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Sandmeyer Reactions. Part 1. A Comparative Study of the Transfer of Halide and Water Ligands from Complexes of Cu^{II} to Aryl Radicals

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Rate constants have been estimated for the transfer to aryl radicals of Cl ligands from $CuCl^+$ and $CuCl_2$ relative to that for the transfer of water ligands from Cu^{2+}: $k^{OH}:k_1^{Cl}:k_2^{Cl} = 1:(59.3 \pm 3.4):(205 \pm 9)$ The rate data indicate that aryl radicals exhibit nucleophilic character during these ligand transfers and that, in the competition between chlorination and hydroxylation, the reactivity–selectivity principle is not obeyed. In competition between $CuBr^+$ and $CuCl^+$ in transferring halide ligands to 4-chlorophenyl radicals a value of $k_1^{Br}/k_1^{Cl} = 2.3$ is estimated; there is no selectivity between bromination and chlorination across a range of aryl radicals. The reactivities of the different copper complexes in ligand-transfer broadly parallel their reduction potentials. The nature of the transition state for ligand-transfer is discussed.

The Sandmeyer reaction has wide laboratory and industrial scale application in the synthesis of functionalised aromatic materials, and our present understanding of its mechanism derives from the work of Waters[1] and Kochi.[2] The former recognised the radical nature of the reaction with its potential for a catalytic cycle in copper; the latter recognised the key inner-sphere ligand-transfer from Cu^{II} by which the new functionality is introduced into the aromatic ring. The mechanism of Sandmeyer chlorination is usually expressed by the propagation steps of Scheme 1.[3]

$$ArN_2^+ + Cu^ICl_2^- \longrightarrow Ar^\bullet + N_2 + Cu^{II}Cl_2 \qquad \text{(i)}$$

$$Ar^\bullet + Cu^{II}Cl_2 \longrightarrow ArCl + Cu^ICl \qquad \text{(ii)}$$

$$Cu^ICl + Cl^- \longrightarrow Cu^ICl_2^- \qquad \text{(iii)}$$

Scheme 1

The mechanism so formulated is an oversimplification. For example, step (i) might conceivably itself be composite and the reduction of the diazonium ion could be an outer-sphere process, in which case the first reduction product would be a diazenyl radical $ArN_2^\bullet$. Diazenyl radicals are known species which have been produced at low temperature by photolysis of diazosulphides ArN_2SAr', and characterised by EPR spectroscopy; they rapidly fragment into nitrogen and aryl radicals.[4,5] Alternatively, the reduction of the diazonium ion could be an inner-sphere process involving the formation of a complex between ArN_2^+ and the Cu^I reductant. Traditionally, the Sandmeyer reaction was formulated as occurring *via* a Cu^I–diazonium complex[6] since precipitation often occurs on mixing the reactants. However, such a precipitate, formed from benzenediazonium ion and CuBr in the presence of an excess of bromide ion, has been shown by an X-ray crystal structure determination to be merely an insoluble salt of composition PhN_2^+ $[Cu_2Br_3]^-$.[7] The material shows no evidence of ligation of the Cu^I by the diazonium ion. Thus, while the observation of a precipitate, in this case, is not evidence for the involvement of an intermediate complex, the possibility that the reduction step is actually an inner-sphere process occurring *via* a transient complex has not been excluded. (Cu^I reductions of inorganic species frequently occur *via* inner-sphere mechanisms.[8,9])

Steps (ii) and (iii) of the mechanism may also be oversimplifications. Copper in both oxidation states forms several complexes with the halide and pseudo-halide ligands used in Sandmeyer reactions,[10] and the actual species involved in a particular circumstance may depend on the conditions of solution chosen and on the halide or pseudo-halide used.

The reduction of diazonium ions by species other than complexes of Cu^I has long been known. Recently, Galli has shown that, in the initial absence of Cu^I, a variety of reductants will initiate Sandmeyer reactions provided that Cu^{II} is present to effect the ligand-transfer.[11] It is not clear from Galli's work, however, that the diazonium ion is always the species initially reduced; some reductants could reduce Cu^{II} also. Since it is known that Fe^{2+} does not reduce Cu^{2+},[8] the initiation of the Sandmeyer reaction by this reductant no doubt does occur *via* initial reduction of the diazonium ion. On the other hand, Galli's finding of initiation by ascorbic acid most probably results from the rapid reduction of Cu^{II} which is a well established reaction.[12–17] Whatever reduction step initiates the process, Cu^I will be produced by the essential ligand-transfer step and so the 'normal' Sandmeyer reductant will intervene and might conceivably supersede the initial reductant unless the latter reduces the diazonium ion significantly faster than does Cu^I.

The usual synthesis of phenols from diazonium ions is by hydrolysis in acid conditions. Here the diazonium ion is heterolysed to produce the aryl cation which is rapidly solvated.[18–20] However, Cohen and co-workers[21] showed that certain phenols, obtained in poor yields in the customary manner, can be usefully synthesised by a homolytic route. In their procedure, the diazonium ion is believed to be reduced to an aryl radical by Cu_2O in the presence of a high concentration of Cu^{2+}. A water ligand from the aquated copper ion is transferred in a manner presumed to be analogous to the Sandmeyer reaction, giving the corresponding phenol. The counter-ion of the Cu^{2+} must not be halide or the normal Sandmeyer halogen transfer supervenes. In addition, for efficient transfer of water, relatively high concentrations of Cu^{2+} are required, which limits the large scale applicability of the reaction.

In this paper we report an investigation into the mechanism of Sandmeyer hydroxylation, comparing it with halogenation, particularly chlorination.

Results and Discussion

The primary method employed was to set up competitive hydroxylation and chlorination reactions by effecting the decomposition of diazonium ions using copper sulphate solution containing added sodium chloride, and to observe the

Table 1 Sandmeyer product ratio for various initiators in the reaction of 4-chlorobenzenediazonium ion with aqueous $CuSO_4$ containing added sodium chloride[a]

Initiator	Yield ArOH (%)	Yield ArCl (%)	Mean [ArCl]/[ArOH]
Catechol	62.3 60.6	16.8 16.8	0.27
Na_2SO_3	53.8 49.2	16.7 14.0	0.30
Ascorbic acid in air	67.0 67.0	20.5 19.8	0.30
air excluded	63.2 60.2	17.7 18.0	0.29

[a] Conditions: $[ArN_2^+] = 0.02$ mol dm^{-3}; [Initiator] = 0.005 mol dm^{-3}; $[Cl^-] = 0.02$ mol dm^{-3}; $[Cu^{2+}] = 0.3$ mol dm^{-3}.

