Novel Redox Reactions of Diazonium Fluoroborates. The Formation of Copper Salt–Azo-compound Complexes: Water-induced Free Radical Aromatic Arylation

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Whereas certain diazonium fluoroborates (ArN_2BF_4) are stable in benzene at room temperature in the presence of equivalent amounts of copper powder, they react slowly on addition of acetone (10% v/v) to the mixture to give precipitates of red complexes of the azo-compounds (ArN:NAr) with ionic copper. In addition, the free azo-compounds and small (<10%) amounts of biaryls (ArPh) can be isolated. The complexes decompose in water or in polar solvents to give the corresponding azo-compounds. In contrast, when the reaction of the diazonium salt is carried out in the presence of water (2 mol. equiv.), either free or bound in the form of hydrated salts, *e.g.* magnesium sulphate monohydrate, high yields of biaryls (ArPh) formed by a free radical path are obtained. Azo-complexes are not formed and are not precursors in this reaction, in which copper acts as catalyst.

These contrasting observations represent extremes of behaviour of diazonium salts in the presence of copper; the use of smaller quantities of water leads to mixtures of products.

The stoicheiometry has been established in each of these reactions and explanations in terms of a series of one-electron, redox reactions of the Waters type are presented.

Similar reactions occur with *p*-chlorobenzenediazonium hexafluorophosphate.

COPPER salt-induced reactions of diazonium salts have been investigated extensively and it is now accepted that the Sandmeyer reaction [1] and the related Meerwein arylation [1] of olefins proceed by a series of one-electron transfer processes involving the formation of aryl radicals. This one-electron transfer mechanism for the Sandmeyer reaction was proposed by Waters [2] in 1942 and has since received ample experimental support.[3]

It is generally assumed that the related Gattermann reaction,[1] in which finely divided copper is used instead of copper(I) salts, proceeds in a similar fashion, although no studies directed at the mechanism of this reaction have been carried out. Copper is also associated with the Pschorr cyclisation [1,4] of diazonium salts. The mechanism of the latter reaction has not been established un-

equivocally in all cases and it appears that heterolytic or homolytic routes can be followed according to circumstance.

It was our intention therefore to investigate the copper-induced decomposition of simple diazonium fluoroborates (ArN_2BF_4) in the presence of an aromatic solvent (Ar'H) under conditions of successful Pschorr-type ring closure, in the expectation that arylation of the solvent would occur. Determination of the composition of the resultant isomeric mixture of biaryls (ArAr') [5] would then allow a decision to be made concerning the nature of the intermediate in the reaction.

Few examples of copper-induced decomposition of simple diazonium fluoroborates in aromatic solvents have been reported. Gilman and Yablunky [6] unsuccessfully attempted to produce an organobismuth compound by

[1] H. Zollinger, ' Diazo and Azo Chemistry, Aliphatic and Aromatic Compounds,' Interscience, New York, 1961; D. C. Nonhebel, *Chem. Soc. Special Publ.*, No. 24, 1970, p. 409.

[2] W. A. Waters, *J. Chem. Soc.*, 1942, 266.

[3] D. C. Nonhebel and W. A. Waters, *Proc. Roy. Soc. (A)*, 1957, **242**, 16.

[4] R. A. Heacock and D. C. Hey, *J. Chem. Soc.*, 1952, 1508.

[5] G. H. Williams, ' Homolytic Aromatic Substitution,' Pergamon, Oxford, 1960.

[6] H. Gilman and H. L. Yablunky, *J. Amer. Chem. Soc.*, 1941, **63**, 949.

decomposition of a diazonium fluoroborate in the presence of bismuth and copper. Starkey and Whaley [7] claimed to have prepared arylcopper compounds by heating a mixture of diazonium fluoroborate in dry benzene or toluene in the presence of copper powder. Experimental details were sparse, and the isomeric composition of a biaryl fraction which was obtained was not determined. These results were later challenged by Warf,[8] who stated that Starkey and Waley had obtained copper(I) fluoroborate rather than the arylcopper. This criticism was supported by little experimental evidence, however, and Makarova and Matveeva [9] have reported that the copper-catalysed decomposition of diazonium fluoroborates in ethyl benzoate gives isomeric 2'- and 4'-substituted biaryls on being heated, but the amount of diazonium fluoroborate accounted for in identified products was very low (3%). Abramovitch and his coworkers [10] on the other hand have more recently reported evidence believed to be indicative of the participation of diradical cations in uncatalysed decompositions of diazonium fluoroborates.

The nature of the copper-induced reaction of diazonium fluoroborate with aromatic solvents was thus not established at the start of this investigation, although Waters [11] concluded in 1939 that the copper- or zinc-induced decomposition of diazonium chlorides in acetone proceeded by way of radicals, and more recently Waters and his coworkers [12] confirmed that the zinc-catalysed decomposition of arenediazonium fluoroborates in acetone leads to aryl radicals.

EXPERIMENTAL

Materials.—Benzene (AnalaR) was dried over sodium and distilled. Fluorobenzene, chlorobenzene, and pyridine were dried and fractionally distilled. AnalaR acetone was used without purification. Nitrobenzene was fractionally frozen and distilled.

Azobenzene (m.p. 67—68°), 4,4'-dichloroazobenzene (m.p. 186—188°; lit.,[13] 188°), and 4,4'-dibromoazobenzene (m.p. 206°; lit.,[13] 205°) were prepared by reduction of the corresponding nitrobenzenes. 4,4'-Dimethylazobenzene had m.p. 144° (lit.,[13] 144°).

Copper powder. Powdered zinc (AnalaR; 16·25 g) was added in portions to a stirred solution of copper sulphate (93·6 g) in water (300 ml) at 0°. The precipitated copper was collected and washed with water, 2M-hydrochloric acid, water, alcohol, and finally ether, and then dried (CaCl₂) *in vacuo*.

