# Alkyl Aryl Sulphides from the Interaction of Aryl Thiocyanates and Alcohols under the Influence of Triphenylphosphine or of Trialkyl Phosphites

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Typical aryl thiocyanates react with primary alcohols in the presence of triphenylphosphine to give hydrogen cyanide, triphenylphosphine oxide, and the corresponding alkyl aryl sulphide in high yield. With propan-2-ol, yields of sulphide are lower on account of the competing elimination reaction which leads to a benzenethiol and propene. t-Butyl alcohol yields exclusively products of elimination. Alcohols in the presence of their phosphite esters give similar results, even with p-dimethylaminophenyl thiocyanate, the one thiocyanate studied that failed to give alkyl aryl sulphide with triphenylphosphine and simple primary alcohols. It is suggested that the observed products arise from collapse of a triphenyl- or trialkoxy-oxythiophosphorane which results from attack of an alcohol molecule on the first-formed triphenyl- or trialkoxy-arylthiophosphonium cyanide.

In extending our investigation of the intramolecular cyclisation of diazo-ketones to those having an *ortho*-thiocyanato-function, we observed that when phenyl thiocyanate and the triphenylphosphine adduct of 2-diazo-4'-nitroacetophenone were heated in refluxing methanol, hydrogen cyanide was evolved and major components of the complex reaction mixture were methyl phenyl sulphide and triphenylphosphine oxide.[1] Presumably, triphenylphosphine, arising from the known [2] dissociation of the adduct, brought about reaction between the aryl thiocyanate and the alcohol according to equation (1).

$$ArSCN + ROH + Ph_3P \longrightarrow$$
$$ArSR + Ph_3P{=}O + HCN \quad (1)$$
$$(I)$$
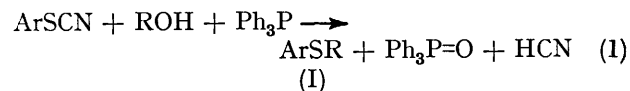
Further investigation has now confirmed this suggestion and has shown that the reaction [equation (1)] is of fairly general application (Table) to the preparation of alkyl aryl sulphides (I) from aryl thiocyanates and primary alcohols. Yields are high, and since aryl thiocyanates are readily available [3] from aromatic amines, the above procedure for the preparation of the sulphides (I) is probably more convenient than most others. For instance, the sulphides (I) are obtainable from arenethiols by alkylation or from alkanethiols by reaction with an aromatic diazonium salt; but overall yields are generally low as the thiols have to be prepared by reduction of sulphonyl chlorides which, if not available by direct sulphonation, have in turn to be obtained from the corresponding amines.

The presence of one *ortho*-substituent on the aromatic thiocyanate has no effect on the yield of the sulphide (I); both *ortho*-methyl- and *ortho*-nitro-phenyl thiocyanates give over 90% yield of the corresponding sulphide (I) with methanol. However yields are lower with mesityl thiocyanate and significant amounts of diaryl disulphide (II) are obtained. Thiols or their oxidation products, the disulphides (II), are also obtained when secondary alcohols are employed, and become the sole product with t-butyl alcohol. With phenyl thiocyanate, triphenylphosphine and a large molar excess of ethylene glycol, there results 2-(phenylthio)ethanol (85%); the latter when treated in the same way provided 1,2-bis-phenylthioethane (78%). In effect, therefore, it is possible to bring about stepwise reaction of the glycolic hydroxy-groups.

All reactions were carried out at 100 °C, or at the reflux temperature of the alcohol if this was below 100 °C. The reaction times given in the Table were determined by following the disappearance of the reactants (t.l.c.) and by the cessation of hydrogen cyanide

[1] W. T. Flowers, G. Holt, M. A. Hope, and C. P. Poulos, *J.C.S. Perkin I*, 1975, 286.

[2] H. J. Bestmann and L. Göthlich, *Annalen*, 1962, **655**, 1, and references cited therein.

