

A Kinetic Template Effect in the Metal Ion-catalysed Reactions of *o*-Bromodiarylazo Compounds with Tertiary Phosphines. ¹³C N.m.r. and X-Ray Structural Studies of *o*-Phosphoniodiarylazo Derivatives.

David W. Allen,* Ian W. Nowell, and Lorraine A. March

Department of Chemistry, Sheffield City Polytechnic, Pond Street, Sheffield, S1 1WB

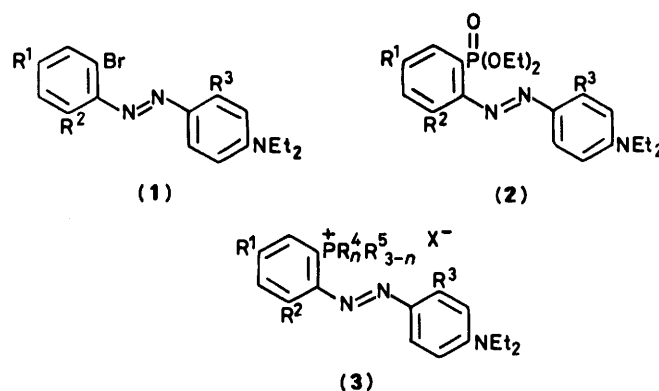
Brian F. Taylor

Department of Chemistry, The University, Brook Hill, Sheffield, S3 7HF

o-Bromodiarylazo compounds react with tertiary phosphines in the presence of either nickel(II) bromide or copper(II) acetate in refluxing ethanol to give the related *o*-phosphoniodiarylazo compounds in good yield. The phosphonium derivatives are also formed in the reactions of the *o*-bromodiarylazo compounds with either [Ni(Ph₃P)₃]Br or [Cu(Ph₃P)_nOAc] (*n* = 2 or 3). The possible involvement of co-ordination-template assisted electron-transfer processes in the reactions is discussed. ¹³C N.m.r. data for the *o*-phosphoniodiarylazo products are also presented, as is also a single crystal X-ray study of one member of the series. Crystals of tri-*n*-butyl [6-(2-acetyl-amino-4-diethylaminophenylazo)-3-bromo-5-methylphenyl]phosphonium bromide are monoclinic, space group *C2/c*, *a* = 25.695(16), *b* = 10.910(11), *c* = 25.363(15) Å, β = 90.63(5)°, *U* = 7 109.2 Å³. The structure was solved using heavy-atom methods in conjunction with least-squares refinement of diffractometer data, giving a final *R* value of 0.069 for 710 observed reflections [*I*/σ(*I*) ≥ 1.5].

While tertiary phosphines and trialkyl phosphites react readily with most alkyl halides to form phosphonium salts and phosphonate esters respectively, the corresponding reactions with aryl halides normally only proceed at elevated temperatures (150–200 °C) in the presence of a transition-metal salt, e.g. Co^{II}Br₂, Ni^{II}Br₂ or Cu^{II}Br₂. These reactions are usually carried out in the absence of a solvent, although reactions leading to arylphosphonium salts have also been carried out in refluxing benzonitrile (b.p. 190 °C).^{1–5} Reactions leading to the formation of arylphosphorus compounds under mild conditions compatible with the presence of sensitive functional groups are, therefore, of some potential interest. Price *et al.* have shown that *o*-bromodiarylazo dyestuffs, e.g. (1; R¹ = H or Br; R² = H or Me; R³ = H or NHAc), react readily with triethyl phosphite in refluxing ethanol in the presence of copper(II) acetate to form the related phosphonate esters (2) in good yield.⁶ The reactions were found to be completely regioselective in that where the diarylazo compound contains two bromine atoms, e.g. (1; R¹ = Br), only the bromine *ortho* to the azo group is replaced by a diethylphosphonate group. The mechanism of these reactions has been studied in detail and found to be rather complex.⁷ The observation that the ethyl group lost from triethyl phosphite is isolated as ethyl acetate and that the bromine displaced from the dyestuff is isolated as [Cu{P(OEt)₃}Br] has led to the proposal of a mechanism involving a concerted nucleophilic attack initially by acetate ion on the co-ordinated phosphite, forming [(RO)₂P = O → Cu], followed by formation of the aryl-phosphorus bond and displacement of the halogen into the co-ordination sphere of copper(I). In related work, Price *et al.*⁸ have also shown that the phosphonate esters (2) are formed in the reactions of the *o*-bromodiarylazo dyestuffs (1) with diethyl phosphite in the presence of copper(I) iodide and sodium acetate in ethanol. We have now investigated the possibility of similar reactions involving tertiary phosphine nucleophiles which would lead to the arylazophosphonium salts (3). A preliminary report of this work has appeared.⁹

