

## Further Studies of the Kinetic Template Effect in the Metal Ion-catalysed Reactions of *ortho*-Donor-substituted Aryl Halides with Tertiary Phosphines. Structural Requirements of the Template

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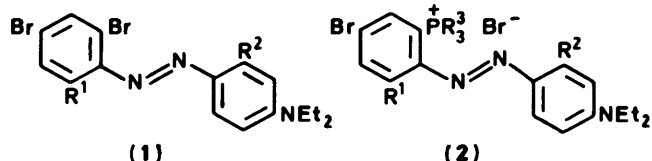
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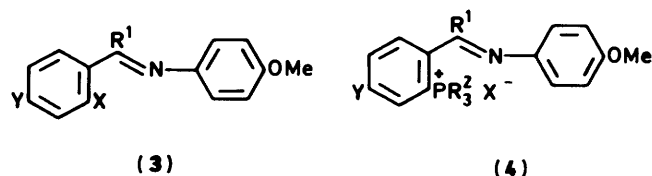
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The reactions of a series of Schiff's bases, derived from *ortho*-chloro-, bromo- or iodo-benzaldehydes and *p*-anisidine, with tertiary phosphines in the presence of nickel(II) bromide in refluxing ethanol proceed with displacement of the *ortho*-halogen to form the related *ortho*-substituted arylphosphonium salts. These reactions appear to be examples of a kinetic template effect in which the Schiff's base moiety aids the catalytic role of the metal ion in promoting the substitution reaction. Introduction of a second donor atom into the substituent group present at the nitrogen of related Schiff's bases inhibits the reactions due to diversion of the metal ion in other modes of coordination. The reactions are also inhibited by steric crowding at the imino-nitrogen. A range of other aryl halides bearing *ortho*-substituents having the potential to act as co-ordination templates has been prepared and their reactions with phosphines in the presence of metal ions studied enabling the rather critical nature of effective template groups to be defined. Detailed  $^{13}\text{C}$  n.m.r. data are also reported for the Schiff's bases and related arylphosphonium salts.

The formation of arylphosphonium salts from the reactions of tertiary phosphines with aryl halides normally only proceeds at elevated temperature (150–200 °C) in the presence of a transition metal salt, e.g. cobalt(II) bromide or nickel(II) bromide, usually in the absence of a solvent.<sup>1–4</sup> In recent work,<sup>5,6</sup> we have shown that when the *o*-bromodiaryldazo dyestuffs (1;  $\text{R}^1 = \text{H}$  or Me,  $\text{R}^2 = \text{H}$  or NHAc) are heated under reflux in ethanol with a range of tertiary phosphines (2 mol equiv.) in the presence of copper(II) acetate or nickel(II) bromide (0.1 mol equiv.), the related diarylazophosphonium salts (2;  $\text{R}^1 = \text{H}$  or Me,  $\text{R}^2 = \text{H}$  or NHAc,  $\text{R}^3 = \text{e.g., Bu, Ph, 2-thienyl}$  or 2-furyl) are formed in good yield. These reactions proceed under mild conditions with complete regiospecific replacement of the halogen *ortho* to the azo group. The *para*-halogen is unaffected. Replacement of the *ortho*-halogen does not occur in the absence of the metal salt catalyst. We have suggested that these reactions involve the operation of a kinetic template effect in which metal ion-promoted replacement of the halogen *ortho* to the azo group is assisted by co-ordination of the metal to an azo nitrogen atom. A related regiospecific replacement under mild conditions occurs in the reaction of triethylphosphite with the dyestuffs (1) in the presence of copper(II) acetate, to give related *o*-diarylazophosphonate ester.<sup>7</sup> The mechanism of these phosphonation reactions has been studied in detail and found to be rather complex.<sup>8</sup>

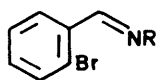


In order to extend our study of the operation of such kinetic template effects in promoting the formation of aryl-phosphorus bonds, we have explored the reactivity towards tertiary phosphines of a range of aryl halides bearing substituents in the *ortho* position which have the potential to co-ordinate to a metal ion catalyst and perhaps to promote facile replacement of the halogen under mild conditions.