[3] See J. L. Wood, *Org. Reactions*, 1943, **3**, 240, for compilation of references.

evolution; in many instances there was a marked ' tailing-off ' and no great precision is therefore claimed for the times quoted. The general scatter of these and the relatively small differences observed for substituents of completely dissimilar electronic character make detailed mechanistic conclusions impossible. However, it may be commented that in the tentative scheme proposed, benzenethiolate ion is required to function first as a leaving group and then at a later stage as a nucleophile, and hence a substituent that facilitates the

recent observations,[12] would then dissociate to give benzenethiolate ion and hence alkyl aryl sulphide (I) and triphenylphosphine oxide (Scheme), rather than phosphine sulphide and ether.

When t-butyl alcohol is employed, the major products are phosphine oxide, arenethiol or disulphide (II) (any of the former usually being converted into the latter during work-up), and isobutene. These products presumably arise by elimination of the alkene from the oxonium precursor (V) or the oxythiophosphorane (VI).

Reactions between aryl thiocyanates (ArSCN) and alcohols (ROH) to give alkyl aryl sulphides (ArSR) (I) [yield (%) of ArSR ^{a}/yield (%) of ArSSAr ^{a} (reaction time ^{b})]

	Ar =	Ph	p-MeC$_6$H$_4$	p-MeO·C$_6$H$_4$	p-Me$_2$N·C$_6$H$_4$	p-NO$_2$C$_6$H$_4$	2,4,6-Me$_3$C$_6$H$_2$
R =	Me	87/0 (8)	93/0 (3)	88/0 (8)	15/80 (10)	82/0 (4)	51/30 (3)
	Et	84/0 (6)				78/0 (7)	55/33 (5)
	Pr	80/0 (3)		86/0 (8)	0/88 (10)	85/0 (8)	68/20 (5)
	Bu	80/0 (3)					
	PhCH$_2$	81/0 (3)			88/0 (6)	62/15 (3)	
	CH$_2$:CH·CH$_2$				70/12(5)		
	Pr^i	70/15 ^{c} (6)	18/18 ^{d} (3)	71/15 (5)	10/86 (12)	80/10 (3)	
	cyclo-C$_6$H$_{11}$			30/58 (5)	0/90 (4)	35/50 (5)	

^{a} Based on initial ArSCN. ^{b} In h. ^{c} All ArSH. ^{d} Some ArSH.

first function may have a deleterious effect on the latter. The evidence does not exclude the possibility of a change in mechanism with change in the substituent, but we note in those reactions which do not lead to alkyl aryl sulphide (I) reaction times are significantly longer. In all cases the yield of phosphine oxide is nearly quantitative.

A number of workers have recently reported the nucleophilic attack of trivalent phosphorus on divalent sulphur resulting, as in equation (2), in the formation of a phosphonium ion (III) and the displacement of an anion, Y$^-$, e.g. phthalimide,[4] $\bar{N}$(SPh)$_2$,[5] PhCO·$\bar{C}$HPh,[6] $\bar{S}$Ph,[7] $\bar{C}$l,[8] and $\bar{C}$N.[9] Such reactions have rarely been carried out in the presence of alcohols, although inter-

$$R\text{-}S\text{-}Y + \geqslant P\colon \longrightarrow \geqslant \overset{+}{P}\text{-}S\text{-}R + Y^- \qquad (2)$$
$$(III)$$
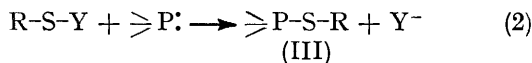
action of diphenyl disulphide and triphenyl phosphine or trimethyl phosphite in methanol has been reported to yield methyl phenyl sulphide.[10] Tanaka has recently attempted the reaction of aryl thiocyanates with triphenylphosphine in methanol solution, but employed only a *catalytic* amount (0.2 mol) of phosphine and did not detect sulphide formation.[11]

Since the reaction of a typical aryl thiocyanate with an alcohol is extremely slow in the absence of triphenylphosphine, the latter presumably reacts with the thiocyanate to provide a phosphonium salt (IV) which with an alcohol should give hydrogen cyanide and an oxythiophosphorane (VI) *via* the oxonium precursor (V). The oxythiophosphorane, in accord with Barton's