Table 2 Variation of phenol yield[a] and product ratio[b] as a function of the ratio [ascorbic acid]/$[4\text{-}ClC_6H_4N_2^+]$

$\frac{[\text{Ascorbic acid}]}{[4\text{-}ClC_6H_4N_2^+]}$	Yield ArOH (%)	[ArCl]/[ArOH]
0.02	39.3	—
0.05	80.7	0.59
0.05[c]	78.9	—
0.05[d]	81.3	—
0.05[e]	80.8	—
0.01	79.3	0.61
0.15	80.4	—
0.25	78.5	0.59
0.50	—	0.65
0.75	81.7	—
1.00	81.6	0.67
1.25	81.1	—
1.50	81.9	0.59
		Mean 0.62 ± 0.06

[a] Conditions: $[ArN_2^+] = 0.02$ mol dm^{-3}; $[Cu^{2+}] = 0.3$ mol dm^{-3}; initiator added after diazonium ion except where indicated otherwise. [b] Conditions: $[ArN_2^+] = 0.02$ mol dm^{-3}; $[Cu^{2+}] = 0.3$ mol dm^{-3}; $[Cl^-] = 0.04$ mol dm^{-3}; initiator added after diazonium ion. [c] Diazonium ion added 30 s after initiator. [d] Diazonium ion added 2 min after initiator. [e] Diazonium ion added 5 min after initiator.

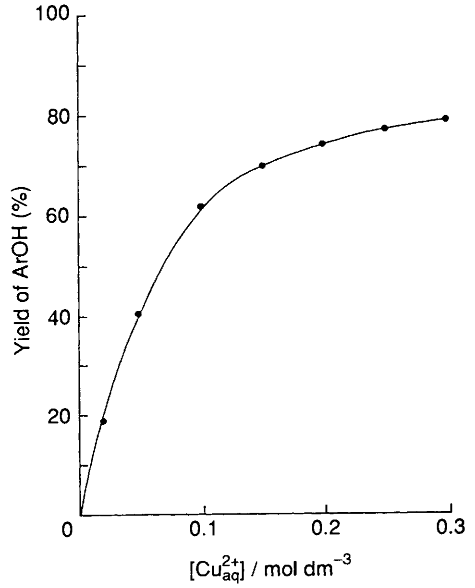

Fig. 1 Variation in the yield of 4-chlorophenol as a function of $[Cu^{2+}]$

relative proportions of phenol and aryl halide produced. Various substituted benzenediazonium ions were used, but 4-chlorobenzenediazonium ion was studied in greatest detail for reasons of convenience in GLC analysis of the products.

Initiation of the Reaction Between Copper Ions and Diazonium Ions.—It was found that if the reaction was initiated, following Cohen *et al.*,[21] by using Cu_2O, a poor reproducibility of the ratio of aryl halide to phenol resulted at low concentrations of added sodium chloride. However, reproducible results were obtained when Cu^I was produced homogeneously by addition of an initiating reductant capable of producing Cu^I. Although some variation of the product ratio [ArCl]/[ArOH] was observed with the nature and amount of reductant (particularly with diazonium ions bearing electron-donating substituents) consistency was obtained with 4-chlorobenzenediazonium ion when reaction was initiated with a variety of reductants (ascorbic acid, catechol, sodium sulphite), which reduce Cu^{2+} (Table 1). Following this finding, ascorbic acid was used routinely as initiator. There is ample precedent for reactions of the system Cu^{2+}/ascorbic acid/O_2,[22] but for the present work it was shown that the relative yields of aryl halide and phenol were independent of the presence or absence of air. By use of rate constants and equilibrium constants from the literature,[16,17,23,24] it was shown by kinetic simulation that added ascorbic acid is converted into dehydroascorbic acid, producing two mole equivalents of Cu^I within 0.5 s of mixing, under the chosen experimental conditions. The product ratio, [ArCl]/[ArOH], was invariant irrespective of whether the diazonium ion was added to the mixture before or shortly after the formation of Cu^I, consistent with slow disproportionation of the latter.[25]

Confirmation of a Catalytic Cycle in Copper Ions.—Table 2 shows the variation in the yield of phenolic product from 4-chlorobenzenediazonium ion (in the absence of added sodium chloride) as the amount of initiating ascorbic acid was varied. Maximum yields of 4-chlorophenol were obtained when much less ascorbic acid than the stoichiometric equivalent of the diazonium ion was used, clear indication of the catalytic cycle anticipated by Waters.[1] In the presence of added chloride, the ratio [ArCl]/[ArOH] is constant (Table 2) over a similar range of concentrations of initiator, implying that the chlorination and hydroxylation processes have a common intermediate (the aryl radical) for which different Cu^{II} species compete (Scheme 2).

$$AH^- + Cu^{II} \longrightarrow A^{\bullet -} + Cu^I + H^+ \quad (AH^- = \text{ascorbate})$$

$$A^{\bullet -} + Cu^{II} \longrightarrow A + Cu^I$$

$$ArN_2^+ + Cu^I \longrightarrow Ar^\bullet + N_2 + Cu^{II}$$

$$Ar^\bullet + Cu^{II}X \longrightarrow ArX + Cu^I \quad (X = Cl, H_2O)$$

Scheme 2

A similar catalytic cycle in copper ions could also be initiated by addition of small quantities of Fe^{2+}(aq); here initial reduction is of the diazonium ion.

The Dependence of the Extent of Hydroxylation on $[Cu^{2+}]$.—The variation in the yield of 4-chlorophenol obtained when 4-chlorobenzenediazonium ion was reacted with different concentrations of Cu^{2+}(aq) is shown in Fig. 1. The amount of ascorbic acid used as initiator was held at 0.25 mole equivalents of the diazonium ion for all concentrations of Cu^{2+}. When $[ClC_6H_4N_2^+] = 0.02$ mol dm^{-3}, yields of 4-chlorophenol were maximised for $[Cu^{2+}] = 0.3$ mol dm^{-3}. These conditions were therefore adopted for subsequent competition experiments.

