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Phosphinodithioformates

IV. Substituent Influence on the Course of the Reaction of Secondary Phosphines with Carbon Disulfide and Base

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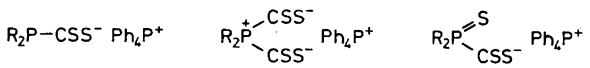
The reaction of secondary phosphines with ethanolic carbon disulfide in the presence of triethylamine gives phosphinodithioformates (I) or phosphoniobisdithioformates (II), depending on the phosphine used. In several cases, the occurrence of an equilibrium mixture of I and II in solution was demonstrated by proton magnetic resonance, infrared, and visible spectroscopy. The position of the equilibrium, as well as the nature of the dithioformate isolated, is dependent primarily on the inductive effects, and to a smaller degree also on the steric effects, of the substituents on phosphorus. Compounds I and II were isolated as tetraphenylphosphonium salts and characterized by means of analytical and spectroscopic data and by their reaction with sulfur to give thiophosphinoyldithioformates (III).

In the first part of this series[1] the reactions of diethylphosphine and diphenylphosphine with carbon disulfide in the presence of triethylamine or potassium phenolate were described. Diphenylphosphine gave diphenylphosphinodithioformates (*e.g.* If), whereas diethylphosphine gave diethylphosphoniobisdithioformates (*e.g.* IIb).



Ia-g IIa-g IIIa-g

R_2P = a: Me_2P b: Et_2P c: Pr^i_2P d: $(NCCH_2CH_2)_2P$
e: $(PhCH_2)_2P$ f: Ph_2P g: PhMeP

The different behaviour of these two secondary phosphines towards carbon disulfide prompted the present study of the influence of R on the structure of the reaction product.

Table 1. Yields, melting points, and elemental analyses for tetraphenylphosphonium *P,P*-disubstituted phosphinodithioformates (I), phosphoniobisdithioformates (II), and thiophosphinoyldithioformates (III).

No.	Compound	Yield, % [a]	M.p., °C [b]	Formula	Analyses (C, H, S)
IIa	$Me_2P(CSS)_2^-Ph_4P^+$	– [c]	149–153	$C_{28}H_{26}P_2S_4$	Found 60.85; 4.78; 23.00 Calc. 60.84; 4.74; 23.21
IIIa	$Me_2P(S)CSS^-Ph_4P^+$	75 [d]	188–192	$C_{27}H_{26}P_2S_3$	Found 63.75; 5.16; 18.81 Calc. 63.75; 5.15; 18.91
IIc	$Pr^i_2P(CSS)_2^-Ph_4P^+$	60 [c]	125–142	$C_{32}H_{34}P_2S_4$	Found 63.20; 5.76; 20.92 Calc. 63.13; 5.63; 21.07
IIIc	$Pr^i_2P(S)CSS^-Ph_4P^+$	60 [e]	142–146	$C_{31}H_{34}P_2S_3$	Found 65.80; 6.15; 17.20 Calc. 65.93; 6.07; 17.03
Id	$(NCCH_2CH_2)_2PCSS^-Ph_4P^+$	55 [d]	115–119	$C_{31}H_{28}N_2P_2S_2$	Found 67.10; 5.15; 11.86 Calc. 67.13; 5.09; 11.56
IIId	$(NCCH_2CH_2)_2P(S)CSS^-Ph_4P^+$	60 [f]	147–149	$C_{31}H_{28}N_2P_2S_3$	Found 63.41; 4.76; 16.28 Calc. 63.46; 4.81; 16.40
Ie	$(PhCH_2)_2PCSS^-Ph_4P^+$	60 [g]	162–167	$C_{39}H_{34}P_2S_2$	Found 74.30; 5.52; 10.37 Calc. 74.50; 5.45; 10.20
IIIe	$(PhCH_2)_2P(S)CSS^-Ph_4P^+$	60 [h]	171–177	$C_{39}H_{34}P_2S_3$	Found 71.02; 5.26; 14.32 Calc. 70.88; 5.19; 14.55
Ig	$PhMePCSS^-Ph_4P^+$	50 [f]	126–130	$C_{32}H_{28}P_2S_2$	Found 71.55; 5.33; 11.65 Calc. 71.35; 5.24; 11.91
IIIg	$PhMeP(S)CSS^-Ph_4P^+$	65 [h]	154–158	$C_{32}H_{28}P_2S_3$	Found 67.40; 4.97; 16.94 Calc. 67.34; 4.94; 16.86