When the dyestuffs (1; R¹ = Br; R² = H or Me; R³ = H or NHAc) are heated under reflux in ethanol with a range of tertiary phosphines (2 mol equiv.) in the presence of copper(II) acetate (0.1 mol equiv.) or nickel(II) bromide (0.1 mol equiv.),



the diarylazophosphonium salts [3; R¹ = Br; R² = H or Me; R³ = H or NHAc; R⁴ = Bu, Ph, 2-thienyl or 2-furyl (*n* = 3); and R⁴ = Ph (*n* = 2) R⁵ = benzyl; X = Br] are formed in good yield in clean reactions. The latter all take place with complete regioselective replacement of the halogen *ortho* to the azo group in (1). The *para*-halogen is not affected. The reactions do not occur in the absence of the metal salt catalyst. The rate of the reactions increases as the concentration of the catalyst increases. Other metal salts, e.g. Fe^{II}Cl₂, Cu^{II}Br₂, Ni^{II} acetate and K₂PdBr₄ fail to catalyse the reactions. In the presence of cobalt(II) bromide, however, the reactions take place but at a very slow rate compared with those catalysed by nickel(II) bromide or copper(II) acetate. The nickel(II)-catalysed reactions also proceed at a much reduced rate if the solvent is changed from ethanol to THF or chloroform. Likewise, the copper(II) catalysed reactions also proceed slowly in chloroform. However, in THF no reaction occurs.

Proof of structure of the phosphonium salts (3) rests on (i) elemental analysis (ii) ¹H, ³¹P, and ¹³C n.m.r. spectroscopy, and (iii) the results of an X-ray crystallographic study of the salt (3; R¹ = Br; R² = Me; R³ = NHAc; R⁴ = Bu, *n* = 3; X = Br).

Experimental

¹³C N.m.r. spectra were recorded on JEOL PFT-100 and Bruker WH-400 spectrometers at 25.15 MHz and 100.6

MHz respectively. ^1H N.m.r. spectra were recorded at 80.13 MHz on a Bruker WP-80SY spectrometer. Chemical shifts are reported on the δ scale with respect to tetramethylsilane (5% w/v) as internal standard in deuteriochloroform solution. Coupling constants are reported in Hz and are accurate to ± 0.73 Hz. ^{31}P N.m.r. spectra were recorded at 40.48 MHz on a JEOL PFT-100 spectrometer. Chemical shifts are recorded with respect to 85% orthophosphoric acid as external standard, and are accurate to ± 0.1 p.p.m.; shifts to highfield are negative in sign.

General Procedure for Formation of *o*-Phosphoniodiarylozo Derivatives.—The *o*-bromodiarylozo dyestuff (10^{-3} mol), tertiary phosphine (2×10^{-3} mol) and either anhydrous nickel(II) bromide (0.1 mol equiv.) or hydrated copper(II) acetate (0.1 mol equiv.) were heated together under reflux in ethanol (10 cm^3) in a nitrogen atmosphere for 5–8 h, until the parent dyestuff was completely converted into the purple phosphonium derivative (t.l.c. Kieselgel, CHCl_3 –HOAc 80:20 as eluant). The reaction mixture was then poured into water (50 cm^3), and extracted with chloroform ($3 \times 5\text{ cm}^3$). The chloroform layer was dried (MgSO_4) and evaporated. The oily residue was triturated several times with dry ether until solid. The phosphonium salt was then recrystallised from chloroform-ethyl acetate (except as stated otherwise). The following salts were characterised (^{31}P and ^{13}C n.m.r. data are presented in Tables 1 and 2). *Tri-n-butyl*[3-bromo-6-(4-diethylaminophenylazo)-5-methylphenyl]phosphonium bromide (67% yield), m.p. 149–50 °C (Found: C, 55.4; H, 7.35. $\text{C}_{29}\text{H}_{46}\text{Br}_2\text{N}_3\text{P}$ requires C, 55.5; H, 7.40%; δ 7.8–6.5 (6 H, m), 3.5 (4 H, q), 2.8 (6 H, m), 2.45 (3 H, s), and 1.7–0.5 (27 H, m).

Triphenyl[3-bromo-6-(4-diethylaminophenylazo)-5-methylphenyl]phosphonium bromide (84%), m.p. 145 °C (ex. H_2O) (Found: C, 58.5; H, 5.20; N, 5.50. $\text{C}_{35}\text{H}_{34}\text{Br}_2\text{N}_3\text{P}\cdot\text{H}_2\text{O}$ requires C, 59.5; H, 5.15; N, 5.95%; δ 8.0–6.0 (21 H, m), 3.4 (4 H, q), 2.7 (3 H, s), and 1.15 (6 H, t).

Treatment of an aqueous solution of the salt with aqueous lithium perchlorate gave the corresponding phosphonium perchlorate, m.p. 131 °C (ex. H_2O) (Found: C, 58.2; H, 4.9; N, 5.5. $\text{C}_{35}\text{H}_{34}\text{BrClN}_3\text{O}_4\text{P}\cdot\text{H}_2\text{O}$ requires C, 57.95; H, 5.00; N, 5.80%).

