

Phosphonation of Aryl Halides by Copper(I) Complexes of Trialkyl Phosphites

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The copper complexes $[\text{Cu}_3(\text{O}_2\text{CMe})_5\{\text{P}(\text{OR})_3\}_2]$ (1; R = Me or Et), $[\text{Cu}(\text{O}_2\text{CMe})\{\text{P}(\text{OR})_3\}(\text{bpy})]$ (2; R = Me or Et) (bpy is 2,2'-bipyridine), and $[\text{Cu}(\text{O}_2\text{CMe})\{\text{P}(\text{OEt})_3\}_2]$ react with certain 2-halogenoazobenzene compounds, ArX, at room temperature to form the corresponding dialkyl arylphosphonates, $\text{ArP}(\text{O})(\text{OR})_2$, and the products, ArH and Ar_2 , of reductive substitution and biaryl coupling. The ester, MeCO_2R , and a copper(I) halide complex (e.g. $[\text{CuX}\{\text{P}(\text{OR})_3\}]$) are also formed. Kinetic studies of the reactions of some of these copper complexes with 2'-acetamido-6-bromo-4'-diethylamino-2,4-dinitroazobenzene in alcohol solution show that the phosphonation reactions are equal concentration second-order processes in each case. The effects of a radical scavenger and of light on the reaction suggest the involvement of radicals in the formation of ArH and Ar_2 , but not in the formation of $\text{ArP}(\text{O})(\text{OR})_2$. The effects of different substituents in ArX, of changes in solvent, and of various additives on these reactions are investigated. A mechanism involving concerted nucleophilic substitution within the co-ordination sphere of copper(I) is proposed.

THE important role of copper, its salts and complexes in effecting transformations of interest in synthetic organic chemistry has been recognised since the discoveries of Ullmann and of Sandmeyer.¹ Despite the widespread and continuing use of these reactions, much remains to be understood about the mode of action of the metal atom, particularly in terms of the processes which may be presumed to occur within the co-ordination sphere of the metal.

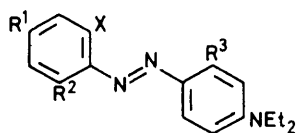
We have shown² that certain types of aryl halides react with trialkyl phosphites in the presence of copper(II) acetate in boiling alcohol solution to form the dialkyl-arylphosphonate. Subsequent investigations³ have established that copper(II) alkanecarboxylates react with trialkyl phosphites in alcohol to form novel, pale blue-

or Et) and $[\text{Cu}(\text{O}_2\text{CMe})\{\text{P}(\text{OR})_3\}(\text{bpy})]$ (2; R = Me or Et) (bpy is 2,2'-bipyridine), and representative examples of the aryl halide substrates, and show here that each of the complexes (1), (2), and $[\text{Cu}(\text{O}_2\text{CMe})\{\text{P}(\text{OEt})_3\}]$ (3), will effect the phosphonation of certain aryl halides at room temperature in solution in the absence of any added phosphite. We have investigated the influence of substituents in the aryl halide substrates, of changes in solvent, of various additives such as radical initiators and radical scavengers, and of changes in the physical conditions (heat, light) on the reaction. Extensive use has been made of high pressure liquid chromatography (h.p.l.c.), particularly in kinetic studies of some of these reactions.

RESULTS

The aryl halide (4a) reacts with copper(II) acetate and triethyl phosphite in boiling ethanol to form the diethyl arylphosphonate (5a), together with a trace (<0.3%) of the reductive substitution product.² At room temperature no reaction was detected in a similar mixture during a comparable period of time (1 h). The trinuclear copper complex (1; R = Et) reacts with the halide (4a) in dry, deoxygenated ethanol under dinitrogen at room temperature to give the phosphonate (5a) as the principal product, together with the reductive substitution product (6a) (5%), and the biaryl coupling product (7a) (6%). Careful analysis of the liquid product mixture after isolation of the azobenzene compounds (5a)–(7a), showed (gas chromatography and mass spectroscopy) the presence of ethyl acetate which was absent at the start of the reaction. The copper(I) complex $[\text{CuBr}\{\text{P}(\text{OEt})_3\}]$ was also isolated from the reaction.