[a] Based on secondary phosphine. The yield of IIa was not determined, since the starting dimethylphosphine was not isolated. [b] With decomposition. [c] Recrystallized from a 9 : 1 ethanol-carbon disulfide mixture. [d] Recryst. from abs. ethanol. [e] Dissolved in ethanol and precipitated with ether. [f] Dissolved in acetone and precipitated with ether. [g] Crude product. [h] Dissolved in methylene chloride and precipitated with ether.

ISOLATION AND CHARACTERIZATION OF TETRAPHENYLPHOSPHONIUM SALTS

The following phosphines were selected for the study: dimethyl-, diethyl-, diisopropyl-, di-*tert*-butyl, bis(2-cyanoethyl)-, dibenzyl-, diphenyl-, methylphenyl-, and dimesitylphosphine. Most of these reacted with carbon disulfide in ethanolic solution at room temperature in the presence of triethylamine and tetraphenylphosphonium chloride, to give salts of type I or II. Dimethyl-, diethyl-,[1] and diisopropylphosphine gave compounds of type II, whereas bis(2-cyanoethyl)-, dibenzyl-, diphenyl-,[1] and methylphenylphosphine reacted to give type I compounds. No reaction took place with di-*tert*-butyl- or dimesitylphosphine.

The compounds isolated (Table 1) were characterized by elemental analysis, proton magnetic resonance (^{1}H NMR) and infrared (IR) spectroscopy, and preparation of *P*-sulfides (III).

The ^{1}H NMR spectra ($CDCl_3$) are given in Table 2. Data for Ia–c are included, since they are present in $CDCl_3$ solutions in equilibrium with IIa–c, respectively, as discussed later. By means of ^{1}H NMR spectroscopy, compounds

Table 2. ^{1}H NMR chemical shifts [a] (τ) and coupling constants (*J*, Hz) of tetraphenylphosphonium *P,P*-disubstituted phosphinodithioformates (I), phosphoniobisdithioformates (II), and thiophosphinoyldithioformates (III) (*ca.* 5 % solutions in $CDCl_3$ at *ca.* 40°C or as stated).

Compound	P–C–C–*H* [b]	P–C–*H* [b]	J_{PCCH}	J_{PCH}	J_{HCCH}	J_{HCH}
Ia		8.56 (d)		2.3		
IIa		7.85 (d)		12.0		
IIIa		8.01 (d)		12.4		
IIb	8.87 (dt)	7.35 (dq)	*ca.* 16.0	*ca.* 13.2	*ca.* 7.6	
IIIb	8.85 (dt)	*ca.* 7.7 (m)	*ca.* 18	–	*ca.* 7.4	
Ic [c]	8.83 (dd)	7.63 (dsep)	12.1	*ca.* 2.6	7.0	
	8.86 (dd)		12.4			
IIc [c]	8.57 (dd)	6.47 (dsep)	14.5	*ca.* 14.2	7.1	
IIIc	8.78 (dd)	7.05 (dsep)	15.6	9.0	7.0	
	8.86 (dd)		16.6			
Ie		6.27 (dd)		2.8		14.0
		6.83 (dd)		3.5		
IIIe [d]		6.18 (dd)		13.7		13.8
		6.33 (dd)		12.8		
IIIe [e]		6.16 (dd)		13.4		13.7
		6.48 (dd)		12.4		
Ig		8.36 (d)		4.2		
IIIg		7.71 (d)		12.3		

[a] The values given are the centres of the multiplets.