Tri-n-butyl[6-(2-acetyl-amino-4-diethylaminophenylazo)-3-bromo-5-methylphenyl]phosphonium bromide (70%), m.p. 182–183 °C (Found: C, 54.5; H, 7.1. $\text{C}_{31}\text{H}_{49}\text{Br}_2\text{N}_4\text{OP}$ requires C, 54.35; H, 7.20%; δ 8.0–6.0 (5 ArH, m), 3.5 (4 H, q), 2.9 (6 H, m), 2.5 (3 H, s), 2.2 (3 H, s), and 1.8–0.6 (27 H, m).

Triphenyl[6-(2-acetyl-amino-4-diethylaminophenylazo)-3-bromo-5-methylphenyl]phosphonium bromide (78%), m.p. 261–262 °C (Found: C, 59.75; H, 5.05. $\text{C}_{37}\text{H}_{37}\text{Br}_2\text{N}_4\text{OP}$ requires C, 59.65; H, 5.00%; δ 7.9–6.7, (18 H, m), 5.9 (2 H, br s), 3.35 (4 H, q), 2.70 (3 H, s), 2.2 (3 H, s), and 1.15 (6 H, t).

Tri-n-butyl[3-bromo-6-(4-diethylaminophenylazo)phenyl]phosphonium bromide (80%), m.p. 199–200 °C (Found: C, 54.25; H, 7.15; N, 6.55. $\text{C}_{28}\text{H}_{44}\text{Br}_2\text{N}_3\text{P}$ requires C, 54.8; H, 7.25; N, 6.85%; δ 8.2–6.6 (7 H, m), 3.55 (4 H, q), 3.0 (6 H, m), and 2.0–0.3 (27 H, m).

Triphenyl[3-bromo-6-(4-diethylaminophenylazo)phenyl]phosphonium bromide (70%), m.p. 278–280 °C (Found: C, 59.85; H, 4.8; N, 6.05. $\text{C}_{34}\text{H}_{32}\text{Br}_2\text{N}_3\text{P}$ requires C, 60.6; H, 4.80; N, 6.25%; δ 8.5–6.1 (22 H, m), 3.4 (4 H, q), and 1.2 (6 H, t).

Tri-n-butyl[6-(2-acetyl-amino-4-diethylaminophenylazo)-3-bromophenyl]phosphonium bromide (66%), m.p. 258–260 °C (Found: C, 53.4; H, 7.0; N, 8.20. $\text{C}_{30}\text{H}_{47}\text{Br}_2\text{N}_4\text{OP}$ requires C, 53.7; H, 7.05; N, 8.35%; δ 8.4–6.3 (6 H, m), 3.55 (4 H, q), 3.1 (6 H, m), 2.3 (3 H, s), and 2.0–0.4 (27 H, m).

Triphenyl[6-(2-acetyl-amino-4-diethylaminophenylazo)-3-bromophenyl]phosphonium bromide (78%), m.p. >300 °C (decomp.) (ex. $\text{EtOH}\cdot\text{H}_2\text{O}$) (Found: C, 58.5; H, 4.8; N, 7.45.

$\text{C}_{36}\text{H}_{35}\text{Br}_2\text{N}_4\text{OP}$ requires C, 59.15; H, 4.85; N, 7.65%; δ 8.5–7.0 (19 H, m), 6.0 (2 H, m), 3.4 (4 H, q), 2.4 (3 H, s), and 1.2 (6 H, t).

Benzyl(diphenyl)[3-bromo-6-(4-diethylaminophenylazo)phenyl]phosphonium bromide (86%), m.p. 240 °C (Found: C, 61.1; H, 4.95; N, 6.1. $\text{C}_{35}\text{H}_{34}\text{Br}_2\text{N}_3\text{P}$ requires C, 61.15; H, 5.00; N, 6.10%; δ 8.2–6.3 (22 H, m), 5.35 (2 H, d, $^2J_{\text{PCH}}$ 15.8 Hz), 3.5 (4 H, q), and 1.25 (6 H, t).

[3-Bromo-6-(4-diethylaminophenylazo)phenyl]tri-2-thienylphosphonium bromide (78%), m.p. 269–270 °C (Found: C, 48.85; H, 3.8; N, 6.0. $\text{C}_{28}\text{H}_{26}\text{Br}_2\text{N}_3\text{PS}_3$ requires C, 48.60; H, 3.80; N, 6.05%; δ 8.5–6.3 (22 H, m), 3.5 (4 H, q), and 1.25 (6 H, t).

Tri-2-furyl[3-bromo-6-(4-diethylaminophenylazo)phosphonium bromide (53%), m.p. >235 °C (decomp.) (Found: C, 51.3; H, 4.25; N, 6.35. $\text{C}_{28}\text{H}_{26}\text{Br}_2\text{N}_3\text{O}_3\text{P}$ requires C, 52.2; H, 4.07; N, 6.5%; δ 8.4–6.5 (22 H, m), 3.5 (4 H, q), and 1.25 (6 H, t).

