalysis Department of Department of General and Organic Chemistry, the H. C. Ørsted Institute. ^{1}H and ^{31}P NMR spectra were obtained on a Bruker HX 90E spectrometer. Tris(dimethylamino)-phosphine and dimethylaminodimethylphosphine were prepared according to the literature.[9] Trimethylphosphine was obtained from its silver iodide complex [10] by pyrolysis. All preparations were performed in a nitrogen atmosphere.

Bis(dimethylamino)methylphosphine. To a stirred solution of $(Me_2N)_2PCl$ [11] (12.4 g) in dry ethyl ether (75 ml), kept at −78 °C, was added MeLi (1.6 M in ether, 50 ml). After 2 h at 20 °C the reaction mixture was set aside for LiCl to precipitate, the solution decanted and the solvent evaporated under reduced pressure. Vacuum distillation through a 15 cm Vigreux column gave $(Me_2N)_2MeP$ (5.4 g, 50 %), b.p. 37−39 °C/13 mmHg (lit.[12] 64−67 °C/49−50 mmHg). According to its ^{1}H NMR spectrum the product contained a small amount of $(Me_2N)_3P$ (3−6 %), but was otherwise pure.

Dipolar ionic compounds (II). The phosphine (4 mmol) in dry ether or pentane (5−10 ml) was cooled to −78 °C and methyl- or phenylisothiocyanate (6 mmol) added with stirring. After 24 h at −20 °C (−78 °C in case of IIc) the colourless or yellow crystals were filtered off, washed with cold ether or pentane and dried 5 min *in vacuo* at 20 °C. The crude compounds were analytically pure except those for which solvents of crystallisation are given in Table 1.

Methiodides (IV). To a methylene chloride or acetone solution of II was added the corresponding isothiocyanate (*ca.* mol:mol) in order to suppress dissociation, and then excess methyl iodide at −78 °C. After 1 h at 20 °C the solvent was evaporated and the residue recrystallized from the solvent given in Table 1.

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