418. *The Constitution of Some Additive Compounds of Tertiary Phosphines.*

By W. Cule Davies and (in part) W. P. Walters.

Comparison of the ease of isolation of the compounds of carbon disulphide with nuclear-substituted aryldialkylphosphines leads to an anomalous series for the effects of the substituents (Czimatis, *Ber.*, 1882, **15**, 2014; Michaelis and Schenk, *Annalen*, 1890, **260**, 1; Davies and Morris, *Bull. Soc. chim.*, 1933, **53**, 980). The effects of substitution on the stabilities of the compounds, now obtained by a quantitative method, give a series of substituents consistent with the usual electronic series.

The compounds lose carbon disulphide in the air and the system is found experimentally to be univariant, so dissociation pressures at various temperatures can be measured and, hence, stabilities compared.

The following equation represents the dissociation of the solid additive compound :

$$\underset{\text{(solid)}}{R'R_2P,CS_2} \rightleftharpoons \underset{\text{(gas)}}{CS_2} + \underset{\text{(liquid)}}{R'R_2P} \rightleftharpoons \underset{\text{(vapour)}}{R'R_2P}$$

Under the conditions of measurement employed (10—100°; 1—200 mm.), carbon disulphide is gaseous, and, in the general case, the phosphine exerts a measurable vapour pressure. On the assumptions that the vapour of the additive compound is completely dissociated (the vapour is not coloured, whereas the solid is intensely coloured) and that the mixture of carbon disulphide and phosphine vapour obeys the gas laws, the system is clearly univariant. There should be a fixed pressure of carbon disulphide over the dissociating compound at each temperature, and the total dissociation pressure measured is the sum of the pressures of carbon disulphide and the vapour of the phosphine. The effect on the dissociation pressure of the solubility of the additive compound in the liquid phosphine has been ignored. Determinations were not made in the temperature region just below the melting point of the additive compound.

The empirical index of stability may be obtained as follows. The stability of the carbon disulphide compound of phenyldimethylphosphine is taken as unity; that of any other compound is then obtained by comparing the temperatures at which the dissociation pressures of the latter and of the standard become 50 mm. In Table I the additive compounds of the dimethyl- and the diethyl-phosphines are given in order of stability. It will be seen that with one exception the m. p.'s of the compounds run parallel to the stabilities in the two groups of compounds. Generally, the colour of the standard substance is deepened or brightened by nuclear substituents and by change to a diethylphosphine.

Table I.

Stabilities, Melting Points, and Colours of Addition Compounds with Carbon Disulphide.

	Empirical index of stability.	M. p. (sealed tube).	Colour.*		Empirical index of stability.	M. p. (sealed tube).	Colour.*
A. *Substituted phenyldimethylphosphines.*				B. *Substituted phenyldiethylphosphines.*			
p-OMe	1·34	119°	Deep orange	*p*-NMe$_2$	1·27	103°	Deep orange
p-Me	1·11	118	Light brown	*p*-OPh	0·77	69	Brown
(Unsub.)	(1·00)	102	Terracotta	*p*-Me	0·62	55	Chocolate
p-OPh	0·97	88	Salmon-pink	(Unsub.)	0·49	45	Brown
p-Br	0·92	96	Orange	*p*-Br †	$<0·4$		—
2 : 5-Me$_2$	0·81	71·5	—				
2 : 4 : 6-Me$_3$	0·55	46	—				

* The colour given is that of the finely powdered substance. In solution in the presence of excess of carbon disulphide the colour is invariably deep red.

† The additive compound was obtained as a solid which was too unstable to be used in the present experiments.

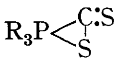
These results show that the following factors affect the stabilities of the additive compounds.

(i) *Nuclear substituents in the* p-*position.* These substituents should exhibit polar and not steric effects. Reference to Table I shows that the stability of the compound is increased by an electron-releasing group (*p*-Me) and diminished by an electron-attracting group (*p*-Br). It may be concluded, therefore, that the reaction between a tertiary phosphine and carbon disulphide is one requiring electron-accession to the side chain (point of attack). The phosphine is the donor molecule, so the co-ordination formula $R_3P \leftarrow S{:}C{:}S$ is impossible. Czimatis's conclusion (*loc. cit.*) that the reactivity of an aryldialkylphosphine towards carbon disulphide decreased with an increase in weight of the aryl group cannot be accepted.

