The Copper-promoted Reaction of *o*-Halogenodiarylazo-compounds with Nucleophiles. Part 1. The Copper-promoted Reaction of *o*-Bromodiarylazo-compounds with Trialkyl Phosphites. A Novel Method for the Preparation of Dialkyl Arylphosphonates[1]

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o-Bromodiarylazo-compounds react with triethyl phosphite in the presence of copper(II) acetate in dry ethanol to give the corresponding *o*-diethylphosphonatodiarylazo-compounds in good yield. Reaction is facilitated by the presence of an *o*'-donor substituent in the *o*-bromodiarylazo-compound. In 10% aqueous ethanol reductive replacement competes with nucleophilic substitution in *o*-bromodiarylazo-compounds having an *o*'-donor substituent but not in those devoid of such a substituent. Under these conditions reduction of the copper(II) acetate to a copper(I) species occurs with liberation of acetic acid. The former *o*-bromodiarylazo-compounds readily undergo reductive substitution in the presence of acetic acid or, better, trifluoroacetic acid and copper(I) acetate or copper–bronze in ethanol, whereas the latter do not. In the presence of acetic acid biaryl coupling competes with reductive substitution and becomes the principal reaction when no acid is present. Neither reductive substitution nor biaryl coupling occur when the copper(I) acetate or copper–bronze are replaced by copper(II) acetate.

SINCE the original discovery by Ullmann,[2] copper and its compounds have been used to promote the nucleophilic replacement of halogen in a variety of aryl halides including *o*-halogenodiarylazo-compounds. Thus, in 1931 Delfs[3] obtained the copper complex of 2-(2-hydroxynaphthyl-1-azo)phenol-4-sulphonic acid by heating an aqueous solution of 1-chloro-2-(2-hydroxynaphthyl-1-azo)benzene-4-sulphonic acid, copper sulphate, sodium hydroxide, and ammonia at 80 °C for 1 h. This early observation of the facile, copper-promoted replacement of halogen in *o*-halogeno-*o*'-hydroxydiarylazo-compounds by a hydroxy-group has since been extended to a variety of nucleophilic species including alkoxide[4-7] phenoxide,[4,5,7,8] β-dicarbonyl,[9] and sulphinate[4] anions, ammonia,[4] and aliphatic[4,5,10] and aromatic[4,5] amines. More recently *o*-cyano-,[11] *o*-nitro-,[12] *o*-alkylsulphonyl-,[13] and *o*-arylsulphonyl-diarylazo-compounds[13] have been prepared by the copper-promoted reaction of *o*-bromodiarylazo-compounds with cyanide, nitrite, and alkyl- and aryl-sulphinate ions, respectively. We now report the preparation of *o*-dialkylphosphonatodiarylazo-compounds by the copper-promoted reaction of *o*-halogenodiarylazo-compounds with trialkyl phosphites, and the extension of this reaction to other aryl halides.

The reaction of alkyl halides with trialkyl phosphites is the most widely used method[14] for the preparation of dialkyl alkylphosphonates but, with few exceptions, aryl halides do not undergo this reaction.[15] A limited number of aryl iodides and bromides react[16] with trialkyl phosphites on prolonged heating at high temperatures in the presence of copper–bronze to give moderate yields of dialkyl arylphosphonates. Similar reactions[17] of certain aryl iodides and bromides with trialkyl phosphites have also been carried out at elevated temperatures in the presence of catalytic amounts of nickel chloride, bromide, or iodide. Reactions of this type are, however, limited in their application because of the sensitivity[18] of substituents such as nitro, azo, amino, hydroxy, *etc.*, towards trialkyl phosphites under these severe conditions.

Arylphosphonic acids have been prepared by the Friedel–Crafts method,[19] by direct phosphonation[20] with phosphonic anhydride, *via* a diazonium salt,[21] and *via* a Grignard reagent or an aryl-lithium compound.[22] *o*-Nitrophenylphosphonic acid has been prepared[23] by the interaction of *o*-dinitrobenzene and triethyl phosphite. These reactions are limited in their application, and none can be employed directly in the synthesis of dialkyl arylphosphonates containing sensitive functional groups.

EXPERIMENTAL

^{1}H N.m.r. spectra were measured on a Hitachi–Perkin-Elmer R-24A spectrometer at 60 MHz or a Varian HA-100 spectrometer at 100 MHz, using tetramethylsilane as internal standard. Mass spectra were recorded with an A.E.I. MS90 spectrometer. Thin layer chromatography was carried out on Eastman Chromagram sheets 13 181 (silica gel) using cyclohexane–chloroform (1 : 1), nitromethane–toluene (7 : 93), and ethyl acetate–light petroleum (3 : 2) as eluants. G.l.c. spectra were obtained with a Pye-Unicam series 104 chromatograph, using Celite (100—120 mesh) coated with 10% silicone E301 as the stationary phase. Evaporations under reduced pressure were carried out with a Buchi Rotavapor. Light petroleum refers to the fraction of b.p. 60—80 °C. Triethyl phosphite was purchased from B.D.H. Chemicals Ltd. and used without purification.

Diethyl [2-(2-*Hydroxynaphthyl*-1-*azo*)*phenyl*]*phosphonate* (*with* A. A. PATEL).—(*a*) A stirred mixture of 1-(2-bromophenylazo)-2-naphthol (23) (3.27 g), triethyl phosphite (6.64 g), tetrakis(acetonitrile)copper(I) perchlorate (3.26 g), and acetonitrile (50 ml) was boiled under reflux for 80 h, cooled, and poured into water (300 ml). The *product* (3.2 g, 83.5%) was separated, washed with water, and crystallised from light petroleum as orange plates (Found: C, 62.5; H, 5.4; N, 7.0; P, 8.4. $C_{20}H_{20}N_2O_4P$ requires C, 62.5; H, 5.45; N, 7.3; P, 8.05%); δ($CDCl_3$) 1.2 (6 H, t, $MeCH_2$), 3.7 (4 H, q, $MeCH_2$), 7.5—7.9 (10 H, m, aromatic), and 13.4 (1 H, s, OH).