[b] Multiplicity of signals in brackets. d = doublet, t = triplet, q = quartet, sep = septet, m = unresolved multiplet.

[c] *Ca.* 10 % solution, 0°C.

[d] *Ca.* 20 % solution.

[e] *Ca.* 12 % solution in $(CD_3)_2SO$.

of the formula I and II are easily distinguished, owing to the differences in coupling constants and chemical shifts. The numerical values of the PCH coupling constants are 2.3 – 4.2 Hz for compounds I and 12.0 – 14.2 Hz for II. The increased value for the latter compounds is attributed to the positive charge on phosphorus.[2] The positive charge also causes a deshielding of the alkyl hydrogens of II relative to those of I, expressed in a considerable displacement of the P – C – *H* signals of II towards lower field. A similar displacement, though smaller, is also found for P – C – C – *H* signals. The *P*-sulfides III show ^{1}H NMR spectra very similar to those of compounds II, although the signals are found at a little higher field for the sulfides, which indicates that the deshielding effect of P^+ in II is greater than that of $P^+ - S^- \longleftrightarrow P=S$ in III.

The ^{1}H NMR spectra were sometimes complicated by second-order splitting or nonequivalence phenomena. Thus, the spectra of Ib, Id, and IIId could not be analysed by first-order treatments, and in several other cases only approximate coupling constants could be obtained. Magnetic nonequivalence was observed in the spectra of Ic, IIIc, Ie, and IIIe (Table 2). In Ic and IIIc the isopropyl groups are equivalent, but the CH_3 groups of each isopropyl group are magnetically nonequivalent, owing to the prochirality of the phosphorus atom. The nonequivalence gives rise to two quartets for the CH_3 signals, with different PCCH coupling constants. In IIc the P atom is no longer prochiral, and consequently the CH_3 groups are magnetically equivalent. The hydrogen atoms of each CH_2 group in Ie and IIIe are nonequivalent for the same reason, and the CH_2 signals appear as the AB part of an ABX spectrum.

Table 3. Characteristic IR absorption bands (cm^{-1} [a]) of tetraphenylphosphonium *P,P*-disubstituted phosphinodithioformates (I), phosphoniobisdithioformates (II), and thiophosphinoyldithioformates (III).

Compounds I – III	$\nu_{as}(-CSS^-)$					$\nu(P=S)$
	I		II		III	III
	KBr	$CHCl_3$ [b]	KBr	$CHCl_3$ [b]	KBr	KBr
a	–	996 s [c]	1052 vs-br	1052 s	1036 s	593 s
b	–	*ca.* 975 m-br	1052 s	1052 s	1043 s	594 m
c	–	986 s	1023 s	1024 m	1019 s/ 1031 s	594 m
d	994 s [c]/ 1008 s	1007 s	–	–	1035 s	624 m
e	1013 s	998 vs [c]	–	–	1041 s	602 s
f	1012 s	1010 s	–	–	1044 s	642 s
g	994 s [c]	1000 s [c]	–	–	1039 s	614 s/ 622 m

[a] vs = very strong, s = strong, m = medium, and br = broad.
[b] *Ca.* 10 % solutions.
[c] Superimposed on a band from Ph_3P^+.