(ii) *Nuclear substituents in the* o-*position.* Comparison of the carbon disulphide compounds of *p*-tolyl-, *p*-xylyl-, and 2 : 4 : 6-trimethylphenyl-dimethylphosphines shows that the introduction of *o*-methyl groups decreases the stability. This result is consistent with theories of steric hindrance.

(iii) *Change from aryldimethyl- to aryldiethyl-phosphine.* This substitution considerably depresses the stability of the additive compound. Such a result is contrary to expectation if the polar effects alone of the alkyl groups are considered. Here, as in (ii), stereochemical, rather than polar, effects determine the stabilities of the additive compounds.

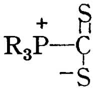
Hantzsch and Hibbert's cyclic formula (I) (*Ber.*, 1907, **40**, 1508) for the additive compounds of carbon disulphide and tertiary phosphines has been criticised by Davies and Morris (*loc. cit.*) on the grounds that it involves quinquecovalent phosphorus, for which it is difficult to assign a space structure. The co-ordination formula (II) is improbable, because the acceptor atom, sulphur, obtains a decet of electrons, four of which are unshared.



(I.)

$R_3P \longrightarrow S{:}C{:}S$

(II.)

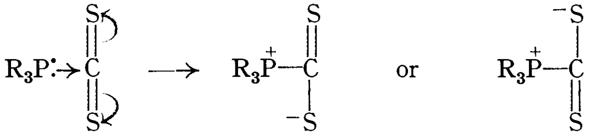


$R_3\overset{+}{P}-C(=S)-S^-$

(III.)

Such a valency group never occurs unless the unshared electrons become inert, and sulphur is too light an element to have inert pairs (Sidgwick and Bowen, *Ann. Reports*, 1931, **28**, 400). An inner-salt formula (III) best explains the formation and properties of the additive compound. Moreover, this type of formula can be applied without exception to other similar additive compounds of tertiary phosphines.

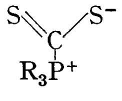
The following is the mechanism of the formation of the compound. In carbon disulphide there is the possibility of an electron deficiency at the carbon atom. Co-ordination of the lone pair of the phosphorus atom then occurs with the depleted octet of the carbon atom :

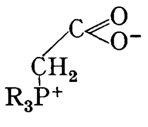


It will be seen that the negative charge may be distributed to either sulphur atom, yielding two forms involving resonance. This would account for the intense colour of the additive compound.

The phosphine–carbon disulphide compounds, unlike the phosphorus betaines, are insoluble in water. They are sparingly soluble in benzene, but soluble in alcohol, acetone, and hydrochloric acid. In the latter a colourless salt, $SH{\cdot}CS{\cdot}PR_3\}Cl$, is formed. The distance apart of the bound ions in the betaine is greater than in the addition compound.

(IV.)



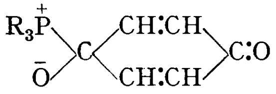


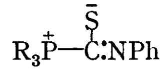
(V.)

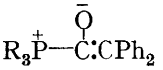
Rotation of the group S:C·S about the C–P link in the latter compound does not affect the distance apart of the bound ions (see IV). On the other hand, the distance apart of the bound ions in the betaine can be increased from that in the most favoured position (V) by rotation of the group $O{:}\overset{|}{C}{\cdot}\bar{O}$ about the C–C link. Such rotation will occur, if necessary, under the influence of an attacking reagent, water or hydrochloric acid. For these reasons the betaine is soluble in water and strongly basic, whilst the phosphine–carbon disulphide compound is insoluble in water and feebly basic.

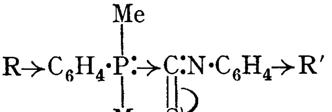
It is unnecessary to assume that, because a tertiary phosphine sulphide may readily be obtained from the addition compound, *e.g.*, by heating with water in a sealed tube (Hofmann, *Phil. Trans.*, 1860, **150**, 409) or with anhydrous fatty acids (Hantzsch and Hibbert, *loc. cit.*), the phosphorus atom in the additive compound is linked directly to the sulphur atom. Most probably, dissociation of the compound into its generators takes place, followed by decomposition of the liberated carbon disulphide, yielding sulphur which then combines with the free phosphine. The great affinity of sulphur for a tertiary phosphine is demonstrated on p. 1792.