A similar elimination would account for the formation of thiol or disulphide when secondary alcohols are employed or when any of the alcohols used is not rigorously dried. The high yield of disulphide (II) from the reaction of p-dimethylaminophenyl thiocyanate and

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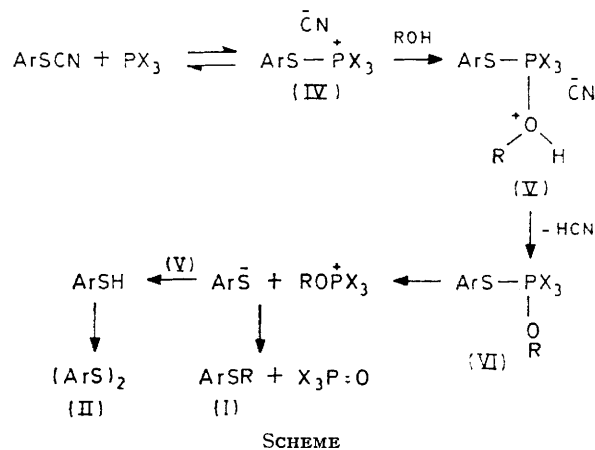
methanol may arise *via* deprotonation of the oxonium precursor (V) by the dimethylamino group of the arenethiolate residue rather than by cyanide ion; this protonated species, or its tautomer, p-dimethylaminobenzenethiol, might then be expected to be a better leaving group than its anion. On the other hand, phosphonium salts containing the much more reactive benzyl and allyl groups might be expected to react even with the feebly nucleophilic p-dimethylaminobenzenethiol to give alkyl aryl sulphide (I); such a suggestion

[4] D. N. Harpp and B. A. Orwig, *Tetrahedron Letters*, 1970, 2691.
[5] J. Almog, D. H. R. Barton, P. D. Magnus, and P. K. Norris, *J.C.S. Perkin I*, 1974, 853.
[6] D. N. Harpp and S. M. Vines, *J. Org. Chem.*, 1974, **39**, 647.
[7] D. N. Harpp and J. G. Gleason, *J. Amer. Chem. Soc.*, 1971, **93**, 2437.

[8] D. C. Morrison, *J. Amer. Chem. Soc.*, 1955, **77**, 181.
[9] W. A. Sheppard, *J. Org. Chem.*, 1961, **24**, 1460.
[10] R. S. Davidson, *J. Chem. Soc. (C)*, 1967, 2131.
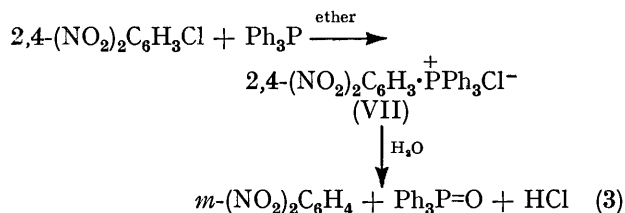[11] K. Tanaka, *Bull. Chem. Soc. Japan*, 1972, **45**, 834.
[12] D. H. R. Barton, D. P. Manly, and D. A. Widdowson, *J.C.S. Perkin I*, 1975, 1568.

accords with the known ease of S_N2 displacement of benzyl and allyl halides.[13] In any event, the behaviour of the p-dimethylaminophenyl thiocyanate appears to be associated with its basicity and not simply with the electronic effect of the substituent since p-methoxy-phenyl thiocyanate gives high yields of the sulphides (I) even with methanol and propanol.

As Parker and Kharasch[14] have done, we attempted to demonstrate the intermediacy of benzenethiolate ions by carrying out some of the reactions in the presence of 1-chloro-2,4-dinitrobenzene; thus, adding the trap in the reaction of phenyl thiocyanate, triphenylphosphine, and n-propanol reduced the yield of the sulphide (I) from 80% to zero, and gave instead a 55% yield of 2,4-dinitrophenyl phenyl sulphide; a similar effect was observed when propan-2-ol was used. These results may be taken to indicate the intermediacy of benzenethiolate ion, but their quantitative significance is uncertain, since in a set of equilibrium reactions such as appears to occur here rapid removal of one of the components may well serve to distort the whole system. 2,4-Dinitrophenyl thiocyanate appears to act as its own trap, since its reaction with triphenylphosphine and alcohol gave diaryl sulphide, ArSAr, which presumably arose by displacement of thiocyanate ion by the benzenethiolate ion.