(*b*) A stirred mixture of 1-(2-iodophenylazo)-2-naphthol (3.7 g), triethyl phosphite (2.5 g), copper(II) acetate (2.0 g), and acetonitrile (200 ml) was boiled under reflux for 30 min when t.l.c. showed reaction to be complete. The *product*, isolated as in the preceding experiment, gave an i.r. spectrum identical with that of authentic material.

Diethyl [8-(2-Hydroxynaphthyl-1-azo)-naphth-1-yl]-phosphonate (*with* P. M. ROWBOTHAM).—A stirred mixture of 1-chloro-8-(2-hydroxynaphthyl-1-azo)naphthalene (24) (3.3 g), triethyl phosphite (2.5 g), copper(II) acetate (2.0 g), and dry ethanol (60 ml) was boiled under reflux for 18 h, cooled, and poured into water (350 ml). The *product* (2.35 g, 55%) was separated, washed with water, and crystallised from light petroleum as red plates (Found: C, 66.3; H, 5.7; N, 6.6; P, 7.0. $C_{24}H_{23}N_2O_4P$ requires C, 66.35; H, 5.35; N, 6.45; P, 7.15%).

*Diethyl {3,5-Dinitro-2-[2-acetylamino-4-*N*-β-(β-methoxyethoxycarbonyl)ethylamino-5-methoxyphenylazo]phenyl}-phosphonate.*—A stirred mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-6-methoxy-*N*-β-(β-methoxyethoxycarbonyl)ethylaniline (2.9 g), triethyl phosphite (1.25 g), copper(II) acetate (1.0 g) and acetonitrile (75 ml) was boiled under reflux for 1 h, and the solvent was then removed under reduced pressure. The residue was dissolved in acetone (200 ml) and water was added to precipitate the product (2.4 g, 75%) which crystallised (thimble) from methanol as glistening black rods (Found: C, 46.5; H, 5.6; N, 12.8; P, 4.9. $C_{25}H_{33}N_6O_{12}P$ requires, C, 46.8; H, 5.2; N, 13.1; P, 5.0%).

TABLE 1

Diethyl phosphonates [(12)—(22)] prepared from *o*-bromodiarylazo-compounds [(1)—(11)]

Diethyl phosphonate	Reaction time/h	Analyses (%) [Found (Calc.)]									
		C		H		Br		N		P	
(12)	1	49.4	49.25	5.8	5.45			15.8	15.65	6.1	5.8
(13)	0.25	48.5	48.6	5.8	5.5			16.8	17.0	6.1	6.25
(14)	8	50.4	50.1	5.1	5.45			14.6	14.6	6.3	6.45
(15)	24	53.8	53.75	6.3	6.15			14.0	14.25	6.3	6.3
(16)	18	53.8	53.75	6.1	6.15			14.0	14.25	6.4	6.3
(17)	1.25	51.0	51.2	6.1	6.0	14.5	14.85	10.5	10.4	5.5	5.75
(18)	8	51.95	52.3	5.8	6.0	16.55	16.6	8.6	8.7	6.2	6.45
(19)	2.0	46.6	46.3	5.2	5.1	14.4	14.0	12.0	12.3	5.1	5.45
(20)	9	46.6	46.8	5.5	5.1	15.8	15.6	11.1	10.9	6.3	6.05
(21)	0.2	52.1	52.05	6.3	6.2	14.8	14.45	10.2	10.1	5.8	5.6
(22)	1.5	60.4	60.75	7.5	7.45			11.7	11.8	6.7	6.55

*Diethyl {3.5-Dinitro-6-[2-acetylamino-4-(*NN*-diethylamino)phenylazo]phenyl}phosphonate* (12).—(*a*) A stirred mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (1) (2.4 g), triethyl phosphite (1.25 g), copper(II) acetate (1.0 g), and dry ethanol (50 ml) was boiled under reflux for 1 h, cooled, and poured into water (800 ml). The *product* (2.4 g, 90%) was separated, washed with water, and crystallised (thimble) from methanol as glistening black rods (Found: C, 49.4; H, 5.8; N, 15.8; P, 6.1%; M^+ 536. $C_{22}H_{29}N_6O_8P$ requires C, 49.15; H, 5.45; N, 15.65; P, 5.95%); $\delta(CDCl_3)$ 1.3 (12 H, t, $MeCH_2$), 2.3 (3 H, s, MeCO), 3.5 (4 H, q, $MeCH_2N$), 4.1 (4 H, q, $MeCH_2O$), and 6.2—8.3 (5 H, m, aromatic). This method was employed to study the effect of substituents on the copper(II) acetate–promoted reaction of the *o*-bromodiarylazo-compounds [(2)—(11)] with triethyl phosphite in dry ethanol. Results are summarised in Table 1.

(*b*) A stirred mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (1) (1.2 g), triethyl phosphite (0.63 g), copper bronze (0.63 g), and dry ethanol (25 ml) was boiled under reflux under nitrogen for 15 min, when t.l.c. showed complete disappearance of the *o*-bromodiarylazo-compound and the formation of a product having the same R_F value as diethyl {3,5-dinitro-6-[acetylamino-4-(*NN*-diethylamino)phenylazo]phenyl}phosphonate (12) together with a small amount of a product having the same R_F value as 3-acetylamino-4-(2,4-dinitrophenylazo)-*NN*-diethylaniline (29). Treatment of the mixture as in (*a*) gave *diethyl {3,5-dinitro-6-[2-acetylamino-4)-*NN*-diethylamino)phenylazo]phenyl}phosphonate* (0.95 g; 71%) as glistening black rods, i.r. and n.m.r. spectra identical with those of authentic material.

(*c*) When the copper–bronze in the previous experiment was replaced by copper(I) acetate no *o*-bromodiarylazo-compound could be detected after 6 h, when t.l.c. showed the principal coloured product to be diethyl {3,5-dinitro-6-[2-acetylamino-4-(*NN*-diethylamino)phenylazo]phenyl}-phosphonate (12) together with a small amount of 3-acetylamino-4-(2,4-dinitrophenylazo)-*NN*-diethylaniline (29) (identical R_F values in a variety of eluants).

(*d*) The 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline used in experiment (*a*) was replaced by 3-acetylamino-4-(2-iodo-4,6-dinitro-phenylazo)-*NN*-diethylaniline (2.65 g). Reaction was complete in 10 min and gave the same *product* in 92% yield, i.r. spectrum identical with that of authentic material.