Table 3 The influence of ionic strength on the product ratio [ArCl]/[ArOH] from reaction of 4-chlorobenzenediazonium ion with Cu^{II}

$[Cl^-]$/mol dm^{-3}	I/mol kg^{-1}	[ArCl]/[ArOH]	I/mol kg^{-1}	[ArCl]/[ArOH]
0.01	1.23	0.14	1.62	0.11
0.04	1.26	0.59	1.62	0.58
0.08	1.30	1.31	1.62	1.32

Table 4 The variation in product ratio [ArCl]/[ArOH] from reaction of 4-chlorobenezendiazonium ion as a function of total added chloride concentration $[Cl^-]_t$

$[Cl^-]_t$/mol dm^{-3}	[ArCl]/[ArOH]	$[Cl^-]_t$/mol dm^{-3}	[ArCl]/[ArOH]
0.01	0.14	0.16	3.31
0.02	0.30	0.18	3.97
0.04	0.59	0.20	4.62
0.06	0.90	0.25	6.15
0.08	1.31	0.30	7.76
0.10	1.69	0.35	9.72
0.12	2.19	0.40	12.71
0.14	2.76		

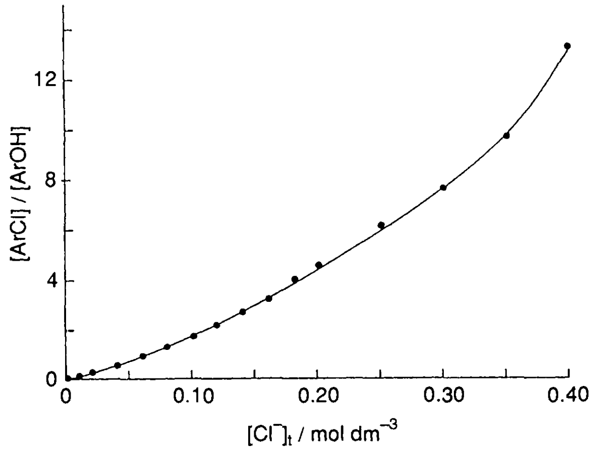

Fig. 2 Variation in the product ratio as a function of the concentration of added chloride for Sandmeyer reaction of 4-chlorobenzenediazonium ion

An Investigation of the Role of Ionic Strength Effects.—Since the reaction mechanism under investigation involves ionic species and significant concentrations of electrolytes are used in the reaction medium, experiments were made to test for ionic strength effects. Copper sulphate at a concentration of 0.3 mol dm^{-3} was the major contributor to the ionic strength (I = 1.2 mol kg^{-1}) and sodium chloride at concentrations in the range 0–0.4 mol dm^{-3} the minor contributor; by comparison, the contributions from other components of the mixture *e.g.* diazonium salt were small. Without other added salts the ionic strength thus varied in the range *ca.* 1.2–1.6 mol kg^{-1}. It was found that for a given concentration of sodium chloride the same ratio [ArCl]/[ArOH] was obtained, within experimental error, irrespective of whether the ionic strength took the value appropriate to the amount of NaCl added, or whether it was adjusted to 1.62 mol kg^{-1} by addition of KNO_3 (Table 3). It is therefore concluded that the effect of ionic strength is not significant for the results to be described. The reaction mixtures had initial and final pH in the range 2.5–3. Raising pH to the gel point by addition of NaOH had no effect on the product ratio or yield.

Competitive Sandmeyer Chlorination and Hydroxylation.—(i) *Relative rates of chlorination and hydroxylation.* Fig. 2 and Table 4 show the non-linear increase in the ratio [ArCl]/[ArOH] as a function of the concentration of added chloride. In order to account for the relative reactivities of different Cu^{II} complexes in ligand-transfer to aryl radicals, information is required on their relative concentrations under given experimental conditions. This is obtainable if the stability constants of the various complexes are known. Cu^{II} forms four weak complexes with Cl^- in aqueous solutions as shown in eqns. (1)–(4).

$$Cu^{2+} + Cl^- \rightleftharpoons CuCl^+;\ K_1 = \frac{[CuCl^+]}{[Cu^{2+}][Cl^-]} \quad (1)$$

$$CuCl^+ + Cl^- \rightleftharpoons CuCl_2;\ K_2 = \frac{[CuCl_2]}{[CuCl^+][Cl^-]} \quad (2)$$

$$CuCl_2 + Cl^- \rightleftharpoons CuCl_3^-;\ K_3 = \frac{[CuCl_3^-]}{[CuCl_2][Cl^-]} \quad (3)$$

$$CuCl_3^- + Cl^- \rightleftharpoons CuCl_4^{2-};\ K_4 = \frac{[CuCl_4^{2-}]}{[CuCl_3^-][Cl^-]} \quad (4)$$

These complexes exhibit different extents of aquation; we formulate them all without water ligands but their presence, where appropriate, is understood. Estimates of K_1 have been obtained by various methods and the results lack consistency;[26] there have been far fewer estimates of K_2–K_4. Recently, however, Ramette[27,28] has determined K_1–K_4 by electrochemical measurements of the solubility of $Cu(IO_3)_2$ in solutions of NaCl of concentrations up to 5 mol dm^{-3}. These results were shown to be in close agreement with values obtained by spectroscopic measurements[29] under comparable conditions when the results for the latter were analysed by the same non-linear regression technique. Consistent values of K_1 and K_2 have also been obtained by others.[30] For these reasons we have used Ramette's values (K_1–K_4 = 2.36, 0.63, 0.48 and 0.08 dm^3 mol^{-1}, respectively) although later we shall consider the consequence for our results of adopting other values.

By employing these constants, the equilibrium distribution of solute species present when varying amounts of NaCl were added to 0.3 mol dm^{-3} aqueous $CuSO_4$ were calculated (Table 5). Under the conditions of our experiments only three Cu^{II} species are present in significant concentration: Cu^{2+}, $CuCl^+$ and $CuCl_2$.

If it is assumed that the chloro-complexes transfer only chloride and not water ligands (*i.e.* the hydroxylation is effected

Table 5 The equilibrium distribution of solute species (mol dm^{-3}) in aqueous $CuSO_4$ (0.3 mol dm^{-3}) for various concentrations of added NaCl[a]

$[Cl^-]_t$	$[Cl^-]$	$[Cu^{2+}]$	$10^2[CuCl^+]$	$10^3[CuCl_2]$	$10^4[CuCl_3^-]$	$10^6[CuCl_4^{2-}]$
0.010	0.006	0.296	0.410	0.015	4.3×10^{-4}	2.0×10^{-5}
0.020	0.012	0.292	0.812	0.060	3.4×10^{-3}	3.2×10^{-4}
0.040	0.024	0.284	1.585	0.236	0.027	5.1×10^{-3}
0.060	0.036	0.276	2.325	0.523	0.089	0.025
0.080	0.048	0.269	3.031	0.913	0.209	0.081
0.100	0.060	0.261	3.705	1.401	0.404	0.194
0.120	0.072	0.254	4.346	1.981	0.688	0.398
0.140	0.085	0.248	4.957	2.648	1.08	0.731
0.160	0.097	0.241	5.538	3.396	1.59	1.24
0.180	0.110	0.234	6.090	4.220	2.23	1.96
0.200	0.123	0.228	6.615	5.114	3.01	2.96
0.250	0.155	0.214	7.812	7.623	5.67	7.02
0.300	0.188	0.200	8.856	10.47	9.43	14.1
0.350	0.221	0.187	9.762	13.58	14.4	25.4
0.400	0.254	0.175	10.542	16.90	20.6	42.0

[a] Calculated using concentration stability constants: $K_1 = 2.36$, $K_2 = 0.63$, $K_3 = 0.48$, $K_4 = 0.88$ dm^3 mol^{-1}, respectively (ref. 27).