Reaction of triphenylphosphine and 1-chloro-2,4-dinitrobenzene in ether [equation (3)] gave the insoluble phosphonium salt (VII) and a soluble red oil, small quantities of which were obtained in all the trapping

$$2,4\text{-}(NO_2)_2C_6H_3Cl + Ph_3P \xrightarrow{\text{ether}}$$
$$2,4\text{-}(NO_2)_2C_6H_3\text{·}\overset{+}{P}Ph_3Cl^-$$
$$\text{(VII)}$$
$$\downarrow \text{H}_2\text{O}$$
$$m\text{-}(NO_2)_2C_6H_4 + Ph_3P{=}O + HCl \quad (3)$$

experiments. The formation of salts such as (VII) by displacement of chlorine has apparently not been reported, although they have been claimed to be intermediates in the reaction of arenediazonium salts with triphenylphosphine [equation (4)].[15] In accord with

$$ArN_2{}^+Cl^- + Ph_3P + H_2O \longrightarrow$$
$$ArH + Ph_3P{=}O + HCl \quad (4)$$
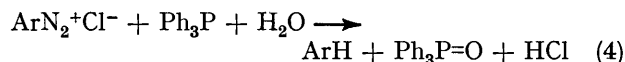
these findings, our phosphonium salt (VII) with water gave m-dinitrobenzene and triphenylphosphine oxide [equation (3)].

The reactions of triphenylphosphine are frequently paralleled by those of trialkyl phosphites. A number of the reactions detailed in the Table were repeated with the appropriate trialkyl phosphite in place of triphenyl-

phosphine; in all cases good yields of the alkyl aryl sulphide (I) were obtained. Thus, tri-isopropyl phosphite, with phenyl and with p-nitrophenyl thiocyanate and propan-2-ol, gave 88 and 85% yields, respectively, of the aryl isopropyl sulphide according to equation (5).

$$ArSCN + ROH + (RO)_3P \longrightarrow$$
$$ArSR + (RO)_3P{=}O + HCN \quad (5)$$
$$\text{(I)}$$
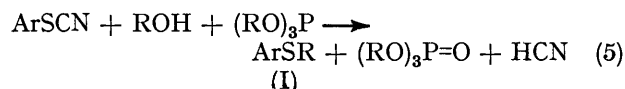
More interestingly, heating p-dimethylaminophenyl thiocyanate with an equimolar quantity of trialkyl phosphite in methanol, in ethanol, and in propan-2-ol gave 91, 90, and 89% yields, respectively, of alkyl aryl sulphide (I), thus vastly improving the yields obtained when triphenylphosphine was employed. The different electronic effects of alkoxy and phenyl groups and the increased opportunities for hydrogen bonding of the former may well make it more difficult for deprotonation of the polyalkoxy-intermediate (V; X = OR) than the triphenyl intermediate (V; X = Ph) by the p-dimethylaminophenylthio-residue, and hence may give an increased opportunity for deprotonation by cyanide ion.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 instrument, [1]H n.m.r. spectra on Perkin-Elmer R20A or Varian HA100 spectrometer, and mass spectra on an A.E.I. MS902 spectrometer. All the known compounds gave satisfactory analytical and spectroscopic data. For products marked with an asterisk, further spectral data are available in Supplementary Publication No. SUP 21876 (5 pp.).*