(*e*)—(*i*) Replacement of the ethanol used in (*a*) by the following solvents gave the same *product* (reaction temperatures and times to complete disappearance of starting material in parentheses); (*e*) DMSO (80 °C, 15 min); (*f*) *N*-methylpyrrolidone (80 °C, 15 min); (*g*) DMF (80 °C, 1 h); (*h*) THF (65 °C, 47 h); and (*i*) chlorobenzene (115 °C, 3 h).

*Reaction of 3-Acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline* (1) *with Triethyl Phosphite in n-Butyl Alcohol.*—A mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (2.4 g), triethyl phosphite (1.25 g), copper(II) acetate (1.0 g), and n-butyl alcohol (60 ml) was stirred at 80 °C for 23 h, when t.l.c. showed complete disappearance of the *o*-bromodiarylazo-compound and the formation of three new blue products, the R_F value of one of which was identical with that of diethyl {3,5-dinitro-6-[2-acetylamino-4-(*NN*-diethylamino)-phenylazo]phenyl}phosphonate (12). After removal of the solvent under reduced pressure, the residue was dissolved in acetone and the solution was poured into water (600 ml). The precipitated solid was separated, washed with water, and dried. Preparative chromatography [Kieselgel GF_{254} (Typ 60) Merck, ethyl acetate–light petroleum (1 : 1)] gave *diethyl {3,5-dinitro-6-[2-acetylamino-4-(*NN*-diethylamino)phenylazo]phenyl}phosphonate* (12), M^+ 536, i.r. spectrum identical with that of authentic material; *ethyl butyl {3,5-dinitro-6-(2-acetylamino-4-*NN*-diethylamino-*

phenylazo]*phenyl*}*phosphonate*, M^+ 564, fragmentation pattern consistent with this structure; and *dibutyl* {3,5-*dinitro*-6-[2-*acetylamino*-4-(NN-*diethylamino*)*phenylazo*]-*phenyl*}*phosphonate*, M^+ 592, fragmentation pattern consistent with this structure.

Reaction of 3-*Acetylamino*-4-(2-*bromo*-4,6-*dinitrophenylazo*)-NN-*diethylaniline* (1) *with Triethyl Phosphate in Cellosolve*.—Replacement of the n-butyl alcohol used in the preceding experiment by cellosolve gave *diethyl* {3,5-*dinitro*-6-[2-*acetylamino*-4-(NN-*diethylamino*)*phenylazo*]-phenyl}phosphonate (12), M^+ 536, i.r. spectrum identical with that of authentic material; *ethyl* β-*ethoxyethyl* {3,5-*dinitro*-6-[2-*acetylamino*-4-(NN-*diethylamino*)*phenylazo*]-*phenyl*}*phosphonate*, M^+ 580, fragmentation pattern consistent with this structure; and *bis*(β-*ethoxyethyl*) {3,5-*dinitro*-6-[2-*acetylamino*-4-(NN-*diethylamino*)*phenylazo*]-*phenyl*}*phosphonate*, M^+ 624, fragmentation pattern consistent with this structure.

Reaction of 3-*Acetylamino*-4-(2-*bromo*-4,6-*dinitrophenylazo*)-NN-*diethylaniline* (1) *with Triethyl Phosphite in Acetonitrile*.—(*a*) A stirred mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (4.8 g), triethyl phosphite (3.8 g), copper(II) acetate (2.0 g), and acetonitrile (50 ml) was boiled under reflux under nitrogen, and the reaction was followed by t.l.c. After 1 h reaction was effectively complete, the sole coloured product being diethyl {3,5-dinitro-6-[2-acetylamino-4-(*NN*-diethylamino)-phenylazo]phenyl}phosphonate (12)ч(R_F values in several eluants identical with those of authentic material).

(*b*) A stirred mixture of triethyl phosphite (3.8 g), copper(II) acetate (2.0 g), and acetonitrile (50 ml) was boiled under reflux under nitrogen for 1 h during which time the original blue solution became colourless and g.l.c. examination showed the mixture to contain triethyl phosphite and triethyl phosphate. 3-Acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (1) (4.8 g) was added and the reaction was followed by t.l.c. After 1 h the *o*-bromodiarylazo-compound had effectively disappeared and the reaction mixture contained both *diethyl* {3,5-*dinitro*-6-[2-*acetylamino*-4-(NN-*diethylamino*)*phenylazo*]-*phenyl*}*phosphonate* (12) and 3-*acetylamino*-4-(2,4-*dinitrophenylazo*)-NN-*diethylaniline* (29) (R_F values in a variety of eluants identical with those of authentic samples).

(*c*)—(*e*) Stirred mixtures of triethyl phosphite [1.65 g, 3.35 g, and 5.0 g respectively, in experiments (*c*), (*d*), and (*e*)], copper(II) acetate (2.0 g), and acetonitrile (50 ml) were boiled under reflux under nitrogen. In experiments (*e*) and (*d*) the originally blue solutions became colourless in 15 min and 1.5 h, respectively, whilst in experiment (*c*) the original blue colour persisted after 5 h, although markedly reduced in intensity. 3-Acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (1) (4.8 g) was added to each experiment and reaction was followed by t.l.c. After 1 h experiment (*c*) contained a mixture of the parent o-*bromodiarylazo-compound*, 3-*acetylamino*-4-(2,4-*dinitrophenylazo*)-NN-*diethylaniline* (29), and *diethyl* {3,5-*dinitro*-6-[2-*acetylamino*-4-(NN-*diethylamino*)*phenylazo*]*phenyl*}-*phosphonate* (12). Experiments (*d*) and (*e*) contained only the latter two *products*.

Reaction of 3-*Acetylamino*-4-(2-*bromo*-4,6-*dinitrophenylazo*)-NN-*diethylaniline* (1) *with Triethyl Phosphite in Ethyl Acetate*.—(*a*) A stirred mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (4.8 g), triethyl phosphite (2.5 g), copper(II) acetate (2.0 g), and ethyl acetate (160 ml) was boiled under reflux for 10 h when t.l.c. showed reaction to be complete and the sole coloured product to be *diethyl* {3,5-*dinitro*-6-[2-*acetylamino*-4-(NN-*diethylamino*)*phenylazo*]*phenyl*}*phosphonate* (12).