Reactions between the same copper complex (1; R = Et) and a variety of other aryl halides (4b–k) in ethanol at room temperature were investigated. These experiments showed that the same classification of halogen-atom reactivity exists in the present instance as had been established previously.² Briefly, this classification may be described as follows. (i) The bromine atom at C-4, *para* to the azo-group in compounds (4b–d) and in compounds



	R ¹	R ²	R ³
(4) X = Br	a NO ₂	NO ₂	NHAc
(5) X = P(O)(OR) ₂	b Br	NO ₂	NHAc
(6) X = H	c Br	Me	NHAc
(7) Dimer	d Br	H	NHAc
	e NO ₂	NO ₂	NH ₂
	f NO ₂	NO ₂	N(Me)Ac
	g Br	NO ₂	H
	h Br	Me	H
	i Br	H	H
	j NO ₂	NO ₂	Me
	k NO ₂	NO ₂	H

green complexes $[\text{Cu}_3(\text{O}_2\text{CR}^1)_5\{\text{P}(\text{OR}^2)_3\}_2]$, from which $[\text{Cu}(\text{O}_2\text{CR}^1)\{\text{P}(\text{OR}^2)_3\}_2]$ can be derived by treatment with a unidentate ligand such as pyridine. Derivatives containing bidentate ligands (biL) of the general formula $[\text{Cu}(\text{O}_2\text{CR}^1)\{\text{P}(\text{OR}^2)_3\}(\text{biL})]$ have also been prepared.³

We describe studies of the reactions between the copper complexes $[\text{Cu}_3(\text{O}_2\text{CMe})_5\{\text{P}(\text{OR})_3\}_2]$ (1; R = Me

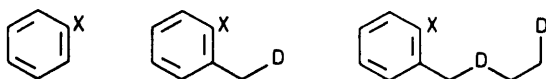
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(4g—i), is uniformly inert to substitution under these conditions.

(ii) The bromine atom at C-2, *ortho* to the azo-group in compounds (4g—k) which have no donor atom or group at C-8, the *ortho*-position of the non-halogen bearing ring, undergoes phosphonation slowly or not at all.

(iii) The bromine atom at C-2 in compounds (4a—f), which have a donor atom (nitrogen) at C-8 in the non-halogen bearing ring, undergoes phosphonation rapidly, unless steric constraints [*e.g.* in compound (4f)] prevent this.

These three categories (types 1, 2, and 3) of aryl halide can be represented as shown in Scheme 1.



SCHEME 1 D represents a donor atom

The importance of steric effects in the reactions of aryl halides of type 3 may be judged from the fact that compounds (4b) and (4c) react equally rapidly with the complex (1; R = Et) but the halide (4d), which lacks a C-6 substituent, reacts with complex (1; R = Et) much more slowly (*ca.* 40 times). A similar difference is observed in the case of aryl halides of type 2; compounds (4g) and (4h) react slowly with the copper complex (1; R = Et), but compound (4i) does not react at all under the same conditions. These observations suggest that the electronic influence of the substituents at C-6 is less important than steric effects in the phosphonation reaction.

The distinction between aryl halides of type 2 and type 3 in the rates of their reaction with the complex (1; R = Et) [a factor of *ca.* 100 in the rate] suggests that the presence of two donor atoms in systems of type 3 provides more favourable circumstances for co-ordination (chelation) than the single donor atom present in the substrates of type 2. However, although the formation of copper complexes by bidentate and by tridentate diarylazo-ligands is well known,⁴ we have been unable to isolate complexes of this kind in the systems under investigation here and we have no positive evidence for their existence as intermediates in the phosphonation.