Aryl Thiocyanates.—Most of these were prepared by the interaction of the corresponding diazonium salt and iron(III) thiocyanate according to the procedure of Korezynski and his co-workers.[16] Phenyl thiocyanate was also prepared according to the method of Soderbach,[17] and its p-dimethyl-amino-derivative was obtained by the procedure of reference 18. Those obtained by the diazotisation procedure usually contained a small proportion of isothiocyanate, as indicated by characteristic broad i.r. band at $\nu_{max.}$ 2 090 cm^{-1}. Simple recrystallisation from ethanol served to remove the iso-compound from the solid thiocyanates. The iso-compound was removed from liquid thiocyanates by treating an ethereal solution of the crude product with benzylamine (0.2 mol. equiv.); most of the resultant thiourea was precipitated. The filtered solution was washed successively with dilute hydrochloric acid, sodium carbonate solution, and water. The residue obtained on concentrating the dried (MgSO$_4$) solution was distilled under reduced pressure, to give the isothiocyanate-free product. This procedure gave more satisfactory results than that of Riemschneider,[19] who used aniline to remove the iso-compound but did not separate the thiourea prior to distillation.

* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

[13] See A. Streitwieser, jun., *Chem. Rev.*, 1956, **56**, 585, for compilation of references.

[14] A. J. Parker and N. Kharasch, *J. Amer. Chem. Soc.*, 1960, **82**, 3071.

[15] L. Horner and H. Hoffmann, *Chem. Ber.*, 1958, **91**, 45.

[16] M. A. Korczynski, F. Kniatowna, and F. Kaminski, *Bull. Soc. chim. France*, 1922, **31**, 1179.

[17] E. Soderback, *Acta Chem. Scand.*, 1954, **8**, 1851.

[18] R. Q. Brewster and W. Schroeder, *Org. Synth.*, 1943, Coll. Vol. II, p. 574.

[19] R. Riemschneider, *J. Amer. Chem. Soc.*, 1956, **78**, 841.

Alcohols.—These were AnalaR or good quality reagent grade and were carefully dried by conventional procedures. 2-(Phenylthio)ethanol was prepared by condensation of sodium benzenethiolate with ethylene chlorohydrin.[20]

Interaction of Aryl Thiocyanates and Alcohols in the Presence of Triphenylphosphine or of Trialkyl Phosphites.—General procedure. The aryl thiocyanate (0.2 mol) and triphenylphosphine or trialkyl phosphite (0.2 mol) in the alcohol (100 ml) were heated under reflux (or at 100 °C with higher boiling alcohols) until t.l.c. indicated disappearance of the reactants. All reactions were carried out under nitrogen and the presence of hydrogen cyanide in the effluent gases was indicated by a positive reaction to Methyl Orange–mercury(II) chloride test paper. In the phenyl thiocyanate–triphenylphosphine–propan-1-ol reaction, the liquid condensed in a trap at -78 °C, characteristic i.r. absorption for hydrogen cyanide [$\nu_{max.}$ 4 000m, 3 279s, 2 779w, 2 597w, 2 105m (C≡N), 1 449s, and 1 379s cm^{-1}]; bands attributable to cyanogen were absent. At the end of the reaction, the excess of alcohol was removed under reduced pressure and the products were separated by one of the two following procedures.

(a) The crude product was taken up in the minimum volume (*ca.* 300 ml) of boiling light petroleum (b.p. 60—80 °C); on cooling the bulk of the phosphine oxide (m.p. and mixed m.p. 153—155 °C) separated, and was removed. Concentration of the filtrate to *ca.* 100 ml gave a second but much smaller crop of the oxide, and the alkyl aryl sulphide was obtained by vacuum distillation of the concentrated filtrate.