Arenediazonium fluoroborates, prepared in the usual way, were purified to constant decomposition point by precipitation from acetone with ether. The products were dried *in vacuo* in the dark and were freshly recrystallised from acetone–ether before use. Their decomposition points agreed with literature values. *p*-Chlorobenzenediazonium hexafluorophosphate was provided by the Ozark–Mahoning Co., Oklahoma.

Reactions of Copper with Diazonium Fluoroborates in Aromatic Solvent–Acetone Mixtures.—The procedure is exemplified by the following experiments, which were carried out at room temperature unless otherwise stated.

(i) p-*Bromobenzenediazonium fluoroborates in benzene.* There was no reaction between the fluoroborate and copper in dry benzene during 72 h. A suspension of *p*-bromobenzenediazonium fluoroborate (9·0 g, 0·033 mol) in benzene (150 ml) and acetone (15 ml) was stirred magnetically. After 2 min copper powder (2·1 g, 0·033 mol) was added. After a few min a reaction occurred with the evolution of nitrogen and precipitation of a voluminous red complex. The reaction was complete after 4 h. The complex (10·4 g) was collected, washed with light petroleum (b.p. 40—60°) and dried *in vacuo* (Found: C, 17·9; H, 2·1; Br, 19·4; N, 6·75%). Evaporation of the filtrate and chromatography of the residue gave 4,4'-dibromoazobenzene (9·73 g), m.p. and mixed m.p. 204°. Treatment of the complex (10·0 g) with acetone (50 ml) caused decomposition with slight effervescence to give a yellow solid (5·074 g); the acetone solution on evaporation gave 4,4'-dibromoazobenzene (0·12 g), m.p. and mixed m.p. 204°. Extraction of the yellow solid with chloroform gave more azo-compound (3·853 g) and left a copper-containing residue (1·221 g). The total yield of 4,4'-dibromoazobenzene was 86%.

(ii) *Toluene-*p-*diazonium fluoroborate in nitrobenzene.* The fluoroborate (6 g) was stirred with copper powder (3 g) in nitrobenzene (100 ml) and acetone (10 ml). After evolution of nitrogen was complete the precipitated red complex was collected, washed with dry benzene, and dried *in vacuo*. The filtrate was washed (H₂O) and dried, and the solvents were removed by distillation through a helix-packed fractionating column. The residue, on distillation, gave an orange solid, b.p. 80—120° at 0·2 mmHg (1·47 g). This on chromatography gave crude 4,4'-dimethylbiphenyl (0·4 g, 15%) which on recrystallisation from light petroleum (b.p. 40—60°) had m.p. and mixed m.p. 119—120°, and 4,4'-dimethylazobenzene (0·65 g), m.p. 141°.

The red complex was treated with water (100 ml) to give a brown solid and a blue solution. The residue was digested with acetone to give copper (1·82 g) and 4,4'-dimethylazobenzene (1·26 g), m.p. and mixed m.p. 141—143° (total yield 64%). A portion of the blue aqueous solution was shown to contain copper(II) ions. The remainder was treated with a saturated solution of potassium chloride at 0°. The colourless precipitate was collected, washed with cold water, and dried. The i.r. spectrum was identical with that of potassium fluoroborate.

(iii) p-*Chlorobenzenediazonium fluoroborate in benzene: reactions of the complex so formed.* The diazonium salt (9 g, 0·04 mol) in benzene (150 ml) and acetone (15 ml) with copper (3·6 g, 0·57 mol) at room temperature gave a red complex, which was collected. The filtrate gave a red solid (1·83 g), m.p. 72—110° which on chromatography on alumina gave 4-chlorobiphenyl (1·02 g, 13·5%), m.p. and mixed m.p. 76°, and 4,4'-dichloroazobenzene (0·77 g, 15%), m.p. and mixed m.p. 184—185°.

[7] E. B. Starkey and W. M. Whaley, *J. Amer. Chem. Soc.*, 1946, **68**, 793.
[8] J. C. Warf, *J. Amer. Chem. Soc.*, 1952, **74**, 3702.
[9] L. G. Makarova and M. K. Matveeva, *Izvest. Akad. Nauk S.S.S.R. Otdel. khim. Nauk*, 1960, 1974 (English trans. p. 1838); 1961, 1772.

[10] R. A. Abramovitch, W. A. Hymers, J. B. Rajan, and R. Wilson, *Tetrahedron Letters*, 1963, 1507; R. A. Abramovitch and J. G. Saha, *Canad. J. Chem.*, 1965, **43**, 3269.
[11] W. A. Waters, *J. Chem. Soc.*, 1939, 864.
[12] B. A. Marshall and W. A. Waters, *J. Chem. Soc.*, 1959, 381; R. O. C. Norman and W. A. Waters, *ibid.*, 1958, 167; P. S. Johnson and W. A. Waters, *ibid.*, 1962, 4652.
[13] I. M. Heilbron, ' Dictionary of Organic Compounds,' Eyre and Spottiswoode, London, 1956.

The red complex did not contain unchanged diazonium salt; its i.r. spectrum showed the presence of $-N=N-$ and BF_4^- (1060 cm^{-1}) systems. It was insoluble in chloroform, carbon tetrachloride, benzene, xylene, light petroleum, ether, and chlorobenzene, and decomposed before dissolving on being warmed in nitrobenzene, dibutyl phthalate, or dimethyl sulphoxide. Acetone, ethanol, water, or dimethylformamide caused immediate decomposition to 4,4'-dichloroazobenzene. All attempts to purify the complex were unsuccessful. Results of microanalysis were inconsistent, as were those of macroanalysis for copper carried out on aqueous solutions of the decomposed complex. Magnetic balance determinations also gave inconsistent results and indicated the presence of copper(II) and copper(I) ions.