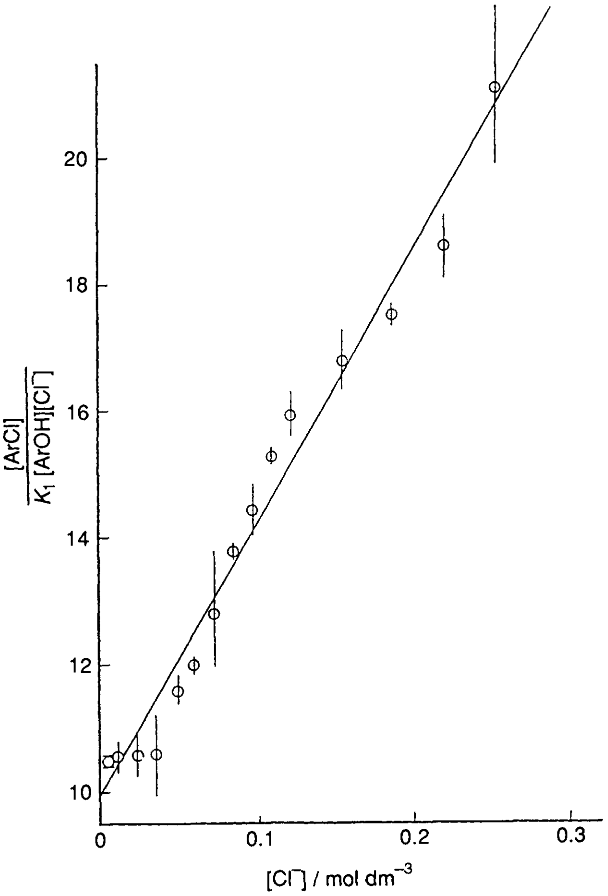

Fig. 3 Regression of $[ArCl]/K_1[ArOH][Cl^-]$ upon $[Cl^-]$ for Sandmeyer reaction of 4-chlorobenzenediazonium ion

only by Cu^{2+}), the rates of ligand-transfer may be written $d[ArCl]/dt = k_1^{Cl}[Ar^{\cdot}][CuCl^+] + k_2^{Cl}[Ar^{\cdot}][CuCl_2]$ and $d[ArOH]/dt = k^{OH}[Ar^{\cdot}][Cu^{2+}]$. Thus, for a kinetically determined process in which the ratio of products equals the ratio of their rates of formation, it follows that eqn. (5) holds.

$$\frac{[ArCl]}{[ArOH]} = \frac{d[ArCl]/dt}{d[ArOH]/dt} = \frac{k_1^{Cl}}{k^{OH}} \times \frac{[CuCl^+]}{[Cu^{2+}]} + \frac{k_2^{Cl}}{k^{OH}} \times \frac{[CuCl_2]}{[Cu^{2+}]} \quad (5)$$

This treatment is valid provided the relative proportions of copper complexes remain essentially constant over the course of reaction. This should occur since rates of equilibration are very fast for Cu^{II} and the proportion of inorganic chloride converted into aryl chloride is small in comparison to the total chloride present (20% in the least favourable case). Substitution of the concentration ratios in eqn. (5) from eqns. (1) and (2) gives eqn. (6).

$$\frac{[ArCl]}{K_1[ArOH][Cl^-]} = \frac{k_1^{Cl}}{k^{OH}} + \frac{K_2 k_2^{Cl}[Cl^-]}{k^{OH}} \quad (6)$$

A simple regression of the left hand side of eqn. (6) upon the equilibrium concentration of chloride (Fig. 3) thus allows an estimation of relative rate constants. The values determined are $k_1^{Cl}/k^{OH} = 9.89 \pm 0.58$, $k_2^{Cl}/k^{OH} = 68.5 \pm 5.8$ and $k_2^{Cl}/k_1^{Cl} = 6.92 \pm 0.72$ where the uncertainties quoted are ±2 standard deviations.

A statistical correction may then be applied to these values to take account of the different numbers of transferable ligands of each kind. It is assumed that Cu^{2+} is $[Cu(OH_2)_6]^{2+}$ and that, owing to the dynamic Jahn–Teller effect,[31] any of the six water ligands may be transferred with equal probability. There is evidence that the chlorine atoms in $[CuCl_2(OH_2)_4]$ in solution are *trans*, occupying equivalent tetragonally extended axial positions and so are presumed to be transferred with equal probability.[32] Thus the statistically corrected relative rate constants for ligand transfer to 4-chlorophenyl radical are evaluatedas $k^{OH}:k_1^{Cl}(\text{corr.}):k_2^{Cl}(\text{corr.}) = 1:(59.3 \pm 3.4):(205 \pm 9)$.*

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* The use of McConnell and Davidson's[33] values in place of Ramette's enables evaluation of the statistically corrected relative rate constants for ligand transfer as $k^{OH}:k_1^{Cl}(\text{corr.}):k_2^{Cl}(\text{corr.}) = 1:(87.2 \pm 5.2):(729 \pm 60)$. Thus the choice of stability constants from divergent estimates affects the relative rate constants only within the order of magnitude.

An identification of a 'better' set of stability constants cannot be made on the basis of the fit of our data since the concentrations of complexes calculated for a range of total chloride concentrations with one set of equilibrium constants are proportional to those calculated with an alternative set. When step-wise stability constants decrease in the order $K_1 > K_2$ *etc.*, it may be shown from the defining equations of the constants and the material-balance equations for Cu and Cl that, to a first approximation and at low total chloride concentration, the equilibrium chloride concentration is given by $[Cl^-] = [Cl^-]_t/\{1 + K_1([Cu^{2+}]_t - [Cl^-]_t)\}$. Elimination of $[Cl^-]_t$ between two such expressions dependent on different estimates of K_1 gives, again to first approximation, $[Cl^-]^A = [Cl^-]^B(1 + K_1^B[Cu^{2+}]_t)/(1 + K_1^A[Cu^{2+}]_t)$ *i.e.* the alternative chloride concentrations are proportional. Since the concentrations of the various complexes are functions of the chloride concentration, these alternative concentrations are also respectively proportional.