(b) The alcohol-free residue was chromatographed on silica gel (80—200 mesh; 80 × 3 cm). Elution with light petroleum (b.p. 60—80 °C) served to remove benzenethiols; the same solvent, sometimes in conjunction with toluene gave a satisfactory separation of alkyl aryl sulphide from diaryl disulphide. Finally triphenylphosphine oxide or trialkyl phosphate was removed by chloroform or chloroform–toluene (1 : 1). The following new alkyl aryl sulphides were prepared: *ethyl* p-*dimethylaminophenyl sulphide,** τ (CDCl$_3$) 2.75 (2 H, d, aromatic *ortho* to SR, *J* 9 Hz), 3.50 (2 H, d, aromatic *ortho* to NMe$_2$, *J* 9 Hz), 7.20 (6 H, s, NMe$_2$), 7.32 (2 H, q, S·CH$_2$·CH$_3$, *J* 6.6 Hz), and 8.82 (3 H, t, S·CH$_2$·CH$_3$, *J* 6.6 Hz), *m/e* 181 (M^+, 73%), 152 (C$_8$H$_{10}$NS$^+$, 100), 136 (C$_7$H$_6$NS$^+$, 15), 120 (C$_8$H$_{10}$N$^+$, 3), and 91 (C$_6$H$_5$N$^+$, 4); p-*dimethylaminophenyl isopropyl sulphide,** τ (CDCl$_3$) 2.65 (2 H, d, aromatic *ortho* to SR, *J* 9 Hz), 3.45 (2 H, d, aromatic *ortho* to NMe$_2$, *J* 9 Hz), 7.0 (1 H, septet, SCHMe$_2$, *J* 6.0 Hz), 7.20 (6 H, s, NMe$_2$), and 8.70 (6 H, d, S·CHMe$_2$, *J* 6.0 Hz), *m/e* 195 (M^+, 50%), 152 (C$_8$H$_{10}$NS$^+$, 100), 136 (C$_7$H$_6$NS$^+$, 12), 120 (C$_8$H$_{10}$N$^+$, 20), 91 (C$_6$H$_5$N$^+$, 13), and 43 (C$_3$H$_7^+$, 73); *allyl* p-*dimethylaminophenyl sulphide,** τ (CDCl$_3$) 2.75 (2 H, d, aromatic *ortho* to SR, *J* 9 Hz), 3.50 (2 H, d, aromatic *ortho* to NMe$_2$, *J* 9 Hz), 4.20 (H$_A$), 5.07 (H$_B$), and 5.15 (H$_C$) (each 1 H, m, H$_A$C:CH$_B$H$_C$ with H$_A$ and H$_C$ *trans*; J_{AB} 9, J_{BC} 1.5, J_{AC} 16 Hz), 6.70 (2 H, d, S·CH$_2$·CH:CH$_2$, *J* 7 Hz), and 7.20 (6 H, s, NMe$_2$), *m/e* 193 (M^+, 31%), 152 (C$_8$H$_{10}$NS$^+$, 100), 136 (C$_7$H$_6$NS$^+$, 13), 120 (C$_8$H$_{10}$N$^+$, 7), and 91 (C$_6$H$_5$N$^+$, 6%). These are pale yellow liquids which decompose on attempted distillation *in vacuo* and which rapidly turn dark. *Benzyl* p-*dimethylaminophenyl sulphide* * formed white needles,

m.p. 92—93 °C [from light petroleum (b.p. 60—80 °C) (Found: C, 73.8; H, 7.1; N, 5.9; S, 13.4. C$_{15}$H$_{17}$NS requires C, 74.0; H, 7.1; N, 5.8; S, 13.2%), τ (CDCl$_3$) 2.85 (2 H, d, aromatic *ortho* to SR, *J* 9 Hz), 2.87 (5 H, m, Ph), 3.50 (2 H, d, aromatic *ortho* to NMe$_2$, *J* 9 Hz), 6.12 (2 H, s, S·CH$_2$Ph), and 7.15 (6 H, s, NMe$_2$), *m/e* 243 (M^+, 39%), 152 (C$_8$H$_{10}$NS$^+$, 100), 136 (C$_7$N$_6$NS$^+$, 12), 120 (C$_8$H$_{10}$N$^+$, 2), and 91 (C$_6$H$_5$N$^+$ or C$_7$H$_7^+$, 17).

In the reaction with phenyl thiocyanate, triphenylphosphine, and t-butyl alcohol, the effluent gases were passed through a sodium hydroxide scrubber to remove hydrogen cyanide and then condensed in a bath at -120 °C (n-pentane–liquid nitrogen). The material in the trap was transferred to a gas cell; its i.r. spectrum showed characteristic bands for isobutene ($\nu_{max.}$ 2 941s, 1 786m, 1 667m, 1 460s, 1 380, 907m, 897s, and 877m cm^{-1}).