A significant feature of these reactions between the aryl halides (4a—k) and the copper complexes (1)—(3) which is revealed by h.p.l.c., used to monitor the evolution of the products with time, is that the formation of both the reductive substitution product (6) and the biaryl coupling product (7) is complete in the early stages of the reaction and does not increase thereafter, although the phosphonation reaction continues to produce the phosphonate (5). A typical example of the results obtained is shown in Table 1. Furthermore, we find that the amount of the biaryl coupling product (7) formed within the shorter period is dependent upon the copper complex used. Taking the halide (4a) as the substrate, the yield of the product (7a) increased from $6 \pm 1\%$ when the complex (1; R = Et) was used, to $24 \pm 1\%$ when complex (2; R = Et) was used (Table 2). Broadly similar results to the foregoing are obtained with the complexes (1; R = Me) and (2; R = Me) as phosphonating agents.

Kinetic and Mechanistic Studies.—Kinetic measurements of the phosphonation of the aryl halide (4a) by complex (1; R = Et) to give the phosphonate (5a) in ethanol solution were made by h.p.l.c. The phosphonation reaction is

an equal concentration second-order process. The rate of the second-order reaction was measured at four temperatures in the range 273—345 K and the results are shown in Table 3. An Arrhenius plot of these results gives the activation energy, $E_a = (74 \pm 20) \text{ kJ mol}^{-1}$. As well as the

TABLE 1

Evolution of products (5a), (6a), and (7a) from the phosphonation of the aryl bromide (4a) (0.20 mmol) by the copper complex (1; R = Et) (0.20 mmol) in solution (20 ml) at 293 K, determined by h.p.l.c.

Time <i>t</i> (min)	Composition (% mol fraction) of sample analysed at time <i>t</i>			
	(4a)	(5a)	(6a)	(7a)
A Daylight; EtOH				
2	86.6	13.5		
5	83.8	14.9	0.5	1.0
7	74.3	24.7	0.5	1.0
11	65.8	30.8	1.2	2.2
28	35.6	57.5	2.6	4.4
61	16.0	74.2	4.3	5.6
124	2.9	86.3	5.0	5.8
160		88.5	5.4	6.1
B Daylight; EtOH; dpbh (0.01 mmol) added				
3	85.9	14.1		
23	40.7	58.2	1.1	
50	5.0	94.1	0.9	
95	0.6	97.7	1.7	
115		98.4	1.6	
C Dark; ethanol				
6	67.4	32.6		
13	43.8	56.1		
36	28.6	71.4		
62	4.4	94.7	1.0	
127		96.8	3.2	
D Daylight; EtOH; P(OEt) ₃ (0.20 mmol) added				
8	68.0	32.0		
38	56.7	43.2		
135	38.5	61.5		
191	20.3	79.7		
E Daylight; THF				
8	36.6	49.5	4.7	9.2
15	31.3	54.2	5.5	9.0
23	27.0	58.3	5.9	8.8
40	20.2	64.9	6.2	8.7
69	16.7	68.4	6.3	8.6
111	13.9	71.2	6.2	8.7
198	12.4	72.8	6.2	8.7

detection of the phosphonate (5a), the use of h.p.l.c. shows simultaneously that the yields of the products (6a) and (7a) (Table 2) decrease at the same time as both the temperature of the reaction and the rate of the phosphonation increase. This suggests that compounds (6a) and (7a) are the kinetically favoured products and that the phosphonate (5a) is thermodynamically favoured, and indicates that the three products (5a), (6a), and (7a) originate from a common intermediate.

The influence of the alkoxy-substituent at phosphorus in the copper complexes (1) was recognised when the phosphonation of the aryl halide (4a) by the complex (1; R = Me) in methanol solution proceeded more slowly (Table 3) than the corresponding reaction of complex (1; R = Et) in ethanol.