The complex obtained from the foregoing experiment was boiled with a mixture of benzene (100 ml), acetone (10 ml), and water (5 ml) for 6 h. Partial decomposition of the complex occurred to give a yellow solid (5·03 g), which on extraction with hot chloroform gave 4,4'-dichloroazobenzene (2·95 g), m.p. and mixed m.p. 186° (total yield 90·4%). Insoluble copper was rejected.

Typical results of related reactions of other diazonium fluoroborates are given in Table 1.

(iv) *Variation in the proportion of copper in reactions with* p-*bromobenzenediazonium fluoroborate.* The results of these experiments are summarised in Figures 1 and 2. In each case *p*-bromobenzenediazonium fluoroborate (1 g, 0·0036 mol) was stirred with benzene (18 ml) and acetone (2 ml) in the presence of various amounts of copper in a flask attached to a nitrometer containing water saturated with nitrogen. Subsequently, the complex was filtered off, and the filtrate chromatographed to give 4,4'-dibromoazobenzene; the complex was treated with water to give more azo-compound.

In some cases the complex decomposed in water with slight effervescence (*ca.* 5—10 ml per g of complex). A series of complementary experiments in which the complex was kept *in vacuo* before decomposition with water indicated that this was due to release of occluded nitrogen in the porous complex rather than to a decomposition process.

Copper-induced Reactions of Diazonium Fluoroborates in the Presence of Hydrated Salts in a Mixture of Benzene and Acetone.—p-*Bromobenzenediazonium fluoroborate; magnesium sulphate monohydrate.* The fluoroborate (9 g, 0·033 mol) and magnesium sulphate monohydrate (15 g, 0·108 mol) were suspended in dry benzene (150 ml) and acetone (15 ml), and the mixture was stirred. After a few min, copper powder (3 g, 0·048 mol) was added. A reaction started immediately with the evolution of nitrogen and was complete after 4 h. A red complex was not formed. The mixture was filtered and the residual magnesium sulphate and copper were rejected.

The filtrate was extracted with 2N-sodium hydroxide solution (3 × 50 ml), which on acidification and extraction with ether gave *p*-bromophenol (0·126 g, 3%) (i.r. spectrum).

The benzene solution was washed with water and dried (MgSO$_4$). Distillation gave 4-bromobiphenyl (3·978 g, 52%), b.p. 110—115° at 0·1—0·2 mmHg, m.p. and mixed m.p. 88—90°.

The undistilled residue on chromatography on alumina with light petroleum (b.p. 40—60°; 500 ml) as eluant gave 4,4'-dibromoazobenzene (0·146 g, 3%), m.p. and mixed m.p. 204—206°.

p-*Nitrobenzenediazonium fluoroborate; magnesium sulphate monohydrate.* The fluoroborate (11·84 g, 0·05 mol) and

magnesium sulphate monohydrate (22·43 g, 0·16 mol) were suspended in dry benzene (150 ml) and acetone (15 ml) and the mixture was stirred. On the addition of copper powder (3·15 g, 0·05 mol), a reaction started immediately with the evolution of nitrogen and was complete after 17 h. A red complex was not formed. The mixture was filtered and the residual magnesium sulphate and copper were rejected.

The filtrate was extracted with 2N-sodium hydroxide solution (3 × 100 ml), which on acidification and extraction with ether (3 × 200 ml) gave *p*-nitrophenol (0·62 g, 9%), m.p. 113° (lit.,[13] 114°).

The benzene solution was washed with water and dried (MgSO$_4$). Concentration gave a red solid (5·89 g), which was dissolved in benzene (15 ml) and adsorbed on an alumina column (30 × 2·5 cm). Elution with light petroleum gave 4-nitrobiphenyl (5·10 g, 51%) as pale yellow needles, m.p. and mixed m.p. 112—113°. Elution with benzene–light petroleum (b.p. 60—80°) (1 : 1; 2200 ml), benzene (1250 ml), benzene–chloroform (1 : 1; 750 ml), and chloroform (900 ml) gave 4,4'-dinitroazobenzene (0·75 g, 11%), m.p. 222—223°.

Benzenediazonium fluoroborate: various quantities of magnesium sulphate monohydrate. The reactions were carried out similarly with benzenediazonium fluoroborate (9 g, 0·05 mol), copper powder (4·7 g, 0·075 mol), benzene (150 ml), and acetone (15 ml). The results are summarised in Table 2.

Measurement of the Ratios of Isomers formed in the Arylation Reactions.—(i) *Phenylation of chloro- and fluorobenzene.* Benzenediazonium fluoroborate (9 g, 0·047 mol) decomposed at room temperature in a mixture of chlorobenzene (124 ml) and acetone (12·4 ml), in the presence of magnesium sulphate monohydrate (15 g, 0·1 mol) and copper powder (4·7 g, 0·075 mol). Fluorobenzene (88 ml) instead of chlorobenzene, and acetone (8·8 ml) were used in a similar experiment. The mixtures were filtered, concentrated (to 5 ml), and adsorbed on alumina (30 × 2·5 cm). Elution with light petroleum (b.p. 40—60°; 1000 ml) and distillation gave mixtures of chlorobiphenyls (2·51 g, 32%) and fluorobiphenyls (2·87 g, 35%), respectively. Analyses were carried out by g.l.c. In the case of the fluorobiphenyls it was not possible to separate the 3- and 4-isomers. The results of the experiments are summarised in Table 5. The method of analysis was checked by examination of mixtures of known composition and found to be satisfactory.