(*b*) A stirred mixture of triethyl phosphite (3.3 g), copper(II) acetate (2.0 g), and ethyl acetate was boiled under reflux under nitrogen for 2 h, during which time the copper(II) acetate dissolved to give an initially blue, and finally colourless solution which was shown by g.l.c. to contain triethyl phosphite and triethyl phosphate. 3-Acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (4.8 g) was added and reaction was followed by t.l.c. After 16 h none of the original *o*-bromodiarylazo-compound could be detected and the mixture contained both *diethyl* {3,5-*dinitro*-6-[2-*acetylamino*-4-(NN-*diethylamino*)*phenylazo*]*phenyl*}*phosphonate* (12) and 3-*acetylamino*-4-(2,4-*dinitrophenylazo*)-NN-*diethylaniline* (29).

Dimethyl {3,5-*Dinitro*-6-[2-*acetylamino*-4-(NN-*diethylamino*)*phenylazo*]*phenyl*}*phosphonate*.—A stirred mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (1) (2.4 g), trimethyl phosphite (1.25 g), copper(II) acetate (1.0 g), and dry methanol (100 ml) was boiled under reflux for 12 h. The mixture was then cooled, and the product was separated and crystallised (thimble) from methanol as glistening black needles (Found: C, 47.5; H, 4.95; N, 16.3; P, 6.3%; M^+ 508. $C_{20}H_{25}N_6O_8P$ requires C, 47.25; H, 4.95; N, 16.55; P, 6.1%).

Diethyl [5-NN-*Diethylamino*-2-(4-*nitrophenylazo*)*phenyl*]-*phosphonate* (28).—(*a*) A stirred mixture of 3-iodo-4-(4-nitrophenylazo)-*NN*-diethylaniline (25) (4.25 g), triethyl phosphite (2.5 g), copper(II) acetate (2.0 g), and dry ethanol (75 ml) was boiled under reflux for 1 h, when t.l.c. showed reaction to be complete. The mixture was filtered while still hot, and the filtrate was diluted with water (500 ml) to precipitate the *product* (3.9 g, 90%) which crystallised (thimble) from methanol as brown rods (Found: C, 54.9; H, 6.4; N, 12.8; P, 7.0%; M^+ 434. $C_{20}H_{27}N_4O_5P$ requires C, 55.3; H, 6.25; N, 12.9; P, 7.15%).

(*b*) When the 3-iodo-4-(4-nitrophenylazo)-*NN*-diethylaniline used in the previous experiment was replaced by 3-bromo-4-(4-nitrophenylazo)-*NN*-diethylaniline (26) (3.8 g) the reaction went to completion in 6 h. The product (3.8 g, 87%) was identical (i.r.) with that from the preceding experiment.

(*c*) A comparable reaction employing 3-chloro-4-(4-nitrophenylazo)-*NN*-diethylaniline (27) failed to go to completion in 24 h. The presence of diethyl-[5-*NN*-diethylamino-2-(4-nitrophenylazo)phenyl]phosphonate in the reaction mixture was demonstrated by t.l.c. A similar experiment using 3-fluoro-4-(4-nitrophenylazo)-*NN*-diethylaniline showed no sign of reaction after 24 h.

3-*Acetylamino*-4-(2,4-*dinitrophenylazo*)-NN-*diethylaniline* (29).—(*a*) A stirred mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (1) (4.8 g), triethyl phosphite (3.3 g), copper(II) acetate (2.0 g), water (5.0 ml), and ethanol (50 ml) was boiled under reflux for 1 h when t.l.c. showed the *o*-bromodiarylazo-compound to have disappeared. The mixture was filtered while still hot and the residue on the filter was washed with ethanol. Crystallisation (thimble) from methanol gave the *product* as glistening black needles (Found: C, 56.3; H, 5.3; N, 20.6%; M^+ 400. Calc. for $C_{18}H_{20}N_6O_5$: C, 56.0; H, 5.05; N, 21.0%); δ($CDCl_3$) 1.3 (6 H, t, $MeCH_2$), 2.25 (3 H, s, *Me*CO), 3.5 (4 H, q, $MeCH_2$), and 6.3—8.2 (6 H, m, aromatic).

(*b*) The preceding experiment was repeated using deuterium oxide (5.0 ml) in place of the water. The i.r.

spectrum of the product was identical with that of the product from the preceding experiment, and its mass spectrum showed considerable enhancement of the molecular ion of M^+ 401.

3-*Acetylamino*-4-(4-*nitrophenylazo*)-NN-*diethylaniline* (30).—A stirred mixture of triethyl phosphite (3.3 g), copper(II) acetate (2.0 g), and acetonitrile (50 ml) was boiled under reflux under nitrogen for 18 h, during which time the initially blue solution became colourless. G.l.c examination of the reaction mixture showed it to contain triethyl phosphate. 3-Acetylamino-4-(2-bromo-4-nitrophenylazo)-*NN*-diethylaniline (4) (4.35 g) was added and the mixture was boiled under reflux for 24 h, cooled, and filtered. Crystallisation (thimble) from methanol gave the product (1.4 g, 39.5%) as glistening black needles (Found: C, 61.4; H, 5.5; N, 19.4%; M^+ 354. Calc. for $C_{18}H_{20}N_5O_3$: C, 61.0; H, 5.7; N, 19.75%), i.r. spectrum identical with that of authentic material.

3-*Acetylamino*-4-{2-[3,5-*dinitro*-2-(2-*acetylamino*-4-NN-*diethylaminophenylazo*)*phenyl*]-4,6-*dinitrophenylazo*}-NN-*diethylaniline* (32).—(*a*) A stirred mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (1) (4.8 g), copper–bronze (2.5 g), and dry ethanol (100 ml) was boiled under reflux under nitrogen for 90 min, cooled, and filtered. Crystallisation (thimble) of the residue from ethanol gave the *product* (2.9 g, 73%) as glistening black rods (Found: C, 54.4; H, 4.8; N, 21.2%; M^+ 798. $C_{36}H_{38}N_{12}O_{10}$ requires C, 54.15; H, 4.8; N, 21.05%); $\delta(CDCl_3)$ 1.22 (12 H, t, *Me*CH$_2$), 2.15 (6 H, s, MeCO), 3.45 (8 H, q, MeC*H*$_2$), and 6.15—8.55 (10 H, m, aromatic).