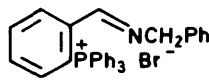


Initial studies<sup>5</sup> centered on a series of Schiff's bases of type (3;  $\text{R}^1 = \text{H}$ ,  $\text{X} = \text{Cl, Br, or I}$ ;  $\text{Y} = \text{H or Cl}$ ) derived from the reactions of halogenobenzaldehydes and *p*-anisidine. On treatment with tributylphosphine or triphenylphosphine (2 mol) in refluxing ethanol in the presence of nickel(II) bromide (0.1 mol), the salts (4) are formed over several hours. Preliminary comparative rate studies using a conductimetric technique indicate that the ease of replacement of the *ortho* halogen is  $\text{I} < \text{Br} < \text{Cl}$ . The related *o*-fluoro Schiff's bases do not undergo the reaction. The isomeric *p*-halocompounds (3;  $\text{R}^1 = \text{H}$ ;  $\text{X} = \text{H}$ ;  $\text{Y} = \text{Cl, Br, or I}$ ) also do not react under these conditions. The dichloro Schiff's base (3;  $\text{R}^1 = \text{H}$ ;  $\text{X} = \text{Y} = \text{Cl}$ ) undergoes a regiospecific replacement of the *ortho*-chlorine to give the salts (4;  $\text{R}^1 = \text{H}$ ;  $\text{R}^2 = \text{Bu or Ph}$ ;  $\text{X} = \text{Y} = \text{Cl}$ ). Unambiguous proof that the *ortho*-chlorine is replaced is provided by alkaline hydrolysis of the tributylphosphonium salt, which proceeds with cleavage from phosphorus of the group most stable as a carbanion<sup>9,10</sup> to give the *para*-chloro Schiff's base (3;  $\text{R}^1 = \text{H}$ ,  $\text{X} = \text{H}$ ;  $\text{Y} = \text{Cl}$ ). The above reactions also proceed in acetonitrile and in methanol, but at a slower rate than in ethanol, and also to some extent in tetrahydrofuran and in chloroform. No reactions occur in the absence of the nickel(II) halide, and as the concentration of this catalyst increases, so does the rate of formation of the phosphonium salt. The reaction of equimolar amounts of preformed bis(phosphine)nickel(II) halide complexes with the *o*-halogeno Schiff's bases leads to a much faster rate of formation of the phosphonium salts. Apart from nickel(II), no other metal ion has been found which significantly catalyses these reactions. In particular, no salt formation was observed when copper(II) acetate was used as the catalyst, in marked contrast to the related reactions of the dyestuffs (1).

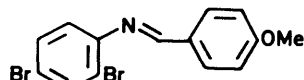
The related Schiff's base (3;  $\text{R}^1 = \text{Me}$ ;  $\text{X} = \text{Br}$ ;  $\text{Y} = \text{H}$ ),



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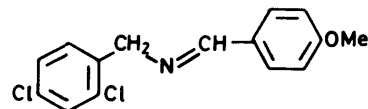


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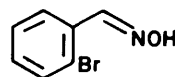


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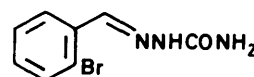
derived from the reaction of *o*-bromoacetophenone with *p*-anisidine in toluene, also undergoes the replacement reaction to give the salts (4; R<sup>1</sup> = Me; R<sup>2</sup> = Ph; X = Br; Y = H), the presence of the methyl group on the azomethine carbon causing no steric effect. However, increased steric crowding at the azomethine nitrogen is found to inhibit the reaction. Thus whereas the Schiff's base (5; R = CH<sub>2</sub>Ph) reacts with triphenylphosphine in the presence of nickel(II) bromide to give the salt (6), the related Schiff's bases [5; R = CH(Me)Ph or Bu<sup>1</sup>] fail to undergo the reaction. Introduction of a second donor site in the imino moiety of the Schiff's base also inhibits the reaction. Thus the Schiff's bases (5; R = CH<sub>2</sub>CH<sub>2</sub>OH, 2-pyridylethyl, 2-benzothiazolyl, or 2-benzimidazolyl) all fail to undergo the substitution reaction on heating with triphenylphosphine in ethanol containing either a catalytic quantity of nickel(II) bromide or in the presence of an equimolar amount of a pre-formed bis(phosphine)nickel(II) halide complex. It would seem that under these conditions, metal ion-promoted hydrolysis of the Schiff's base predominates, to give the aldehyde and free amino compound. These results imply that when the Schiff's base bears a second donor group which is capable of co-ordinating with the metal ion, especially when the formation of a chelate complex is possible, then the metal ion is diverted from its catalytic role. Support for this view is found in the reactions of the *o*-halogenoaryl Schiff's bases (7) and (8), derived from  $\alpha,\omega$ -diamines. These compounds have the potential to form



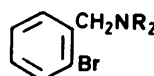
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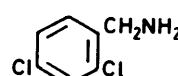
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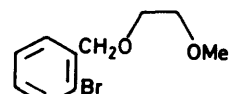
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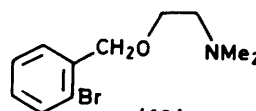
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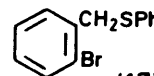
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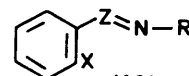
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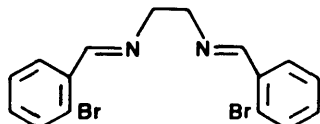
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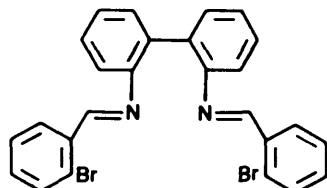
(17)



(18)



(7)



(8)

respectively five- and seven-membered ring chelate complexes with the metal ion, and do not undergo the substitution reaction on treatment with a tertiary phosphine in the presence of nickel(II) bromide. Instead, it is found that these substrates undergo hydrolysis to form 2-bromobenzaldehyde and the respective diamine.

