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Reactions of Aminophosphines with Carbon Disulfide

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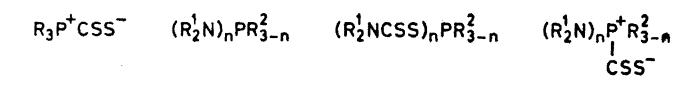
The reactions of several alkyl and aryl substituted aminophosphines with carbon disulfide have been studied. Dipolar addition compounds (aminophosphoniodithioformates) have been isolated when alkyl groups are bound to phosphorus. These compounds rearrange at room temperature to yield insertion products ((thiocarbamoylthio)-phosphines), which have also been obtained when aryl groups are bound to phosphorus. The structures of the compounds have been determined by infrared and proton magnetic resonance spectroscopy and, for the insertion compounds, by hydrolysis experiments. The reaction with carbon disulfide failed for diphenylaminodiphenylphosphine and this fact, together with other observations, are discussed in terms of a possible mechanism proposed for the insertion reaction.

The reactions of tertiary aliphatic phosphines with carbon disulfide, to give addition compounds, have been known for more than a century.[1] Several structures for these red compounds were proposed, until Margulis and Templeton by X-ray analysis [2] showed the structure of the triethylphosphine adduct to be (I), *i.e.* the dipolar structure proposed by one of the authors in 1937.[3] A similar structure was inferred, from infrared and dipole moment studies, for the red addition compounds obtained with other trialkylphosphines.[4,5] The infrared spectra of these compounds have in common a strong absorption band near 1050 cm^{-1}, assigned to the antisymmetric stretching vibration of the dithiocarboxylate group.[4]



I II III IV

Table 1. Reaction products of aminophosphines with carbon disulfide. Dipolar compounds and their methiodides.

Compound	M.p., °C	Yield %	Analyses										$-CSS^-$ or $-CSSMe$ IR frequencies (cm^{-1} in CH_2Cl_2)
			C		H		N		S		I		
			found	calc.	found	calc.	found	calc.	found	calc.	found	calc.	
$(Me_2N)_3P^+CSS^-$	49–50 [a]	90 [b]	34.91	35.14	7.50	7.58	17.24	17.56	25.89	26.79			1047 vs [e]
$(Me_2N)_3P^+CSSMe\ I^-$	116–117	60 [c]	25.23	25.21	5.47	5.55	11.03	11.03	16.63	16.82	33.18	33.29	1081 s
$(Me_2N)_2EtP^+CSS^-$	54–55 [a]	35 [b]	37.22	37.47	7.59	7.64	12.60	12.49	28.09	28.59			1053 vs
$(Me_2N)_2EtP^+CSSMe\ I^-$	99–100	80 [c]	26.17	26.25	5.38	5.48	7.63	7.66	17.51	17.50	34.93	34.65	1081 s
$(Me_2N)Me_2P^+CSS^-$	69–70 [a]	65 [b]	32.98	33.13	6.64	6.68	7.62	7.73	35.29	35.38			1057 s
$(Me_2N)Me_2P^+CSSMe\ I^-$	126–127	60 [d]	22.32	22.30	4.71	4.68	4.33	4.33	20.00	19.84	39.09	39.27	1086 s
$(Et_2N)Et_2P^+CSS^-$	56–58 [a]	90 [b]	45.50	45.54	8.52	8.49	5.77	5.91	27.42	27.01			1060 s
$(Et_2N)Et_2P^+CSSMe\ I^-$	56–57	65 [c]	31.79	31.67	6.35	6.11	3.71	3.69	16.58	16.91	33.41	33.46	1085 s

[a] Rearranges after melting. [b] From ether (crude product). [c] From 1-butanol/ether. [d] From acetone/ether. [e] vs = very strong, s = strong.