^{13}C N.m.r. Data.—The ^{13}C n.m.r. chemical shifts of the aryl carbons of the parent dyes and phosphonium salts are reported in Table 1. Signals were assigned using the standard techniques of off-centre double resonance, substitution, e.g. $\text{R}^1 = \text{H}$ or Me and substitution parameters.¹⁰ To assist in the assignment, the ^{13}C spectra of the salts $[\text{PPh}_4]\text{Br}$ and $[\text{PhPBu}_3]\text{Br}$ were also recorded. Chemical shifts of $\text{Bu}^n\text{-P}^+$ and Ph-P^+ plus those of the remaining carbons in the dyestuffs are reported in Table 2.

Ring A. With one exception [compound (10)] all the signals are sharp and exhibit phosphorus coupling. As found in *o*-tolylphosphines,¹¹ the substituent *ortho* to the phosphorus has a marked effect on the value of $^2J_{\text{PC}}$, i.e. $^2J_{\text{PC}} = 2\text{--}3$ Hz, $^2J_{\text{P}^+\text{C}} = 7\text{--}12$ Hz.

Ring B. In a number of cases the signals of the carbons *ortho* to the azo-group are broad. There appears to be no set pattern for the broadening although it usually occurs with triphenylphosphonium, trifurylphosphonium, triethienylphosphonium, and diphenyl(benzyl)phosphonium salts and in three cases amide substituents. However, not all amide compounds or triphenylphosphonium salts exhibit broadening.

Probably there is some form of restricted rotation in these dyestuffs, the restriction depending on phosphine bulk and relative orientation of the amide group, but how this would explain the broadening of C-2 in compound (10) is not obvious.

X-Ray Structural Study of *Tri-n-butyl*[6-(2-acetyl-amino-4-diethylaminophenylazo)-3-bromo-5-methylphenyl]phosphonium bromide.—Crystal data. $\text{C}_{31}\text{H}_{49}\text{Br}_2\text{N}_4\text{OP}$, $M_r = 684.51$, Monoclinic, space group $C2/c$, $a = 25.695(16)$, $b = 10.910(11)$, $c = 25.363(15)$, $\beta = 90.63(5)^\circ$, $U = 7109.2\text{ \AA}^3$, $\text{Mo-K}\alpha \lambda = 0.71069\text{ \AA}$, $D_m = 1.27$, $D_c = 1.28\text{ g cm}^{-3}$, $Z = 8$, $\mu(\text{Mo-K}\alpha) = 2.28\text{ mm}^{-1}$, $F(000) = 2848$.

X-Ray intensity measurements. Crystal quality was poor and great difficulty was found in selecting a crystal suitable for data collection. Eventually a crystal of approximate dimensions (distances to faces from centre) $0.05(100, \bar{1}00) \times 0.06(001, 00\bar{1}) \times 0.17\text{ mm}(010, 0\bar{1}0)$ was mounted with the b axis coincident with the ω axis of a Stöe Stadi 2 two-circle diffractometer. Data were collected using monochromated $\text{Mo-K}\alpha$ radiation and the background- ω scan-background technique. Corrections for Lorentz and polarisation effects were applied but no corrections for absorption were made. The crystal was found to be weakly diffracting and of 331 unique reflections collected only 710 had $I/\sigma(I) \geq 1.5$ and these were used in the subsequent structure analysis.

Structure determination and refinement. Interpretation of a three-dimensional Patterson map readily afforded the positions of the two bromine atoms in the asymmetric unit. The remaining non-hydrogen atoms were located from successive electron-density maps. The poor quality of the data prevented satisfactory location of the hydrogen atoms and only the

Table 1. N.m.r. data for aryl carbons and ^{31}P chemical shifts for phosphonium salts*