(ii) p-*Bromophenylation of nitrobenzene.* The experiment was performed in triplicate. *p*-Bromobenzenediazonium fluoroborate (8 g) in nitrobenzene (250 ml) and acetone (25 ml) reacted overnight with copper powder (3 g) and magnesium sulphate monohydrate (25 g). After filtration and washing (H$_2$O), the solution was dried and distilled to give a mixture of isomeric 4-bromonitrobiphenyls (2·73 g), b.p. 138—150° at 0·3 mmHg (Found: N, 5·1. Calc. for $C_{12}H_8BrNO_2$: N, 4·8%). A portion of the homogenised product was analysed by a u.v. spectrophotometric method as described later. A second portion (1·55 g) was chromatographed on alumina. Elution with light petroleum (b.p. 40—60°) gave 4,4'-dibromoazobenzene (0·02 g), m.p. and mixed m.p. 206°, further elution (400 ml) gave yellow crystals (1·24 g) and 4-bromo-4'-nitrobiphenyl, m.p. and mixed m.p. 175—176° (0·2 g). The yellow crystals, on fractional crystallisation from light petroleum (b.p. 60—80°), gave 4'-bromo-3-nitrobiphenyl (0·05 g) as almost colourless

[14] H. Meerwein, V. Hederich, and K. Wunderlich, *Arch. Pharm.*, 1958, **291**, 541.

needles, m.p. and mixed m.p. 87—91°, and 4′-bromo-2-nitrobiphenyl (0·45 g) as yellow prisms, m.p. and mixed m.p. 64—65°.

Duplicate experiments gave mixtures of bromonitro-biphenyls for which the following analytical figures were obtained: (i) N, 4·7; (ii) N, 4·8%.

The isomeric compositions of the mixtures of bromo-nitrobiphenyls were determined by the method described in ref. 15. Calibration spectra of the three pure isomers, provided by Professor D. H. Hey, in absolute ethanol were recorded in the range 220—330 nm. The concentrations of the solutions employed and the values of the maximum molecular extinction coefficients were as follows:

	$10^5 \times$ Concn. (mol l^{-1})	$\lambda_{max.}$/ nm	$\varepsilon_{max.}$
4′-Bromo-2-nitrobiphenyl	2·499	238	19,890
4′-Bromo-3-nitrobiphenyl	1·241	254	28,450
4-Bromo-4′-nitrobiphenyl	2·891	308	18,070

The spectra of the three homogenised experimental mixtures (1, 2, and 3) were then recorded, the concentrations of the solutions being about $2·5 \times 10^{-5}$ mol l^{-1}.

The results of the analyses are given in Table 4. The accuracy of the determinations was checked by analysing mixtures of known composition and also by the method previously described, and found to be satisfactory ($\pm 2\%$ for each isomer).

Attempted Preparation of Azobenzene–Copper(I) Fluoroborate Complex.—Benzenediazonium fluoroborate (9 g) was stirred with phenylcopper [16] (6·5 g) in dry benzene (150 ml) under nitrogen. After the vigorous reaction had subsided the mixture was stirred for 80 h. The tarry precipitate (7·28 g) was intractable; distillation of the filtrate gave biphenyl (2·6 g), m.p. and mixed m.p. 70°.

Preparation of 4,4′-Dibromoazobenzene–Copper(I) Fluoroborate Complex.—A solution of copper(I) fluoroborate (cf. ref. 8) was first prepared as follows. Copper(I) oxide (7·0 g) suspended in nitromethane (12 ml) and boron trifluoride–ether complex (12 g) was warmed under reflux for 2 h. The green filtrate was concentrated *in vacuo* to *ca.* 10 ml and filtered, and 4,4′-dibromoazobenzene (1·60 g) in benzene (300 ml) was added to the stirred filtrate to give a red precipitate. This was collected, washed with light petrol-eum (b.p. 40—60°), and dried (P$_2$O$_5$) (yield 1·73 g).

The i.r. spectrum of the product was identical with that of the complex obtained from a typical reaction of copper with *p*-bromobenzenediazonium fluoroborate, and behaved similarly on hydrolysis; *viz.* 1·30 g gave 4,4′-dibromoazobenzene (0·49 g), m.p. and mixed m.p. 210—211° and a filtrate which contained 0·099 g of ionic copper (Cu–azo-compound ratio 1·08 : 1). A typical complex gave a ratio of 1·31 : 1.

DISCUSSION

Simple diazonium fluoroborates (ArN$_2$BF$_4$; Ar = Ph, *p*-BrC$_6$H$_4$, *p*-ClC$_6$H$_4$, *p*-MeC$_6$H$_4$, *p*-NO$_2$·C$_6$H$_4$, or *o*-MeC$_6$H$_4$) did not react at room temperature under the influence of copper powder (1 equiv.) in benzene even during 72 h. On addition of acetone (10% by volume of the aromatic solvent) a reaction occurred at room temperature with evolution of nitrogen and precipitation of a voluminous red solid. The rate of the reaction was

[15] J. I. G. Cadogan, D. H. Hey, and G. H. Williams, *J. Chem. Soc.*, 1954, 794.

irreproducible and occasionally there was an induction period of several hours which was followed by a vigorous reaction. Such irreproducibility appeared to be a function of the physical state of the copper.

The soluble portion of the reaction mixture contained small quantities of the azo-compound (ArN:NAr) (Table 1) corresponding to the diazonium salt together

TABLE 1

Reactions of diazonium fluoroborates with copper in benzene–acetone

XC$_6$H$_4$·N=N·C$_6$H$_4$X

X in XC$_6$H$_4$N$_2$BF$_4$	Cu *	(%) From complex	Free	Ar accounted for (%)
H	1·6	56	19·5	75·5
4-Cl	1·4	42·5	14	56·5
4-Br	1·0	60	15	75
4-Me	0·7	45·5	14	59·5
4-Br †	1·5	43·5	19	62·5
4-Cl †	1·4	38	33	71
4-Br ‡	1·4	60·5	7	80·5

* Mol. equiv. w.r.t. ArN$_2$BF$_4$. † MeCOEt was used instead of Me$_2$CO. ‡ 4-Bromobiphenyl (13%) was also isolated.

with small yields of the corresponding biaryl (ArPh) (*ca.* 10%).