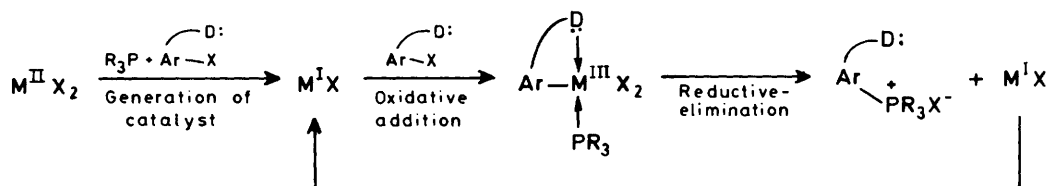
The very critical nature of the donor atom and its position with respect to the *ortho*-halogen for the promotion of a template-assisted replacement reaction is illustrated by studies of the reactivity of a number of related systems. Thus both Schiff's base system (9) and (10) fail to undergo conversion to phosphonium salts, presumably because neither is able to be involved in the appropriate mode of metal co-ordination (*e.g.* the formation of a five-membered ring involving the nitrogen and the *ortho*-halogen) to promote the reactions leading to replacement of the *ortho*-halogen. The oxime (11) and semicarbazone (12) are similarly unreactive.

The *o*-halogenobenzylamines (13; R = H or Me) and (14),

whilst having a nitrogen atom in the same relative position as in the reactive Schiff's bases, also fail to undergo conversion to the related phosphonium salts. Replacement of nitrogen by either oxygen, as in *o*-bromobenzyl alcohol, and the ethers (15) and (16), or by sulphur, as in (17), has no effect in promoting the substitution reactions, these compounds being inert on prolonged reflux in ethanol with triphenylphosphine, in the presence of nickel(II) ion.

Thus it would appear that such metal-ion promoted substitution reactions require a very specific template of type (18; Z = CH or N; R = non-sterically crowded alkyl or aryl). It is of interest to note that the reactions of the diarylazo template systems (1)<sup>6</sup> appear to be much less sensitive to the presence of additional donor centres *e.g.* (1; R<sup>2</sup> = NHCOMe) than those of the Schiff's bases, and also that the reactions of the former are catalysed by both copper(II) acetate and nickel(II) bromide, whereas nickel(II) is required specifically for the reactions of the Schiff's bases. Clearly some very subtle co-ordination chemistry is involved in these reactions. It is highly probable that electron-transfer processes<sup>11</sup> are also involved, in which the metal ion is initially reduced to a lower oxidation state, *e.g.* Ni<sup>I</sup> (the active catalytic species) which then undergoes a co-ordination template-assisted oxidative insertion into the carbon-halogen bond, followed by formation of the phosphorus-carbon bond in a reductive-elimination of the phosphonium salt, with regeneration of the catalyst, as in the Scheme.

Whereas the reduction of copper(II) to copper(I) by phosphorus(III) compounds is well-known,<sup>12</sup> the related reduction of nickel(II) to nickel(I) in the absence of an additional reducing agent is less well-documented. However, it is known that nickel(I) complexes are formed in the reactions of certain nickel(II) halides with polydentate phosphines,<sup>13,14</sup> and also that the nickel(0) complex [Ni{(EtO)<sub>3</sub>P<sub>4</sub>}] is formed when nickel(II) chloride is heated in triethylphosphite.<sup>15</sup> Oxidative-



addition of aryl halides to nickel(0) and nickel (I) species is now well established,<sup>16-18</sup> as is also the formation of arylphosphonium salts from arylnickel(II) and arylnickel(III) intermediates.<sup>18,19</sup> In the reactions of the above *o*-halogeno Schiff's bases, we have observed that the rate of phosphonium salt formation increases rapidly when the Schiff's base is treated with the nickel(I) complex  $[\text{Ni}(\text{Ph}_3\text{P})_3\text{Br}]$ , (accessible by reduction of  $[\text{Ni}(\text{Ph}_3\text{P})_2\text{Br}_2]$  with sodium borohydride in ethanol).<sup>20</sup> This result lends 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 the imino nitrogen of the Schiff's base has a key role in stabilising the lower oxidation state and in promoting the subsequent reactions leading to phosphonium salt formation.

### Experimental

<sup>13</sup>C N.m.r. spectra were recorded on JEOL PFT-100 and Bruker AM-250 spectrometers at 25.15 MHz and 62.9 MHz respectively. Chemical shifts are reported on the  $\delta$  scale with respect to tetramethylsilane (5% w/v) as an internal standard in deuteriochloroform. Coupling constants are reported in Hz and are accurate to  $\pm 0.73$  Hz. <sup>31</sup>P N.m.r. spectra were recorded on a Bruker AM-250 at 101.3 MHz. Chemical shifts are reported with respect to 85% orthophosphoric acid as an external standard; shifts to high frequency are positive in sign. All chemical shifts are accurate to  $\pm 0.1$  p.p.m. <sup>1</sup>H N.m.r. spectra were recorded on a Bruker WP80 SY spectrometer at 80 MHz. Chemical shifts are reported on the  $\delta$  scale with respect to tetramethylsilane as an internal standard in deuteriochloroform. High resolution mass spectra were recorded using a Kratos MS80 mass spectrometer coupled to a DS/55 data system, with perfluorokerosene as the reference compound.