Compd.	R ¹	R ²	R ³	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C-12	$\delta(^{31}\text{P})$
(1)	H	Br	H	149.1 ^a	122.7 ^b	135.5	124.9 ^b	131.0	118.7	143.2	126.1	110.9	150.6 ^a			
(2)		Br	NHAc	151.7 ^a	122.0 ^b	135.3	123.0 ^b	131.1	118.5	130.4 ^c	135.3 ^c	100.9	148.8 ^a	106.5	136.0 [†]	
(3)		PPh ₃ ⁺	H	154.4	117.6	137.7	122.8	139.9	118.8	142.2	127.4 [†]	111.2	152.3			23.1
(4)		PPh ₃ ⁺	NHAc	153.6	118.0	137.4	122.0	140.7	119.9	131.6 ^d	142.0 ^d	100.8	154.0	108.1	118.3	22.9
(5)		PBu ₃ ⁺	H	154.2	117.7	134.9	122.8	138.2	118.4	142.6	127.3 [†]	111.8	152.2			32.4
(6)		PBu ₃ ⁺	NHAc	154.5	117.1	134.9	122.0	138.6	118.3	142.2	142.1	100.6	154.1	109.2	131.3	32.2
(7)	Me	Br	H	150.3 ^a	117.7 ^b	133.0 ^e	119.4 ^b	133.0 ^e	132.6	142.7	125.5	110.7	150.7 ^a			
(8)		Br	NHAc	148.8 ^a	118.5 ^b	133.3 ^e	119.7 ^b	133.7 ^e	133.2	130.3 ^b	136.8 ^b	100.6	151.8 ^a	106.4	129.6 [†]	25.0
(9)		PPh ₃ ⁺	H	151.6	111.6	137.1	122.0	142.2	138.3	141.0	126.0	111.0	152.0			
(10)		PPh ₃ ⁺	NHAc	152.1	114.6 [†]	136.7	120.9	142.8	142.8	131.1 ^a	140.2 ^a	100.5	153.7	107.8	120.6 [†]	24.0
(11)		PBu ₃ ⁺	H	153.8	116.5	138.3	120.8	141.3	133.3	142.3	126.4	111.6	152.1			32.3
(12)		PBu ₃ ⁺	NHAc	153.8	117.6	133.2	120.2	141.6	131.4	141.6	141.6	100.2	154.1	109.0	131.0	32.1
(13)	H	P(2-Furyl) ₃ ⁺	H	154.3	113.5	136.6	122.5	140.7	120.2	142.0	127.6 [†]	111.8	152.7			-18.8
(14)	H	P(2-Th) ₃ ⁺	H	153.4	120.7	136.1	122.5	140.1	118.6	142.5	128.2 [†]	111.6	152.6			2.0
(15)	H	PPh ₂ (CH ₂ Ph) ⁺	H	154.0	117.8	137.7	122.7	139.4	118.6	142.9	127.4 [†]	111.7	152.4			22.8

* Superscript letters: assignments interchangeable. The numbering of the carbon atoms differs from the crystallographic numbering and the systematic numbering for these compounds. † Signal broad at ambient. ‡ Obscured by other signals; ^{31}P — ^{13}C coupling constants in parentheses.

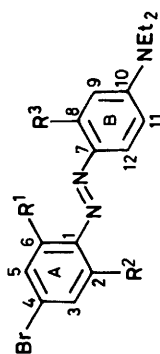


Table 2. ¹³C N.m.r. data for side-chain substituents (p.p.m.)

N(CH ₂ CH ₃) ₂	44.8—45.6
N(CH ₂ CH ₃) ₂	12.6—12.8
NHCOCH ₃	25.4—26.2
NHCOCH ₃	168.3—170.5
[P(C ¹ H ₂ C ² H ₂ C ³ H ₂ C ⁴ H ₃) ₃] ⁺	C-1 22.0—22.2 (50)
	C-2 24.5 (5)
	C-3 28.3 (17)
	C-4 13.4—13.6
[P(C ₆ H ₅) ₃] ⁺	C-1 119.4—121.5 (92)
	C-2,6 133.4—133.7 (10)
	C-3,5 130.3 (13)
	C-4 134.3—135.1 (3)
CH ₃ -Aryl	18.6—21.4
[P(2-Thienyl) ₃] ⁺	C-1 119.5 (118)
	C-2 147.0 (12)
	C-3 130.4 (17)
	C-4 140.9 (6)
[P(2-Furyl) ₃] ⁺	C-1 132.3 (52) C-2 113.7 (11)
	C-3 130.1 (24) C-4 153.3 (9)
[PPh ₂ (CH ₂ Ph)] ⁺	Phenyl C-1 119.0 (87)
	C-2 133.8 (10)
	C-3 130.0 (12)
	C-4 131.1 (6)
	Benzyl CH ₂ 33.3 (48)
	128.1 (9) 128.5 (5)
	128.9 (4) 134.5 (3)

Table 3. Final fractional co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses.

Atom	x	y	z
Br(1)	2 905(2)	4 608(5)	3 140(1)
Br(2)	1 280(2)	2 734(5)	5 110(1)
P	2 449(4)	504(14)	3 508(3)
N(1)	2 904(8)	-908(23)	4 371(7)
N(2)	3 317(9)	-983(26)	4 616(8)
N(3)	4 783(13)	-4 574(40)	3 995(12)
N(4)	4 254(91)	-1 080(28)	5 093(9)
O	5 043(10)	-1 551(31)	5 391(9)
C(1)	1 787(11)	1 639(31)	4 898(11)
C(2)	2 064(10)	986(31)	5 287(9)
C(3)	2 447(11)	134(31)	5 113(9)
C(4)	2 566(9)	39(27)	4 555(8)
C(5)	2 309(10)	826(28)	4 201(8)
C(6)	1 928(9)	1 642(29)	4 391(9)
C(7)	2 716(11)	-697(36)	5 542(11)
C(8)	4 688(14)	-985(37)	5 426(12)
C(9)	4 625(13)	134(40)	5 816(13)
C(11)	3 665(11)	-1 898(33)	4 471(10)
C(12)	3 543(12)	-2 822(37)	4 047(12)
C(13)	3 907(13)	-3 691(36)	3 917(11)
C(14)	4 399(13)	-3 726(37)	4 167(12)
C(15)	4 535(12)	-2 779(37)	4 548(11)
C(16)	4 164(12)	-1 911(34)	4 682(10)
C(141)	4 564(16)	-5 710(51)	3 722(17)
C(142)	4 633(16)	-5 431(50)	3 113(17)
C(143)	5 454(15)	-4 264(47)	4 019(15)
C(144)	5 456(23)	-5 095(62)	4 433(23)
C(21)	2 141(13)	1 748(39)	3 111(13)
C(22)	1 535(13)	1 389(41)	3 033(13)
C(23)	1 318(18)	2 678(50)	2 730(18)
C(24)	730(27)	2 673(69)	2 758(25)
C(31)	2 312(13)	-1 035(41)	3 315(12)
C(32)	1 845(14)	-1 413(42)	3 522(13)
C(33)	1 741(28)	-2 645(68)	3 229(28)
C(34)	1 271(22)	-2 995(59)	3 449(22)
C(41)	3 201(15)	1 097(45)	3 479(14)
C(42)	3 345(40)	605(89)	3 147(38)
C(43)	4 036(36)	1 079(78)	3 197(36)
C(44)	4 291(39)	480(85)	3 113(40)