The precipitated red solid, the nature of which is independent of the aromatic solvents used, did not contain unchanged diazonium salt, contained the $-N=N-$ and BF$_4^-$ systems, and was very sensitive to moisture or polar solvents. No evidence for the chemical incorporation of acetone in the complex was found. The role of acetone in the reaction therefore remains obscure: in the absence of other evidence it is assumed to be that of a solvent. The complex was insoluble in benzene, light petroleum, dry ether, chlorobenzene, chloroform, and carbon tetrachloride. Reaction with solvents such as water, acetone, ethanol, or dimethylformamide caused decomposition to give high yields (*ca.* 65—90% based on ArN$_2$BF$_4$) of the azo compound, together with copper(II) fluoroborate and a small amount of metallic copper. A slight effervescence occurred during the decomposition of the complex, but the quantity of gas evolution was only a few ml and is attributed to adsorption of nitrogen by the porous complex. All attempts to purify this complex by crystallisation failed since the material was either decomposed by the solvent or failed to dissolve. The determination of the magnetic properties of the complex by use of a magnetic balance indicated the presence of copper(I) and copper(II) ions. Microanalytical results for the complex were inconsistent, as were the results of determinations of copper content, made on the hydrolysed material.

From these results it appeared that the complex was heterogeneous, particularly since different analyses were obtained for different portions of the same product. Such inconsistencies in the product are not surprising in view of the heterogeneity of the reaction.

The stoicheiometry of the reaction was established in

[16] H. Gilman and J. M. Straley, *Rec. Trav. chim.*, 1936, **55**, 821.

part by noting the variation in volume of nitrogen evolved with change in the amount of copper used. The results (Figure 1) indicate that the volume of nitrogen evolved increases with increase in the amount of copper until 0·5
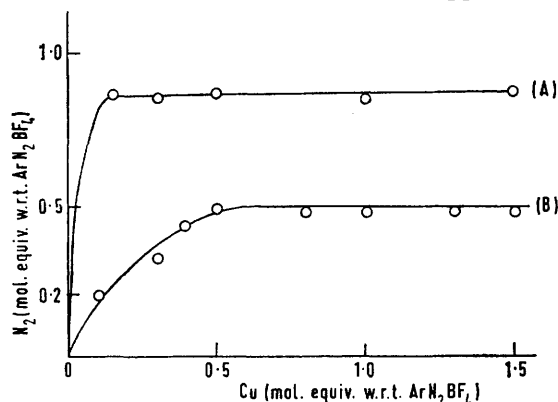

FIGURE 1   Nitrogen evolution in reactions of p-bromobenzene-diazonium fluoroborate (A) in the presence and (B) in the absence of magnesium sulphate monohydrate

mol of copper per mol of diazonium salt is used; 0·5 mol of nitrogen per mol of salt is then obtained. Further quantities of the metal do not then produce more than 0·5 mol. equiv. of nitrogen. In each of these experiments the weight of complex was also measured, as was the yield of free azo-compound in solution. In each case also the complex was subsequently treated with water to give more azo-compound. The results are summarised in Figure 2. The amount of the free azo-compound
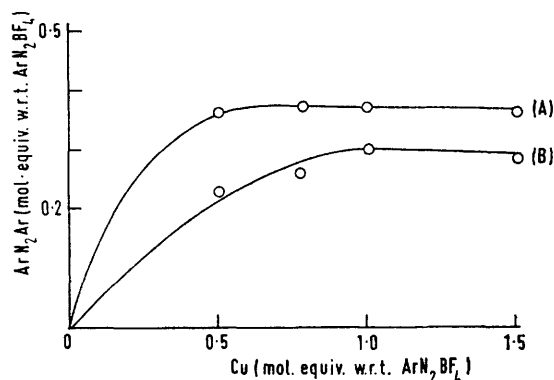

FIGURE 2   Reaction of copper with p-bromobenzenediazonium fluoroborate: (A) total ArN_2Ar; (B) ArN_2Ar from complex

decreases with the increase in the amount of copper used, and the amount of azo-complex reaches a constant value when 1 mol. equiv. of copper is used. The constant value (ca. 0·4 mol. equiv.) of total azo-compound is attained, however, after the addition of only 0·5 mol. equiv. of copper.
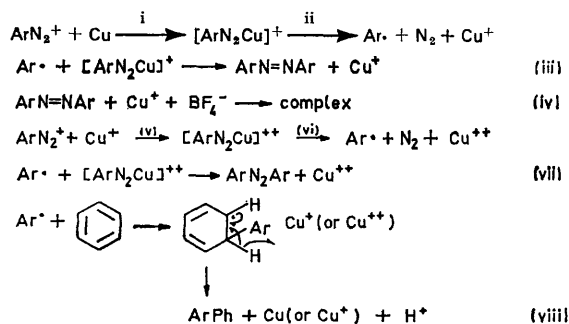
In all these experiments decomposition of the azo-complex gave fluoroborate anion and copper, both free and as copper(II) ion. The latter was estimated by titration and good accountances were obtained. Copper-induced decomposition of an equimolar mixture of

[17] E. Pfeil and O. Velten, *Annalen*, 1949, **562**, 163; **565**, 183.

benzene- and p-bromobenzene-diazonium fluoroborate under standard conditions gave the cross-product, 4-bromoazobenzene, in addition to the two possible symmetrical azo-compounds.