**Preparation of Potential Templates.**—The following compounds were prepared as previously described: 2-Bromobenzyl-*N,N*-dimethylamine,<sup>21</sup> 2-bromobenzaldehyde semi-carbazone,<sup>22</sup> 2-bromobenzyl phenylsulphide,<sup>23</sup> (2-fluorobenzylidene)aniline,<sup>24</sup> *N*-(2-chlorobenzylidene)-4-methoxyaniline,<sup>25</sup> *N*-(2-bromobenzylidene)-4-methoxyaniline,<sup>26</sup> *N*-(2-iodobenzylidene)-4-methoxyaniline,<sup>27</sup> *N*-(2,4-dichlorobenzylidene)-4-methoxyaniline,<sup>28</sup> 2-bromobenzaldehyde oxime,<sup>29</sup> 2-(2-bromobenzoyloxy)-*N,N*-dimethylethylamine,<sup>30</sup> 2-Bromobenzylamine and 2,4-dichlorobenzylamine were obtained commercially. The following compounds appear to be new:

**2-(2-Bromobenzoyloxy)-1-methoxyethane (15).** To a solution of sodium (0.7 g) in 2-methoxyethanol (25 cm<sup>3</sup>) was added 2-bromobenzyl bromide (5 g), and the resulting mixture heated under reflux for 2 h. The cooled reaction mixture was then poured into water (100 cm<sup>3</sup>) and the product extracted with chloroform (4  $\times$  15 cm<sup>3</sup>). Evaporation of the dried chloroform extract gave an oil which was purified by distillation under reduced pressure to give the *bromo ether* (4.16 g, 85%), as a pale yellow liquid, b.p. 98 °C at 0.4 mmHg (Found: C, 48.95; H, 5.45. C<sub>10</sub>H<sub>13</sub>BrO<sub>2</sub> requires C, 48.95; H, 5.35%;  $\delta_{\text{H}}$  = 4.2–4.8 (m, 4  $\times$  ArH), 6.5 (2 H, s), 7.2 (4 H, br s), and 7.4 (3 H, s).

**Schiff's Bases.** These were prepared by heating together equimolar quantities of the 2-halogenoaryl carbonyl compound

and primary amine in either ethanol or toluene, in the presence of a trace of toluene-*p*-sulphonic acid as a catalyst, (with removal of liberated water using a Dean-Stark trap). In most cases, the products crystallised on cooling, and were purified by further recrystallisation. In a few cases, the products were oils which could not be purified sufficiently for satisfactory micro-analysis and so were characterised by <sup>1</sup>H n.m.r. and high resolution mass spectrometry. The <sup>1</sup>H n.m.r. spectra of all of these compounds exhibited a characteristic signal at  $\delta \approx 8.5$ –9.0 due to the azomethine proton.

**2,4-Dibromo-*N*-(4-methoxybenzylidene)aniline (9).** This had m.p. 87–88 °C (from EtOH) (Found: C, 45.6; H, 2.95; N, 3.7; C<sub>14</sub>H<sub>11</sub>Br<sub>2</sub>NO requires C, 45.55; H, 3.0; N, 3.8%);  $\delta_{\text{H}}$  8.2 (1 H, s), 8.1–6.4 (7 H, m), and 3.85 (3 H, s).

**2,4-Dichloro-*N*-(4-methoxybenzylidene)benzylamine (10).** This had m.p. 41 °C (from EtOH) (Found: C, 61.25; H, 4.45; N, 4.75. C<sub>15</sub>H<sub>13</sub>Cl<sub>2</sub>NO requires C, 61.2; H, 4.45; N, 4.75%);  $\delta_{\text{H}}$  8.3 (1 H, s); 7.9–6.7 (7 H, m), 4.8 (2 H, s), and 3.8 (3 H, s).

***N*-(2-Bromobenzylidene)benzylamine (5; R = PhCH<sub>2</sub>),** isolated as an oil [Found:  $M^+(\text{Br})$ , 275.0148. C<sub>14</sub>H<sub>12</sub>BrN requires  $M(\text{Br})$ , 275.0134];  $\delta_{\text{H}}$  8.75 (1 H, s), 8.2–7.0 (9 H, m), and 4.8 (2 H, s).

***N*-(2-Bromobenzylidene)-*t*-butylamine (5; R = Bu<sup>t</sup>).** This was isolated as an oil [Found:  $M^+(\text{Br})$ , 241.0295. C<sub>11</sub>H<sub>14</sub>BrN requires  $M(\text{Br})$ , 241.0291];  $\delta_{\text{H}}$  8.1 (1 H, s), 8.15–7.10 (4 H, m), and 8.3 (9 H, s).

***N*-(2-Bromobenzylidene)-1-phenylethylamine [5; R = CH(Me)Ph].** This was isolated as an oil [Found:  $M^+(\text{Br})$ , 289.0312. C<sub>15</sub>H<sub>14</sub>BrN requires  $M(\text{Br})$ , 289.0290];  $\delta_{\text{H}}$  8.75 (1 H, s), 8.25–7.95 (1 H, m), 7.7–6.9 (8 H, m), 4.6 (1 H, q), and 1.6 (6 H, d).

***N*-(2-Bromobenzylidene)-2-hydroxyethylamine (5; R = CH<sub>2</sub>-CH<sub>2</sub>OH).** This was isolated as an oil [Found:  $M^+(\text{Br})$ , 228.9926. C<sub>9</sub>H<sub>10</sub>BrNO requires  $M(\text{Br})$  228.9925];  $\delta_{\text{H}}$  8.6 (1 H, s), 7.95 (1 H, m), 7.6–7.0 (3 H, m), and 4.8 (4 H, m).

