N-Isothiocyanatoamines

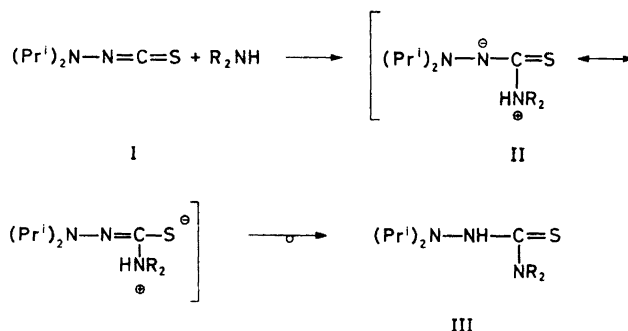## X. The Reaction between N-Isothiocyanatodiisopropylamine and Phosphines

UFFE ANTHONI, OTTO DAHL,
CHARLES LARSEN and PER HALFDAN NIELSEN

*Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen,
The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark*

N-Isothiocyanatodiisopropylamine reacts with trimethyl- and triethylphosphine with formation of dipolar adducts. The structure of the adduct with triethylphosphine was established by spectroscopic methods and by conversion to the hydrochloride and the methiodide. On treatment with diethyl- or diphenylphosphine, N-isothiocyanatodiisopropylamine was reduced to diisopropylammonium thiocyanate with concurrent oxidation of the phosphines to the corresponding tetraalkyldiphosphanes. It is shown that the band in the infrared spectrum around 2500 cm^{-1} usually taken as indicative of the presence of a SH group may in some instances be confused with the absorption arising from the NH$_2{}^+$ group, appearing also as sharp and well-defined bands in the same spectral region.

In previous papers of this series [1,2] we have assumed the reactivity of the NCS group in N-isothiocyanatodiisopropylamine (I) towards nitrogen in primary and secondary amines, hydrazines, *etc.* to originate chiefly from the tendency to form resonance stabilized dipolar intermediates such as II. However, owing to the great mobility of the proton on the positively charged nitrogen atom, these intermediates cannot be isolated but rearrange to the usual thioamide form (III).

An intermediate similar to II was successfully invoked to explain the dimerization of N-isothiocyanatodimethylamine,[3] but in this case cyclization to a triazole prevented isolation of the intermediate. Infrared spectra of (I) dissolved in tertiary amines as, *e.g.*, pyridine showed that the strong band at *ca.* 2040 cm^{-1} assigned to the asymmetric stretching mode of the N=C=S group was barely influenced. On the other hand, bases such as N,N'-methylenedipiperidine caused this absorption to disappear within 15 min at room temperature and at the same time a new strong band appeared at 1561 cm^{-1}. However, this initial addition reaction appeared to be followed

$(Pr^i)_2N-N=C=S + R_2NH \longrightarrow \left[(Pr^i)_2N-\overset{\ominus}{N}-\underset{\underset{\oplus}{HNR_2}}{\overset{|}{C}}=S \longleftrightarrow \right.$

I   II

$\left. (Pr^i)_2N-N=\underset{\underset{\oplus}{HNR_2}}{\overset{|}{C}}-\overset{\ominus}{S} \right] \xrightarrow{\quad\sigma\quad} (Pr^i)_2N-NH-\underset{NR_2}{\overset{|}{C}}=S$

III

by rearrangements (*cf.* the analogous reaction with isothiocyanates [4]) and was postponed for a detailed study. We wish to report here on the reaction between (I) and phosphines which are known to exhibit an enhanced reactivity relative to amines in analogous reactions. Thus, isothiocyanates [5,6] and carbon disulfide [7] form reasonably stable adducts with tertiary phosphines, but not — at least at room temperature — with the corresponding amines.

Trimethylphosphine (IVa) and triethylphosphine (IVb) react readily at room temperature with (I) to give the 1:1 adducts, Va and Vb, but triphenylphosphine was under similar conditions recovered unchanged after 24 h.