The reactions of aminophosphines of the general type II ($n = 1-3$) with carbon disulfide have not been systematically studied. Some papers[6-10] describe the reaction of selected aminophosphines with carbon disulfide to give colourless products, which are generally claimed to be insertion products having the structure III. Nöth and Vetter[7] have presented some support for such a structure for a compound obtained from carbon disulfide and tris-dimethylaminophosphine: The same compound (III, $R^2 = Me_2N$, $R^1 = Me$, $n = 2$) was obtained from dimethylaminodichlorophosphine and sodium dimethyldithiocarbamate. In contrast, Smith[8] has assumed a dipolar structure (IV, $R^2 = Ph$, $R^1{}_2N$ = 3-azabicyclo[3,2,2]non-3-yl, $n = 1$) for the colourless product obtained from the corresponding aminophosphine and carbon disulfide. In some cases a transient red colour has been observed[6,7,10] on mixing carbon disulfide and the aminophosphine, but so far only colourless products have been isolated.

The present paper describes the preparation and characterization of red dipolar products (IV), as well as colourless insertion products (III), formed by the reactions of a variety of aminophosphines (II, $n = 1$, 2, 3; R^1 and R^2 = Me, Et, Ph) with carbon disulfide. The structures of the compounds have been assigned by proton magnetic resonance (NMR) spectroscopy and by infrared (IR) spectroscopy and the structures are further supported by chemical reactions.

Dipolar compounds. A red colour was formed in most cases when an ethereal solution of an aminophosphine was mixed with carbon disulfide. Red crystalline 1:1 adducts (Table 1) could be isolated when the solutions were kept at, or below, 0°C. In the case of bis-(dimethylamino)phenylphosphine a faint red colour was developed when carbon disulfide was added at 0°C, but no stable red compound could be isolated. Colour changes were not observed in the cases of dimethyl-, diethyl- or diphenylaminodiphenylphosphine. A decrease in reactivity towards carbon disulfide on passing from alkyl- to aryl-substituted phosphorus has previously been established from reactions involving tertiary phosphines; thus dimethylphenylphosphine forms a stable red carbon disulfide adduct[5] whilst methyldiphenylphosphine and triphenylphosphine do not react with carbon disulfide.[11,12]

The general structure of the red compounds was indicated by their NMR spectra (Table 3). The presence of a large coupling ($J_{PNCH} = 9-11$ Hz) between phosphorus and the α-hydrogens on the *N*-alkyl groups shows that the P–N bonds are intact. A similar large coupling constant has been reported for other aminophosphines and aminophosphonium compounds.[13,14] The splitting has been proved by decoupling experiments to be due to a coupling to phosphorus and not a nonequivalence phenomenon.[15] The coupling constants J_{PCH} and J_{PCCH} and the chemical shifts found for the *P*-alkyl groups are close to those found for the *P*-methiodides of the corresponding aminophosphines, showing that the red compounds most probably are phosphonium compounds. In accordance with this structure (IV) is the fact that the dipolar compounds react with methyl iodide to give *S*-methyl derivatives and not *P*-methyl derivatives, as shown by the appearance of a singlet resonance peak, due to the new methyl group, in the NMR spectra of the methiodides. Finally, in the IR spectra of these compounds, the characteristic strong absorption band due to the $-CSS^-$ grouping is found in the region 1047 – 1060 cm^{-1}. The band

disappears on *S*-methylation and a new band, characteristic of the $-CSSCH_3$ grouping,[4] appears at slightly higher wavenumbers (Table 1).