(*b*) Repetition of the preceding experiment in the presence of water (10 ml) gave a similar result (i.r. spectrum of *product* identical with that of authentic material).

(*c*) When experiment (*a*) was repeated using copper(I) acetate (2.45 g) in place of the copper–bronze, after 1 h t.l.c. showed the mixture to contain 3-acetylamino-4-{2-[3,5-dinitro-2-(2-acetylamino-4-*NN*-diethylaminophenylazo)phenyl]-4,6-dinitrophenylazo}-*NN*-diethylaniline (32) together with minor amounts of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (1) and 3-acetylamino-4-(2,4-dinitrophenylazo)-*NN*-diethylaniline (29). The *product*, isolated as in (*a*), (2.4 g, 64%) had an i.r. spectrum identical with that of authentic material.

3-*Acetylamino*-4-{2-[5-*bromo*-3-*nitro*-2-(2-*acetylamino*-4-NN-*diethylaminophenylazo*)*phenyl*]-4-*bromo*-6-*nitrophenylazo*}-NN-*diethylaniline* (33).—A stirred mixture of 3-acetylamino-4-(2,4-dibromo-6-nitrophenyl-azo)-*NN*-diethylaniline (8) (2.55 g), copper–bronze (1.25 g), and ethanol (50 ml) was boiled under reflux for 1 h and filtered while still hot. Crystallisation (thimble) of the residue from ethanol gave the product (1.5 g, 69%) as glistening green prisms (Found: C, 50.1; H, 4.3; Br, 18.2; N, 16.4. $C_{36}H_{38}Br_2N_{10}O_6$ requires C, 49.9; H, 4.4; Br, 18.45; N, 16.15%).

In an attempted preparation of 4-{2-[5-bromo-3-nitro-2-(4-*NN*-diethylaminophenylazo)phenyl]-4-bromo-6-nitrophenylazo}-*NN*-diethylaniline from 4-(2,4-dibromo-6-nitrophenylazo)-*NN*-diethylaniline under similar conditions to those employed in the preceding experiment, little or no reaction could be detected by t.l.c. after 6 h.

Copper-promoted Reactions of 3-*Acetylamino*-4-(2-*bromo*-4,6-*dinitrophenylazo*)-NN-*diethylaniline* (1) *in Ethanol–Acetic Acid and Ethanol–Trifluoroacetic Acid*.—(*a*) A stirred mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (4.8 g), copper–bronze (2.5 g), acetic acid (1.2 g), and dry ethanol (100 ml) was boiled under reflux under nitrogen for 90 min, when t.l.c. showed complete disappearance of the *o*-bromodiarylazo-compound and the formation of two products having R_F values identical with those of authentic 3-acetylamino-4-(2,4-dinitrophenylazo)-*NN*-diethylaniline (29) and 3-acetylamino-4-{2-[3,5-dinitro-2-(2-acetylamino-4-*NN*-diethylaminophenylazo)-phenyl]-4,6-dinitrophenylazo}-*NN*-diethylaniline (32), respectively. The mixture was cooled, filtered, and the residue extracted (thimble) with acetone. The acetone extracts were evaporated on a steam-bath while maintaining constant volume by the addition of ethanol. When crystallisation occurred the mixture was filtered while still hot to obtain 3-*acetylamino*-4-(2,4-*dinitrophenylazo*)-NN-*diethylaniline* (29) (1.4 g; 35%), i.r. and n.m.r. spectra identical with those of authentic material. On cooling, the filtrate deposited 3-*acetylamino*-4-{2-[3,5-*dinitro*-2-(2-*acetylamino*-4-NN-*diethylaminophenylazo*)*phenyl*]-4,6-*dinitrophenylazo*}-NN-*diethylaniline* (32) (0.9 g, 22%), i.r. and n.m.r. spectra identical with those of authentic material.

(*b*) When the preceding experiment was repeated using trifluoroacetic acid (2.3 g) in place of acetic acid, t.l.c. after 30 min showed complete disappearance of the *o*-bromodiarylazo-compound and the formation of a product having an R_F value identical with that of 3-acetylamino-4-(2,4-dinitrophenylazo)-*NN*-diethylaniline, together with a very faint trace of a product having an R_F value identical with that of 3-acetylamino-4-{2-[3,5-dinitro-2-(2-acetylamino-4-*NN*-diethylaminophenylazo)phenyl]-4,6-dinitrophenylazo}-*NN*-diethylaniline. The mixture was cooled, filtered, and the residue was crystallised (thimble) from ethanol to obtain 3-acetylamino-4-(2,4,-dinitrophenylazo)-*NN*-diethylaniline (3.3 g, 82.5%) as glistening black needles, i.r. and n.m.r. spectra identical with those of authentic material.

(*c*) A stirred mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (1.2 g), copper(I) acetate (1.2 g), trifluoroacetic acid (2.3 g), and dry ethanol (25 ml), was boiled under reflux under nitrogen for 6 h and filtered while still hot. Crystallisation (thimble) of the residue from ethanol gave 3-*acetylamino*-4-(2,4-*dinitrophenylazo*)-NN-*diethylaniline* (0.65 g; 65%) as glistening black needles, i.r. and n.m.r. spectra identical with those of authentic material.

(*d*) A stirred mixture of 3-acetylamino-4-(2-bromo-4,6-dinitrophenylazo)-*NN*-diethylaniline (1.2 g), copper(II) acetate (0.5 g), acetic acid (0.6 g), and dry ethanol (25 ml) was boiled under reflux under nitrogen for 24 h, during which time no reaction was detected by t.l.c.

Diethyl 2-Methoxycarbonylphenylphosphonate (*with* P. A. MACK).—A stirred mixture of methyl-*o*-iodobenzoate (26.2 g), copper(II) acetate (20.0 g), triethyl phosphite (49.8 g), and dry ethanol (100 ml) was boiled under reflux under nitrogen for 4 h, when g.l.c. showed the reaction to be effectively complete. After removal of the solvent under reduced pressure, distillation of the residual oil gave main fraction, b.p. 80—140 °C at 0.25 mmHg. This was redistilled through a heated, 8-in Dufton column to obtain the product (23.0 g, 84%) as a colourless oil, b.p. 145 °C at 0.4 mmHg (Found: C, 53.1; H, 6.1; P, 11.5. $C_{12}H_{17}O_5P$ requires C, 52.95; H, 6.3; P, 11.4%); δ 1.3 (6 H, t, *Me*CH$_2$), 3.85 (3 H, s, MeO), 4.1 (4 H, q, MeC*H*$_2$), and 7.45—8.25 (4 H, m, aromatic). Under comparable conditions *o*-iodoaniline failed to react with triethyl phosphite.

