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Phosphinodithioformates

I. Reactions of Secondary Phosphines with Carbon Disulfide in the Presence of Bases

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Diphenylphosphine reacts with carbon disulfide in the presence of weak bases to give diphenylphosphinodithioformates (I) whereas diethylphosphoniobisdithioformates (II) are obtained from diethylphosphine. Triethylammonium, potassium, and tetraphenylphosphonium salts have been isolated and characterized by infrared and proton magnetic resonance spectroscopy and by electrical conductivity measurements. Reactions of (I) and II with sulfur give diethyl- and diphenylthiophosphinoyldithioformates, respectively. A mechanism is suggested for the reaction leading to (I) and II.

Phosphinodithioformates, R_2PCSS^-, which may be regarded as phosphorus analogues of dithiocarbamates, would be of considerable interest not only as metal chelating agents but also as starting materials for the preparation of organic compounds containing the R_2PCS-group. Whilst phosphinoformates and some of their derivatives are known [1,2] very little has been published on phosphinodithioformates. Noltes [3] has prepared a phenylzinc derivative and Schumann *et al.*[4] a triphenyltin derivative of diphenylphosphinodithioformic acid. Both compounds were obtained by insertion of carbon disulfide into a metal-phosphorus bond. Malatesta [5] has obtained a maroon compound, tentatively formulated as $((C_2H_5)_2PCSS)_2Ni$, from the reaction of diethylphosphine with carbon disulfide in ether, extraction of the solution with aqueous ammonia and subsequent addition of nickel ions. The compound could not be obtained pure. Very recently, Kramolowsky [6] has described some alkali-metal salts of diphenylphosphinodithioformic acid, which are obtained as dioxan solvates from alkali-metal diphenylphosphides and carbon disulfide at low temperatures. Kramolowsky has also described a barium salt, as well as diphenylthiophosphinoyldithioformates and bisdiphenylphosphinodithioformatonickel(II) obtained from reactions of the alkali-metal diphenylphosphinodithioformates with sulfur and nickel salts, respectively.

Reactions of secondary phosphines with carbon disulfide in the presence of weak bases such as triethylamine have been studied and the results obtained using diphenylphosphine and diethylphosphine are reported here.

When diphenylphosphine, carbon disulfide, and triethylamine were mixed in ether solution a high yield of triethylammonium diphenylphosphinodithioformate (Ia) was obtained. Ia is stable

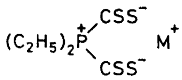
$$(C_6H_5)_2P{-}CSS^- M^+$$

Ia-c

a: $M = (C_2H_5)_3NH$
b: $M = K$
c: $M = (C_6H_5)_4P$

at room temperature when kept in a closed tube. However, decomposition to the starting materials occurs when Ia is either dried *in vacuo* or heated. The potassium salt (Ib) has been prepared by us essentially in the same way as by Kramolowsky,[6] as well as directly from diphenylphosphine, carbon disulfide, and potassium phenolate in ether at room temperature. Ib is obtained non-solvated by the latter method. It is rather hygroscopic and decomposes in the presence of water, but is otherwise stable at room temperature. The compound Ib could be transformed to the stable Ic by double decomposition using tetraphenylphosphonium chloride.

The compounds IIa-c were obtained from diethylphosphine by reactions similar to those used for the preparation of Ia-c. However, IIc was most conveniently prepared directly from



IIa-c

a: $M = (C_2H_5)_3NH$
b: $M = K$
c: $M = (C_6H_5)_4P$

diethylphosphine, carbon disulfide, tetraphenylphosphonium chloride and triethylamine in ethanol. IIa is stable at −25°C but decomposes at room temperature within a few days to carbon disulfide, triethylamine and an as yet unidentified yellow oil. The compounds IIb and IIc are stable at room temperature.

The assignments of structure Ia-c and IIa-c to the compounds mentioned above are based on their elemental analyses, their electrical conductivities, and their infrared (IR) and proton magnetic resonance (NMR) spectra. The electrical conductivities of acetone solutions of Ic and IIc are comparable to that found for tetraphenylphosphonium picrate under the same conditions (see Experimental) showing that the salts are 1:1 electrolytes in acetone. Moreover, the triethylammonium and potassium salts could be converted to the tetraphenylphosphonium salts in high yields indicating that the same anion was present in Ia-c as well as in IIa-c. The IR spectra (KBr) of all these compounds showed a very strong band in the region 1000−1060 cm^{-1}. This band, which was assigned to the $-CSS^-$ antisymmetric stretching

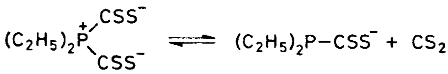
Table 1. NMR chemical shifts [a] (τ, ppm) and coupling constants (J, Hz) of diethylphosphoniobisdithioformates and related compounds.