The addition of a radical scavenger, 1,1-diphenyl-2-picrylhydrazyl, (dpph), (0.01 mmol) to the reaction (293 K) between the complex (1; R = Et) (0.20 mmol) and the aryl

halide (4a) (0.20 mmol) resulted in the complete suppression of the biaryl coupling product (7a), strong inhibition of the reductive substitution, and a slight acceleration of the phosphonation reaction (Table 1B). This indicates that radicals are involved in the biaryl coupling reaction and possibly in the reductive substitution as well.

triethyl phosphite to form the complex (3) and triethyl phosphate; in separate experiments it was shown that this complex (3) reacts with the aryl halide (4a) to give the phosphonate (5a) and small quantities of compounds (6a) and (7a). It would appear that, in the presence of an equimolar proportion of triethyl phosphite at room tempera-

TABLE 2

Final yield (%) of reductive substitution (6) and biaryl coupling (7) products from the reactions of aryl halides (4) with copper complexes in solution

Complex	Halide	Solvent	Additive	Light (L) Dark (D)	Temp. (K)	Yield (%)	
						(6)	(7)
(1; R = Et)	(4a; X = Br)	EtOH		L	273	11.4	12.2
(1; R = Et)	(4a; X = Br)	EtOH		L	293	5.4	6.1
(1; R = Et)	(4a; X = Br)	EtOH		L	310	4.3	
(1; R = Et)	(4a; X = Br)	EtOH		L	345	2.6	
(1; R = Me)	(4a; X = Br)	MeOH		L	293	3.4	7.0
(1; R = Et)	(4a; X = I)	EtOH		L	293	2.1	2.5
(1; R = Et)	(4e; X = Br)	EtOH		L	293	5.4	3.7
(1; R = Et)	(4k; X = Br)	EtOH		L	293		
(1; R = Et)	(4a; X = Br)	THF		L	293	6.2	8.6
(1; R = Me)	(4a; X = Br)	THF		L	293	5.2	27.5
(1; R = Et)	(4a; X = Br)	EtOH	dpph (5%)	L	293	1.6	
(1; R = Et)	(4a; X = Br)	EtOH	P(OEt) ₃	L	293	0.4	
(1; R = Et)	(4a; X = Br)	EtOH		D	293	3.2	
(2; R = Et)	(4a; X = Br)	EtOH		L	293	3.4	23.9
(2; R = Et)	(4a; X = Br)	EtOH		D	293	7.0	1.0
(2; R = Et)	(4a; X = Br)	EtOH	dpph (7%)	L	293	3.5	30.9
(2; R = Et)	(4a; X = Br)	EtOH	dpph (92%)	L	293		
(2; R = Et)	(4e; X = Br)	EtOH		L	293		10.3
(3; R = Et)	(4a; X = Br)	EtOH		L	293	2.6	12.3

Further support for the intervention of radicals was obtained when the reaction (293 K) between the complex (1; R = Et) and the aryl halide (4a) was carried out in the dark (Table 1C). Again, the biaryl coupling was suppressed and the reductive substitution was inhibited, but

TABLE 3

Second-order rate constant, k_{obs} , $\text{l mol}^{-1} \text{s}^{-1}$ for phosphonate production in alcohol (ROH) solution from reaction of copper complexes with the aryl halide (4a)

Copper complex	Aryl halide (4a)		T/K	$k_{\text{obs}}/$ $\text{l mol}^{-1} \text{s}^{-1}$
	R	X		
(1)	Et	Br	273	$(6.2 \pm 1.8) \times 10^{-5}$
(1)	Et	Br	293	$(7.5 \pm 0.9) \times 10^{-4}$
(1)	Et	Br	310	$(7.9 \pm 0.7) \times 10^{-3}$
(1)	Et	Br	345	$(2.2 \pm 0.3) \times 10^{-2}$
(1)	Me	Br	293	$(1.0 \pm 0.1) \times 10^{-4}$
(1)	Et	I	293	$(3.1 \pm 0.7) \times 10^{-4}$
(2)	Et	Br	293	$(3.1 \pm 0.7) \times 10^{-5}$
(3)	Et	Br	293	$(1.5 \pm 0.2) \times 10^{-4}$