Table 1. Assignments of some infrared bands (KBr, cm^{-1}) of reaction products from *N*-isothiocyanatodiisopropylamine and tertiary phosphines.[a]

Assignment	Va	Vb	VI	VII
$\nu(N-H)$	—	—	2790m 2710wbr	—
$\nu(C=N)$	1470s	1474s	1447vs	1488vs
$\delta(CH_3)$	1286m	—	—	—
CH_3CH_2-P	—	1265w 1257w	1283m 1258w	1280w 1264w
$\nu(C-S^-)$	910vs	934vs	—	—
$\nu_{as}(P-C)$	767m	776s 758s	780s 768s 754s	792m 767m 757vs

[a] The following abbreviations have been used to designate the intensities: vs=very strong, s=strong, m=medium, w=weak, br=broad, and ν=stretching and δ=deformation, for the type of vibration involved.

This latter result is consistent with the low reactivity of triphenylphosphine towards related compounds such as carbon disulfide. On standing at room temperature, only Vb is completely stable for an extended period, whilst Va slowly liquefies. On heating to the melting point both compounds develop

Table 2. Assignments of the NMR spectra (CDCl$_3$, τ-values) of reaction products from *N*-isothiocyanatodiisopropylamine and tertiary phosphines together with some related compounds.[a]

| | Alkyl bonded to phosphorus | | | | | | | Alkyl bonded to nitrogen | | | | |
| | CH$_3$ | | | | CH$_2$ | | | CH$_3$ | | | CH | |
	τ ppm	M	J_{PH} Hz	J_{HH} Hz	τ ppm	M	J_{PH} Hz	τ ppm	M	J_{HH} Hz	τ ppm	M
I								8.81	2	6.2	6.72	7
(CH$_3$)$_3$P[b]	9.11	2	2.7									
Va	8.18	2	12.4					8.92	2	6.4	5.09	7
(C$_2$H$_5$)$_3$P[b]	9.04	—	13.7	7.6	8.8	—	0.5					
Vb	8.84	2×3	16.0	7.3	7.87	2×4	12.0	8.93	2	6.2	5.22	7
VI	8.69	2×3	18.0	7.2	7.36	2×4	12.5	8.62	2	6.5	6.07	7
VII	8.75	2×3	18.0	7.3	7.53	2×4	11.7	8.74	2	6.8	5.17	7
VIII	8.92	2×3	16.8	7.4	7.73	2×4	12.0					
IX					7.83	2×4	12.5	8.90	2	6.6	5.6	

[a] The following abbreviations have been used: M=multiplicity of signal, J=coupling constants. The roman numerals correspond to the following compounds: I = *N*-isothiocyanatodiisopropylamine, Va and Vb=adducts of I with trimethyl- and triethylphosphine, VI and VII = products from the reaction of Vb with hydrogen chloride and methyliodide, VIII=adduct from triethylphosphine and carbon disulfide, IX=adduct between triethylphosphine and isopropylisothiocyanate.

[b] Hendrickson *et al.*[13]