The IR spectra were recorded in KBr and in $CHCl_3$ solutions. In KBr, each of the compounds I–III showed a strong, rather broad band between 975 and 1052 cm^{-1}. This band was absent in the spectra of the corresponding phosphines and phosphonium salts and is tentatively assigned to the $-CSS^-$ asymmetric stretching vibration ($\nu_{as}(-CSS^-)$, Table 3).[3,4] The position of the band is at lower frequencies (975–1013 cm^{-1}) for type I salts than for type II and III salts (1019–1052 cm^{-1}). For both compounds I and II this band was found at approximately the same positions in $CHCl_3$ as in KBr (Table 3). However, for IIa–c a new band, which is close to that of $\nu_{as}(-CSS^-)$ in the spectra of Id–g and due to the presence of Ia–c, appeared when the spectra were recorded in $CDCl_3$. The difference in position of the $\nu_{as}(-CSS^-)$ band for type I and II compounds, although of unknown origin, is useful for characterization. A medium to strong band between 593 and 642 cm^{-1} found only in the spectra of IIIa–g is assigned [5] to the P=S stretching vibration (ν(P=S)).

DISCUSSION OF PRODUCT TYPE AND EQUILIBRIUM DATA

In the ^1H NMR spectra of IIa–c, recorded in $CDCl_3$ or $(CD_3)_2SO$ solutions, two sets of signals were observed. The relative intensities of the two sets varied with temperature, concentration, and solvent. One of the sets practically disappeared when an excess of carbon disulfide was added. This behaviour suggests the occurrence of the equilibrium (1) in these solvents, and, as discus-

$$\underset{\text{II}}{R_2\overset{+}{P}\!\!<\!\!\begin{matrix}CSS^-\\CSS^-\end{matrix}} \rightleftharpoons \underset{\text{I}}{R_2P{-}CSS^-} + CS_2 \quad (1)$$

sed in the previous section, both ^1H NMR and IR spectra of IIa–c in $CHCl_3$ solution were consistent with this interpretation. The presence of free carbon disulfide in $CHCl_3$ solutions of IIa–c was established by the appearance of a very strong band at 1520 cm^{-1} (ν_{as} (SCS)). Visible spectroscopy was used to establish the presence of only two absorbing species in equilibrium. As shown in Fig. 1, isosbestic points appeared when carbon disulfide was gradually removed from a solution of IIb and carbon disulfide in $(CH_3)_2SO$, which indicated the presence of an equilibrium between Ib (λ_{max} *ca.* 440 mμ) and IIb (λ_{max} *ca.* 490 mμ). However, the overlap of the bands from I and II and the presence of a strong band nearby precludes a quantitative treatment.

The ratio of I to II could be obtained from the ^1H NMR spectra in the cases shown in Table 4. For a given R this ratio increases when (1) the temperature is raised; (2) the concentration is lowered; or (3) a less polar solvent is used. These results are in agreement with an endothermic dissociation of II to the less polar compounds $I + CS_2$. A substituent influence on the ratio, *i.e.* on the position of the equilibrium (1), also follows from Table 4. It is seen that the ratio of I to II measured under similar conditions increases from R = Me to R = $PhCH_2$. Spectra of Ig (R_2P = PhMeP) in the presence of a great excess of carbon disulfide showed no signals due to IIg. This absence