Reactions in the Presence of 1-Chloro-2,4-dinitrobenzene.—These were carried out as in the general procedure except that 1-chloro-2,4-dinitrobenzene (0.02 mol) was included. Work-up by the chromatographic procedure enabled the unsymmetrical diaryl sulphides to be isolated by elution with light petroleum (b.p. 60—80 °C)–toluene (7 : 3); phenyl thiocyanate, triphenylphosphine, and 1-chloro-2,4-dinitrobenzene with propyl and isopropyl alcohols provided 2,4-dinitrophenyl phenyl sulphide, m.p. 119—121 °C (from ethanol) (lit.,[21] 121 °C) (56 and 31%, respectively). There also resulted diphenyl disulphide (23 and 45%, respectively), m.p. 58—60 °C (from ethanol) (lit.,[22] 62.5—63.5° C) and unchanged phenyl thiocyanate (18 and 11%, respectively) was recovered by elution with light petroleum–toluene (9 : 1). Yields of triphenylphosphine oxide were 76 and 79%, respectively. When p-dimethylaminophenyl thiocyanate was substituted for the simple phenyl derivative in the propan-1-ol reaction, p-dimethylaminophenyl 2,4-dinitrophenyl sulphide (70%), m.p. 175—176 °C (lit.,[23] 175—176 °C) separated from the cool mixture. More (*ca.* 1%) of this material was isolated by chromatography of the residue, which also gave triphenylphosphine oxide (72%) and unchanged thiocyanate (20%).

1-Chloro-2,4-dinitrobenzene and Triphenylphosphine.—The chlorodinitro-compound (8.1 g, 0.04 mol) and triphenylphosphine (10.48 g, 0.04 mol) were stirred in dry ether (200 ml) at 18—24 °C for 12 h. The yellow solid (4.27 g, 23%) was separated, washed with a little ether, and identified as 2,4-*dinitrophenyl*(*triphenyl*)*phosphonium chloride,** m.p. 205—207 °C (decomp.), $\nu_{max.}$ 2 900m, 1 605m, 1 590m,
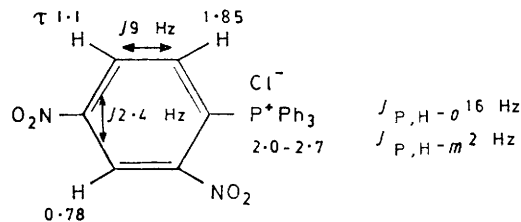
1 585s, 1 482m, 1 450s, 1 350s, 1 190w, 1 160w, 1 125w, 1 100s, 995m, 960m, 915w, 870w, 860w, 831s, 760s, 748s, 740s, 715s, 700m, 690s, and 682s cm^{-1} (see diagram for n.m.r. data), and the ether filtrate was evaporated to give an involatile red oil, $\nu_{max.}$ 3 521m, 3 448m, 3 080s, 1 724m,

[20] A. H. Ford-Moore, R. A. Peters, and R. W. Wakelin, *J. Chem. Soc.,* 1949, 1754.
[21] R. W. Bost, J. O. Turner, and R. D. Norton, *J. Amer. Chem. Soc.,* 1932, **54,** 1986.

[22] E. Campaigne, J. Tsurugi, and W. W. Meyer, *J. Org. Chem.,* 1961, **26,** 2486.
[23] C. M. Buess and N. Kharasch, *J. Amer. Chem. Soc.,* 1950, **72.** 3529.

1 526s, 1 439m, 1 342s, 1 104s, 733s, 714s, and 693s cm⁻¹. The phosphonium salt (3 g) was heated under reflux with water (50 ml) for 20 min. Steam distillation gave *m*-dinitrobenzene (0.9 g, 83%), m.p. and mixed m.p. 87—89 °C, in the distillate. The non-volatile residue was extracted with chloroform (3 × 40 ml); evaporation of the dried (Na$_2$SO$_4$) extract provided triphenylphosphine oxide (1.49 g, 84%), identical (mixed m.p. and i.r. spectra) with authentic material.