a strong smell of phosphine indicating dissociation to the starting materials I and IV. Treatment of Vb with hydrogen chloride and methyl iodide afforded a hydrochloride (VI) and a methiodide (VII), respectively. The infrared and NMR spectra of these compounds were recorded and the results listed in Table 1 and Table 2.
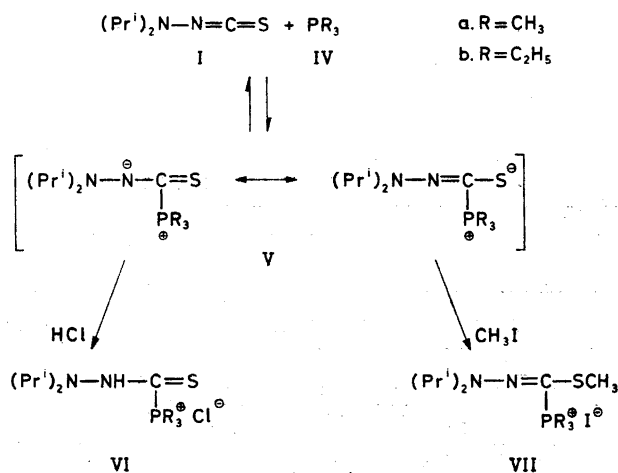
When one of the phosphines IVa or IVb react with (I) there are four possible sites of attack to be considered. The possibility that the nitrogen atom of the diisopropylamino group is involved in the reaction can at once be excluded; this would lead to a trialkyl (diisopropylamino)phosphonium thiocyanate, and the infrared spectrum was devoid of absorption in the region around 2000 cm^{-1} expected from the thiocyanate group. Next, if the phosphine attacks the carbon atom of the N=C=S group the resonance stabilized adduct V is obtained. Finally, attack on sulfur or nitrogen of the same group would lead to dipolar adducts with negatively charged carbon. The two latter possibilities seem excluded by the observation that treatment with methyl iodide leads to S-methylation and treatment with hydrogen chloride to N-protonation, as will be apparent from the evidence discussed below. We therefore propose V, VI, and VII to have phosphorus bonded to the carbon atom of the original isothiocyanate group.

The infrared spectrum of VI displayed two peaks in the high-frequency region assigned (Table 1) to NH stretching vibrations. The possibility that they arise instead from CH stretching vibrations was unambiguously excluded by comparison with the infrared spectra of V and VII. This is a very low position for such bands, but it is not entirely unexpected in view of the neighbouring positively charged phosphorus atom. A very weak, broad peak centered at 2075 cm^{-1} points to [8] the additional presence of negligible amounts of S-protonated material. The position of the bands arising from the C=N stretching vibrations of V—VII is the same as the counterpart in thioamides and thioureides [9] (B band) and well within the region earlier proposed for such bands (1400—1600 cm^{-1}). When the spectrum of Vb is compared to that of VII this band is displaced towards higher frequencies in the latter compound. This is also expected from the increasing double bond character following the S-methylation, but the shift is much smaller than observed for other thioamide groupings.[9] We take this to indicate the following resonance structures to be of significance for VII:
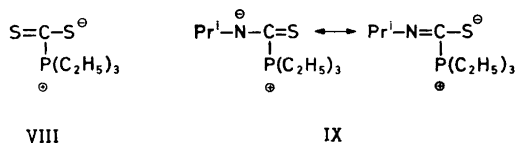
$$(Pr^i)_2N{-}N{=}C{-}SCH_3 \quad \longleftrightarrow \quad (Pr^i)_2\overset{\oplus}{N}{=}N{-}C{-}SCH_3$$
$$\underset{\underset{\oplus}{PR_3}}{|} \qquad\qquad\qquad \underset{PR_3}{\|}$$

If we instead compare the spectra of Vb and VI it is seen that salt formation induces a shift of the C=N stretching band towards lower frequencies. This is in accord with the proposal that treatment of Vb with hydrogen chloride results in N-protonation, i.e. diminished double bond character of the C=N bond.

A few other infrared bands are of interest. Thomas and Chittenden [10] proposed a band of medium intensity in the range 1272—1333 cm^{-1} to be typical of the methyl group bonded to phosphorus, but two weak bands in the region of 1250 cm^{-1} for ethyl groups in the same surroundings. Jensen and Nielsen [7,11] have previously found the corresponding values to be 1290 cm^{-1} for adducts of trimethylphosphine with carbon disulfide and diselenide, and 1240—1260 cm^{-1} for the triethylphosphine adducts. The agreement of

these data and those now reported in Table 1 is excellent. The very strong bands in the spectra of Va and Vb at 910 cm^{-1} and 934 cm^{-1} have no counterparts in the same neighbourhood in the spectra of VI and VII. We attribute these bands to mixed vibrations, involving mainly CS stretching, and note that the corresponding bands in the adducts of phosphines with carbon disulfide are shifted about 100 cm^{-1} towards higher frequencies in accord with the higher double bond character of the CS bands in the latter substances. The location of the typical well-defined bands originating from the asymmetric P—C stretching vibrations are in the range appropriate for alkyl groups bonded to positively charged phosphorus.[7,10-12] The multiplicity of bands observed in Vb—VII is probably the result of the presence of rotational isomers.[12]