the phosphonation proceeded at the same rate as in the reaction with dpph. The addition of triethyl phosphite (1 mmol) to the reaction between the complex (1; R = Et) (1 mmol) and the halide (4a) (1 mmol) in ethanol at room temperature resulted in the suppression of both products (6a) and (7a) (Table 1D). The production of the phosphonate (5a) under these conditions is slightly slower than when there is no excess of free triethyl phosphite present. It is known³ that the complex (1; R = Et) reacts with

the trinuclear complex (1; R = Et) reacts to form the complex (3); concurrently, triethyl phosphite probably serves as a radical scavenger, suppressing both the reductive substitution and biaryl coupling reactions. The rate of the reaction between the complex (3) and the aryl halide (4a) to form the phosphonate (5a) is slower (Table 3) than when the trinuclear complex (1; R = Et) is used.

The role of the solvent in the phosphonation reaction is significant. When carried out in tetrahydrofuran (THF) at room temperature the phosphonation is no longer a simple second-order reaction; the formation of the phosphonates (5a; R = Et) and (5a; R = Me) by the reaction of the aryl halide (4a) with the complexes (1; R = Et) and (1; R = Me), respectively, proceeded more slowly in THF than in ethanol (Table 1E). The reaction in THF was accompanied by a significant increase in the yield of the biaryl coupling and reductive substitution products (Table 2), suggesting that solvent-cage effects are important in these radical reactions.

The effect of different substituents on the progress of the reaction was determined. Phosphonation of the iodide analogue of the aryl bromide (4a) by the copper complex (1; R = Et) was slower than phosphonation of the bromide (4a) itself, and the yield of the biaryl coupling and reductive substitution products (6a) and (7a) was also lower. The effect of replacing the acetyl-amino-group at C-8 by an amino-group, giving compound (4e), and by hydrogen, giving compound (4k), a type 2 halide, was to arrest the phosphonation reaction in the order (4a) < (4e) << (4k). The slow phosphonations of the halides (4e) and (4k) were not second-order equal-concentration reactions. The yields of the biaryl coupling products from compounds (4e) and (4k) decrease in the order (4a) (6.1%) > (4e) (3.5) > (4k) (0).

The addition of benzyl bromide, a type 1 halide, to the trinuclear complex (1; R = Et) in ethanol at room tempera-

ture did not produce any $\text{PhCH}_2\text{P}(\text{O})(\text{OEt})_2$, but, rather, caused decomposition of the copper complex to $[\text{Cu}_2(\text{O}_2\text{CMe})_4]$ and $[\text{Cu}(\text{O}_2\text{CMe})\{\text{P}(\text{OEt})_3\}_2]$. Similarly, *n*-butyl bromide can be recovered unchanged from a neat mixture with pure liquid complex (3). These observations demonstrate clearly the distinction between the three types of halide and emphasize the importance of the presence of two donor atoms on the substrate in addition to the halogen.

Phosphonation Reactions of $[\text{Cu}(\text{O}_2\text{CMe})\{\text{P}(\text{OR})_3\}(\text{bpy})]$ (2).—The reaction between the yellow copper(I) complex (2; $\text{R} = \text{Et}$) and 2-acetamido-6'-bromo-4-diethylamino-2',4'-dinitroazobenzene (4a) at room temperature in light proceeds more slowly (Table 3) than the corresponding reactions of the complexes (1; $\text{R} = \text{Et}$) and (3) with the aryl halide (4a). At the same time, the total yield of 2-acetamido-4-diethylamino-2,4'-dinitroazobenzene (6a) and its dimer (7a) increases markedly (Table 2). The reaction stops after half the aryl halide (4a) has been consumed, at which point the products 2-acetamido-4-diethylamino-6-diethylphosphonato-2',4'-dinitroazobenzene (5a) and (7a) are present in *ca.* equal amounts together with a small yield of the azobenzene (6a). In the dark, the reaction continues until the aryl halide (4a) is essentially completely consumed, at which point (24 h) the products comprise the phosphonate (5a) (92%) together with the azobenzene (6a) (7%) and its dimer (7a) (1%). Closer investigation of the dark reaction by h.p.l.c. showed that the formation of the dimer (7a) reached a maximum (53% after 80 min) and then decreased. The production of the phosphonate (5a) does not follow second-order kinetics in the dark. In both the light and the dark, the yield of the dimer (7a) was substantial (>15%) even after short (5 min) reaction times. The biaryl compound (7a) does not react with the complex (2; $\text{R} = \text{Et}$) in the light at room temperature, or in the dark in the presence of added bromide ion, triethyl phosphite, or *N*-bromosuccinimide. Similar results were obtained from the reaction between the complex (2; $\text{R} = \text{Me}$) and the aryl halide (4a) in methanol in the light and in the dark.