Table 6 Relative rate data[a] for ligand transfers to 4-substituted phenyl radicals from copper complexes[b]

	Substituent	k_1^{Cl}/k^{OH}	k_2^{Cl}/k^{OH}	k_2^{Cl}/k_1^{Cl}	$k^{OH}:k_1^{Cl}(corr):k_2^{Cl}(corr)$	$k_2^{Cl}(corr)/k_1^{Cl}(corr)$
1	NO_2	3.59 ± 0.44	17.4 ± 4.0	4.9 ± 1.3	1:21.5 ± 2.6:52.3 ± 12.0	2.43 ± 0.62
2	CN	4.01 ± 0.19	18.3 ± 4.3	4.6 ± 1.1	1:24.1 ± 1.1:55.0 ± 12.9	2.29 ± 0.54
3	CO_2Et	6.41 ± 0.46	40.8 ± 19.3	6.36 ± 3.9	1:38.5 ± 2.8:122 ± 58	3.18 ± 1.95
4	Cl	9.89 ± 0.58	68.5 ± 5.8	6.92 ± 0.72	1:59.3 ± 3.4:205 ± 9	3.46 ± 0.36
5	F	11.9 ± 0.8	79.9 ± 13.0	6.73 ± 1.2	1:71.3 ± 2.4:240 ± 38	3.36 ± 0.6
6	H	23.1 ± 1.1	238 ± 58	10.3 ± 2.6	1:139 ± 7:714 ± 116	5.13 ± 1.3
7	Me	32.7 ± 4.8	493 ± 32	15.1 ± 3.0	1:196 ± 28:1478 ± 191	7.53 ± 1.5

[a] Quoted uncertainties are ±two standard deviations for entries 1, 4, 5, 7 and 8 where measurements were made at 6–15 chloride concentrations; for entries 2, 3 and 6 uncertainties are estimated experimental errors for measurements made at 2 chloride concentrations. [b] The distribution of Cu^{II} species was calculated using Ramette's concentration stability constants (ref. 27).

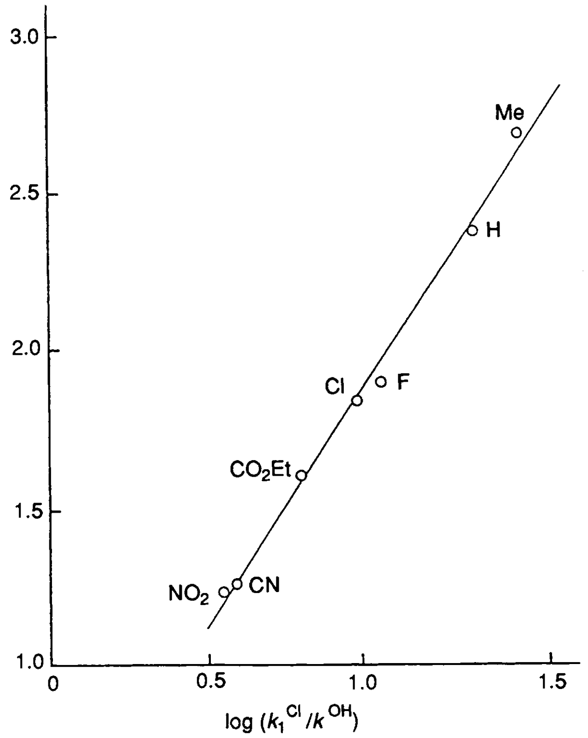

Fig. 4 Correlation of relative rates of ligand transfer from Cu^{II} complexes to 4-substituted phenyl radicals

(ii) *Substituent effects.* Determinations of relative rate constants analogous to those described above for ligand-transfers to 4-chlorophenyl radicals, were made for a further four 4-substituted radicals, the substituents being NO_2, F, Me and OMe; additionally, relative rate constants for three other 4-substituents (H, CO_2Et and CN) were found from measurements at only two chloride concentrations by solving eqn. (6) for the two concentrations, simultaneously. The results, obtained using Ramette's stability constants for the chlorocopper(II) complexes are given in Table 6.

As can be seen, the relative rate constants are substituent-dependent. For the 4-NO_2 substituent, there is little discrimination between $CuCl^+$ and $CuCl_2$: were the radical completely unselective, k_2^{Cl}(corr.)/k_1^{Cl}(corr.) would take a value of unity. The 4-CN substituent confers similar behaviour. The remaining radicals are more selective showing relatively easier abstraction of Cl from both $CuCl^+$ and $CuCl_2$, by comparison with abstraction of water from aquated Cu^{2+}, as the substituent becomes more electron-donating. Across the range of seven substituents from NO_2 to Me (OMe will be discussed separately) the reactivity of aryl radicals with $CuCl_2$ is proportional to that with $CuCl^+$ (Fig. 4). The correlation of Fig. 4 is given by eqn. (7).

$$\log k_2^{Cl}/k^{OH} = (0.380 \pm 0.084) + (1.485 \pm 0.058) \log k_1^{Cl}/k^{OH} \quad (7)$$
$$(100R^2 = 99.2;\ F = 649.8,\ F_{99.9} = 47.18)$$

The substituent dependence of neither k_1^{Cl}/k^{OH} nor k_2^{Cl}/k^{OH} is correlated by the simple Hammett equation, but correlation of the data from NO_2 to Me was achieved using Taft's 'bisected' substituent constants, σ_I and the various σ_R.[34] The results were best fitted by expressions using σ_R^+ or σ_R^0. Eqn. (8a and b)[*] apply to k_1^{Cl}/k^{OH}, with the latter marginally the better:

$$\log k_1^{Cl}/k^{OH} = (1.318 \pm 0.051) - (1.131 \pm 0.089)[\sigma_I + (0.509 \pm 0.085)\sigma_R^+] \quad (8a)$$

$$\log k_1^{Cl}/k^{OH} = (1.344 \pm 0.049) - (1.118 \pm 0.087)[\sigma_I + (0.757 \pm 0.123)\sigma_R^0] \quad (8b)$$

Similarly, k_2^{Cl}/k^{OH} is given by eqns. (9a and b),[*] with the former marginally the better.