Table 2 summarizes the chemical shifts and the spin coupling constants for the NMR spectra of the adducts of phosphines with N-isothiocyanatodiisopropylamine. The table includes data for the adducts derived from triethylphosphine and carbon disulfide (VIII) or isopropylisothiocyanate (IX), both with closely related structures. The data for IX are not complete because of a pronounced tendency for dissociation in solution. If we compare this result with the observed stability of Vb under the same conditions it can be concluded that the dimethylamino group exerts a stabilizing influence on the adduct, most probably by a resonance mechanism analogous to that depicted above for VII which will tend to enhance the double bond character of the bond between the phosphine and the N=C=S group.

$$S=\overset{\ominus}{C}-S \qquad Pr^i-\overset{\ominus}{N}-C=S \longleftrightarrow Pr^i-N=C-\overset{\ominus}{S}$$
$$\underset{\oplus}{P(C_2H_5)_3} \qquad \underset{\oplus}{P(C_2H_5)_3} \qquad \underset{\oplus}{P(C_2H_5)_3}$$

$$\text{VIII} \qquad\qquad\qquad \text{IX}$$

Hendrickson et al.[13] have shown that in the case of ethyl groups bonded to a quaternary phosphorus atom the CH_3 and CH_2 proton resonances yield essentially first order patterns. It was possible also in the present case to distinguish the triplets and quadruplets arising from the H—H and [31]P—H couplings, but the figures in Table 2 should nevertheless be taken with some reservation. This is due partly to the deviations from the first order patterns which were apparent from the unequal spacings, and partly to the presence of the strong doublet from CH_3 resonance of the diisopropylamino group in the middle of the area covered by the multiplets from the other CH_3 proton resonance signals.
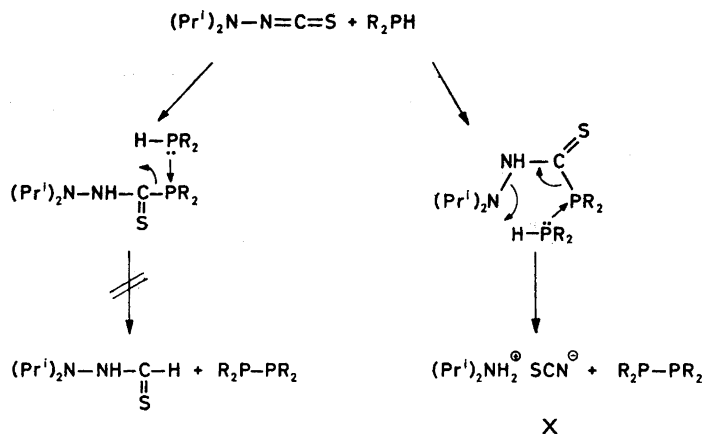
The chemical shift of the methylene protons of the ethyl groups bonded to phosphorus is $\tau = 8.8$ ppm in free triethylphosphine (Table 2). Three of the other compounds, Vb, VIII, and IX have in common a dipolar structure with a positive charge on phosphorus and a negative on sulfur or nitrogen. In these compounds a downfield shift of about 1 to 7.7—7.9 ppm is observed, which is clearly an intermediate case to that of compounds with full phosphonium ion structure, such as tetraethylphosphonium iodide, for which a shift of 1.4 to 7.35—7.5 ppm has been reported.[13] In this connection it is