Inner-salt formulæ can be given to the phosphine compounds of *p*-benzoquinone (VI), which have now been made, of organic thiocarbimides (VII) (Hofmann, *loc. cit.*), and of diphenylketen (VIII) (Staudinger and Meyer, *Helv. Chim. Acta*, 1919, **2**, 612). These compounds are crystalline substances, insoluble in water, but soluble in hydrochloric acid.


(VI.)


$R_3\overset{+}{P}—\overset{\overset{-}{S}}{C}{:}NPh$
(VII.)


$R_3\overset{+}{P}—\overset{\overset{-}{O}}{C}{:}CPh_2$
(VIII.)


$R{\rightarrow}C_6H_4{\cdot}\overset{\overset{Me}{|}}{\underset{\underset{Me}{|}}{P}}{:}{\rightarrow}\underset{\underset{S}{\|}}{C}{:}N{\cdot}C_6H_4{\rightarrow}R'$
(IX.)

The negative charge can only be transferred to one atom. This may account for the feebler colour, cream or pale yellow, of these compounds.

It has already been shown that the reaction between carbon disulphide and a nuclear-substituted aryldialkylphosphine was favoured by electron-accession towards the phosphorus atom. By considering the arylthiocarbimides as substituted carbon disulphides, it is to be expected, therefore, that the reaction between a phosphine and a nuclear-substituted arylthiocarbimide would be facilitated by electron-recession from the point of attack (see IX). This conclusion has now been verified.

To be capable of forming with tertiary phosphines additive products of the type under discussion, a compound must possess a carbon atom situated in a conjugated system, such as in carbon disulphide or *p*-benzoquinone, with such atoms or groups which would lead to electron-deficiency at that carbon. The thiocarbonyl group alone is insufficient, and dimethyl-γ-pyrone does not combine with a phosphine. There is no evidence of combination of triethylphosphine with carbon dioxide, even at low temperature, doubtless because of the weaker electronic effects of the carbonyl than of the thiocarbonyl group. For a similar reason, phenylcarbimide does not form an additive compound with a phosphine.

The reactivity of the tertiary bases of the elements of Group V*b* is in the order phosphine>arsine>amine (Davies and Lewis, J., 1934, 1599), which explains why amines and arsines do not combine with carbon disulphide; *e.g.*, triethylarsine does not react with carbon disulphide even at low temperature. *p*-Benzoquinone with certain tertiary amines yields compounds to which Bennett and Willis (J., 1929, 256) have given inner-salt formulæ. Whereas, however, the reaction of *p*-benzoquinone with an amine is slow, that with a phosphine is violent and almost instantaneous.

EXPERIMENTAL.

Dissociation Pressure Measurements (with W. P. WALTERS).—The static isoteniscope (Smith and Menzies, *J. Amer. Chem. Soc.*, 1910, **32**, 1412) was used with a modified procedure to suit the present compounds. The pressure in a system connected to an accurately constructed pressure gauge was adjusted by admission of air or by suction to be equal to the pressure exerted by the substance contained in a bulb, which was separated from the main system by a U-tube of mercury as confining liquid. Equality of pressure was indicated by the surfaces of the mercury in the limbs of the U-tube being in the same horizontal plane, observation being made with a travelling microscope. The bulb and U-tube were immersed in a vigorously stirred water-bath, of which the temperature was thermostatically controlled. Instead of " boiling out " the air in the bulb, as recommended by Smith and Menzies, the whole apparatus was completely evacuated at a temperature where the pressure exerted by the substance was negligible. During this operation, the confining liquid was manipulated from the U-tube into a side-tube. The temperature was then raised so that the dissociation pressure of the substance was about 5 mm., and the whole apparatus again evacuated. Finally, the confining liquid was run back into the U-tube. Complete absence of air was thus ensured. Readings of dissociation pressures at various temperatures up to 100° were then taken.

It was shown in an experiment with one of the additive compounds that dissociation-pressure readings taken following a moderately long second evacuation agreed with those following a prolonged evacuation which produced considerable free phosphine. Care was always taken that sufficient liquid phosphine was present to saturate the gaseous phase with its vapour.

For measurements of the vapour pressures of tertiary phosphines, the second evacuation was carried out at 100°. A reading was taken at this temperature, followed by other observations at lower temperatures.