The aminophosphines, in their ability to give dipolar addition compounds with carbon disulfide, bear more resemblance to tertiary phosphines than to trialkylphosphites or phosphorus trichloride. While tertiary phosphines and tris(dialkylamino)phosphines react exothermically with carbon disulfide, no reaction could be induced between the latter compound and trimethylphosphite or phosphorus trichloride.[11] The same trend is found in the behaviour of these phosphorus compounds towards methyl iodide, when the only compounds forming stable quaternary salts are tertiary phosphines and aminophosphines in which the substituents bound to phosphorus are not more electron attracting than amino groups.[16] The reason for the high stability of phosphonium derivatives of aminophosphines may be an electron density displacement from the lone pair on nitrogen into the empty *d*-orbitals on phosphorus, *i.e.* that the phosphonium derivatives are resonance stabilized by some $p\pi - d\pi$ double bond formation. In contrast, such resonance stabilization would be much smaller for trialkylphosphites and phosphorus trichloride due to the increased electronegativity of oxygen and chlorine over that of nitrogen. Evidence for partial double bond formation in an aminophosphonium compound comes from an X-ray study of $(H_2N)_3P^+ - BH_3^-$.[17] The N–P bond length in this compound (1.65 Å) is shorter than the generally accepted N–P single bond length (1.78 Å).[18]

Insertion compounds. The reactions of aminophosphines with excess carbon disulfide, when performed at room temperature or at higher temperatures, generally resulted in colourless or faintly yellow compounds. In cases where the red dipolar compounds could be isolated at lower temperatures they were transformed to colourless compounds on keeping at room temperature or by gentle heating. The dialkylaminodiphenylphosphines which did not give dipolar compounds reacted with carbon disulfide to give colourless compounds, although with a lower rate than those for the analogous *P*-alkyl compounds. Diphenylaminodiphenylphosphine, however, was recovered unchanged after 24 h in boiling carbon disulfide. The colourless compound obtained from dimethylaminodimethylphosphine was rather unstable and was not isolated

Table 2. Reaction products of aminophosphines with carbon disulfide. Insertion products.

Compound	M.p., °C	Yield, %	Analyses							
			C		H		N		S	
			found	calc.	found	calc.	found	calc.	found	calc.
$(Me_2NCSS)_2PEt$	113–114	85 [a]	32.28	32.05	5.72	5.68	9.35	9.33		
$Me_2NCSSPMe_2$	26– 28	50 [b]	31.79	33.13	6.78	6.68	7.80	7.73		
$Et_2NCSSPEt_2$	11– 13	quant.[c]	45.71	45.54	8.64	8.49	6.04	5.91	27.58	27.01
$Me_2NCSSPPh_2$	124–125	80 [b]	59.10	59.00	5.40	5.28	4.63	4.59	21.19	21.00
$Et_2NCSSPPh_2$	103–104	65 [b]	61.18	61.25	6.16	6.05	4.26	4.20	19.13	19.23

[a] From acetone. [b] From ether. [c] Crude product.

in a pure state. However, the presence of the compound in $CDCl_3$ solutions was unequivocally established by NMR techniques (see below). The new compounds prepared in this work are listed in Table 2.

Inspection of the NMR spectra of these compounds and of several compounds prepared according to directions given in the literature (Table 3) reveals that the coupling between the phosphorus and the *N*-alkyl protons, which is large in both the aminophosphines and the dipolar compounds, has disappeared. This fact strongly indicates that the N–P bond(s) have been broken, *i.e.* that an insertion reaction has taken place. The chemical shift of the *N*-alkyl protons has been changed downfield from the region $\tau = 6.90 - 7.50$ ppm, found for the aminophosphines and the dipolar compounds, to a position close to that of the signals originating from Me_2N in $Me_2NCSSMe$ or Et_2N in $Et_2NCSSMe$ (Table 3). These facts indicate that the CS_2 molecule has been inserted into the N–P bond as shown in structure III, *i.e.* that a C–N bond and not a C–P bond has been formed. Additional support for the structure III was obtained from hydrolysis experiments in the presence of nickel ions. The hydrolyses of the insertion products proceeded quickly in aqueous ethanol, containing triethylamine and nickel chloride, to give high yields of the respective bis-(dialkyldithiocarbamato)-nickel(II) complexes. The reaction scheme is given in eqn. 1 for the monoaminophosphine cases (III, $n = 1$).

$$2\ R^1_2NCSSPR^2_2 + Ni^{2+} + 2\ H_2O + 2\ Et_3N \longrightarrow [(R^1_2NCSS)_2Ni] + 2\ R^2_2PHO + 2\ Et_3NH^+ \quad (1)$$

Other possible structures for the insertion products, *e.g.* $R^1_2NSC(S)PR^2_2$ or $R^1_2NC(S)P(S)R^2_2$, would not be expected to give dithiocarbamato compounds by hydrolysis.