Diethyl 2-Nitrophenylphosphonate.—(*a*) A stirred mixture of 2-iodonitrobenzene (10 g), triethyl phosphite (9.95 g), copper(II) acetate (8.0 g), and dry ethanol was boiled under reflux for 6 h, when g.l.c. showed reaction to be complete. After removal of the solvent under reduced pressure, the residual oil crystallised on cooling. Crystallisation from light petroleum gave the *product* (8.3 g, 80%) as fawn plates (Found: C, 46.3; H, 5.7; N, 5.5; P, 12.1%; M^+ 259. $C_{10}H_{14}NO_5P$ requires C, 46.35; H, 5.45; N, 5.4; P, 11.95%); $\delta(CDCl_3)$ 1.35 (6 H, t, Me), 4.2 (4 H, q. MeCH_2), and 7.4—8.35 (4 H, m, aromatic).

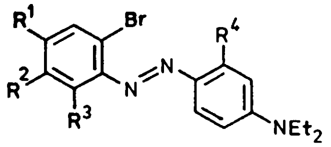
(*b*) When the 2-iodonitrobenzene in the preceding experiment was replaced by 2-bromonitrobenzene, reaction proceeded to completion in 24 h. The i.r. spectrum of the product was identical with that of authentic material.

Diethyl 9,10-*Dioxoanthracen*-1-*yl phosphonate* (*with* P. M. Rowbotham).—A stirred mixture of 1-bromoanthraquinone (2.85 g), triethyl phosphite (2.5 g), copper(II) acetate (2.0 g), and dry ethanol (60 ml) was boiled under reflux for 18 h. The mixture was then filtered while still hot and the solvent was removed under reduced pressure. The residual green solid was stirred with hydrochloric acid (200 ml, 5N), the mixture was filtered, and the filtrate was extracted with chloroform. After removal of the solvent from the dried (magnesium sulphate) chloroform extracts the *product* (1.6 g, 46.5%) was obtained as a colourless solid, which crystallised from light petroleum as colourless needles (Found: C, 62.5; H, 5.2; P, 9.2%; M^+ 344. $C_{18}H_{17}O_5P$ requires C, 62.8; H, 5.0; P, 9.0%); $\delta(CDCl_3)$ 1.4 (6 H, t, *Me*CH$_2$), 4.35 (4 H, q, MeCH_2), and 7.7—8.65 (7 H, m, aromatic).

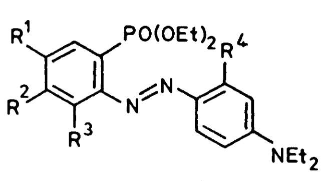
RESULTS

In the presence of copper(II) acetate, (1) reacts with triethyl phosphite in boiling, dry ethanol to give (12) in good yield. The reaction is remarkably clean and no deoxygenation or cyclisation reactions were observed such as might be expected[17,18] when triethyl phosphite reacts with a compound containing two nitro-groups and an *o*-nitrodiarylazo-system. This can doubtless be attributed to the mild conditions under which the reaction occurs. The scope of the reaction with regard to *o*-bromodiarylazo-compounds is broad and is illustrated by the results summarised in Table 1. Several features are noteworthy. (*a*) In those reactions where the diarylazo-compound contains two bromine atoms [(6)—(10)], only the bromine atom *ortho* to the azo-group is replaced by a diethylphosphonate group; the *p*-bromine atom is unaffected. (*b*) Polar effects of substituents are markedly different from those anticipated[24] in uncatalysed nucleophilic replacement reactions [(1), (4), (5), (6), (10), and (11)]. (*c*) The replacement reaction is sensitive to the steric effects of substituents in the benzene ring carrying the bromine atom. Those compounds [(1), (6), (8), (10), and (11)] in which R³ is a group other than hydrogen react more readily than do the comparable unsubstituted compounds, irrespective of the polar nature of the substituent. (*d*) The presence of an acetylamino- or an amino-group in the *ortho'* position facilitates reaction to a remarkable degree [(1) and (2) *vs.* (3); (6) *vs.* (7); (8) *vs.* (9)].

o'-Donor substituents other than acetylamino- and amino-groups are also effective and (23) reacts with triethyl phosphite under similar conditions to give diethyl 2-(2-hydroxynaphthyl-1-azo)-phenylphosphonate. Compound (24) reacts even more rapidly to give the corresponding diethyl phosphonate.



(1)—(11)



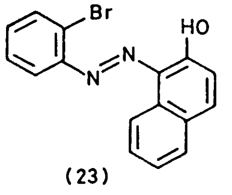
(12)—(22)

(1), (12) $R^1 = R^3 = NO_2$, $R^2 = H$, $R^4 = NHCOMe$
(2), (13) $R^1 = R^3 = NO_2$, $R^2 = H$, $R^4 = NH_2$
(3), (14) $R^1 = R^3 = NO_2$, $R^2 = R^4 = H$
(4), (15) $R^1 = NO_2$, $R^2 = R^3 = H$, $R^4 = NHCOMe$
(5), (16) $R^1 = R^3 = H$, $R^2 = NO_2$, $R^4 = NHCOMe$
(6), (17) $R^1 = Br$, $R^2 = H$, $R^3 = Me$, $R^4 = NHCOMe$
(7), (18) $R^1 = Br$, $R^2 = R^4 = H$, $R^3 = Me$
(8), (19) $R^1 = Br$, $R^2 = H$, $R^3 = NO_2$, $R^4 = NHCOMe$
(9), (20) $R^1 = Br$, $R^2 = R^4 = H$, $R^3 = NO_2$
(10), (21) $R^1 = Br$, $R^2 = H$, $R^3 = Et$, $R^4 = NHCOMe$
(11), (22) $R^1 = R^3 = Me$, $R^2 = H$, $R^4 = NHCOMe$

Ease of halogen replacement follows the anticipated[25] sequence I > Br > Cl, a feature illustrated by the reaction of (25)—(27) with triethyl phosphite in the presence of copper(II) acetate in boiling, dry ethanol. The iodo-compound reacts completely in 1 h to give (28). The same product is obtained from the bromo-compound in 6 h, whilst reaction of the chloro-compound is incomplete after 24 h. The fluoro-compound fails to react. A similar sequence is observed with ethyl *o*-halogenobenzoates.