profitable to compare with the methiodide VII and the hydrochloride VI which show the corresponding signals at 7.53 and 7.36 ppm, respectively. These figures might be tentatively interpreted to mean that only the hydrochloride has full phosphonium character, which agrees with the resonance picture proposed above on infrared evidence. The charge transfer back into the expanded valence shell of phosphorus from the lone pair of the nitrogen atom of the diisopropylamino group is not possible in the hydrochloride because protonation has occurred on the nitrogen atom. The spin-spin coupling constants for the $^{31}P-H$ coupling have values slightly below those reported for tetramethyl- and tetraethylphosphonium ions,[13] and fully substantiate the presence of quaternary phosphorus in these compounds.

These conclusions are adequately supported by the value of the chemical shift for the methylidyne proton of the isopropyl group bonded to nitrogen. Whilst the τ-values of the methyl groups are nearly constant (8.6—8.9) the methylidyne proton is strongly deshielded by the coordination with phosphines, apparent from a downfield shift from 6.72 to 5.09 ppm (Va) or 5.22 ppm (Vb). A virtually identical value is found for the methiodide VII (5.17 ppm) which shows the resonance effect triggered by the empty d-orbitals of the phosphorus atom and the intermediate CN double bond to be operative both in V and VII. This resonance effect must necessarily disappear in the case of the hydrochloride (VI) which has no CN double bond, and in line with this idea the signal occurs at a much higher field (6.07 ppm).

When N-isothiocyanatodiisopropylamine is allowed to react with secondary phosphines such as diethyl- or diphenylphosphine we would, by analogy with the reaction sequence I→II→III, expect formation of representatives of the hitherto unknown class of thiocarbazoylphosphines. Issleib and Harzfeld [6] have recently shown that the analogous thiocarbamoylphosphines arise in the parallel reaction between secondary phosphines and phenylisothiocyanate. However, we obtained proof that the phosphines were converted instead by (I) to tetraethyl- and tetraphenyldiphosphane, identified by conversion to the diphosphanedioxides with atmospheric oxygen. In accordance with this the same phosphine-free, crystalline product, X, was obtained in both reactions. The formation of X must therefore be ascribed to the reducing action of the secondary phosphines on the thiocarbazoylphosphine, which is undoubtedly the initial product. We tentatively propose the reactivity of the phosphorus atom of the thiocarbazoylphosphine in a nucleophilic attack by secondary phosphine to originate in the electronegativity of the thiocarbazoyl group. A parallel reaction is that between chlorodiphenylphosphine and diphenylphosphine which proceeds readily at 100°C with elimination of hydrogen chloride and formation of tetraphenyldiphosphane.[14]

When formulating the possible reaction paths leading to (X) it was taken into account that isocyanates and isothiocyanates have been shown[15] to oxidize triethylstannane to hexaethyldistannane, while at the same time undergoing reduction to the formamides or thioformamides. In the present case, hydrogen transfer to the diisopropylamino group of (I) is a priori equally possible as transfer to the carbon atom of the NCS group with formation of the thioformhydrazide. The following possibilities should thus be considered:

$$(Pr^i)_2N-N=C=S \; + \; R_2PH$$

$$(Pr^i)_2N-NH-\underset{\underset{S}{\|}}{C}-PR_2$$

H–PR₂ (above with lone pair)