Table 4. Selected bond distances (Å) and angles (°)

Bond distances (Å) E.s.d.'s ca. 0.03 Å			
Br(2)-C(1)	1.85	N(1)-N(2)	1.23
C(1)-C(2)	1.41	N(2)-C(11)	1.39
C(1)-C(6)	1.34	C(11)-C(12)	1.50
C(2)-C(3)	1.43	C(11)-C(16)	1.39
C(3)-C(4)	1.46	C(12)-C(13)	1.38
C(3)-C(7)	1.57	C(13)-C(14)	1.41
C(4)-C(5)	1.40	C(14)-C(15)	1.46
C(4)-N(1)	1.43	C(14)-N(3)	1.42
C(5)-C(6)	1.41	C(15)-C(16)	1.39
C(5)-P	1.83	C(16)-N(4)	1.40
P-C(21)	1.86	N(4)-C(8)	1.40
P-C(31)	1.78	C(8)-O	1.11
P-C(41)	2.04	C(8)-C(9)	1.58
Bond angles (°) E.s.d.'s ca. 2°			
Br(2)-C(1)-C(2)	118	C(31)-P-C(41)	118
Br(2)-C(1)-C(6)	118	C(4)-N(1)-N(2)	114
C(2)-C(1)-C(6)	122	N(1)-N(2)-C(11)	118
C(1)-C(2)-C(3)	117	N(2)-C(11)-C(12)	123
C(2)-C(3)-C(4)	120	N(2)-C(11)-C(16)	120
C(2)-C(3)-C(7)	118	C(12)-C(11)-C(16)	117
C(4)-C(3)-C(7)	122	C(11)-C(12)-C(13)	120
C(3)-C(4)-C(5)	118	C(12)-C(13)-C(14)	121
C(3)-C(4)-N(1)	120	C(13)-C(14)-C(15)	119
C(5)-C(4)-N(1)	121	C(13)-C(14)-N(3)	120
C(4)-C(5)-C(6)	119	C(15)-C(14)-N(3)	120
C(4)-C(5)-P	114	C(14)-C(15)-C(16)	119
C(6)-C(5)-P	126	C(15)-C(16)-C(11)	123
C(1)-C(6)-C(5)	121	C(15)-C(16)-N(4)	121
C(5)-P-C(21)	107	C(11)-C(16)-N(4)	115
C(5)-P-C(31)	114	C(16)-N(4)-C(8)	129
C(5)-P-C(41)	100	N(4)-C(8)-O	124
C(21)-P-C(31)	117	N(4)-C(8)-C(9)	111
C(21)-P-C(41)	98	O-C(8)-C(9)	125

phosphorus and bromine atoms were given anisotropic temperature factors. Scattering factors were calculated using an analytical approximation¹² and the weighting scheme adopted was $w = 0.1562[\sigma^2(F_o) + 0.0358(F_o)^2]$ with $\sigma(F_o)$ from counting statistics. Full-matrix least-squares refinement gave the final $R = 0.069$ and $R' = 0.074$. Final atomic parameters are listed in Table 3, selected bond distances and angles are given in Table 4.

Supplementary data available [No. SUP. 56065 (2 pp.)]: thermal parameters. See Instructions for Authors (1984), Section 4, *J. Chem. Soc., Perkin Trans. I*, 1984, Issue 1. Structure factors available from the editorial office on request.