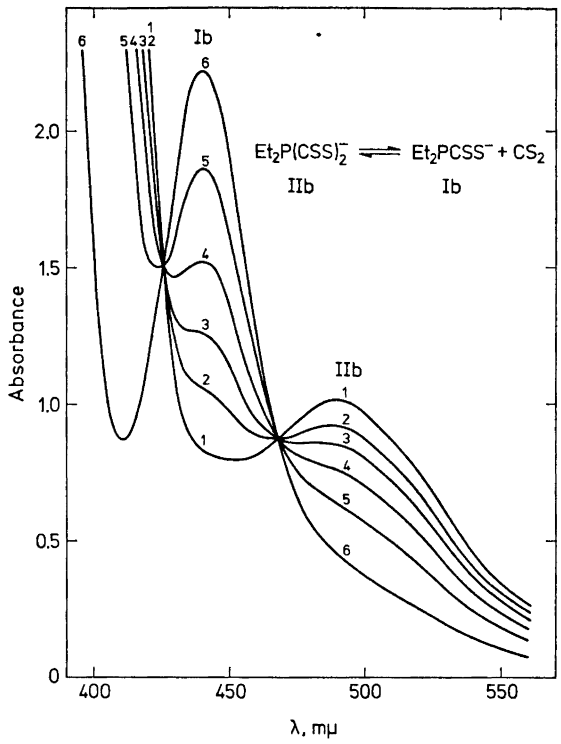


Fig. 1. Visible absorption spectra of IIb (5.3×10^{-2} M) with varying amounts of CS_2 in $(CH_3)_2SO$ solutions (25°C). 1: 30.8 mg IIb and *ca.* 14 mg CS_2 in 10 ml $(CH_3)_2SO$. 2 – 6: CS_2 gradually removed by bubbling nitrogen through the solution for increasing time lengths (3 – 45 min).

shows that the ratio in this case is even greater than for $R = PhCH_2$. Although equilibrium measurements were not performed in ethanolic solutions, the results from preparation of the salts I and II indicate that the equilibrium in ethanol is likewise markedly influenced by the nature of R.

A variation of R is expected to displace the equilibrium if it changes the nucleophilic reactivity of the phosphorus atom towards carbon disulfide. Such a change may be discussed in terms of steric, resonance, and inductive effects of R. Steric hindrance probably accounts for the lesser amount of II in the equilibrium mixture in $CDCl_3$ when $R = Pr^i$ as against Me and Et (Table 4). A lower solubility of II than of I in ethanol can account for the fact that only the former type of product was isolated in these cases. This assumption is also supported by the fact that a 1:1 molar ratio of $Pr^i{}_2PH$ and CS_2 gave IIc in nearly 100 % yield (based on CS_2). Di-*tert*-butylphosphine and dimesitylphosphine did not react with carbon disulfide. In accordance with previous reports on compounds containing the $Bu^t{}_2P$ group, [6] this unreactivity may be due to severe steric hindrance even to approach of the first carbon disulfide molecule. Steric hindrance, however, can hardly explain why

Table 4. Effect of substituent, temperature, concentration, and solvent on the position of the equilibrium (measured on the Ph_4P^+ salts by ^1H NMR spectroscopy):

$$R_2P(CSS)_2^- \rightleftharpoons R_2PCSS^- + CS_2$$
II I

Compounds I-II (R)	Solvent	x_0(II) × 10^2 [a]	t, °C	% II [b]	% I [b]
a (Me)	$(CD_3)_2SO$	2.30	40	87	13
»	$CDCl_3$	2.61	40	62	38
»	$CDCl_3$	2.61	0	86	14
»	$CDCl_3$	2.61	−40	94	6
b (Et)	$(CD_3)_2SO$	2.82	40	*ca.* 85	*ca.* 15 [c]
»	$CDCl_3$	2.83	40	*ca.* 60	*ca.* 40
»	$CDCl_3$	2.83	0	*ca.* 80	*ca.* 20
c (Pr^i)	$(CD_3)_2SO$	0.76	40	45	55
»	$CDCl_3$	2.64	40	25	75
»	$CDCl_3$	1.36	40	19	81
»	$CDCl_3$	0.69	40	*ca.* 10	*ca.* 90
»	$CDCl_3$	2.64	0	60	40
e ($PhCH_2$)	$CDCl_3$	2.38 [d]	40	*ca.* 0 [e]	*ca.* 100
»	$CDCl_3$	2.38 [d]	0	*ca.* 5	*ca.* 95
»	$CDCl_3$	2.38 [d]	−40	*ca.* 15	*ca.* 85

[a] Initial mol fraction of II.
[b] Estimated uncertainty ±3 %.
[c] Estimated from the CH_2 signal of Ib: τ = *ca.* 8 (m).
[d] x_0 (I) with excess CS_2 added ($x_0(CS_2) = 8.7 \times 10^{-2}$).
[e] Estimated from the CH_2 signals of IIe. These are clearly resolved in a 5 : 1 $CDCl_3 - CS_2$ solution at −40°C: τ = 5.95 (d), J_{PCH} = *ca.* 16 Hz.