Compound	Solvent	CH_3CH$_2$P	CH$_3$$CH_2$P	J_{HCCH}	J_{PCH}	J_{PCCH}
$(C_2H_5)_2P(CSS)_2^-$ $(C_6H_5)_4P^+$ [b]	$(CD_3)_2CO/CS_2$ (5:1)	8.93 (2×3[c])	7.43 (2×4)	7.5	13.3	15.9
»	$(CD_3)_2SO/CS_2$ (5:1)	8.98 (2×3)	7.51 (2×4)	7.6	13.3	16.1
$(C_2H_5)_2P(CSS)_2^-K^+$	$(CD_3)_2CO/CS_2$ (5:1)	8.88 (2×3)	7.39 (2×4)	7.5	13.4	16.0
$(C_2H_5)_2P(S)CSS^-$ $(C_6H_5)_4P^+$	$(CD_3)_2CO$	8.91 (2×3)	*ca.* 7.7[d]	*ca.* 7.5	—	*ca.* 17
»	$CDCl_3$	8.85 (2×3)	*ca.* 7.7[d]	*ca.* 7.4	—	*ca.* 18
$(C_2H_5)_3\overset{+}{P}CSS^-$	$(CD_3)_2CO/CS_2$ (5:1)	8.78 (2×3)	7.55 (2×4)	7.6	12.4	17.2

[a] The values given in the table are the centres of the multiplets.
[b] The chemical shifts for the complex tetraphenylphosphonium signals have been omitted. The integral showed the correct ratio between the aromatic and aliphatic protons.
[c] Multiplicity of the signal.
[d] The spectrum showed a second order pattern, and first order treatment were only possible for the CH_3 signals.

vibration, was found in the region 1048—1060 cm^{-1} for IIa-c, a position close to that found for the corresponding band in the spectrum of $(C_2H_5)_3P^+-CSS^-$.[7] The analogous band exhibited by the compounds Ia-c occurred at sligthly lower wavenumbers (1001—1016 cm^{-1}). The NMR spectra of IIb and IIc (in acetone-d_6 and DMSO-d_6) are given in Table 1 together with the spectrum of $(C_2H_5)_3P^+-CSS^-$ for comparison. The proton coupling constants and chemical shifts of the latter compound are in agreement with those of IIb and IIc and thus substantiate the formulation of IIa-c as phosphonium compounds.

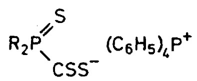
In addition to the signals from IIb and IIc the NMR spectra showed some poorly resolved signals which appeared in two regions centered at about $\tau=8$ and 9 ppm and which disappeared when carbon disulfide was added to the solutions. By varying the temperature (40—100°C) of a DMSO-d_6 solution of IIc it was shown that the intensities of these signals, relative to those from the ethyl groups of IIc, increased when the temperature was raised. This behaviour, which was shown to be reversible, is assumed to be due to a reversible dissociation of II to carbon disulfide and III, *vide* eqn. 1. Even at 100°C, however, the dissociation



(1)

II III

was far from complete, and no salts containing the anion III have hitherto been isolated. When IIc was treated with sulfur at room temperature a *P*-sulfide of III (IVa) was obtained. This result provides further evidence for the equilibrium formulated above



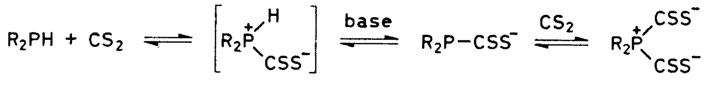
a: $R=C_2H_5$

b: $R=C_6H_5$

IV a-b

in eqn. 1. Similarly IVb was obtained from Ic and sulfur. The IR spectra (KBr) of IVa and IVb showed bands, which had no counterparts in the spectra of Ic and IIc, at 594 cm^{-1} and 642 cm^{-1}, respectively, and accordingly were assigned to the P=S stretching vibration. The electrical conductivities, as well as the NMR spectrum of IVa (Table 1), are in accordance with the postulated structure. The successful preparation of these derivatives shows that the compounds Ia-c and IIa-c contain, or are able to dissociate to compounds containing, trivalent phosphorus.