The reaction has been successfully applied to other aryl halides having *o*-donor functions, *e.g.* ethyl *o*-iodo- and *o*-bromo-benzoates, *o*-iodo- and *o*-bromo-nitrobenzenes, and 1-bromoanthraquinone, but fails with simple aryl halides.

In alcoholic solvents other than ethanol, *e.g.* butanol and cellosolve, treatment of (1) with triethyl phosphite in the presence of copper(II) acetate gives a mixture of the three possible esters of 3,5-dinitro-6-(2-acetylamino-4-*NN*-diethylaminophenylazo)phenylphosphonic acid. Ester



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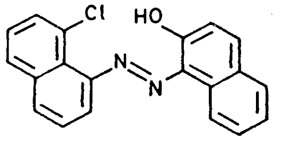

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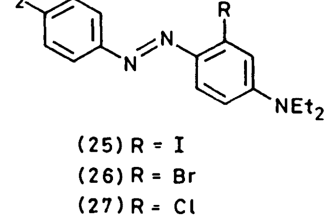
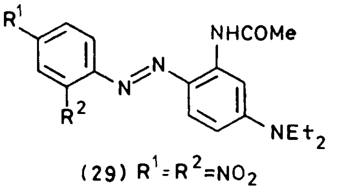


(25) R = I
(26) R = Br
(27) R = Cl
(28) R = PO(OEt)₂

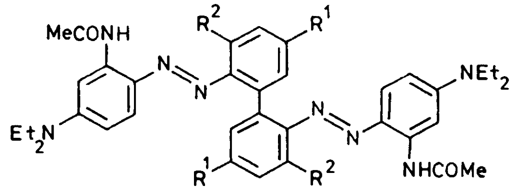
exchange occurs before reaction of the trialkyl phosphite with the *o*-bromodiarylazo-compound, and is promoted [26] by the copper salt. The problem is avoided by suitable choice of phosphite ester and alcohol, and (1) reacts with trimethyl phosphite in the presence of copper(II) acetate in boiling, dry methanol to give dimethyl {3,5-dinitro-6-[2-acetylamino-4-(*NN*-diethylamino)phenylazo]phenyl}phosphonate in good yield.



(29) $R^1 = R^2 = NO_2$
(30) $R^1 = NO_2$, $R^2 = H$
(31) $R^1 = Br$, $R^2 = NO_2$

When (1) is treated with triethyl phosphite and copper(II) acetate in boiling, 10% aqueous ethanol, (29) is produced in addition to (12). Reductive substitution of this type is not uncommon in copper-promoted reactions of aryl halides and is usually associated [25,27,28] with the presence of hydrogen donors in the reaction mixture. In the present instance it is directly attributable to a change in solvent from dry to 10% aqueous ethanol.

Hydrated copper(II) acetate has relatively low solubility in dry ethanol but dissolves readily in the presence of triethyl phosphite to give a blue solution which is not decolourised on prolonged boiling. When water is added the solution rapidly becomes colourless, indicating reduction of copper(II) to copper(I), and triethyl phosphate can be detected in the solution. Addition of (1) results in the formation of a mixture of (12) and (29). In boiling, dry ethanol, however, (1) reacts with triethyl phosphite in the presence of copper(I) acetate to give only (12). It appears, therefore, that the formation of (29) is associated with the acetic acid produced by the reduction of the copper(II) acetate. In fact (29) is produced, together with the Ullmann coupling product, (32), when (1) is treated with acetic acid in the presence of copper(I) acetate in boiling, dry ethanol. When the acetic acid is replaced by trifluoroacetic acid, (29) is the sole product. No reaction occurs in either case in the absence of copper(I) acetate, or when the latter is replaced by copper(II) acetate. The formation of the Ullmann coupling product (32) in the former of these experiments was unexpected, since this product had not been detected in any of the earlier reactions. However, (1) readily undergoes Ullmann coupling in boiling, dry ethanol in the presence of copper–bronze or copper(I) acetate. In the latter case a small amount of the reduction product (29) is also produced. Again no reaction occurs if the copper–bronze or copper(I) acetate are replaced by copper(II) acetate.



(32) $R^1 = R^2 = NO_2$
(33) $R^1 = Br$, $R^2 = NO_2$

In the presence of copper–bronze (8) also readily undergoes Ullmann coupling in boiling ethanol to give (31). Reaction is complete in 1 h and involves only the bromine atom *ortho* to the azo-group in the parent diarylazo-compound. That in the *para*-position remains unaffected after 24 h reflux. Under similar conditions (9) fails to react, and is recovered unchanged after 6 h.

The copper–bronze-promoted Ullmann coupling of (1) is almost completely suppressed in the presence of triethyl phosphite, when the principal product is (12). Both Ullmann coupling and reductive substitution occur when (1) is treated with copper–bronze and acetic acid in boiling, dry ethanol. Replacement of the acetic acid by trifluoroacetic acid results in almost exclusive formation of (29).

Reduction of copper(II) acetate by triethyl phosphite has also been observed in solvents other than 10% aqueous ethanol, *e.g.* acetonitrile and ethyl acetate. The reduction appears to be slow, and dependent upon the triethyl phosphite concentration (Table 2). Addition of (1) to the three solutions (Table 2) gives, in each case, a mixture of (12) and (29). In the first experiment a considerable amount of the *o*-bromodiarylazo-compound remains unchanged. In contrast, when a mixture of (1), triethyl phosphite, copper(II) acetate, and acetonitrile is raised to the boil, reaction is complete in 1 h and the sole product is (12), implying that the reaction (1)→(12) occurs more rapidly in acetonitrile than does reduction of copper(II) to copper(I). Similar results are obtained when the acetonitrile is replaced by ethyl acetate.