Discussion of the Structure.—While poor crystal quality precludes a detailed discussion of the structure of the cation, the following features are, nevertheless, noteworthy. Both the azo and the amido groupings are approximately co-planar (Figure) with the C(11)-C(16) ring [the dihedral angles between the C(11)-C(16) mean plane and the C(9), C(8), O, N(4) and C(11), N(2), N(1), C(4) mean planes are 5.0° and 6.70° respectively]. This planarity facilitates hydrogen bonding between the azo and the amido groups. Although hydrogen atoms have not been included in the refinement, a peak is found on the final difference Fourier map which can be attributed to the amido hydrogen and is situated in an ideal position for a significant interaction with N(2). Other features in the geometry would appear to reflect the presence of a strong interaction of this type and, in particular, there is a marked asymmetry in the exocyclic angles at C(16) [C(15)-C(16)-N(4), 121°; C(11)-C(16)-N(4), 115°]. In contrast, the C(1)-C(6) and the C(11)-C(16) rings are not co-planar, the dihedral angle between the two phenyl rings

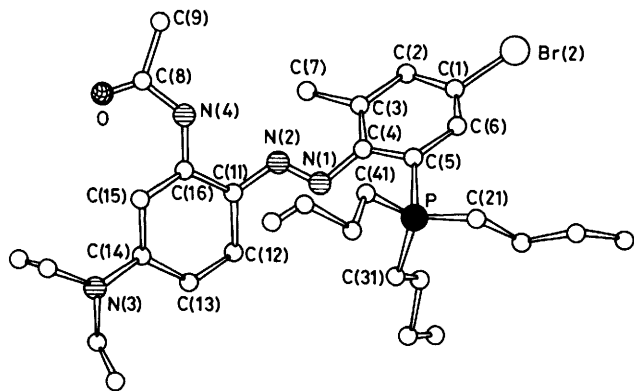


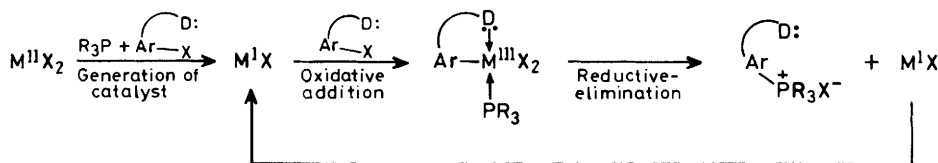
Figure. Structure of phosphonium cation

being 48° . This would appear to reflect an attempt at minimising the interactions between the azo grouping and (i) the methyl group located at C(3), (ii) the butyl chains.

There does not appear to be any significant interactions between the bromide ions and the phosphonium cations, the closest $P^+ \cdots Br^-$ distance being 4.4 \AA .

Discussion of the Mechanism of Phosphonium Salt Formation.—The formation of the above *o*-phosphoniodyarylazo compounds (3) has much in common with the related reactions of *o*-bromodiaryldazo compounds with triethyl phosphite in ethanol, catalysed by copper(II) acetate.⁶ There are, nevertheless, some significant points of difference and it is clear that some very specific co-ordination chemistry is involved. Price *et al.* have shown that in the reactions with triethyl phosphite, only those dyestuffs in which $R^2 \neq H$ undergo the reaction readily, and also that those in which $R^3 = \text{NHAc}$ (or some other potential co-ordinating group) react faster than those in which $R^3 = H$. These reactions are also only catalysed by copper(II) acetate. In the above reactions with phosphines, however, it is not necessary to have a group R^2 other than hydrogen at C(6) and both copper(II) acetate and nickel(II) bromide function as catalysts. Furthermore, whereas dyestuffs in which $R^3 = \text{NHAc}$ react faster with phosphines in the presence of copper(II) acetate than those in which $R^3 = H$, the reverse is the case for the related reactions catalysed by nickel(II) bromide.

It is likely that these reactions involve electron-transfer catalysis¹³ in which the metal is initially reduced to a lower oxidation state, e.g. Ni^I or Cu^I (the active catalytic species), which then undergoes a co-ordination template-assisted oxidative insertion into the carbon–bromine bond, followed by formation of the phosphorus–carbon bond in a reductive-elimination of the product, with regeneration of the catalyst, as in the Scheme.



Scheme.

Reduction of copper(II) to copper(I) by phosphorus(III) compounds is well-known,¹⁴ and Price *et al.* have recently demonstrated that the reaction of trialkyl phosphites with copper(II) acetate in alcohol media leads to the formation of

mixed-valence complexes of the type $[Cu_3(OAc)_5\{(RO)_3P\}_2]$ which involve both Cu^I and Cu^{II} .¹⁵ These complexes have been shown to react with the dyestuffs (1) to form the phosphonates (2) in alcoholic media at room temperature.⁷ The related reduction of nickel(II) to nickel(I) in the absence of an external reducing agent is less well-documented, but it has been shown that nickel(I) complexes are formed in the reactions of certain nickel(II) halides with polydentate phosphines.^{16,17} In addition, it has been shown that the nickel(0) complex $[Ni\{(EtO)_3P\}_4]$ is formed when nickel(II) chloride is heated in triethyl phosphite.¹⁸ Oxidative-addition of aryl halides to nickel(0) and nickel(I) species is now well-established,^{19–21} and so too is the formation of arylphosphonium salts from arylnickel(II) and arylnickel(III) intermediates.^{21,22}