It is worth mentioning that some of the insertion products, when treated with nickel salts in anhydrous solvents, formed red to brown solutions, indicating complex formation. However, no well defined compounds could be isolated; in the presence of water the colour immediately turned green and the dithiocarbamato complexes precipitated.

The IR spectra of the insertion products showed many strong bands in the region 1550 – 800 cm^{-1}; no attempt was made to assign these absorptions to individual groups in the molecules. However, in the region 1040 – 1060 cm^{-1}, where the dipolar compounds IV absorb strongly due to the presence of the $-CSS^-$ groups, no strong bands were found. The absence of a strong band in that region can, therefore, be taken as indicative of the formation of an insertion product, rather than a dipolar product, in the reaction of an aminophosphine with carbon disulfide. The compound described by Smith [8] showed no absorption in the IR spectrum between 1010 and 1120 cm^{-1} and is therefore without doubt an insertion compound, and not a dipolar compound as assumed by Smith. This conclusion is in accordance with the facts that, firstly, the compound is colourless whilst all compounds hitherto described, which contain the $P^+ - CSS^-$ grouping, are red and, secondly, no dipolar carbon disulfide adduct has so far been isolated from a phosphorus compound bearing two *P*-phenyl groups.

Possible mechanisms for the insertion reaction. Several experiments were performed in order to elucidate the conditions necessary for the insertion

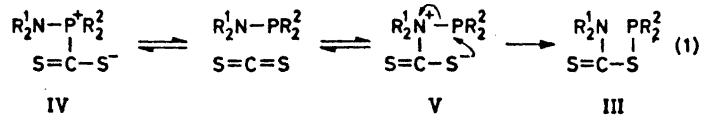
Table 3. NMR chemical shifts [a] (τ, ppm) and coupling constants (*J*, Hz) of aminophosphines and their reaction products with carbon disulfide and methyl iodide (*ca.* 5 % solutions in $CDCl_3$ at *ca.* 40°C or as stated).

Compound	CH_3CH_2N	CH_3CH_2N/CH_3N	CH_3CH_2P	CH_3CH_2P/CH_3P	J_{PNCH}	J_{PCH}	J_{PCCH}	J_{HCCH} (N)	J_{HCCH} (P)	CH_3S
$(Me_2N)_3P$		7.50 (2) [b]			9.1					
$(Me_2N)_3\overset{+}{P}CSS^-$ (0°C)		7.14 (2)			9.2					
$(Me_2N)_3\overset{+}{P}CSSMe\ I^-$		7.02 (2)			9.9					7.06 (1)
$(Me_2NCSS)_2PNMe_2$		7.15 (2)			8.4					
		6.43 (1)			0					
$(Me_2NCSS)_3P$		6.53 (1)			0					
$(Me_2N)_3\overset{+}{P}Me\ I^-$		7.15 (2)		7.77 (2)	10.2	14.4				
$(Me_2N)_2PEt$		7.35 (2)	[c]	[c]	8.9					
$(Me_2N)_2\overset{+}{P}(Et)CSS^-$ (0°C)		7.15 (2)	8.62 (2×3)	*ca.* 7.3 [d]	9.6	*ca.* 12	17.8		7.6	
$(Me_2N)_2\overset{+}{P}(Et)CSSMe\ I^-$		7.00 (2)	8.58 (2×3)	*ca.* 6.9 [d]	10.1	*ca.* 12	20.2		7.5	7.03 (1)
$(Me_2NCSS)_2PEt$		6.50 (1)	8.77 (2×3)	7.70 (2×4)	0	11.6	11.1		*ca.* 7.4	
$(Me_2N)_2\overset{+}{P}(Et)Me\ I^-$		7.13 (2)	8.74 (2×3)	*ca.* 7.3 [d]	10.0	*ca.* 14	20.5			
				7.76 (2)		13.0				
$(Me_2N)_2PPh$		7.20 (2)			9.3					
$(Me_2NCSS)_2PPh$		6.52 (1)			0					
Me_2NPMe_2		7.47 (2)		8.93 (2)	9.4	4.8				
$Me_2N\overset{+}{P}(Me_2)CSS^-$ (0°C)		7.15 (2)		7.87 (2)	10.9	12.2				
$Me_2N\overset{+}{P}(Me_2)CSSMe\ I^-$		6.99 (2)		7.30 (2)	10.7	13.4				7.07 (1)
$Me_2NCSSPMe_2$		6.52 (1)		8.49 (2)	0	9.1				
$Me_2N\overset{+}{P}Me_2\ I^-$		7.15 (2)		7.70 (2)	11.1	13.5				