It appears that the decay of the biaryl compound (7a), which is observed in the dark reaction, is due to interruption of the photochemically-induced radical formation. These radicals take a finite time to decay. The observed yield of compound (7a) is proportional to the amount of aryl radical in solution. Coupling of these aryl radicals occurs when the sample is removed for analysis by h.p.l.c. in the light.

Judged by the yield of the phosphonate (5a), phosphonation of the bromide (4a) by the complex (2; $\text{R} = \text{Et}$) is more rapid in the dark than in the light. This is further confirmation for the formation of an intermediate which is common to the phosphonation, reductive substitution, and biaryl coupling reactions. In the dark, the radical coupling is inhibited. To test this we have investigated the effect of adding a radical scavenger (dpph) on the reaction between the complex (2; $\text{R} = \text{Et}$) and the aryl bromide (4a) in ethanol in daylight. At low concentrations ($\text{Cu} : \text{dpph } ca. 14 : 1$), the scavenger had no significant influence on the distribution of the products, but at higher concentrations ($\text{Cu} : \text{dpph } ca. 1 : 1$) neither the azobenzene (6a) nor its dimer (7a) was formed, but phosphonation to give the phosphonate (5a) proceeded at the same rate as in the dark reaction. These experiments establish that the radical reaction leading to compound (6a) differs from that leading to its dimers (7a) in that the former does not require light.

The reaction between the complex (2; $\text{R} = \text{Et}$) and 2'-amino-6-bromo-4'-diethylamino-2,4-dinitroazobenzene (4e)

was slower than the corresponding reaction with complex (1; $\text{R} = \text{Et}$), and produced more biaryl coupling to give the corresponding dimer (7e) (10%). There was no detectable reaction at room temperature between complex (2; $\text{R} = \text{Et}$) and the 6-bromo-4'-diethylamino-2,4-dinitroazobenzene (4k) (type 2).