***N*-(2-Bromobenzylidene)-2-(2-pyridyl)ethylamine [5; R = CH<sub>2</sub>CH<sub>2</sub>(2-C<sub>5</sub>H<sub>4</sub>N)].** This was isolated as an oil [Found:  $M^+(\text{Br})$ , 290.0252. C<sub>14</sub>H<sub>13</sub>BrN<sub>2</sub> requires  $M(\text{Br})$ , 290.0243];  $\delta_{\text{H}}$  8.55 (1 H, s), 7.95 (1 H, m), 7.7–6.7 (7 H, m), 4.05 (2 H, t), and 3.2 (2 H, t).

**2-Amino-*N*-(2-bromobenzylidene)benzo[b]thiazole (5; R = 2-C<sub>7</sub>H<sub>4</sub>NS).** This was obtained as yellow crystals, m.p. 196–197 °C (from toluene) [Found:  $M^+(\text{Br})$ , 317.9674. C<sub>14</sub>H<sub>9</sub>BrN<sub>2</sub>S requires  $M(\text{Br})$ , 317.9651].

**2-Amino-*N*-(2-bromobenzylidene)benzo[b]imidazole (5; R = 2-C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>).** This was obtained as pale yellow crystals, m.p. 208 °C (from EtOH) (Found: C, 56.0; H, 3.35; N, 14.0. C<sub>14</sub>H<sub>10</sub>BrN<sub>3</sub> requires C, 56.0; H, 3.35; N, 14.0%).

***N,N'*-Bis-(2-bromobenzylidene)ethane-1,2-diamine (7).** This was obtained as white crystals, m.p. 99 °C (from EtOH) (Found: C, 48.85; H, 3.75. C<sub>16</sub>H<sub>14</sub>Br<sub>2</sub>N<sub>2</sub> requires C, 48.75; H, 3.60%);  $\delta_{\text{H}}$  8.65 (2 H, s), 8.0 (2 H, m), 7.7–7.0 (6 H, m), and 4.05 (4 H, s).

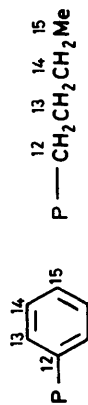
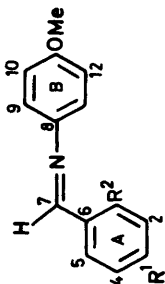
***N,N'*-Bis-(2-bromobenzylidene)biphenyl-2,2'-diamine (8).** This was obtained as pale yellow crystals, m.p. 108 °C (from EtOH) (Found: C, 60.25; H, 3.45; N, 5.30. C<sub>26</sub>H<sub>18</sub>Br<sub>2</sub>N<sub>2</sub> requires C, 60.25; H, 3.45; N, 5.40%);  $\delta_{\text{H}}$  8.5 (2 H, s), and 8.0–6.5 (16 H, m).

***N*-[1-(2-Bromophenyl)ethylidene]-4-methoxyaniline (3; R<sup>1</sup> = Me, X = Br, Y = H).** This was isolated as an oil, *m/z* 305

Table. <sup>13</sup>C N.m.r. spectroscopic data for Schiff's bases and related phosphonium salts.

Compd.	R <sup>1</sup>	R <sup>2</sup>	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	OMe	C-12	C-13	C-14	C-15	δ <sub>p</sub>	Other carbons	
A	H	H	128.6 <sup>a</sup>	128.5 <sup>a</sup>	130.9	128.5 <sup>a</sup>	128.6 <sup>a</sup>	136.3	158.2	144.8	122.1	114.3	158.2	55.4	122.5	133.0	129.9	134.0	25.9		
B	Cl	Cl	133.6 <sup>a</sup>	128.4 <sup>b</sup>	129.8 <sup>b</sup>	128.4 <sup>b</sup>	127.0 <sup>b</sup>	135.8 <sup>a</sup>	154.5	144.7	122.4	114.4	158.6	55.4	(95)	(10)	(13)	(3)			
C	Br	Br	125.8	128.7 <sup>a</sup>	131.9 <sup>a</sup>	128.7 <sup>a</sup>	127.6 <sup>a</sup>	134.7	156.9	144.4	122.5	114.4	158.6	55.4	22.0	24.2	23.3	13.0	33.7		
D	PPh <sub>3</sub>	PPh <sub>3</sub>	114.0	136.4	132.1	136.4	136.1 <sup>a</sup>	140.4	153.0	139.4	121.6	114.2	159.3	55.4	(52)	(5)	(17)				
E	PBu <sub>3</sub>	PBu <sub>3</sub>	113.8	135.7 <sup>a</sup>	131.5	134.3	135.4 <sup>a</sup>	149.6	156.0	140.9	122.0	114.6	159.3	55.2							
F	Cl	H	129.6 <sup>a</sup>	128.9 <sup>a</sup>	135.0 <sup>b</sup>	128.9 <sup>a</sup>	129.6 <sup>a</sup>	136.9 <sup>b</sup>	156.4	114.5	122.2	144.4	158.5	55.4							
G	Cl	Cl	137.0 <sup>a</sup>	129.2 <sup>b</sup>	136.1 <sup>a</sup>	129.2 <sup>b</sup>	129.7 <sup>b</sup>	132.0 <sup>a</sup>	153.0	114.1	122.4	144.4	158.7	55.4							
H	PPh <sub>3</sub>	PPh <sub>3</sub>	116.2	138.0 <sup>a</sup>	137.9	136.1	137.6 <sup>a</sup>	138.9	152.1	138.4	121.8	114.2	159.3	55.3	121.9	132.9	130.0	134.3	25.5		
I	PBu <sub>3</sub>	PBu <sub>3</sub>	116.8	137.6 <sup>a</sup>	137.7	134.8	134.9 <sup>a</sup>	138.8	155.3	141.0	122.7	115.1	160.0	55.6	(96)	(9)	(13)	(3)			
J	Br	H	125.3	131.9 <sup>a</sup>	129.8 <sup>a</sup>	131.9 <sup>a</sup>	129.8 <sup>a</sup>	135.4	156.3	144.5	122.2	114.4	158.5	55.4	22.6	24.8	23.7	13.5	34.5		
K	H	PPh <sub>3</sub>	113.8	138.4 <sup>a</sup>	132.1	136.0	136.1 <sup>a</sup>	139.3	154.9	145.9	119.3	128.4	126.8	*	(50)	(4)	(17)				
L	H	PPh <sub>3</sub>	124.3 <sup>†</sup>	139.3 <sup>a</sup>	132.3	136.7	<sup>a</sup>	141.3	157.2 <sup>‡</sup>	137.0	120.2	113.6	161.9	55.2	121.6	132.2	129.4	133.6	26.6		
M	H§	PPh <sub>3</sub>	113.9	138.5	131.9	136.1	135.3	139.6	157.6	135.4	128.1 <sup>a</sup>	128.2 <sup>a</sup>	126.9		(96)	(9)	(13)	(3)	21.7	17.0	
			(93)	(12)	(14)	(3)	(12)	(4)											25.5	(Me)	
																				61.4	(CH <sub>2</sub> )