TABLE 2

Reaction of copper(II) acetate with triethyl phosphite in boiling acetonitrile

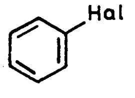
Molar ratio triethyl phosphite : copper(II) acetate	Time/h	Colour of solution
1 : 1	5	pale blue
2 : 1	1.5	colourless
3 : 1	0.25	colourless

Conversion of (1) into (12) by reaction with triethyl phosphite in the presence of copper(II) acetate proceeds readily in solvents such as dimethyl sulphoxide, dimethylformamide, and *N*-methylpyrrolidone, and more slowly in tetrahydrofuran and chlorobenzene. Salts of other metals, including iron, cobalt, nickel, and zinc, fail to promote the reaction.

DISCUSSION

The function of copper in promoting the biaryl coupling, nucleophilic substitution, and reductive replacement of aryl halides has been the subject of debate [25,27] for many years. Various mechanisms have been proposed including involvement of four-centre transition states,[25,29,30] polarisation of the carbon–halogen bond by co-ordination of the latter to copper in a simple [24,31] or chelate [32,33] complex, interaction of the aryl halide with a solvated copper(I) oligomeric species,[28] and intervention of copper aryls.[27,34] None, however, satisfactorily accounts for all the known facts. The results of the present work serve to draw attention to some of the outstanding problems in this area and make it clear that attempts to rationalise the various reactions in terms of a single mechanism are unlikely to succeed.

For the purposes of this discussion aryl halides are divided into three classes: Type I, those in which the halogen does not occupy a potentially chelating position relative to any donor groups which may be present in the molecule (34); Type II, those in which the halogen occupies a potentially chelating position relative to one donor group in the molecule (35); and Type III, those in which the halogen is so located relative to two donor groups in the molecule that, in principle, the possibility exists of its being involved in the formation of an annelated, copper chelate complex (36). The rationale for this classification is the very marked difference in reactivity of comparable aryl halides of the three types in copper-promoted reactions. Thus, under the mild conditions employed throughout this work, Type I aryl halides [exemplified by the bromine atoms *para* to the azo-group in (6)—(10)] are uniformly inert. Type II aryl halides [exemplified by the bromine atoms *ortho* to the azo-group in (3), (7), and (9)] are susceptible to nucleophilic substitution by triethyl phosphite but fail to undergo reductive replacement or biaryl coupling reactions. Comparable Type III aryl halides [exemplified by the bromine atoms *ortho* to the azo-group in (1), (2), (6), (8), (10), and (11)] undergo all three reactions and nucleophilic substitution by triethyl phosphite proceeds much more rapidly than in the analogous Type II *o*-bromodiarylazo-compounds. However, examination of Table 1 reveals that a subdivision of the Type III aryl halides is necessary. Thus, those Type III *o*-bromodiarylazo-compounds having substituents other than hydrogen in the 6-position [(1), (2), (6), (8), (10), and (11)] react with triethyl phosphite much more rapidly than do those in which the 6-position is occupied by hydrogen [(4) and (5)]. Since the polar character of the 6-substituent has little influence this appears to be a steric effect, and it may be inferred that structure (37) is more favourable for reaction to occur than structure (38). A similar conclusion may be drawn with regard to Type II aryl halides from related work [35] on copper-promoted nucleophilic replacement reactions of *o*-bromodiarylazo-compounds. Furthermore, the results obtained with *o*-iodoaniline on the one hand and methyl-*o*-iodobenzoate, *o*-iodonitrobenzene, and 1-bromoanthraquinone on the other, make it necessary to restrict the definitions of Types II and III aryl halides to those in which the halogen atom is so located relative to a donor group in the molecule that, in principle, the possibility exists of its being involved in the formation of a six-membered chelate ring.



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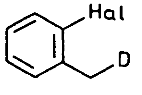

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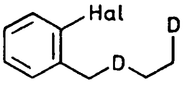
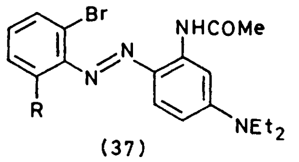


(36)

(D = donor atom)

It is tempting to rationalise the behaviour of *o*-bromodiarylazo-compounds of Types II and III in terms of polarisation of the carbon–halogen bond resulting from involvement of the latter in copper complex formation [(39) and (40)]. However, attempts to isolate copper complexes of *o*-bromodiarylazo-compounds from the various media in which the reactions have been carried out were uniformly unsuccessful. This does not, of course, preclude the possible intervention of transient complexes of these types, but present evidence does not unequivocally justify this conclusion. Furthermore, such a rationalisation fails to provide a satisfactory explanation for the different behaviour of Type II and Type III aryl halides in Ullmann coupling and reductive replacement reactions.



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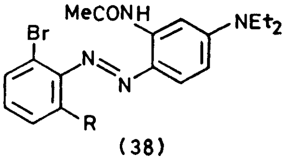
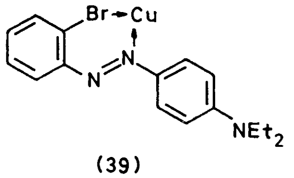


(38)

So far as the state of the copper is concerned, it is clear that copper(II) fails to promote biaryl coupling or reductive replacement under the conditions employed here. On the present evidence little further can be said, since copper–bronze and copper(I) acetate promote both reactions, but it is reasonable to infer that radical processes are involved, at least in the biaryl coupling reaction. It is equally difficult to draw any firm conclusions regarding the function of copper in promoting nucleophilic substitution of the aryl halides by triethyl phosphite. The results described here make it abundantly clear that redox processes are involved in the reaction of triethyl phosphite with copper(II) acetate. It would, therefore, be unwise to speculate on the nature of the active species. It is, however, of considerable interest to note that all three types of reaction can take place simultaneously in a single reaction mixture.



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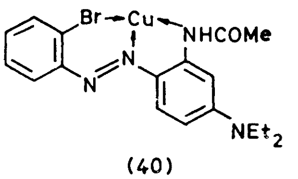

(40)

The work described here provides a novel, facile method for the preparation of dialkyl arylphosphonates and serves to highlight a number of outstanding problems in the field of copper catalysis. Elucidation of these problems awaits the outcome of continuing studies.

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