Tertiary Phosphines.—Aryldialkylphosphines were prepared by interaction of methyl- or ethyl-magnesium halides with aryldichlorophosphines. The latter were prepared by the method of Michaelis (*Ber.*, 1879, **12**, 1009), but whereas phenyl-, *p*-tolyl-, and *p*-methoxyphenyl-dichlorophosphines were isolated by Grüttner and Wiernik's distillation method (*Ber.*, 1915, **48**, 1473), it was found better to isolate the *p*-xylyl, *p*-bromophenyl, *p*-phenoxyphenyl, and *p*-dimethylaminophenyl compounds by an extraction method (Davies, this vol., p. 462).

Additive Compounds with Carbon Disulphide.—The following general method was adopted for the preparation of these compounds. A solution of 1·5 c.c. of purified carbon disulphide in 3 c.c. of pure dry benzene was added at once to a solution of 1 c.c. of the tertiary phosphine in 5 c.c. of benzene. A deep red coloration immediately appeared. In some cases (reactive phosphines) the whole solidified to a crystalline mass, but in others (less reactive phosphines), cooling to − 10° caused the separation of the solid additive compound. The compound was collected on a filter, washed with 5 c.c. of benzene–carbon disulphide (4 : 1), and transferred to a porous plate, where it was rapidly pressed out and finely pulverised. During the last operation, carbon disulphide vapour was allowed to pour down over the compound. The bulb of the isoteniscope was quickly charged with about 0·3 g. of the powder, and then sealed to the isoteniscope U-tube, which was finally attached to the main system and pressure gauge.

On no account should the mixture be heated during the preparation. Recrystallisation is only possible from moderately hot solutions in alcohol or acetone containing excess of carbon disulphide. Even then it is unsatisfactory, except for triethylphosphine–carbon disulphide which is relatively stable.

Analysis.—The instability of some of the additive compounds made desirable a method of analysis in which exposure to the air was reduced to a minimum. About 0·1 g. of the substance, immediately after it had been powdered, was transferred to a weighed test-tube with a constricted neck, which was then sealed. The sealed tube was reweighed, and broken under a mixture of 10 c.c. of acetone and 2 c.c. of methyl iodide. The mixture was well shaken for 15 minutes, and washed with water into 20 c.c. of light petroleum, which was then repeatedly extracted with water. The aqueous extract was titrated against silver nitrate with chromate as indicator. The amount of iodine ion corresponds to that of methylphosphonium iodide formed and hence to that of the tertiary phosphine contained in the additive compound.

The *compounds* given below have not previously been described. Czimatis (*loc. cit.*) failed to obtain the third in a state of sufficient purity for analysis, and he could not obtain the fourth as a solid.

Carbon disulphide compound, $R'{\cdot}C_6H_4{\cdot}PR_2,CS_2$, with	M. p. (sealed tube).	Phosphine, %.	
		Found.	Calc.
p-Methoxyphenyldimethylphosphine	119°	68·6	68·8
p-Bromophenyldimethylphosphine	96	74·4	74·0
Phenyldiethylphosphine	45	68·4	68·6
p-Tolyldiethylphosphine	55	70·3	70·3

Results.—Dissociation pressures, *p* mm. (± 0·2 mm.), at several temperatures, *t*° (± 0·1°), of the additive compounds are given in Table II. The pressure readings have been corrected to mm. of mercury at 0° if the correction is greater than 0·2 mm.

Corresponding pressures and temperatures satisfy linear equations of the type $\log_{10}p = A - B/T$, indicating that the heat absorbed, L, in the dissociation is constant over the range of temperature employed. It was found that the value of L varies slightly for different compounds. However, the values are scarcely comparable, because they were obtained over different ranges

TABLE II.

Dissociation Pressures of the Compounds of Carbon Disulphide and Aryldialkylphosphines.