From the results presented above it is evident that rather weak bases such as triethylamine or potassium phenolate are able to promote the reaction between secondary phosphines and carbon disulfide to give phosphinodithioformates. Experiments have shown that even pyridine is sufficiently basic to promote the reaction. Due to the low acidity of secondary phosphines ($pK_a = 21.7$ and 33.7 for $(C_6H_5)_2PH$ and $(C_2H_5)_2PH$, respectively [8]) it seems unlikely that these reactions proceed *via* a phosphide ion, as is the case in the reactions studied by Kramolowsky.[6] A more plausible mechanism seems to be that shown in eqn. 2. The first step in the reaction may be an electrophilic attack of carbon disulfide on phosphorus



(2)

A B C

to give an unstable adduct (A) similar to those formed by tertiary aliphatic phosphines.[9] In the presence of a base A may be converted to B. When R = ethyl, B behaves like a tertiary aliphatic phosphine and reacts further with carbon disulfide to form C. When R = phenyl, B behaves like a diphenylalkylphosphine which, according to experiments with diphenylmethylphosphine,[10] does not react with carbon disulfide at room temperature.

EXPERIMENTAL

The analyses were carried out in the microanalysis department of this laboratory. The sulfur analyses in some cases were lower than the calculated values and showed some variation, probably because the compounds easily decompose with loss of carbon disulfide on heating. The infrared spectra were obtained on a Perkin-Elmer model 337 grating infrared spectrophotometer, the KBr-disc technique being used. The following abbreviations are used: $\nu(-CSS^-)$ = the $-CSS^-$ antisymmetric stretching vibration, $\nu(P=S)$ = the P=S stretching vibration, vs = very strong, s = strong and m = medium. The proton magnetic resonance spectra were obtained on a Varian A-60 A instrument from approximately 10 % solutions at *ca.* 40°C, with tetramethylsilane as internal standard. The conductance measurements were carried out with a Radiometer type CDM 2d conductivity meter using 1.0×10^{-3} molar solutions in acetone-carbon disulfide (9:1) at 25°C. Tetraphenylphosphonium picrate, $\Lambda_{mol} = 163$ $cm^2ohm^{-1}mol^{-1}$, was used as a 1:1 standard electrolyte. All preparations were carried out in a nitrogen atmosphere. The ether was purified by column chromatography (Al_2O_3, Woelm basic, activity 1). Carbon disulfide, acetone, and ethanol were commercial analytically pure reagents. The melting points (uncorrected) were determined on a Büchi melting point apparatus.

Diphenylphosphine was prepared from triphenylphosphine and sodium in liquid ammonia at *ca.* −80°C,[11] and was liberated from its sodium salt by the addition of excess ammonium chloride. The ammonia was allowed to evaporate and the residue taken up with ether. The ether extract was filtered and the solvent evaporated. The remaining oil was purified by distillation *in vacuo* to give an 80 % total yield of diphenylphosphine, b.p. 100−103°C at 1 mm Hg.

Triethylammonium diphenylphosphinodithioformate (Ia). Diphenylphosphine (1.86 g, 10^{-2} mol), carbon disulfide (0.80 ml, 1.3×10^{-2} mol) and triethylamine (2.8 ml, 2×10^{-2} mol) were dissolved in ether (6 ml). Within a few minutes the product separated as an oil which crystallized on cooling. The mixture was kept at −25°C for 4 days and was then centrifuged. The red-orange crystals obtained were washed with an ether-carbon disulfide mixture (10:1) and dried in a flow of nitrogen. The yield was almost quantitative; m.p. 62−66°C (in a closed capillary tube). (Found: C 62.65; H 7.06; N 3.64; S 16.38. Calc. for $C_{19}H_{26}NPS_2$: C 62.77; H 7.21; N 3.85; S 17.64). $\nu(-CSS^-)$: 1001 cm^{-1} (vs). Ia is very soluble in acetone, ethanol, and chloroform, nearly insoluble in carbon disulfide and ether and decomposes in water. Owing to the similar solubilities of Ia and Ic in acetone or ethanol, Ic precipitated only in a poor yield when saturated solutions of Ia in ethanol or acetone and tetraphenylphosphonium chloride in ethanol were mixed. Partial evaporation of the reaction mixture gave impure products contaminated with Ia.