$$(Pr^i)_2N-NH-\underset{\underset{S}{\|}}{C}-H \; + \; R_2P-PR_2$$

$$(Pr^i)_2NH_2^{\oplus} \; SCN^{\ominus} \; + \; R_2P-PR_2$$

X

　　The product (X) had the elemental composition $C_7H_{16}N_2S$ which is compatible with both reaction paths. In order to exclude a dimeric, or a trimeric structure a mass spectrum was recorded. The main peaks were observed at m/e 28, 45 (base peak), 59, 71, 87, and 101 (molecular peak) and show that X decomposes when introduced in the mass spectrometer. The isotopic composition of the peaks excluded the presence of sulfur. We therefore supposed the spectrum to be that of diisopropylamine and comparison with the mass spectrum of an authentic sample showed good agreement. The NMR spectrum of X in $CDCl_3$ showed, in addition to the bands from the diisopropylamine group (doublet centered at $\tau=8.57$ ppm, septuplet at 6.65 ppm) a very broad band at *ca.* $\tau=2$ ppm corresponding to two hydrogen atoms. In conjunction with the products arising from destruction of X in the mass spectrometer, this evidence is clearly in favour of X being diisopropylammonium thiocyanate. This was finally confirmed by comparison of the melting point, infrared, and NMR spectra with those of an authentic sample prepared from diisopropyl-ammonium chloride and potassium thiocyanate.

　　The infrared spectrum of X presented some rather unusual features which will be discussed shortly. The bands originating from the thiocyanate ion were established by comparison to the infrared spectrum of diisopropylammonium chloride as a very strong band at 2075 cm⁻¹ (KBr) originating from the CN stretching vibration and a weak, but sharp band at 750 cm⁻¹ from the CS stretching vibration. The remainder of the spectrum, which is identical for diisopropylammonium chloride and thiocyanate, is due to the diisopropyl-ammonium ion. It displays a sharp, well-defined band of medium strength at 2495 cm⁻¹ displaced to 1917 cm⁻¹ on deuteration (by recrystallization from deuterium oxide). This is highly characteristic of a band originating from an SH stretching vibration, but must obviously instead be correlated with the presence of the protonated group. The band was barely influenced when the spectrum of X was recorded in chloroform. Thus, the presence of a band at ca. 2500 cm⁻¹ cannot be taken as evidence for an SH grouping in compounds where the NH_2^+ grouping is present. This result makes some

earlier conclusions questionable, for example, that thiourea is S- rather than N-protonated because of the presence of the 2500 cm^{-1} band.[16] Indeed it has been shown,[8] that bands due to SH stretching vibrations should be displaced to *ca.* 2100 cm^{-1} in compounds where strong hydrogen bonding can occur.

EXPERIMENTAL

Conditions and equipment used for the physical measurements were those described in part II of this series.[17]

All preparations with phosphines were carried out in a nitrogen atmosphere. The diethylether used was freshly distilled from lithium aluminium hydride.

Trimethylphosphoniodiisopropylthioformhydrazonate (Va). N-Isothiocyanatodiisopropylamine (2 mmol, 0.32 g) was dissolved in ether (10 ml). Trimethylphosphine, generated directly from the silver iodide adduct [18] (2.5 mmol, 0.80 g), was bubbled through the solution carried by a slow stream of nitrogen. A colourless precipitate was slowly formed. After cooling in an ice-bath for 2 h the adduct was isolated by centrifugation, washed several times with ether and dried. Yield 0.18 g. Recrystallization from dry acetone-ether furnished colourless crystals, m.p. 130−132°C (decomp.). (Found: C 51.00; H 9.89; N 12.09; S 13.46. Calc. for $C_{10}H_{23}N_2PS$: C 51.26; H 9.89; N 11.95; S 13.69).

Triethylphosphoniodiisopropylthioformhydrazonate (Vb). Triethylphosphine (2 mmol, 0.24 g) was added to a solution of N-isothiocyanatodiisopropylamine (2 mmol, 0.32 g) in ether (15 ml). The adduct crystallized slowly from the yellow solution. After cooling for 2 h in an ice-bath the compound was isolated by centrifugation, washed with pentane and dried. Yield 0.25 g. Recrystallization from ether gave colourless crystals, m.p. 108.5−109.5°C (decomp.). (Found: C 56.70; H 10.88; N 10.16; S 11.48. Calc. for $C_{13}H_{29}N_2PS$: C 56.48; H 10.58; N 10.14; S 11.60). The *hydrochloride* (VI) was precipitated in nearly quantitative yield by mixing equimolar amounts of Vb in ether and hydrogen chloride in ether. The m.p. of the colourless, hygroscopic product is 152−156°C. (Found: Cl 10.99. Calc. for $C_{13}H_{30}ClN_2PS$: Cl 11.34).