It is possible at this stage to postulate a reaction scheme which accounts for the results discussed so far. It is assumed that the primary process is a redox reaction, involving transfer of one electron from copper to the diazonium cation to give a diazonium cation–copper complex which is relatively stable at room temperature [reaction (i)], in which copper acts as the donor. Decomposition of this complex, which is much more rapid at higher temperatures, with complete transfer of an electron then gives an aryl radical, copper(I) ion, and nitrogen [reaction (ii)]. Similar stabilisation of diazonium cations by copper(I) ions has been invoked by Nonhebel and Waters,[3] and by Pfeil and Velten [17] in rationalisations of the Sandmeyer–Meerwein reactions. It is then assumed that the aryl radical in the main does not have an opportunity of attacking the solvent but reacts immediately with a further stabilised diazonium cation to give the azo-compound which appears mainly as the copper(I) complex [reactions (iii) and (iv)]. This reaction probably occurs in a ' cage ' at the metal surface.

Evidence in favour of a cage reaction arises from the results of the decomposition of p-nitrobenzenediazonium fluoroborate in benzene, which gave, in addition to a high yield of 4,4′-dinitroazobenzene, small amounts of 4-nitrophenyl and, significantly, 4,4′-dinitrobiphenyl. Toluene-p-diazonium fluoroborate in nitrobenzene similarly gave a small quantity of 4,4′- dimethylbiphenyl, and p-bromobenzenediazonium fluoroborate in benzene gave 4,4′-dibromobiphenyl. The isolation of symmetrical biaryls derived only from the diazonium salt clearly shows that all of the aryl radicals do not become free in the accepted sense, since it is well known that free radical combination reactions to give symmetrical biaryls are not favoured in the presence of aromatic solvents.

In order to satisfy the observed stoicheiometry (Figures 1 and 2), which requires the consumption of 0·5 mol. equiv. of copper to produce approximately 0·5 mol. equiv. of nitrogen and 0·4 mol. equiv. of azo-compound, it is necessary to make the reasonable assumption that copper(I) ion is also effective in the reduction of the diazonium cation [reactions (v)—(vii)].

$$ArN_2^+ + Cu \xrightarrow{\text{i}} [ArN_2Cu]^+ \xrightarrow{\text{ii}} Ar\cdot + N_2 + Cu^+$$

$$Ar\cdot + [ArN_2Cu]^+ \longrightarrow ArN=NAr + Cu^+ \qquad \text{(iii)}$$

$$ArN=NAr + Cu^+ + BF_4^- \longrightarrow complex \qquad \text{(iv)}$$

$$ArN_2^+ + Cu^+ \xrightarrow{\text{(vi)}} [ArN_2Cu]^{++} \xrightarrow{\text{(vii)}} Ar\cdot + N_2 + Cu^{++}$$

$$Ar\cdot + [ArN_2Cu]^{++} \longrightarrow ArN_2Ar + Cu^{++} \qquad \text{(viii)}$$

$$ArPh + Cu(or\ Cu^+) + H^+ \qquad \text{(viii)}$$

SCHEME

The relationship between free and complexed azo-compound (Figure 2) is now rationalisable: below 0·5 mol. equiv. of copper there is incomplete consumption of the salt. At 0·5 mol. equiv. of copper, both copper and copper(I) ion are acting as reducing agents to give an almost theoretical yield of azo-compound which complexes only with copper(I) ion. As the amount of copper used in the reaction is increased (0·5—1·0 mol. equiv.) so there is less need for copper(I) ions to act as the one-electron source, so that the amount of complexed azo-compound increases at the expense of the free azo-compound, the total amount remaining constant. The heterogeneity of the reaction product is also explicable on this basis.

The reaction is thus extremely complicated, particularly since some arylation of the solvent also occurs. This is also formulated as a redox reaction which involves oxidation of the intermediate cyclohexadienyl radical by copper(I) or copper(II) ions (Scheme), thus recalling similar oxidations by copper(II) ion in the Sandmeyer and Meerwein reactions.[1] This arylation reaction is therefore a means of restoring zero-valent copper to the system and explains why an almost theoretical yield of nitrogen is obtained during the reaction without the production of an equivalent amount of azo-compound (80%; Figures 1 and 2).

With regard to the azo-compound–copper(I) complex produced in the reaction it is noteworthy that Cowdrey and Davies[18] have reported the formation of an unstable and uncharacterised complex of azobenzene and copper(I) chloride, while a stable 1 : 1 complex of azomethane and copper(I) chloride is well known and its structure has been established by X-ray crystallography.[19] In this investigation two possible synthetic routes to the 1 : 1 complex of an azobenzene and copper(I) fluoroborate were examined. In the first, copper(I) fluoroborate was treated with 4,4′-dichloroazobenzene in nitromethane to give a red unstable product which gave an i.r. spectrum identical with that of the complex obtained from the copper-induced decomposition of p-chlorobenzenediazonium fluoroborate. Further, the synthesised product decomposed in water to give the component materials. The second attempt at synthesis was unsuccessful and involved the reaction of phenylcopper[16] with a suspension of benzenediazonium fluoroborate in benzene. An azo-complex was not formed and biphenyl was obtained. This result is pertinent to the discussion of the mechanism of the reactions already described, because an alternative route to the azo-compounds could involve the prior formation of an arylcopper derivative which could then react with the electrophilic diazonium group:

$$ArN_2^+ + Cu \longrightarrow ArCu + N_2$$

$$ArN_2^+ + ArCu \longrightarrow ArN_2Ar + Cu^+$$
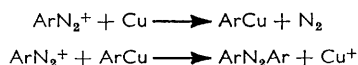
It is noteworthy that the related reaction of zinc diaryls proceeds in this fashion.[20]

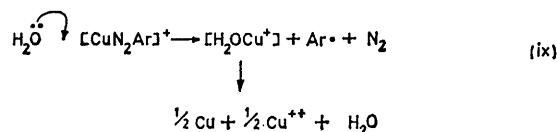$$Ar_2Zn + 2Ar'N_2^+ \longrightarrow 2Ar'N_2Ar + Zn^{++}$$

Clearly, this type of reaction is not favoured in our reac-

tions, particularly since arylcopper derivatives, if formed, would have been expected to react with the acetone present in the system to give aryl carbinols, which were not detected. Kochi[21] similarly discounts the participation of arylcopper derivatives in the Sandmeyer reaction.