Phenyldimethylphosphine–carbon disulphide.

t	25·2°	37·2°	44·1°	49·8°				
p, mm.	2·0	5·0	11·5	20·5				
t	44·9° *	49·4°	54·8°	59·2°	65·2°	68·5°	70·9°	74·6°
p, mm.	13·0	19·0	29·0	40·0	62·5	88·25	110·2	143·6

$\log_{10}p = 13\cdot459 - 3935/T$; $L = 17{,}990$ cals./g.-mol.

p-*Tolyldimethylphosphine–carbon disulphide.*

t	34·6°	44·9°	59·3°	64·4°	69·5°	74·2°	79·95°
p, mm.	2·5	7·6	22·5	39·0	55·9	77·05	115·8

$\log_{10}p = 13\cdot561 - 4050/T$; $L = 18{,}510$ cals./g.-mol.

p-*Xylyldimethylphosphine–carbon disulphide.*

t	36·2°	42·0°	46·0°	52·9°	57·3°	60·4°	63·4°	65·5°
p, mm.	11·5	22·0	32·9	67·7	105·8	144·2	198·9	251·4

$\log_{10}p = 16\cdot432 - 4758/T$; $L = 21{,}750$ cals./g.-mol.

2 : 4 : 6-*Trimethylphenyldimethylphosphine–carbon disulphide.*

t	14·0°	24·2°	29·0°	32·7°	37·8°	38·2°	40·2°
p, mm.	5·0	17·0	29·0	45·0	77·8	79·7	99·1

$\log_{10}p = 16\cdot245 - 4462/T$; $L = 20{,}400$ cals./g.-mol.

p-*Bromophenyldimethylphosphine–carbon disulphide.*

t	39·6°	46·8°	52·2°	57·0°	62·2°	66·4°	71·0°	75·0°
p, mm.	9·4	19·3	32·2	49·5	75·3	113·1	170·4	246·5

$\log_{10}p = 14\cdot795 - 4321/T$; $L = 19{,}750$ cals./g.-mol.

p-*Methoxyphenyldimethylphosphine–carbon disulphide.*

t	61·3°	70·4°	75·0°	80·0°	87·0°	92·0°
p, mm.	6·3	15·5	24·7	39·7	79·0	131·6

$\log_{10}p = 16\cdot416 - 5229/T$; $L = 23{,}900$ cals./g.-mol.

p-*Phenoxyphenyldimethylphosphine–carbon disulphide.*

t	40·0°	47·0°	52·3°	58·0°	63·4°	67·5°	72·2°
p, mm.	7·3	14·1	24·7	43·8	72·9	105·7	162·0

$\log_{10}p = 15\cdot435 - 4569/T$; $L = 20{,}890$ cals./g.-mol.

Phenyldiethylphosphine–carbon disulphide.

t	13·5°	20·6°	25·1°	29·5°	33·1°	36·2°
p, mm.	6·4	15·0	26·2	44·0	67·9	100·8

$\log_{10}p = 17\cdot075 - 4666/T$; $L = 21{,}330$ cals./g.-mol.

p-*Tolyldiethylphosphine–carbon disulphide.*

t	22·2°	29·7°	32·1°	36·1°	39·8°	45·1°
p, mm.	10·0	21·2	28·5	42·1	58·9	102·7

$\log_{10}p = 15\cdot046 - 4152/T$; $L = 18{,}980$ cals./g.-mol.

p-*Phenoxyphenyldiethylphosphine–carbon disulphide.*

t	30·5°	37·3°	41·5°	45·5°	50·0°	54·8°	58·2°
p, mm.	8·3	18·2	27·8	43·0	65·0	108·3	156·9

$\log_{10}p = 15\cdot984 - 4574/T$; $L = 20{,}910$ cals./g.-mol.

p-*Dimethylaminophenyldiethylphosphine–carbon disulphide.*

t	45·0°	51·2°	61·0°	66·5°	72·0°	77·0°
p, mm.	2·2	4·1	10·5	18·3	28·9	48·0

$\log_{10}p = 14\cdot895 - 4633/T$; $L = 21{,}170$ cals./g.-mol.

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* This set of determinations was made with another sample of the compound; it will be seen that the measurements are reproducible with fair accuracy.

of temperature, and the effect of the phosphine vapour is a complicating factor. Furthermore, in some cases, the additive compound was so unstable that the figures given can only be approximate.

Values of the vapour pressures of some aryldimethylphosphines are given in Table III. Even with the most volatile phosphine (phenyldimethylphosphine), the vapour pressure in the temperature range under investigation is small compared with the total dissociation pressure of the corresponding additive compound. The vapour pressures of aryldiethylphosphines up to 100° are almost negligible.

TABLE III.