Et_2NPEt_2	8.97 (3)	7.07 (2×4)	[c]	[c]	8.7			7.0		
$Et_2\overset{+}{N}P(Et_2)CSS^-$ (0°C)	8.78 (3)	6.77 (2×4)	8.77 (2×3)	7.40 (2×4)	10.2	*ca.* 11.3	18.5	7.2	7.4	
$Et_2\overset{+}{N}P(Et_2)CSSMe\ I^-$	8.70 (3)	6.61 (2×4)	8.63 (2×3)	7.00 (2×4)	11.0	12.2	20.2	7.1	7.5	7.02 (1)
$Et_2NCSSPEt_2$	8.70 (3)	*ca.* 6.05 [e]	[c]	[c]				7.2		
$Et_2NCSSPEt_2$ (in CS_2)	8.77 (3)	6.15 (4)	[c]	[c]	0			7.0		
$Et_2\overset{+}{N}P(Et_2)Me\ I^-$	8.77 (3)	6.75 (2×4)	8.72 (2×3)	7.37 (2×4)	10.8	11.5	*ca.*	7.2	7.5	
				7.77 (2)		12.5	19.2			
Me_2NPPh_2		7.37 (2)			9.5					
$Me_2NCSSPPh_2$		6.53 (2)			1.8					
$Me_2NCSSPPh_2$ (in CS_2)		6.62 (1)			0					
Et_2NPPh_2	9.05 (3)	6.91 (2×4)			9.7			7.1		
$Et_2NCSSPPh_2$	8.71 (3)	*ca.* 6.1 [e]						7.2		
$Et_2NCSSPPh_2$ (in CS_2)	8.78 (3)	6.24 (4)			0			7.1		
PMe_3 [f] (pure liquid)				9.11 (2)		2.7				
PEt_3 [f] (pure liquid)			9.04 [c]	8.8 [c]		0.5	13.7		7.6	
$\overset{+}{P}Me_4\ I^-$ [f]				7.53 (2)		14.4				
$\overset{+}{P}Et_4\ I^-$ [f]			8.72 (2×3)	7.48 (2×4)		13	18		7.3	
$Me_2NCSSMe$		6.52 (1)								7.36 (1)
$Et_2NCSSMe$	8.72 (3)	*ca.* 6.1 [e]						7.1		7.37 (1)
$Et_2NCSSMe$ (in CS_2)	8.76 (3)	6.14 (4)						7.1		7.48 (1)