$$\log k_2^{Cl}/k^{OH} = (2.366 \pm 0.083) - (1.736 \pm 0.144)[\sigma_I + (0.441 \pm 0.087)\sigma_R^0] \quad (9a)$$

$$\log k_2^{Cl}/k^{OH} = (2.402 \pm 0.087) - (1.719 \pm 0.155)[\sigma_I + (0.647 \pm 0.138)\sigma_R^+] \quad (9b)$$

We consider first the slopes of these correlations which represent the differences in reaction constants (ρ values) for the two types of ligand-transfer. Assuming it to be unlikely that the transfers of Cl and H_2O ligands would have opposite substituent dependences, the negative slopes of eqns. (8a and b) and (9a and b) could conceivably arise in two ways: either (i), the transfers of both Cl and H_2O ligands are assisted by electron-withdrawing substituents, *i.e.* each process has a positive reaction constant ρ, but the transfer of H_2O has the larger value; or (ii), the transfer of both types of ligand is assisted by electron-donating substituents *i.e.* each process has a negative reaction constant ρ, but the transfer of Cl has the larger absolute magnitude. Since overall, in each ligand-transfer, the result is a reduction of Cu^{II} to Cu^I and since $CuCl_2$, the strongest oxidant (E^0 = 0.45 V),[†] reacts faster than $CuCl^+$

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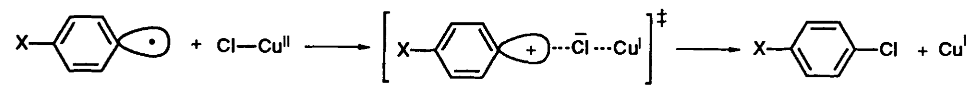
[*] Statistical results for eqns. (8a), (8b), (9a) and (9b) are as follows: (8a), ($100R^2 = 98.2$; $F = 110.9$, $F_{99.9} = 61.25$); (8b), ($100R^2 = 98.3$; $F = 116.4$, $F_{99.9} = 61.25$); (9a), ($100R^2 = 97.9$; $F = 94.23$, $F_{99.9} = 61.25$); (9b), ($100R^2 = 97.6$; $F = 81.15$, $F_{99.9} = 62.15$).

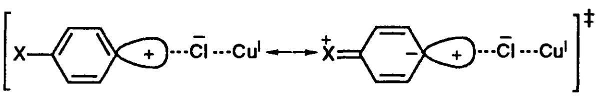
[†] Reduction potentials for $CuCl_2$ and $CuCl^+$ were calculated from Ramette's stability constants for the complexes[27] and those of Gunter and Zuberbühler[35] for chlorocopper(I) complexes. Yandell[36] calculated values based on the latter with McConnell and Davidson's values[33] which differ by only 0.01 V.



Scheme 3

($E^0 = 0.34$ V) which in turn reacts faster than Cu^{2+} ($E^0 = 0.16$ V),[37] it appears that the copper complexes exhibit electrophilic character and the aryl radicals nucleophilic character in the transition states for these ligand-transfers (Scheme 3). Thus case (ii) is believed to be appropriate to the present results, *i.e.*, the rates of both kinds of ligand-transfer are increased by electron-donating substituents in the aryl ring, chlorination showing the larger substituent dependence. This rationale implies that the competitive ligand-transfers comprise a failure of the reactivity–selectivity principle as the slower-reacting radicals exhibit the lower selectivity.

Aliphatic carbon-centred radicals are oxidised to carbonium ions by Cu^{2+}.[38,39] Owing to the greater electronegativity of the σ-SOMO (sp^2 rather than p or sp^3), complete oxidation of aryl radicals does not occur but we suggest that in the transition states for ligand-transfer the carbocationic character at the reaction centre increases relative to the ground state. The observation of a dependence of the relative rate constants on σ_R^+ is consistent with such an increase for if, on passage to the transition state, the σ-SOMO is depleted in electron-density, the electronegativity of the reactive carbon will increase, incurring a polarisation of the orthogonal π-orbital which would be partly stabilised by mesomeric donation from appropriate substituents (Scheme 4).

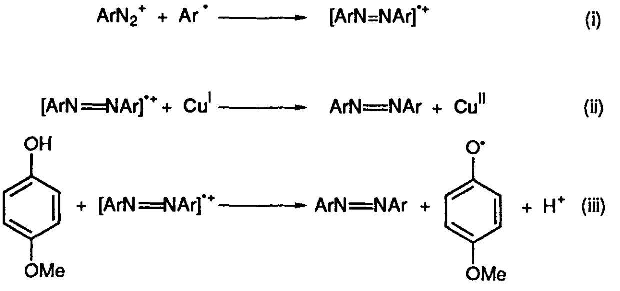


Scheme 4

The fact that, in comparison with the inductive effect, the mesomeric effect plays a relatively small and indirect role in the stabilisation of cationic character in the transition states is reflected in the small coefficient of σ_R^+ in both eqns. (8a) and (9a). By definition (*via* σ^0), correlations involving σ_R^0 relate to situations with a lack of direct conjugation between reaction site and substituent. Eqns. (8b) and (9b) thus give an alternative account of the indirect role of substituents' mesomeric effects in stabilising the transition states for ligand transfer. It should be noted, however, that the coefficient of σ_R^+ or of σ_R^0 is constant, within the statistical uncertainty, between eqns. (8a) and (9a) and between (8b) and (9b). This implies that the relative importance of inductive and mesomeric effects in stabilising the increased positive charge in the aryl moieties of the transition states for ligand-transfer, stays essentially the same irrespective of whether Cl is abstracted from $CuCl^+$ or from $CuCl_2$. Pross[40] has shown how an increase in charge separation in a transition state, relative to reactants and products, may result in breakdown of the reactivity–selectivity principle.