The methiodide (VII) was prepared by treatment with methyl iodide in ether and recrystallized from chloroform-ether. The m.p. is 104−105°C. (Found: C 40.22; H 7.81; I 30.51. Calc. for $C_{14}H_{32}IN_2PS$: C 40.19; H 7.71; I 30.33).

Triethylphosphonioisopropylthioformimidate (IX). The preparation was performed as described for Vb using isopropylisothiocyanate and triethylphosphine. Cooling in a dry-ice bath gave a poor yield (*ca.* 10 %) of slightly yellow crystals with m.p. 58.5−59.5°C after recrystallization from ether-pentane. The compound is rather unstable (smells of triethylphosphine) and could not be obtained quite pure. (Found: C 53.85; H 10.01; N 6.57; S 14.94. Calc. for $C_{10}H_{22}NPS$: C 54.76; H 10.11; N 6.39; S 14.62).

Reaction of N-isothiocyanatodiisopropylamine with diethylphosphine. N-Isothiocyanato-diisopropylamine (5 mmol, 0.79 g) was added with stirring to a cooled solution of diethyl-phosphine [19] (7 mmol) in ether (20 ml). An exothermic reaction took place and colourless crystals separated slowly from the solution. After 5 h at room temperature they were isolated and washed several times with ether. Yield *ca.* 0.47 g. Recrystallization from acetone-ether furnished colourless crystals, m.p. 89−90°C. Repeated preparations showed some variation in the analytical figures. (Found: C 52.05, 52.56; H 10.22, 10.05; N 17.23, 16.66; S 18.57, 19.62). The compound (X) was identified as diisopropylammonium thiocyanate (see later). The filtrate from X, upon evaporation of the solvent, gave some more X and a yellow oil. An infrared spectrum of the oil (in dichloromethane) showed, in addition to absorptions from X, bands due to diethylphosphine (ν_{P-H} at 2305 cm^{-1}) and presumably tetraethyldiphosphane dioxide ($\nu_{P=O}$ at 1170 and 1145 cm^{-1}), formed by air oxidation of tetraethyldiphosphane. No N−H absorption above 3200 cm^{-1} was present, and accordingly the presence of diisopropylthiocarbazoyldiethylphosphine could be excluded.

Diisopropylammonium thiocyanate. Diisopropylammonium chloride (1.0 g) in methanol was mixed with potassium thiocyanate (1.4 g) in methanol. The slurry was evaporated to dryness, the residue extracted with chloroform, and the chloroform solution evaporated to give 1.2 g of the crude product. Recrystallization from acetone-ether yielded colourless

crystals, m.p. 89—91°C. A mixture with X showed no depression of the m.p., and the infrared spectra were identical. (Found: C 52.63; H 10.10; N 17.22; S 19.40. Calc. for $C_7H_{16}N_2S$: C 52.45; H 10.07; N 17.47; S 20.00).

Reaction of N-*isothiocyanatodiisopropylamine with diphenylphosphine.* Diphenylphosphine [14] (4 mmol, 0.75 g) was added to *N*-isothiocyanatodiisopropylamine (2 mmol, 0.32 g) in ether (10 ml). After 4 h at room temperature the colourless crystals formed were filtered off and washed with ether. Yield 0.20 g (65 %) of *diisopropylammonium thiocyanate*, m.p. 89—91°C (identified by m.p. and infrared spectrum). A stream of oxygen was bubbled through the filtrate for 1 h. The crystals which formed were filtered off and washed with ether. Yield 0.30 g (40 %) of *tetraphenyldiphosphane dioxide*, m.p. 158—165°C. The compound was identified by comparison of the m.p. and infrared spectrum with those of an authentic sample (m.p. 167°C).[14]

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