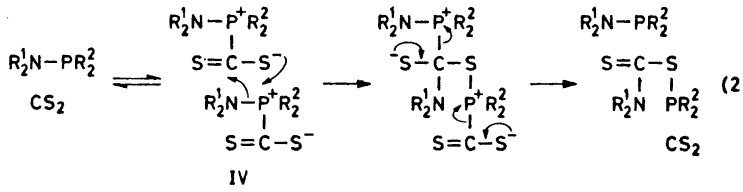
[a] The values given in the table are the centres of the multiplets. [b] Multiplicity of the signals. [c] Second order pattern. [d] Partly hidden by other signals. [e] Broad and unresolved, probably due to hindered rotation about the C—N bond.[20] [f] Ref. Hendrickson.[19]

reaction to take place. The reaction was found not to occur when the aminophosphines were converted to their *P*-methiodides or *P*-sulfides. These results indicate either that an electrophilic attack on phosphorus occurs in some stage of the insertion reaction, or that the positively charged phosphorus atom in these derivatives inhibits an electrophilic attack on the neighbouring nitrogen atom. The reaction was inhibited also when the nitrogen atom was substituted with two phenyl groups. Substituting alkyl groups on the nitrogen with phenyl groups is expected to exert only a small effect on the availability of the lone pair on phosphorus but a much larger effect on the availability of the lone pair on nitrogen, towards electrophilic reagents. Provided that this assumption is correct, these experiments indicate that the insertion reaction proceeds *via* an electrophilic attack of CS_2 on nitrogen, as proposed briefly by Hudson and Searle:[25]



According to this mechanism the dipolar compound IV is not an intermediate, but is formed in a competing reaction to the insertion reaction. The relative amounts of the two types of dipolar products (IV and V) present in solutions would depend on the relative nucleophilicity of nitrogen and phosphorus towards the sp hybridized carbon of CS_2. Alkylation experiments [22,23] have shown that phosphorus generally is the more nucleophilic of the two towards sp^3 hybridized carbon. The isolation of the dipolar compounds IV indicates that this is also true in the case of *sp* hybridized carbon. Electrophilic attack on nitrogen in aminophosphines is not unknown, however. The reactions with hydrogen halides,[23] acetyl chloride,[21] benzaldehyde,[24] and some reactions with isocyanates,[25] are all consistent with a mechanism involving initial electrophilic attack on nitrogen, as is the reaction leading to the formation of V. The last step in this reaction, the nucleophilic substitution on phosphorus, is facilitated by the conversion of the amino group to a good leaving group by quaternisation. This last step, being irreversible, will result in a displacement of the equilibria to the right.

An alternative mechanism for the insertion reaction may be one in which the dipolar compound is formed as an intermediate, further reaction taking place by a bimolecular nucleophilic attack of the negatively charged sulfur on the positive phosphorus atom:



This mechanism, which is proposed by Vetter and Nöth for the reaction of tris-(dimethylamino)phosphine with carbon disulfide,[7] is considered less likely for the following reasons: i) Assuming the reversible formation of IV to be fast relative to the further reactions it is expected, that an increase in the concentration of IV would increase the rate of formation of the insertion product. However, the rate (followed by NMR spectroscopy) is not increased to a measurable degree when Me_2NPPh_2 reacts with CS_2 in $Cl_2C=CCl_2$ in the presence of $Et_3P^+-CSS^-$, in spite of the similarity of $Et_3P^+-CSS^-$ and IV. ii) The rearrangement of $(Me_2N)_2P^+EtCSS^-$ yields $(Me_2N)_2PEt$ and $(Me_2NCSS)_2PEt$ without any detectable amounts (by NMR spectroscopy) of $Me_2NCSSPEtNMe_2$. Assuming mechanism (2) to be correct, $Me_2NCSSPEtNMe_2$ should therefore form a dipolar product ($Me_2NCSSP^+Et(NMe_2)CSS^-$) with CS_2 readily. However, a formation of such a dipolar product from $Me_2NCSSPEtNMe_2$ is unlikely because the closely related compound, $Et_2NCSSPEt_2$, is unreactive towards CS_2. It is worth mentioning that the rearrangement of $(Me_2N)_3P^+CSS^-$ similarly gave mixtures of $(Me_2N)_3P$, $(Me_2NCSS)_2PNMe_2$, and $(Me_2NCSS)_3P$ without any detectable amounts of $Me_2NCSSP(NMe_2)_2$ (by NMR spectroscopy). iii) The kinetics of the reaction are not compatible with mechanism (2). The rearrangement of $Et_2NP^+Et_2CSS^-$ in CH_2Cl_2 (measured by following the disappearance of $Et_2NP^+Et_2CSS^-$ by visible spectroscopy) is first order ($\log[Et_2NP^+Et_2CSS^-] = -kt + C$) in the presence of a large excess of CS_2, whilst this is not the case when the addi-