The behaviour of the 4-methoxyphenyl radical is anomalous. Although the value of the ratio [ArCl]/[ArOH] increases rapidly with the concentration of added chloride (as expected from the net electron-donating character of the substituent), at a fixed chloride concentration the ratio also increases with the amount of initiator employed (Table 7). The values of k_1^{Cl}/k^{OH} and k_2^{Cl}/k^{OH} evaluated for 4-methoxyphenyl radical under conditions identical to those for other radicals are not correlated with the values of Table 6 by eqns. (7), (8) and (9). Furthermore, it was noticed that the maximum percentage yields of combined Sandmeyer products from 4-methoxyphenyl radical (*i.e.*, 4-methoxyphenol and 4-chloroanisole) were low when compared with those from other radicals, such as 4-methylphenyl and 4-chlorophenyl radicals, under similar conditions. Gas chromatographic analysis revealed a third product, the mass spectrum of which proved it to be 4,4′-dimethoxyazobenzene. Its amount increased with increase in the amount of initiator used (Table 7). The results given in Table 7 indicate that 4,4′-dimethoxyazobenzene is formed at the expense of both Sandmeyer products but that the total amount of reactant diazonium ion accounted for as identified products when reaction goes to completion is 80 ± 5%, comparable to the previously mentioned radicals. The formation of 4,4′-dimethoxyazobenzene thus appears to be competitive with the formation, by ligand-transfer, of the Sandmeyer products. Nonhebel and Waters[41] have made a similar observation.*

We propose that the competition is due to the intervention of reactions (i) and (ii) of Scheme 5 which divert 4-methoxyphenyl radicals from Sandmeyer products. We shall show in a later paper that 4-methoxybenzenediazonium ion is the slowest of those studied to be reduced by Cu^I. Thus 4-methoxyphenyl radicals are produced in the presence of significant concentrations of unreacted diazonium ion. Packer and co-workers[42] have measured a rate constant of 4×10^6 dm^3 mol^{-1} s^{-1} for the addition of 4-methylphenyl radical to the corresponding diazonium ion and a similar rate constant is reasonably expected for the addition of 4-methoxyphenyl radical to its diazonium percursor.



Scheme 5

An additional reaction of 4-methoxyphenyl radicals, competitive with the ligand-transfers, is not expected to cause variation in the ratio of the two ligand-transfer products. To account for the observed variation, we propose that a small fraction of the 4-methoxyphenol produced by ligand-transfer is lost by oxidation to the corresponding phenoxyl radical. The loss does not need to be great to account for variation in the Sandmeyer product ratio. For 4-methoxyphenyl radical, the discrimination between the chloride- and water-ligand transfer is expected, from the nature of the substituent, to be greater than for the other radicals studied. Thus phenol yields are intrinsically low and the product ratio [ArCl]/[ArOH] takes relatively high values. Small changes in [ArOH] thus cause changes in the ratio which are large and noticeable.

Flitman and Frieden[12] reported oxidation of 4-methoxyphenol by Cu^{2+} but such oxidation is too slow on the time-scale of the present reactions to represent the means of loss of the phenol; we therefore propose that the species which oxidises 4-

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* We thank a referee for drawing our attention to this paper.

Table 7 Variation of yields and product ratios with the amount of initiator used for reaction[a] of 4-methoxybenzenediazonium ion with aqueous copper sulphate containing added sodium chloride

$\frac{[\text{Ascorbic acid}]}{[4\text{-MeOC}_6\text{H}_4\text{N}_2^+]}$	Yield[b] ArOH (%)	Yield[b] ArCl (%)	Yield[b] ArN=NAr (%)	[ArCl]/[ArOH]	ArN_2^+ accountable (%)
0.050	5.52	31.7	1.11	5.7	39.4
0.075	5.62	42.6	2.19	7.6	52.6
0.125	5.15	52.3	3.86	10.2	65.2
0.250	3.63	55.4	10.9	15.3	80.8
0.375	2.76	51.1	16.1	18.5	86.1
0.500	2.08	39.3	19.6	18.9	80.6
0.750	1.20	26.3	24.5	21.9	76.5
1.000	1.09	24.6	25.3	22.6	76.3

[a] Conditions: $[ArN_2^+] = 0.02$ mol dm^{-3}; $[CuSO_4] = 0.3$ mol dm^{-3}; $[Cl^-] = 0.12$ mol dm^{-3}. [b] Based on diazonium ion.

Table 8 The variation in proportions of Sandmeyer products from 4-chlorobenzenediazonium and Cu^{II} as a function of the concentration of total equimolar mixed halide[a]

$[\text{Halide}]_t$/ mol dm^{-3}	[ArBr]/[ArCl]	[ArBr]/[ArOH]	[ArCl]/[ArOH]
0.01	1.09	0.077	0.084
0.02	1.11	0.174	0.156
0.04	1.25	0.370	0.297
0.08	1.29	0.834	0.645
0.12	1.36	1.40	1.03
0.16	1.42	2.14	1.51
0.20	1.45	2.89	1.99
0.30	1.55	5.59	3.61
0.40	1.65	8.82	5.33
0.50	1.74	12.60	7.23

[a] Conditions: $[4\text{-ClC}_6\text{H}_4\text{N}_2^+] = 0.02$ mol dm^{-3}; $[Cu^{2+}]_t = 0.30$ mol dm^{-3}; [ascorbic acid] = 0.005 mol dm^{-3}.

methoxyphenol is the 4,4′-dimethoxyazobenzene cation-radical [Scheme 5(iii)].

Competitive Sandmeyer Bromination.—A comparison of Sandmeyer bromination with chlorination and hydroxylation in the manner described above is hampered by the lack of reliable stability constants for bromocopper(II) complexes. Bromide is expected to form weaker complexes than does chloride.[43] Libuš and Maciejewski[44] have determined a value for K_1^{Br} (0.87 dm^3 mol^{-1} at infinite dilution) by spectroscopic means, and have examined its dependence on the concentration of other added electrolytes. The value decreases through a minimum with increasing ionic strength. However, the value of K_1^{Cl} determined by the same procedure (1.63 dm^3 mol^{-1})[45] is small by comparison with Ramette's value[27] of 2.36 dm^3 mol^{-1} used in the present work. We have thus taken the value of 0.87 dm^3 mol^{-1} as indicative of K_1^{Br} for our conditions, the neglect of ionic strength effects compensating, to some unspecified extent, for the relatively low estimate given by the spectroscopic method.

Competitive experiments were carried out using 4-chlorobenzenediazonium ion similar to those described above but where, in place of added NaCl, equimolar NaCl and NaBr were used. The reaction products were thus 4-chlorophenol, 1,4-dichlorobenzene and 4-chlorobromobenzene. The mean product ratios from duplicated experiments are given in Table 8. A limited number of other substituted diazonium ions was also used at a very low total concentration of added equimolar halides; the mean product ratios are given in Table 9. It is evident from Table 8 that as the concentration of mixed halide increases and aryl halides are produced at the expense of phenol, there is a selectivity in favour of aryl bromide. This doubtless implies increasing concentrations of complexes with a greater capacity for transfer of a bromide ligand than the chlorocopper(II) complexes present can transfer Cl. However, without firm knowledge of stability constants of bromocopper(II) complexes the factors of relative concentrations and relative intrinsic reactivities cannot be disentangled.