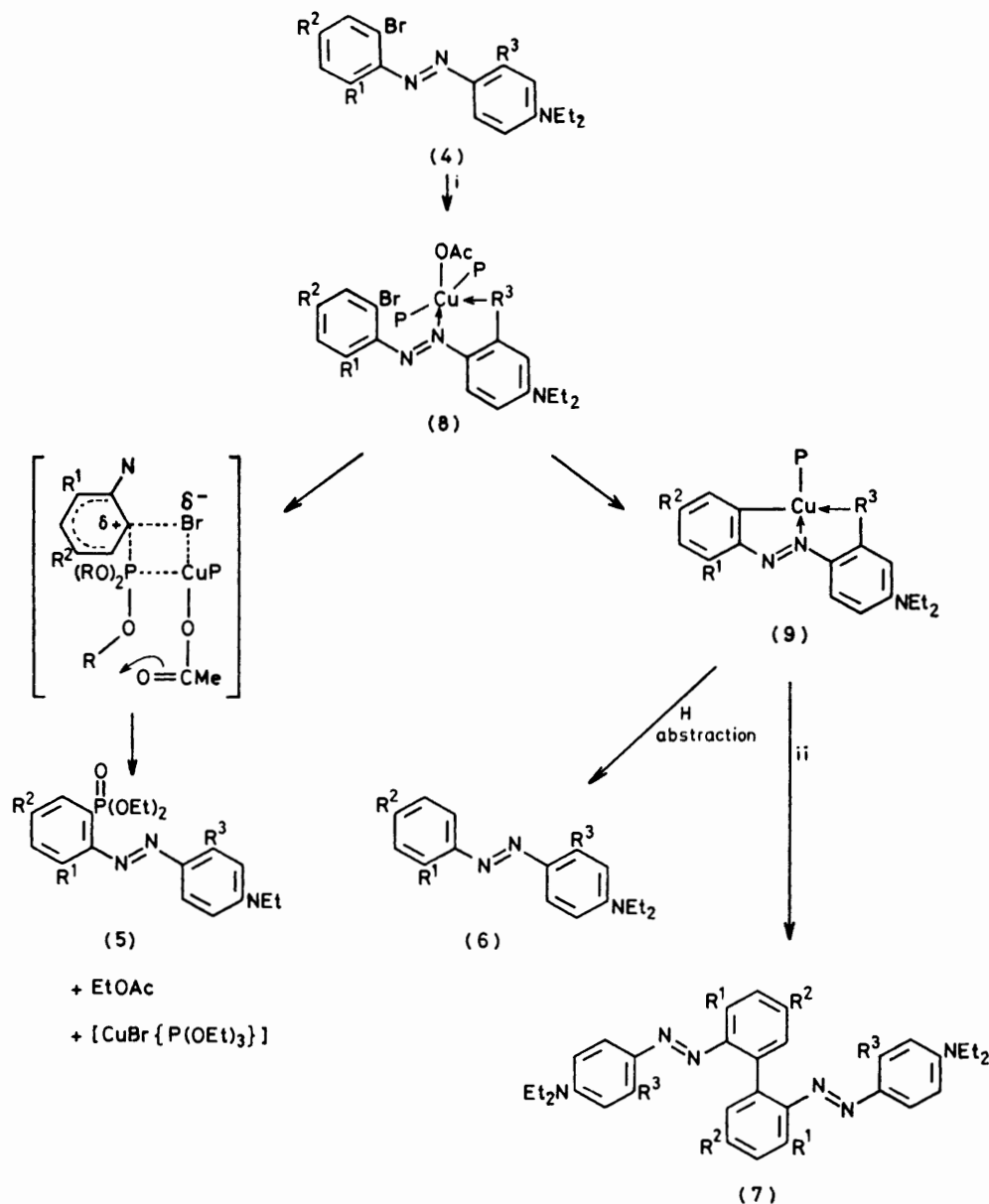
DISCUSSION

Any survey of what has been discovered⁵ about the role of copper and its compounds in promoting nucleophilic displacement in aryl halides shows both that there is a great deal of confusion and that it is unlikely that the various reactions can be rationalized in terms of a single simple mechanism.

In the reactions considered here, it is clear that there must be a common precursor to the three types of azobenzene product (5), (6), and (7). Detailed studies of the copper complexes (1), (2), and (3) have shown³ that the alcohol solvent, in which the reactions are carried out, plays a significant role in their behaviour in solution. There is no evidence for the dissociation of phosphite ligands from any of these compounds in solution. Consequently, since these stoichiometric phosphonation reactions were carried out in the absence of any free (or added) phosphite ligand, it is clear that phosphonation must occur within the co-ordination sphere of the metal atom. The products of reaction between complex (1; $\text{R} = \text{Et}$) and the aryl bromide (4a) include $[\text{CuBr}\{\text{P}(\text{OEt})_3\}]$ and ethyl acetate, in addition to compounds (5a), (6a), and (7a). This suggests that the common precursor (8) mentioned above contains both copper and the aryl halide as shown in Scheme 2. A model for the precursor (8) is provided by the complexes $[\text{Cu}(\text{O}_2\text{CMe})\{\text{P}(\text{OEt})_3\}(\text{biL})]$, which are obtained together with $[\text{Cu}(\text{O}_2\text{CMe})_2(\text{biL})]$ from the reaction between the complex (1; $\text{R} = \text{Et}$) and biL (biL is 1,2-diaminobenzene or 2,2'-bipyridine) in ethanol. The observations that the ethyl group lost from triethyl phosphite is isolated as ethyl acetate and that the bromine lost from the aryl bromide (4a) is isolated as $[\text{CuBr}\{\text{P}(\text{OEt})_3\}]$, are consistent with a concerted nucleophilic attack on the co-ordinated phosphite which is thereby transformed to a phosphonate. Such a conversion is probably accompanied by co-ordination isomerisation as shown in Scheme 3.