Potassium diphenylphosphinodithioformate (Ib). Diphenylphosphine (1.86 g, 10^{-2} mol) and carbon disulfide (0.60 ml, 10^{-2} mol) were added successively to a stirred suspension of potassium phenolate (1.32 g, 10^{-2} mol) in ether (30 ml). The mixture slowly turned red. Stirring was continued for 3 days to complete the reaction. The brick-red crystals were then isolated by centrifugation, washed with ether and dried *in vacuo*. Yield 2.7 g (90 %), m.p. *ca.* 180°C (decomp.). The compound could not be obtained in a totally pure state, and all attempts to purify it by recrystallisation were unsuccessful. (Found: C 51.05; H 3.44; S 20.06. Calc. for $C_{13}H_{10}KPS_2$: C 51.98; H 3.36; S 21.35). $\nu(-CSS^-)$: 1016 cm^{-1} (vs). Ib is very soluble in ethanol and acetone, sligthly soluble in chloroform, insoluble in carbon disulfide and ether and decomposes in water.

Tetraphenylphosphonium diphenylphosphinodithioformate (Ic). Solutions of Ib (0.30 g, 10^{-3} mol) in abs. ethanol (3 ml) and tetraphenylphosphonium chloride (0.41 g, 1.1×10^{-3} mol) in abs. ethanol (1 ml) were mixed. The potassium chloride, which precipitated immediately, was removed by centrifugation and extracted with hot abs. ethanol (3 ml). The combined solutions were heated to the boiling point and sufficient abs. ethanol was then added to dissolve any crystals formed. Orange-red crystals separated on cooling. They were isolated by centrifugation, washed with abs. ethanol and dried *in vacuo*. Yield 0.47 g (80 %), m.p. 127–130°C (decomp.). (Found: C 73:81; H 5.13; S 10.38. Calc. for $C_{37}H_{30}P_2S_2$: C 73.98; H 5.03; S 10.68). $\nu(-CSS^-)$: 1012 cm^{-1} (s). $\Lambda_{mol}=$ 138 $cm^2ohm^{-1}mol^{-1}$. Ic is soluble in acetone, ethanol, and chloroform and insoluble in carbon disulfide and ether.

Tetraphenylphosphonium diphenylthiophosphinoyldithioformate (IVb). To a solution of Ic (0.60 g, 10^{-3} mol) in a 5:2 methylene chloride-carbon disulfide mixture (6 ml) was added a solution of sulfur (0.04 g, 1.3×10^{-3} mol) in carbon disulfide (2 ml). Dark reddish lilac crystals separated almost at once. They were isolated by centrifugation, washed with carbon disulfide and dried *in vacuo*. Yield 0.48 g (75 %), m.p. 166–168°C (Found: C 70.00; H 4.85; S 14.98. Calc. for $C_{37}H_{30}P_2S_3$: C 70.21; H 4.78; S 15.20). $\nu(-CSS^-)$: 1044 cm^{-1} (s); $\nu(P=S)$: 642 cm^{-1} (s). $\Lambda_{mol}=137$ $cm^2ohm^{-1}mol^{-1}$. IVb is very soluble in chloroform, moderately soluble in acetone and insoluble in ethanol, ether, carbon disulfide, and water.

Diethylphosphine was prepared according to the directions given in the literature.[12]

Triethylammonium diethylphosphoniobisdithioformate (IIa). Diethylphosphine (0.90 g, 10^{-2} mol) was added to a stirred solution of excess carbon disulfide (10 ml) and triethylamine (5 ml) in ether (25 ml) at −25°C. The product separated within a few minutes. It was filtered off, washed with ether-carbon disulfide (3:1) and dried *in vacuo*. Yield: 2.8 g (80 %) of red crystals, which, after recrystallisation from an acetone-carbon disulfide mixture (5:1), melted at 53–57°C (decomp.). (Found: C 41.80; H 7.69; N 4.05; S 36.37. Calc. for $C_{12}H_{26}NPS_4$: C 41.96; H 7.63; N 4.08; S 37.34). $\nu(-CSS^-)$: 1060 cm^{-1} (vs), 1048 cm^{-1} (vs). IIa is very soluble in acetone, chloroform, and ethanol, sligthly soluble in carbon disulfide, insoluble in ether and decomposes in water. A solution of IIa (10^{-3} mol) in ethanol (15 ml), when mixed with a solution of tetraphenylphosphonium chloride (2×10^{-3} mol) in ethanol (3 ml), gave an 80 % yield of *IIc* (identified by m.p. and IR spectrum).