Vapour Pressures of Tertiary Phosphines.

*Phenyldimethylphosphine.**

t	100·0°	90·0°	82·6°	69·6°	65·2°	60·2°	53·2°
p, mm.	41·5	28·5	19·0	9·5	6·5	4·5	2·5

p-*Tolyldimethylphosphine.*

t	100·4°	90·0°	83·1°	76·4°	70·3°	58·4°
p, mm.	21·75	13·0	10·2	6·6	5·0	1·7

2 : 4 : 6-*Trimethylphenyldimethylphosphine* : 100·1°/6 mm.; 74·9°/3 mm.
p-*Bromophenyldimethylphosphine* : 99·0°/17·5 mm.; 70·3°/7·3 mm.; 55·0°/4 mm.

* In a distillation of this phosphine, the b. p. was found to be 82—83°/18—20 mm., agreeing well with the value of the vapour pressure at 82·6° obtained with the isoteniscope. The calculated value of the b. p. of the phosphine, 107°/50 mm. (Jackson, Davies, and Jones, J., 1931, 2109) may be shown graphically to be in agreement with the present determinations.

Triethylphosphine–phenylthiocarbimide.—Triethylphosphine (1 c.c.) was added to a solution of 1 c.c. of phenylthiocarbimide in 5 c.c. of ether. The oil which separated solidified when the mixture was cooled to 0°. The compound (Hofmann, *loc. cit.*) forms pale yellow crystals, m. p. 61° (from ether).

*Triethylphosphine–*p-*tolylthiocarbimide.*—When a mixture of the phosphine (0·75 c.c.), *p*-tolylthiocarbimide (0·9 c.c.), and ether (5 c.c.) was cooled to 0°, very pale yellow needles, m. p. 88—90°, of the *compound* (Found : C, 62·6; H, 8·7. $C_{14}H_{22}NSP$ requires C, 62·9; H, 8·3%) separated.

*Triethylphosphine–*p-*nitrophenylthiocarbimide.*—A precipitate (1·3 g.) of the *compound* was obtained immediately when the phosphine (0·75 c.c.) was added to a saturated ethereal solution of *p*-nitrophenylthiocarbimide (0·9 g.). Recrystallised from ether or alcohol–ether, it formed lemon-yellow needles, m. p. 97° (Found : C, 52·3; H, 6·7. $C_{13}H_{19}O_2N_2SP$ requires C, 52·3; H, 6·4%).

*Triethylphosphine–*p-*benzoquinone.*—A buff-coloured precipitate was obtained when the generators were mixed in ether. The precipitate was stable when kept under ether, but became gummy and then hardened to a black mass when the ether was removed (the compound of diphenylketen and this phosphine behaved similarly according to Staudinger and Meyer, *loc. cit.*). The precipitate obtained when solutions of the generators in acetone were mixed was stable, but darkened slightly on keeping. The *compound* [Found : H, 8·7; *M* (ebullioscopic in ethyl alcohol), 224. $C_{12}H_{19}O_2P$ requires H, 8·5%; *M*, 226] blackened at 170° and appeared to melt at about 180°. As is often the case with certain organic phosphorus compounds, this substance was difficult in combustion and low results were obtained for carbon.

*Tri-*n-*butylphosphine–*p-*benzoquinone.*—When excess of ether was added to a mixture of the phosphine (0·5 c.c.), *p*-benzoquinone (0·2 g.), and alcohol (10 c.c.), a cream-coloured crystalline precipitate of the *compound* separated (Found: C, 69·0; H, 10·3. $C_{18}H_{31}O_2P$ requires C, 69·6; H, 10·1%); it blackened at 170° and melted to a black liquid at 180—190°.

p-*Tolyldimethylphosphine–*p-*benzoquinone.*—The *compound* gradually separated from a mixture of the phosphine (1 c.c.), *p*-benzoquinone (0·4 g.), and alcohol (20 c.c.) as cream-coloured glistening leaflets (Found: C, 68·8; H, 6·9. $C_{15}H_{17}O_2P$ requires C, 69·2; H, 6·6%). It does not melt up to 250°, and is slightly soluble in alcohol, but insoluble in acetone.