Table 5. Correlation of inductive effect of R with product and equilibrium data from the reaction:

$$R_2PH + 2\ CS_2 \xrightarrow{Et_3N + Ph_4PCl} \underset{\text{I}}{R_2PCSSPh_4P} + CS_2 \rightleftharpoons \underset{\text{II}}{R_2P(CSS)_2Ph_4P}$$

R_2PH	$\sum\sigma^*$(R) [a]	Product isolated from ethanol	% (I) in $CDCl_3$ [b]
$Pr^i{}_2PH$	−0.38	II	75 [c]
Et_2PH	−0.20	II	*ca.* 40 [c]
Me_2PH	0	II	38 [c]
$(PhCH_2)_2PH$	0.43	I	*ca.* 100 [d]
PhMePH	0.60	I	*ca.* 100 [d]
Ph_2PH	1.20	I	
$(NCCH_2CH_2)_2PH$	1.60 [e]	I	

[a] Taft σ^* values.[7]
[b] Measured by ^1H NMR spectroscopy at *ca.* 40°C.
[c] Solutions of II, mol fraction of I+II *ca.* 2.6×10^{-2}.
[d] Solutions of I, mol fraction *ca.* 2.6×10^{-2}, with an excess of CS_2 added (mol fraction *ca.* 10^{-1}).
[e] From Ref. 9.

$(NCCH_2CH_2)_2PH$, $(PhCH_2)_2PH$, Ph_2PH, and PhMePH give compounds of type I and not II, because the hindrance is probably not greater than for $Pr^i{}_2PH$. Resonance effects, although generally small for third-row elements conjugated to carbon, could explain the low nucleophilic reactivity of phosphorus in If, but not in Id and Ie. Inductive effects, however, may explain the results. The inductive effect of R may be described by the Taft σ^* values,[7] which have been shown to give a satisfactory measure of the nucleophilicity of tertiary phosphines towards ethyl iodide in acetone.[8] In Table 5, the secondary phosphines are listed in order of increasing σ^* values of R. It is seen that the products isolated from phosphines with $\sum\sigma^*(R)$ higher than *ca.* 0.4 are of type I, whereas phosphines with $\sum\sigma^*(R)$ of *ca.* 0 and lower give products of type II. The last column shows that inductive effects largely determine the position of the equilibrium, although steric effects are operating as well.

EXPERIMENTAL

The analyses were carried out in the Microanalysis Department of this laboratory. Infrared spectra were obtained on a Perkin-Elmer 337 Grating Infrared Spectrophotometer, proton magnetic resonance spectra on a Varian A-60A instrument, and visible spectra on a Unicam SP 800 A Ultraviolet Spectrophotometer. The ^1H NMR spectrum of IIIe was obtained from a 20 % solution in $CDCl_3$ because the outer lines of the AB part (the CH_2 signals) of the ABX spectrum were weak, owing to a $J_{AB}/\Delta\nu_{AB}$ ratio of 1.5. A spectrum recorded in $(CD_3)_2SO$ ($J_{AB}/\Delta\nu_{AB} = 0.72$) confirmed the assignments. All preparations involving free phosphines were performed in a nitrogen atmosphere. Solvents used for equilibrium measurements were deoxygenated by bubbling nitrogen through the stirred solvents for 1 h.