Superscript letters: assignment interchangeable. \* No OMe substituent on ring, (ref. 33). † Signal broad at ambient. ‡ Schiff's base carbon also has a methyl substituent. § Benzyl substituent at Schiff base nitrogen. <sup>31</sup>P-<sup>13</sup>C coupling constants in parentheses.



[ $M^+$  ( $^{81}\text{Br}$ )]. Due to coincidence of reference signals, it was not possible to record an accurate mass for the molecular ion. The  $^1\text{H}$  n.m.r. spectrum indicated that a mixture of isomers was present:  $\delta_{\text{H}}$  7.8—6.4 (8 H, m), 3.8 and 3.7 (both s, MeO), and 2.6 and 2.45 (both s, Me). This substrate was characterised by its subsequent conversion to the related phosphonium salt (see below).

**Reactions of Schiff's Bases with Phosphines: General Procedure.**—The Schiff's base (1 mmol), tertiary phosphine (2 mmol) and anhydrous nickel(II) bromide (0.1 mol. equiv.) were heated together under reflux in ethanol (10 cm<sup>3</sup>) in a nitrogen atmosphere for 5—8 h, and the progress of the reaction was monitored by t.l.c. [Kieselgel;  $\text{CHCl}_3$ -EtOH (80:20) as the eluant]. The reaction mixture was then poured into water (50 cm<sup>3</sup>) containing KBr (0.5 g), and extracted with ether (2 × 20 cm<sup>3</sup>) in order to remove non-ionic impurities. The aqueous layer was then extracted with chloroform (3 × 10 cm<sup>3</sup>). The chloroform layer was dried ( $\text{MgSO}_4$ ) and evaporated. The oily residue was then triturated several times with dry ether until it solidified. The phosphonium salt was then recrystallised from chloroform-ethyl acetate (except as stated otherwise). The following salts were characterised ( $^{31}\text{P}$  and  $^{13}\text{C}$  data are presented in the Table).

**N-(4-Chloro-2-triphenylphosphoniobenzylidene)-4-methoxyaniline bromide (4; R<sup>1</sup> = H, R<sup>2</sup> = Ph; Y = Cl, X = Br).** M.p. > 267 °C (decomp.) (Found: C, 65.6; H, 4.3; N, 2.55.  $\text{C}_{32}\text{H}_{26}\text{BrClNOP}$  requires C, 65.45; H, 4.45; N, 2.4%;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.9 (1 H, s), 8.85—6.8 (18 H, m), 6.7—6.0 (4 H, deceptively simple [AX]<sub>2</sub> system), and 3.70 (3 H, s).

**N-(2-Triphenylphosphoniobenzylidene)benzylamine bromide (6).** This was characterised as the tribromomercurate(II) salt, m.p. 205—207 °C (from  $\text{CHCl}_3$ ) (Found: C, 42.3; H, 2.85; N, 1.4.  $\text{C}_{32}\text{H}_{27}\text{Br}_3\text{HgNP}$  requires C, 42.85; H, 3.05; N, 1.55%;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.55 (1 H, s), 8.5—6.4 (24 H, m), and 3.9 (2 H, s).

**4-Methoxy-N-( $\alpha$ -methyl-2-triphenylphosphoniobenzylidene)aniline bromide (4; R<sup>1</sup> = Me, R<sup>2</sup> = Ph; Y = H, X = Br).** M.p. > 265 °C (decomp.) (Found: C, 69.5; H, 5.15; N, 2.45.  $\text{C}_{33}\text{H}_{29}\text{BrNOP}$  requires C, 69.95; H, 5.15; N, 2.45%;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.60—8.52 (1 H, m), 8.27—8.18 (1 H, m), 7.84—7.12 (15 H, m), 6.5—5.1 (4 H, deceptively simple [AX]<sub>2</sub> system), 3.69 (3 H, s), and 2.34 (3 H, s).