Molecular-weight Determinations.—Cryoscopic determinations in acetophenone (Morgan and Lammert, *J. Amer. Chem. Soc.*, 1924, **46**, 381) with several phosphine–carbon disulphide compounds show them to be dissociated (Table IV a). The effect of nuclear substitution on the degree of dissociation is that which would be expected from the results given on p. 1787. The cryoscopic determinations of Hantzsch and Hibbert (*loc. cit.*) for the nitrobenzene solution of triethylphosphine–carbon disulphide indicate some dissociation. Since, however, nitrobenzene is an unsatisfactory solvent, a determination has now been made in benzene, in which there is considerable dissociation.

The effect on the degree of dissociation of nuclear substituents in the additive compounds of arylthiocarbimides and triethylphosphine was found by ebullioscopic determinations in acetone (Table IV b) with a simple ebullioscope (Swietoslawski, *Bull. Soc. chim.*, 1931, **49**, 1563; obtained from "Prolabo," Paris). The methyl group diminishes, and the nitro-group increases, the stability of the compound.

TABLE IV.

	Concn. (g./1000 g.).	Δt.	M. Found.	M. Calc.	Degree of dissociation.
(a) *Cryoscopic Determinations.*					
Solvent: acetophenone (constant = 6·25° per 1000 g.).					
Et_3P,CS_2	8·197	0·300°	171	194	0·13
,,	24·591	0·850	181	194	0·07
$PPhMe_2,CS_2$	8·718	0·450	121	214	0·77
,,	17·436	0·835	130·5	214	0·64
,,	26·154	1·210	135	214	0·59
p-$MeO\cdot C_6H_4\cdot PMe_2,CS_2$	7·975	0·345	144·5	244	0·69
,,	23·925	0·945	158	244	0·54
Solvent: benzene (constant = 4·9° per 1000 g.).					
Et_3P,CS_2	5·196*	0·225	113	194	0·72
(b) *Ebullioscopic Determinations.*					
Solvent: acetone (constant = 1·71° per 1000 g.).					
$PhNCS,Et_3P$	13·030	0·121°	184	253	0·38
p-$NO_2\cdot C_6H_4\cdot NCS,Et_3P$	14·317	0·087	281	298	0·06
p-$C_6H_4Me\cdot NCS,Et_3P$	12·673	0·123	176	267	0·52

* A more concentrated solution could not be made.

Phenyldimethylphosphine–carbon disulphide is not appreciably soluble in benzene. The 2 : 4 : 6-trimethyl homologue, however, gives a *colourless* solution in benzene, and is, therefore, completely dissociated. This conclusion was confirmed by a cryoscopic determination.

Conductivity of Triethylphosphine–Carbon Disulphide.—Drs. J. F. J. Dippy and F. R. Williams kindly made the following determinations with acetone solutions of the additive compound at 25°: For $v = 20$ and 100 litres/g.-mol., molecular conductivity = 0·015 and 0·019 respectively. (The specific conductivity of the acetone was 0·55 gemmho.) The very small conductivity can be attributed to the presence of free phosphine produced by dissociation of the compound, since a substance with an inner-salt structure must be non-conducting.

Formation of Tertiary Phosphine Sulphides.—A phosphine solution in benzene can be accurately estimated even in the presence of phosphine sulphide, by the following method. The solution was shaken with a known excess of 0·1N-hydrochloric acid, the acid layer separated, the benzene washed with water, and the acid and washings titrated against 0·1N-borax, with methyl-red as indicator.

A 0·2M-solution in benzene of phenyldimethylphosphine was mixed at 25° with an equal volume of a 0·2M-solution of sulphur in benzene. Reaction was complete in less than 30 secs. With phenyldi-*n*-amylphosphine, where the steric effects of the alkyl groups should be great, the reaction was again complete in this time. It is concluded that the reaction between a tertiary phosphine and sulphur is practically instantaneous.

Attempts to prepare New Additive Compounds.—There was no evidence of combination between tri-*n*-butylphosphine and the following substances dissolved or suspended in ether, even at − 80°, at which temperature dissociation of any additive compound would be less: benzophenone, dimethyl-γ-pyrone, thiourea, thiosinamine, thiocarbanilide, 4 : 4′-bisdimethylaminothiobenzophenone (cf. Schönberg and Krüll, *Ber.*, 1926, **59**, 1403), sodium diethyldithiocarbamate, and *p*-dimethylaminobenzylidenerhodanine.

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