The following secondary phosphines were prepared by previously published methods: dimethylphosphine,[10] diethylphosphine,[11] diisopropylphosphine,[12] di-*tert*-butylphosphine,[13] bis(2-cyanoethyl)phosphine,[14] diphenylphosphine,[1] and dimesitylphosphine.[15]

Methylphenylphosphine was prepared from triphenylphosphine by stepwise dearylation and alkylation. To a stirred solution of sodium (0.5 mol) in liquid ammonia (0.5 l), cooled in an acetone-dry ice bath, was added triphenylphosphine (0.25 mol). After 15 min solid ammonium chloride (0.25 mol) was added and then methyl iodide (0.25 mol). The nearly colourless solution was treated with more sodium (0.5 mol), and the mixture was stirred for 1 h. The dark red-brown solution was decolourized by addition of solid ammonium chloride (0.75 mol), and the ammonia was allowed to evaporate. Extraction of the residue with benzene (2 × 100 ml) followed by distillation gave methylphenylphosphine (45 %), b.p. 62.5–63°C/13 mmHg (lit.[16] 59–60°C/10 mmHg), and methyldiphenylphosphine (13 %), b.p. 94–96°C/0.5 mmHg (lit.[17] 160°C/15 mmHg). Methylphenylphosphine was characterized by its ^1H NMR spectrum (*ca.* 10 % in $CDCl_3$, *ca.* −57°C): CH_3, $\tau = 8.61$ (dd), $J_{PCH} = 2.7$ Hz, $J_{HPCH} = 7.8$ Hz; PH, $\tau = 5.68$ (dq), $J_{PH} = 220$ Hz, $J_{HPCH} = 7.8$ Hz; Ph, $\tau = 2.1-2.6$ (m).

Dibenzylphosphine was prepared from dibenzylphosphine oxide[18] by thermal disproportionation. The oxide (11.5 g, 0.05 mol) was stirred magnetically in a 50 ml flask and heated in an oil bath to *ca.* 200°C for 2 h. After cooling, sodium hydroxide pellets (*ca.* 1 g) were added, and the flask was attached to a distillation apparatus having a 10 cm Vigreux column. The system was evacuated to *ca.* 0.1 mmHg and the flask reheated to 200°C. Within *ca.* 20 min dibenzylphosphine (3.1–3.4 g, 60–65 %) was collected, b.p. 114–115°C/0.15 mmHg (the lit.[11] b.p. of 115–120°C/3 mmHg seems erroneous). ^1H NMR spectrum (*ca.* 10 % in $CDCl_3$, *ca.* −35°C): CH_2, $\tau = 7.09$ (dd), $J_{PCH} = 2.0$ Hz, $J_{HPCH} = 7.1$ Hz; PH, $\tau = 6.43$ (dquin), $J_{PH} = 209$ Hz, $J_{HPCH} = 7$ Hz; Ph, $\tau = 2.58$ (s). According to the ^1H NMR spectrum, impurities accounted for less than 5 % of the signals. The residue from the distillation was extracted with 2 N aqueous sodium hydroxide and the filtered solution acidified. The precipitate was recrystallized from abs. ethanol to give a *ca.* 70 % yield of dibenzylphosphinic acid, m.p. 191–192°C (lit.[19] 191.5–192.3°C).

Preparation of tetraphenylphosphonium salts I and II. The salts were prepared analogously to the preparation of tetraphenylphosphonium diethylphosphoniobisdithioformate (IIb).[1] The only modifications introduced were that the amount of solvent was generally reduced to about half of that used for IIb and in some cases (Id and Ig) it was necessary to cool the reaction mixture to −25°C for several hours to obtain a crystalline product. No red colour was observed when di-*tert*-butylphosphine or dimesitylphosphine was used, either at room temperature or at −25°C after 48 h. More than 90 % of the dimesitylphosphine was recovered unchanged (IR and m.p.) by evaporation and extraction with pentane. Solvents for recrystallization, yields, melting points, and analyses are given in Table 1.

Preparation of tetraphenylphosphonium salts III. The salts I or II were dissolved in a 5:1 methylene chloride-carbon disulfide mixture, and sulfur was added in a slight excess. After ½ – 1 h the solution was evaporated to dryness, and the residue was freed of remaining sulfur by extraction with carbon disulfide. Solvents for recrystallization, *etc.*, are given in Table 1.

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