Under conditions of low total mixed sodium halide concentration such that only monohalocopper(II) complexes are likely to be present in significant amounts, it may be shown by an analysis analogous to that given above that [ArBr]/[ArCl] is given by eqn. (10) *i.e.* for a given total halide ratio and total

$$\frac{[\text{ArBr}]}{[\text{ArCl}]} = \frac{k_1^{Br}K_1^{Br}(1 + K_1^{Cl}[\text{Cu}^{2+}]_t)}{k_1^{Cl}K_1^{Cl}(1 + K_1^{Br}[\text{Cu}^{2+}]_t)} \times \frac{[\text{Br}^-]_t}{[\text{Cl}^-]_t} \quad (10)$$

Cu^{2+} concentration [ArBr] and [ArCl] are proportional. The constant of proportionality was estimated, from the initial gradient of the plot of [ArBr] *vs.* [ArCl], as 1.15 for equimolar halide concentrations. Equating this quantity to the right hand side of eqn. (10) gave, after insertion of Ramette's K_1^{Cl}, Libuš' K_1^{Br}, and the experimental concentration $[Cu^{2+}]_t = 0.3$ mol dm^{-3}, a value of $k_1^{Br}/k_1^{Cl} = 2.3$. [The use of Libuš' K_1^{Cl} (1.63 dm^3 mol^{-1}) reduced this ratio to 1.38]. Previously the reactivity of copper(II) bromide relative to chloride in ligand-transfer to alkyl radicals in CH_3CN has been found to be 4.[39] However, the distribution of the various complexes is very different in CH_3CN, higher complexes occurring in significant concentrations.[46] Galli[47] estimated a relative reactivity of *ca.* 3 in Sandmeyer reactions, although no consideration was given to the distribution of reactive complexes. It thus seems that the reactivity differential between copper(II) bromides and chlorides may increase in the higher complexes.

The results of Table 9 show that, across the range of substitution considered, the 4-substituted aryl radicals exhibit a variation in selectivity for both types of halogen transfer over water transfer, comparable with that observed for chloride alone. But there is no selectivity between the two types of halogen transfer. This implies that k_1^{Br}/k^{OH} is described by a Hammett–Taft equation with a slope (relative reaction constant) essentially equal to that of eqns. (8a and b). The difference between the halide transfers would therefore appear to reside essentially in the inorganic moieties of the transition states. The lack of reliable stability constants for bromocopper complexes in both oxidation states precludes the calculation of a reduction potential for the couple $CuBr^+/CuBr$ to test the generality of the correspondence observed for the aqua- and chloro-copper complexes.

Conclusion

Evidence has been given which indicates that the homolytic formation of phenols under Sandmeyer conditions is directly comparable with the well-known halogenation reaction:

Table 9 The substituent dependence of the Sandmeyer products from substituted diazonium ions

4-Substituent	[ArBr]/[ArCl]	[ArBr]/[ArOH]	[ArCl]/[ArOH]
OMe	1.14	0.548	0.480
F	1.13	0.220	0.194
Cl	1.11	0.174	0.156
CO_2Et	1.15	0.118	0.103

[a] Conditions: $[ArN_2^+] = 0.02$ mol dm^{-3}; $[Cu^{2+}] = 0.3$ mol dm^{-3}; [ascorbic acid] = 0.005 mol dm^{-3}; $[Cl^-]_t = [Br^-]_t = 0.01$ mol dm^{-3}.

Sandmeyer hydroxylation and halogenation are competitive processes. However, the transfer of a halide ligand occurs more rapidly than the transfer of a water ligand and at high halide concentrations phenol formation is minor, consistent with long known synthetic results. Rate constants have been evaluated for the transfer of chloride ligands from mono- and di-chlorocopper(II) relative to the transfer of water from aquated copper(II) and for the transfer of bromide from monobromocopper(II) relative to the transfer of chloride from the analogous chloro-complex. The dependence of these relative rate constants on substitution in the diazonium ion indicates that halide transfer has a greater sensitivity to substituent effects than transfer of water and that the selectivity between halide- and water-transfer is greater for the faster reacting radicals, *i.e.*, the reactivity–selectivity principle fails. It is inferred that, in the transition states for these ligand-transfer processes, electron transfer occurs between the nucleophilic aryl radicals and the electrophilic copper complexes.

When copper(II) is reduced to copper(I) the coordination number is expected to decrease from 6 to 4. The transfer of the ligand is thus envisaged as occurring *via* a re-orientation, within the activated complex subsequent to electron transfer, of a nucleophile (Cl^- or H_2O) released from coordination to copper, rather than as an atom abstraction process. The rate of ligand transfer is faster the larger the standard reduction potential of the copper complex involved. It thus appears that the barriers to reaction are largely thermodynamically determined, although kinetic factors, such as ligand polarizability may also have a role.

Experimental

Materials.—Diazonium tetrafluoroborates were prepared by diazotisation of the appropriate anilines (0.1 mol) in H_2SO_4 (75–100 cm^3, 2.5 mol dm^{-3}) followed by precipitation with $NaBF_4$,[48] and were purified by dissolution in acetone and reprecipitation by addition of diethyl ether.[49] All other reagents were commercial materials used as supplied.

Sandmeyer Reactions.—The general procedure was to take 100 cm^3 of a stock solution of $CuSO_4{\cdot}5H_2O$ in water (0.3 mol dm^{-3} for most experiments) and to dissolve in it appropriate quantities of sodium chloride (or chloride plus bromide). To the vigorously stirred solution was added 0.02 mol of the appropriate diazonium salt. When the solution became homogeneous, ascorbic acid was added, either as the solid or in solution in a small quantity of water. Evolution of nitrogen was immediate and oily or solid organic products appeared. Ethyl acetate (50 cm^3) was added to dissolve these, followed by an aliquot of a standard solution, in the same solvent, of a suitable internal standard for GC analysis. The mixture was transferred to a tap-funnel, shaken well, then separated.

The organic layer was analysed by GC. Chromatographic conditions depended on the substrate: phenols and halobenzenes having the substituents NO_2, CN, CO_2Et and MeO were analysed using a column packed with 1% DEGA on Gaschrom Q, carrier gas N_2 (*ca.* 40 cm^3 min^{-1}) at temperatures appropriate to the analytes, with 4-chlorophenol as internal standard. Products substituted by Me, F, Cl, H and MeO were analysed on a column packed with 10% SE30 on Gaschrom Q, carrier gas N_2 (*ca.* 40 cm^3 min^{-1}), at suitable temperatures. Here the internal standard used was biphenyl. The gas chromatograph employed was a Pye Unicam model PU 4500 served by a Shimadzu C-R1B integrator, and was calibrated using standard solutions of authentic materials.

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