It is noteworthy that azobenzene forms unstable complexes with silver fluoroborate and with copper(I) and silver perchlorates: $PhN_2Ph-CuClO_4$, $3PhN_2Ph-2AgClO_4$, and $3PhN_2Ph-2AgBF_4$. The formation of an azobenzene–copper(I) fluoroborate complex was not reported.[22]

Copper-induced Decompositions of Diazonium Fluoroborates in the Presence of Water.—We have concluded that most of the aryl radicals formed by decomposition of the stabilised diazonium cation are not free in the generally accepted sense, and that a small proportion only escape to react with the solvent. The question now arises as to why *any* of these radicals escape. Since the reaction mixture undoubtedly contained small amounts of water, it was possible that this reagent encouraged rapid decomposition of the stabilised diazonium cation in such a manner that free aryl radicals were formed [equation (ix)].

$$H_2\overset{\cdot\cdot}{O} \; \uparrow \; [CuN_2Ar]^+ \longrightarrow [H_2OCu^+] + Ar\cdot + N_2 \qquad (ix)$$
$$\downarrow$$
$$\tfrac{1}{2}\,Cu + \tfrac{1}{2}\,Cu^{++} + H_2O$$

This is equivalent to the conversion of cuprous to cupric iron and copper(0) by water. Such reasoning led to a study of the reactions of diazonium fluoroborates in the presence of benzene, acetone (10% v/v), copper, and water (up to 1 equiv.). Thus the reaction of water with p-bromobenzenediazonium fluoroborate in the presence of copper, acetone, or benzene led to the evolution of much larger amounts of nitrogen with the formation of 4-bromobiphenyl (30%), p-bromophenol (33%), 4,4′-dibromoazobenzene (7%), and bromobenzene. Application of this procedure to other simple diazonium fluoroborates (ArN_2BF_4; Ar = Ph, p-MeC_6H_4, or p-ClC_6H_4) led to similar results.

The formation of phenols in these cases can be attributed to the competitive reaction of the diazonium salt with water.[23] In an attempt to reduce the concentration of the water in the system, hydrated salts were used, including magnesium sulphate monohydrate, magnesium sulphate heptahydrate, zinc sulphate heptahydrate, sodium sulphate decahydrate, and iron(II) sulphate heptahydrate. The results are summarised in Table 2.

Thus the multiphase mixture of p-bromobenzenediazonium fluoroborate, copper powder (1 mol. equiv.), benzene (25 mol. equiv.), acetone (2·5 mol. equiv.), and

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magnesium sulphate monohydrate (2 mol. equiv.), remarkably, gave a 44% yield of 4-bromobiphenyl together with some 4,4′-dibromoazobenzene (9%), p-bromophenol (2%), and bromobenzene (10%).

These conditions of reaction, when applied to other related diazonium fluoroborates (ArN_2BF_4; Ar = Ph, p-ClC$_6$H$_4$, p-MeC$_6$H$_4$, o-MeC$_6$H$_4$, or p-NO$_2$·C$_6$H$_4$), similarly gave the corresponding biaryls (ArPh) in high yields.

system by the addition of water, either free or bound in hydrated salts, is further supported by the following observations:

(a) The copper-induced decompositions of benzenediazonium fluoroborate in benzene–acetone in the presence of increasing amounts of magnesium sulphate monohydrate (0·5 ⟶ 2 equiv.) led to an increasing yield of biphenyl and a decreasing yield of azo-complex (Figure 3).

TABLE 2

Copper-induced reactions of diazonium fluoroborates in the presence of water and various hydrated salts

Ar in ArN$_2$BF$_4$	Cu *	Source of H$_2$O *	ArPh (%)	ArN:NAr (%)	ArOH (%)	Ar accounted for (%)
p-ClC$_6$H$_4$	1·4	H$_2$O (3·0)	28	8	25	61
p-BrC$_6$H$_4$	1·4	H$_2$O (4·8)	28	13	35	76
p-ClC$_6$H$_4$	1·4	MgSO$_4$,H$_2$O (3·3)	39	20		59
p-ClC$_6$H$_4$	1·4	Na$_2$SO$_4$,10H$_2$O (3·3)	25	13	10	48
p-ClC$_6$H$_4$	1·4	FeSO$_4$,7H$_2$O (3·3)	39	19	5	63
p-ClC$_6$H$_4$	1·4	ZnSO$_4$,7H$_2$O (3·3)	32	18	17	67
Ph	1·6	Na$_2$SO$_4$,10H$_2$O (2·3)	26	13		
p-ClC$_6$H$_4$	1·4	MgSO$_4$,H$_2$O (3·2) †	42		4	
p-BrC$_6$H$_4$	1·4	MgSO$_4$,H$_2$O (3·3)	52	3	3	58
p-BrC$_6$H$_4$	1·0	MgSO$_4$,H$_2$O (3·3) ‡	52		Trace	68
p-NO$_2$·C$_6$H$_4$	1·0	MgSO$_4$,H$_2$O (3·3)	51	11	9	71
o-MeC$_6$H$_4$	0·75	MgSO$_4$,H$_2$O (2·3)	25			
Ph	1·6	MgSO$_4$,7H$_2$O (0·5) §	22	27	11	60

* Mol. equiv. w.r.t. ArN$_2$BF$_4$. † Under N$_2$. ‡ Reaction in Me$_2$CO–PhH (30% v/v); PhBr (16%) was also formed. § Finely divided material. Large crystals gave high yields of the azo-complex.

It was further observed that the amount of biaryl formed increased with the increase in the amount of magnesium sulphate monohydrate used up to a maximum of 2 mol. equiv., after which further increases in the proportion of salt produced no further increase in the

(b) The addition of *anhydrous* magnesium sulphate to the copper-induced reactions of diazonium fluoroborates did not give biaryls in high yield; rather, the usual formation of azo-complex was observed (Table 3).