This rearrangement would generate a nucleophilic centre at phosphorus, suitable for attack on the carbocationic centre in the C-halogen bond of the aryl halide (4). In separate experiments, we have shown that an external nucleophile (bromide or acetate) does not cause transformation of the co-ordinated phosphite in the complex (1; $\text{R} = \text{Et}$). The alternative product of nucleophilic attack on the co-ordinated phosphite, in which the P-Cu bond is retained, requires that subsequent attack on the aryl halide is carried out by an oxygen nucleophile. Although there is precedent⁶ for such a transformation, we regard it as less likely in the reactions considered here.

There is increasing evidence to show that arylcopper

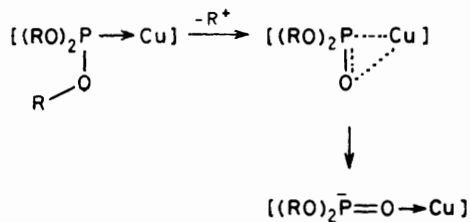


Reagents i, [Cu₃(O₂CMe)₅{P(OR)₃}₂]; ii, hν
SCHEME 2

species are intermediates in the Ullmann biaryl coupling reaction.⁵ Recently, an aryl copper compound similar to (9) was isolated⁷ from the reaction between CuX (X = Br, I, or O₂CMe) and 4-bromo-4'-diethylamino-2-lithio-6-methylbenzene (10). Addition of a 2-iododiarlyl-azo compound to this arylcopper compound (10) resulted in the formation of both the reductive substitution and biaryl coupling products. The present experiments suggest that light is involved only in the coupling of aryl radicals.

Others⁸ have observed that the addition of Cu²⁺ to the Ullmann condensation of halogenoanthraquinones with amines in the presence of copper(I) compounds increases the catalytic activity of the copper(I) species.

It is suggested that a complex between copper(I) and copper(II) is involved. Our observation that the mixed valence complex [Cu₃(O₂CMe)₅{P(OEt)₃}₂] (1) causes more rapid phosphonation of the bromide (4a) than



SCHEME 3

the simple copper(I) complex $[\text{Cu}(\text{O}_2\text{CMe})\{\text{P}(\text{OEt})_3\}_2]$ (3), which can be derived from complex (1) (Table 3), provides substantial support for the increased activity, but does not explain how this arises.

EXPERIMENTAL

The preparations of the copper complexes, the aryl halides (4), the aryl phosphonates (5), and the products of reductive substitution (6) and biaryl coupling (7) have been described.^{2,3} All solvents were purified by distillation, dried, and purged with deoxygenated, dry dinitrogen before use. Reagents were of the highest available purity. Reactions, which were carried out in Schlenk tubes under anaerobic conditions, were commonly monitored by thin layer chromatography on Polygram Sil G/u.v. 254 pre-coated plastic sheets using toluene–nitromethane (4 : 1) and ethyl acetate–light petroleum (b.p. 40–60 °C) (3 : 2) as eluants. H.p.l.c. was undertaken using a Hewlett-Packard 1080B instrument with LiChrosorb RP18 columns. Samples for h.p.l.c. were prepared by eluting an aliquot (1 ml) of the reaction mixture through a short (4 cm) column of alumina

(Grade 0) with acetonitrile to remove any active copper species.

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