**4-Methoxy-N-(2-triphenylphosphoniobenzylidene)aniline bromide (4; R<sup>1</sup> = H, R<sup>2</sup> = Ph; Y = H; X = Br).** M.p. 249 °C (Found: C, 67.45; H, 5.1;  $\text{C}_{32}\text{H}_{27}\text{BrNOP}\cdot\text{H}_2\text{O}$  requires C, 67.35; H, 5.1%;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.6 (1 H, s), 8.5—7.0 (19 H, m), 6.7—5.9 (4 H, deceptively simple [AX]<sub>2</sub> system), and 3.7 (3 H, s).

**4-Methoxy-N-(2-tributylphosphoniobenzylidene)aniline bromide (4; R<sup>1</sup> = H, R<sup>2</sup> = Bu; Y = H; X = Br).** M.p. 103—105 °C (Found: C, 63.5; H, 8.05; N, 2.8.  $\text{C}_{26}\text{H}_{39}\text{BrNOP}$  requires C, 63.40; H, 8.0; N, 2.85%;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.9 (1 H, s), 8.25—7.82 (4 H, m), 7.45—6.97 (4 H, deceptively simple [AX]<sub>2</sub> system), 3.87 (3 H, s), 3.02—2.80 (6 H, m), 1.60—1.40 (12 H, m), and 0.95—0.84 (9 H, m).

**N-(4-Chloro-2-tributylphosphoniobenzylidene)-4-methoxyaniline bromide (4; R<sup>1</sup> = H; R<sup>2</sup> = Bu; Y = Cl; X = Br).** M.p. 198—199 °C (Found: C, 58.95; H, 7.20; N, 2.57.  $\text{C}_{26}\text{H}_{38}\text{BrClNOP}$  requires C, 59.24; H, 7.25; N, 2.65%;  $\delta_{\text{H}}(\text{CDCl}_3)$  8.9 (1 H, s), 8.4—7.55 (3 H, m), 7.5—6.8 (4 H, deceptively simple [AX]<sub>2</sub> system), 3.85 (3 H, s), 3.3—2.7 (6 H, m), 1.8—1.2 (12 H, m), and 1.1—0.7 (9 H, m). The salt (200 mg) was dissolved in ethanol (3 cm<sup>3</sup>) and treated with aqueous sodium hydroxide (30% w/v; 2 cm<sup>3</sup>), and the resulting mixture allowed to stand at room temperature for 7 days. It was then poured into water (15 cm<sup>3</sup>) and the mixture extracted with ether (2 × 10 cm<sup>3</sup>) and the dried ether extract was evaporated and the residue recrystallised from ethanol to give *N*-(4-chlorobenzylidene)-4-methoxyaniline, m.p. 123 °C, identical with an authentic sample.

**$^{13}\text{C}$  N.m.r. Spectroscopic Data.**—The  $^{13}\text{C}$  n.m.r. chemical shifts of the parent Schiff's bases and related phosphonium salts are reported in the Table. Signals were assigned using the standard techniques of Spin Echo Fourier Transform (S.E.F.T.), (with a delay time of  $1/J$ ).<sup>31,32</sup>

**Ring A.** With one exception (compound L), all the signals are sharp, and, in the case of the phosphonium salts, exhibited coupling to phosphorus. As noted previously in related *o*-phosphoniodylazo derivatives (2),<sup>6</sup> the substituent *ortho* to phosphorus in the phosphonium salts has a marked effect on the value of  $^2J_{\text{PC}}$ .

Compound L, in which the Schiff base carbon bears a methyl substituent, shows a marked chemical shift change of ca. 8 p.p.m. for C-1 with respect to the other triphenylphosphonium salts. Furthermore, this signal is broader and there is a signal missing for one of the aryl ring-carbons. It is probable that the methyl substitution causes some form of restricted ring rotation and this would account for the broadening of the C-1 signal; also as seems likely, the missing signal corresponds to C-5 which should also be broadened and would account for its loss.

For compounds H and I, it is possible that the phosphonium salt could be formed either *ortho*- or *para*- to the Schiff's base substituent on the aryl ring. Substitution parameters for  $\text{PPh}_3$  and  $\text{PBu}_3$  on compound B show that a *para*-phosphonium salt should give a chemical shift for C-5 of 129 p.p.m. whilst an *ortho*-phosphonium salt of compound F gives a chemical shift of 113 p.p.m. Whilst multiple substitution in rings can give rise to large errors when using substitution parameters, the lack of any CH resonance in compounds H and I below 134 p.p.m. and the fact that C-6 always exhibited a coupling constant  $^2J_{\text{PH}}$  of 4—5 Hz would strongly indicate that the phosphonium salt has been formed *ortho*- to the Schiff's base substituent.

**Ring B.** Unlike the *ortho*-phosphoniodylazo derivatives (2), no broadening of the aryl carbon signals is observed in any of the compounds studied. Changes in chemical shift of C-9, C-10, and C-11 are very small. Variations in C-8 are more marked and probably reflect changes in the relative orientation of the rings due to variation in the bulk of the *ortho*-substituent on Ring A.