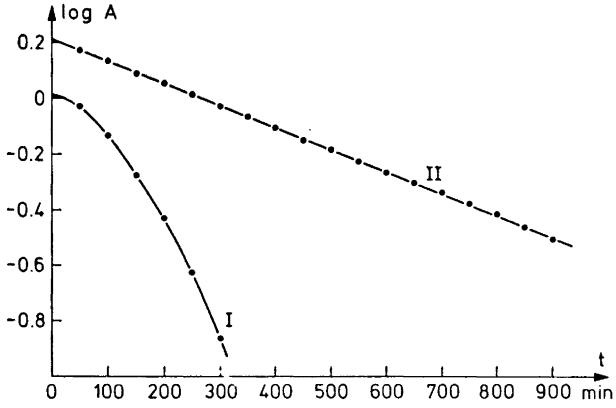


Fig. 1. The rearrangement $Et_2NP^+Et_2CSS^- \rightarrow Et_2NCSSPEt_2$ followed by visible spectroscopy. A = absorption of $Et_2NP^+Et_2CSS^-$ at 487 mμ (maxima) in CH_2Cl_2, 25°C.
I: $[Et_2NP^+Et_2CSS^-]_{t=0} = 2.87 \times 10^{-3}$ mol·l^{-1}.
II: $[Et_2NP^+Et_2CSS^-]_{t=0} = 2.87 \times 10^{-3}$ mol·l^{-1}, $[CS_2]_{t=0} = 2.00$ mol·l^{-1}.

tion of CS_2 is omitted (Fig. 1). Were the mechanism of type (2), then the same rate expression would be expected in both cases.

The rearrangement of $R^1{}_2\overset{+}{N}PR^2{}_2CSS^-$ ($R^1 = R^2 = Me$ or Et), in the absence of an excess of CS_2, did not follow a simple reaction order expression in the

dipolar compound, neither when performed in CH_2Cl_2 nor in more polar solvents (acetone and acetone with added tetrabutylammonium iodide). Providing that the mechanism (1) is the correct one, this fact indicates that none of the steps in (1) is much slower that the other steps, because otherwise a simple first or second order reaction most probably would result. In the absence of more kinetic evidence, however, further conclusions concerning the mechanism cannot be drawn.

EXPERIMENTAL

The analyses were carried out in the Microanalysis Department of this laboratory. The proton magnetic resonance spectra were obtained using a Varian A-60A or a Perkin-Elmer R 12 instrument with tetramethylsilane as internal standard. The infrared spectra were recorded on a Perkin-Elmer model 337 grating infrared spectrophotometer and the visible absorption measurements on a Perkin-Elmer model 137 UV ultraviolet-visible spectrophotometer. All preparations with *P*-aliphatically substituted aminophosphines were carried out in a nitrogen atmosphere.

The following *aminophosphines* were prepared by methods previously reported: Tris(dimethylamino)phosphine,[26] bis(dimethylamino)ethylphosphine,[27] bis(dimethylamino)phenylphosphine,[16] dimethylaminodimethylphosphine,[26] diethylaminodiethylphosphine,[22] dimethylaminodiphenylphosphine,[16] diethylaminodiphenylphosphine,[22] and diphenylaminodiphenylphosphine.[28]

Dipolar compounds (IV). These compounds were prepared by the following general procedure. The aminophosphine (4 mmol) in dry ether (10 ml) was cooled to −80°C and carbon disulfide (1 ml) was added with stirring. The resulting faintly red solution was placed in a refrigerator for 2 h at −25°C, after which the red crystals that had separated were filtered off, washed several times with cold ether and quickly dried *in vacuo* at room temperature. Melting points, analyses, and yields are given in Table 1. The compounds could be stored for several months at −25°C without rearrangement. The *methiodides* of the dipolar compounds were prepared by dissolving the appropriate dipolar compound in methylene chloride at −80°C and adding excess methyl iodide. After 1 h at room temperature the solution was evaporated to dryness and the residue recrystallized to give dark red crystals of the methiodides. Melting points, analyses and yields are given in Table 1. The compounds are stable for several months at room temperature.