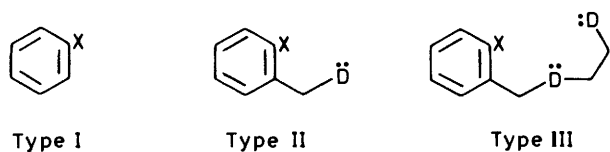
In the light of the reported reactions of the mixed Cu^{II}, Cu^I -phosphite complexes with the dyestuffs (1), we have explored the related reactions of the nickel(I) complex $[Ni(Ph_3P)_3Br]$ (accessible by reduction of $[Ni(Ph_3P)_2Br_2]$ with sodium borohydride in ethanol)²³ and some copper(I) phosphine complexes. When equimolar amounts of the nickel(I) complex and dyestuffs are heated together in ethanol, the phosphonium derivatives (3) are formed rapidly. The reaction proceeds very slowly at room temperature, probably as a result of the insolubility of the nickel(I) complex in ethanol at this temperature. Again it was noted that in these reactions, the phosphonium derivatives are formed more rapidly from the dyestuffs in which $R^3 = H$ compared with those in which $R^3 = \text{NHAc}$. Copper(I) complexes derived from the reaction of triphenylphosphine and copper(II) acetate in alcohol solvents have been known for some time.²⁴ When a solution of copper(II) acetate in ethanol is heated with triphenylphosphine (3–4 mol equiv.), the blue colour of the copper(II) reagent is rapidly discharged, and the resulting solution contains the copper(I) complexes $[Cu(PPh_3)_nOAc]$ ($n = 2$ or 3). Addition of the dyestuffs (1) to such solutions, followed by a period of refluxing also results in formation of the phosphonium derivatives (3) although the rate of conversion is noticeably slower than with the nickel(I) complex. In reactions attempted using copper(II) bromide as the catalyst, no phosphonium salt formation was observed, the highly insoluble phosphine-copper(I) complex $[Cu(Ph_3P)Br]$ being isolated. T.l.c. studies of the reaction mixture indicate that the dyestuffs is converted into a hydrobromide during this process.

The results of these experiments lend some support to the above suggestion of an *in situ* reduction of the metal from the +2 oxidation state, in which intramolecular co-ordination involving an azo nitrogen of the dyestuff plays an important role in stabilising the lower oxidation state, and also in promoting the subsequent reactions leading to phosphonium salt formation.

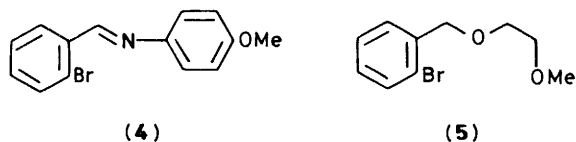
The importance of the availability of an appropriate donor centre in the organic substrate has been explored by Price *et al.*⁶

in the case of the reaction of a range of halogenoaromatic compounds with phosphites in the presence of copper(II) acetate. It has been shown that for these reactions to take place under mild conditions, the aryl halide should have a substituent

in the *ortho* position to the halogen which is able to be involved in intramolecular co-ordination with the metal with the formation of a five or six-membered chelate system. In the phosphonate reactions, Price⁶ has classified aryl halides as being of Type 1, Type 2, or Type 3.



Type 1 halides, not having the desired *ortho*-substituent, are inert in these reactions. The type II halides, having one suitably disposed donor atom are found to undergo the phosphonation reactions slowly, whereas the type III systems, having two appropriate donors, react readily. Thus, *e.g.* whereas the dyestuff (1; R¹ = Br; R² = Me; R³ = H) (a type II halide) only reacts slowly with triethyl phosphite in the presence of copper(II) acetate, the related compound (1; R¹ = Br, R² = Me; R³ = NHAc) (a type III halide) undergoes the reaction at a much faster rate. This state of affairs also seems to apply in the copper(II)-catalysed reactions leading to the phosphonium salts (3), but does not apply in the nickel(II)-catalysed reactions, presumably a reflection of the differing co-ordination preferences of copper and nickel. We have also shown that other type II halides, *e.g.* the Schiff's base (4)⁹ undergo a nickel(II)-catalysed reaction with tertiary phosphines in ethanol to give the related phosphonium salts. However, these reactions do not occur in the presence of copper(II) acetate. The type (III) halide (5), on the other hand, appears to be unreactive when treated with triphenylphosphine in the presence of either nickel(II) bromide or copper(II) acetate.²⁵



In conclusion, it is worth commenting that the above metal-catalysed reactions are clear examples of the rather elusive 'kinetic template effect.' Our studies in this area are continuing in the hope of defining more clearly the factors responsible for the selectivity of such reactions.

Acknowledgements

We thank Dr. R. Price (ICI, Organics Division) for gifts of chemicals and helpful discussions and the S.E.R.C. for an equipment grant (I. W. N.).

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Received 5th March 1984; Paper 4/356