**Schiff's Base Carbon.** Variations in the chemical shift of C-7 are not large with the exception of the triphenylphosphonium salts, again reflecting a steric bulk interaction.

**Other Carbon Signals.** The signals for the other carbons in the molecule—methoxy, phenyl, and butyl side chains, show no abnormal chemical shift behaviour and correspond closely to values found for the *ortho*-phosphoniodylazo derivatives.<sup>6</sup>

## Acknowledgements

P. E. C. thanks the S.E.R.C. for a research studentship. We thank Dr. R. Price and colleagues (I.C.I. Organics Division) for helpful discussions.

## References

- Y. Hirusawa, M. Oku, and R. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1957, **30**, 667.
- L. Horner, G. Mummthney, H. Moses, and P. Beck, *Chem. Ber.*, 1966, **99**, 2782.
- L. Horner and U. M. Duda, *Tetrahedron Lett.*, 1970, 5177.
- P. Beck, in 'Organic Phosphorus Compounds,' eds. G. M. Kosolapoff and L. Maier, Wiley-Interscience, 1972, vol. 2, and references therein.
- Preliminary communication: D. W. Allen, I. W. Nowell, L. A. March, and B. F. Taylor, *Tetrahedron Lett.*, 1982, **23**, 5479.
- D. W. Allen, I. W. Nowell, L. A. March, and B. F. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1984, 2523.
- N. Hall and R. Price, *J. Chem. Soc., Perkin Trans. 1*, 1979, 2634.

- 8 J. A. Connor, D. Dubowski, A. C. Jones, and R. Price, *J. Chem. Soc., Perkin Trans. I*, 1982, 1143.
- 9 W. E. McEwen, G. Axelrad, M. Zanger, and C. A. VanderWerf, *J. Am. Chem. Soc.*, 1965, **87**, 3948.
- 10 W. E. McEwen, K. F. Kumli, A. Blade-Font, M. Zanger, and C. A. VanderWerf, *J. Am. Chem. Soc.*, 1964, **86**, 2378.
- 11 M. Chanon and M. L. Tobe, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 1.
- 12 K. K. Chow, W. Levason, and C. A. McAuliffe, in 'Transition Metal Complexes of Phosphorus, Arsenic, and Antimony Ligands,' ed. C. A. McAuliffe, MacMillan, 1973, and references therein.
- 13 L. Sacconi and S. Midollini, *J. Chem. Soc., Dalton Trans.*, 1972, 1213.
- 14 L. Sacconi, A. Orlandini, and S. Midollini, *Inorg. Chem.*, 1974, **13**, 2850.
- 15 T. M. Balthazor and R. C. Grabiak, *J. Org. Chem.*, 1980, **45**, 5425.
- 16 M. Foa and L. Cassar, *J. Chem. Soc., Dalton Trans.*, 1975, 2572.
- 17 T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 6319.
- 18 T. T. Tsou and J. K. Kochi, *J. Am. Chem. Soc.*, 1979, **101**, 7547.
- 19 L. Cassar and M. Foa, *J. Organomet. Chem.*, 1974, **74**, 75.
- 20 F. Caballero, M. Gomez, and P. Royo, *Transition Met. Chem. (Weinheim, Ger.)*, 1977, **2**, 130.
- 21 F. C. Copp, B.P. 881265.
- 22 H. Rupa and F. Bernstein, *Helv. Chim. Acta*, 1930, **13**, 457.
- 23 T. H. Fisher and J. C. Martin, *J. Am. Chem. Soc.*, 1966, **88**, 3382.
- 24 N. S. Kozlov, V. D. Pak, V. V. Mashevskii, and P. N. Plaksina, *Khim-Farm Zh.*, 1973, **7**, 15; (*Chem. Abstr.*, 1973, **79**, 78478).
- 25 M. Nakamura, K. Komatsu, Y. Gondo, H. Ohta, and Y. Ueda, *Chem. Pharm. Bull.*, 1967, **15**, 585.
- 26 A. S. Al-Tai, D. M. Hall, and A. R. Mears, *J. Chem. Soc., Perkin Trans. 2*, 1976, 133.
- 27 N. S. Kozlov, V. D. Pak, and V. V. Mashevskii, *Dokl. Akad. Nauk. B.S.S.R.*, 1972, **16**, 1020, (*Chem. Abstr.*, 1973, **78**, 29516).
- 28 D. R. Patel, P. S. Satpanthi, P. B. Patel, and J. J. Trivedi, *J. Inst. Chem. (India)*, 1976, **48**, 305.
- 29 J. Schnekenburger, *Fresenius Z. Anal. Chem.*, 1973, **263**, 23.
- 30 F. C. Copp and G. C. Coker. B.P. 924961.
- 31 R. Benn and H. Günther, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 355.
- 32 E. Breitmaier and W. Voelter, 'Monographs in Modern Chemistry,' vol. 5, '<sup>13</sup>C N.M.R. Spectroscopy,' ed. H. F. Ebel, Verlag Chemie, Weinheim, Ger., 2nd Edition, 1978.
- 33 D. W. Allen and P. G. Smithurst, unpublished work.

Received 20th January 1986; Paper 6/133