Insertion compounds. The following compounds were prepared according to the directions given in the literature: $(Me_2NCSS)_2PNMe_2$,[7] $(Me_2NCSS)_3P$,[7] and $(Me_2NCSS)_2PPh$.[10] *Bis((N,N-dimethylthiocarbamoyl)thio)ethylphosphine (III, n=2, R^1=Me, R^2=Et)* was prepared by adding excess carbon disulfide to a solution of bis-(dimethylamino)ethylphosphine in ether at 25°C. After 2 h the colourless crystals were filtered off and recrystallized from dry acetone. *((N,N-Dimethylthiocarbamoyl)thio)dimethylphosphine (III, n=1, R^1=R^2=Me)* was prepared by effecting the rearrangement of the dipolar compound in boiling carbon disulfide. After *ca.* 1 min a yellow solution was formed. The solution, after filtration and evaporation, gave a semi-solid product which was recrystallized from dry ether. The colourless compound turned brown within a few hours even at −25°C and satisfactory analytical results have not been obtained. Attempts to purify the compound by vacuum distillation (b.p. *ca.* 80°C at 2 mm Hg) did not improve the analytical values and resulted in excessive decomposition in the distillation flask. The insertion compound, as well as the dipolar compound, decomposed to a red-brown oil on keeping at room temperature for a few days. *((N,N-Diethylthiocarbamoyl)thio)diethylphosphine (III, n=1, R^1=R^2=Et)* was obtained from the dipolar compound by standing the latter, without solvent, at 25°C for 6 h. The *((N,N-dialkylthiocarbamoyl)thio)diphenylphosphines (III, n=1, R^1=Me or Et, R^2=Ph)* were prepared by dissolving the appropriate aminophosphine (2 mmol) in ether (5 ml) and adding excess carbon disulfide (1 ml). After 4 days at room temperature the colourless crystals formed were isolated and

recrystallized from ether. Analyses, melting points and yields of the new insertion compounds are given in Table 2.

Hydrolysis of the insertion products. The following general procedure was used. The insertion product, dissolved in ethanol, was treated with an equivalent amount of nickel chloride in water and sufficient triethylamine was then added to give a slurry with pH 4–5. The precipitated bis-(dialkyldithiocarbamato)nickel(II) complex was filtered off and washed with ethanol and water and then recrystallized from dimethylformamide. The identities of the complexes were established by comparing their IR spectra and melting points with those of authentic samples, prepared from sodium dialkyldithiocarbamate and nickel chloride. The following yields of recrystallized complexes were obtained:

	Yield of Ni-complex (%)
$(Me_2NCSS)_2PNMe_2$	79
$(Me_2NCSS)_3P$	47
$(Me_2NCSS)_2PEt$	72
$(Me_2NCSS)_2PPh$	73
$Me_2NCSSPMe_2$	80
$Et_2NCSSPEt_2$	74
$Me_2NCSSPPh_2$	86
$Et_2NCSSPPh_2$	81

The filtrate from the hydrolysis of $Me_2NCSSPPh_2$ was treated with aqueous hydrogen peroxide and then made alkaline with sodium hydroxide. After filtration and evaporation to dryness the residue was dissolved in a minimal amount of water and acidified with 4 N HCl. The colourless crystals formed were filtered off, washed with water and dried. A yield of 35 % of Ph_2POOH, m.p. 185–188°C (lit.[29] 190–192°C) and an IR spectrum identical with that of an authentic sample, was obtained.

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