Potassium diethylphosphoniobisdithioformate (IIb). Diethylphosphine (1.0 g, 1.1×10^{-2} mol) and carbon disulfide (2.5 ml, 4×10^{-2} mol) were added to a stirred suspension of potassium phenolate (1.32 g, 10^{-2} mol) in ether (50 ml). The mixture turned red almost at once and red crystals were formed. Stirring was continued overnight to complete the reaction. The carmine-red crystals were filtered off, washed with ether and dried *in vacuo*. Yield 2.2 g (80 %), m.p. *ca.* 95°C with decomposition (in a closed capillary tube). The compound was only obtained in an approximately pure state. Several attempts to purify it by recrystallisation were unsuccessful. (Found: C 25.17; H 3.63; S 42.38. Calc. for $C_6H_{10}KPS_4$: C 25.69; H 3.59; S 45.73). $\nu(-CSS^-)$: 1054 cm^{-1} (vs). IIb is very soluble in acetone and ethanol, sligthly soluble in chloroform and ether, insoluble in carbon disulfide and decomposes in water. IIb (10^{-3} mol) and tetraphenylphosphonium chloride (1.2×10^{-3} mol) were mixed in a 6:1 ethanol-carbon disulfide mixture (7 ml). The precipitate immediately formed was washed with water-ethanol mixture, to remove potassium and tetraphenylphosphonium chlorides, and dried *in vacuo*. The remaining crystals were identified by m.p. and IR spectroscopy to be *IIc*. Yield 70 %.

Tetraphenylphosphonium diethylphosphoniobisdithioformate (IIc). Diethylphosphine (0.90 g, 10^{-2} mol) was added to a stirred solution of tetraphenylphosphonium chloride (4.0 g, 1.1×10^{-2} mol), carbon disulfide (2 ml, 3.3×10^{-2} mol) and triethylamine (2 ml, 1.4×10^{-2} mol) in abs. ethanol (50 ml). The red crystals, which separated almost at once, were filtered off, washed with abs. ethanol and dried *in vacuo*. Yield 4.9 g (85 %). After recrystallization from an ethanol-carbon disulfide mixture (10:1) the compound melted at *ca.* 110°C with decomposition (in a closed capillary tube). (Found: C. 61.79; H 5.27; S 22.18. Calc. for $C_{30}H_{30}P_2S_4$: C 62.04; H 5.21; S 22.08). $\nu(-CSS^-)$: 1052 cm^{-1} (s). $\Lambda_{mol}=147$ cm^{2}ohm^{-1}mol^{-1}. IIc is very soluble in acetone and chloroform, slightly soluble in ethanol and insoluble in ether.

Tetraphenylphosphonium diethylthiophosphinoyldithioformate (IVa). A solution of IIc (0.58 g, 10^{-3} mol) in acetone (5 ml) and a solution of sulfur (0.032 g, 10^{-3} mol) in carbon disulfide (2 ml) were mixed. The solution was allowed to stand for 3 h at room temperature and then evaporated to dryness *in vacuo*. The red crystals were recrystallized from an ethanol-carbon disulfide mixture (5:1), washed with the same solvent and dried *in vacuo*. Yield 0.39 g (70 %), m.p. 131–133°C (in a closed capillary tube). (Found: C 64.81; H 5.71; S 17.73. Calc. for $C_{29}H_{30}P_2S_3$: C 64.90; H 5.63; S 17.92). $\nu(-CSS^-)$: 1043 cm^{-1} (s); $\nu(P=S)$: 594 cm^{-1} (m). $\Lambda_{mol}=156$ cm^{2}ohm^{-1}mol^{-1}. IVa is very soluble in acetone, ethanol and chloroform, insoluble in ether, carbon disulfide, and water.

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