TABLE 3

Copper-induced reactions of diazonium fluoroborates with anhydrous magnesium sulphate *

Ar in ArN$_2$BF$_4$ † (9 g)	ArPh (%)	ArN:NAr (%)		Ar accounted for (%)
		From complex	From solution	
p-BrC$_6$H$_4$ ‡	21	50	3	74
Ph	11	63	4	78
p-ClC$_6$H$_4$	22	50	5	77

* 4 Mol. equiv. w.r.t. ArN$_2$BF$_4$. † PhH (150 ml), Me$_2$CO (15 ml), 1·5 mol. equiv. Cu w.r.t. ArN$_2$BF$_4$ in each experiment.

(c) In the absence of copper and in the presence of hydrated salts no reaction occurred.

(d) The azo-complex is not decomposed by hydrated salts in benzene to give biaryls, but is hydrolysed in the usual way to give the parent azo-compound; thus it is not a precursor in the arylation reaction.

(e) The use of magnesium sulphate heptahydrate in the copper-induced reaction led to a four-fold increase in the yield of phenol over that obtained from the reaction involving the monohydrate.

(f) The free-radical nature of the intermediate involved in the hydrated salt-induced reactions was determined by estimation of the ratios of isomers produced in the p-bromophenylation of nitrobenzene, the phenylation of chlorobenzene, and the phenylation of fluorobenzene,
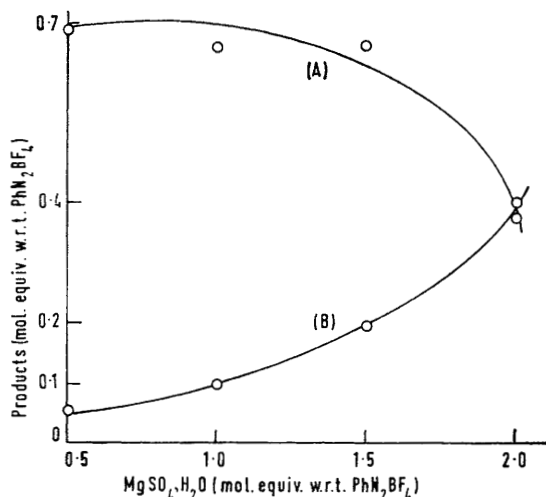

FIGURE 3 Reaction of copper with benzenediazonium fluoroborate: (A) PhN$_2$Ph from complex; (B) Ph$_2$

yield of biaryl. It was also demonstrated (Figure 1), that the role of copper in these reactions is catalytic, as is required by equation (viii), the efficiency of the catalyst being reduced by the presence of the bulky inorganic salt.

The conclusion that radical arylation is induced in this

by use of a u.v. spectrophotometric method in the first case and of g.l.c. for the halogenobiphenyls. The results are summarised in Tables 4 and 5 together with the corresponding ratios of isomers produced by standard free radical arylations of these compounds.

TABLE 4

p-Bromophenylation of nitrobenzene

	Ratios of isomeric 4-bromonitrobiphenyls		
Source of Ar·	2'-	3'-	4'-
ArN_2BF_4–Cu–$MgSO_4,H_2O$	64	14	22
(25°)	65	15	20
	64	15	21 *
(Ar·CO_2)₂ (80°) [24]	58	13	29

* Also resolved by chromatography on alumina.

TABLE 5

Phenylation of chlorobenzene and fluorobenzene

	Chlorobiphenyls			Fluoro-biphenyls 3- and	
Source of Ar·	2-	3-	4-	2-	4- *
PhN_2BF_4–Cu–$MgSO_4,H_2O$ (20°)	65	20	15	56	44
PhN_2Cl–NaOH (5°) [25,26]	63	25	12	54	46
(PhCO_2)₂ (80°) [25]	50	32	18		

* 3- and 4- Isomers not resolved by g.l.c.

The reaction schemes outlined [reactions (i)—(iv)] are in accord with accepted mechanisms of the Sandmeyer and Meerwein reactions which also involve the intermediacy of systems of the type $[ArN_2Cu^+]$. In these cases water-induced decompositions also occur with the result that the aryl radicals present interact with different species, *e.g.* halide ion or olefin.

It is therefore concluded that the inclusion of water in copper-induced decompositions of diazonium fluoroborates leads to rapid preferential decomposition of the initial copper-stabilised diazonium cation to give free aryl radicals and nitrogen. The competing reaction, that of aryl radicals with the stabilised diazonium cation to give the azo-compound, becomes of less importance as the proportion of water available is increased.

In addition to reactions of diazonium fluoroborates, those of *p*-chlorobenzenediazonium hexafluorophosphate were briefly studied. It was thus shown (Table 6) that the latter behaved in a similar manner to the corresponding fluoroborate both in the presence and in the absence of added hydrated magnesium sulphate.

TABLE 6

Reactions of *p*-chlorobenzenediazonium hexafluorophosphate *

				ArN=NAr (%)		Ar
	Time			From		accounted
$MgSO_4,H_2O$	(h)	N_2	ArPh	complex	Free	for (%)
0	48			0·39	0·08	94
0	19	0·44		0·29	0·16	88
2·0	2	0·92	0·50	0	0·16	82

* All quantities in mol. equiv. w.r.t. ArN_2PF_6 [0·01 mol in PhH (150 ml) and Me_2CO (5 ml) with 1 mol. equiv. Cu].

A referee has pointed out that a mechanism based on the intermediacy of an arylcopper [27] cannot be ruled out if we assume that the observed absence of products of reactions of arylcopper with acetone can be discounted on the grounds of slow reaction. It could then be argued that the function of water is merely to suppress the formation of arylcopper in some unspecified way. This may be so.

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