Metal Ions and Complexes in Organic Reactions. Part VII.[1] Copper-promoted Hydrogen Transfer from Aromatic Donors to Halides

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Copper-promoted hydrogen transfer from various aromatic donors to aryl bromides, *e.g.*, in 2,4,6-collidine or dimethylacetamide at ~170°, resulted in reductive substitution, ArBr ⟶ ArH (up to ~80%), sometimes in competition with nucleophilic substitution by the reductants, and (in the case of *o*-bromonitrobenzene) with a small amount of Ullmann-type coupling of the halide. Copper(I) oxide or the metal were the most effective of the copper species examined, and both dissolved during reaction. Unsaturated substituents, particularly *o*-NO_2, greatly enhanced reducibility. α-Bromo-ketones readily underwent similar reduction. Fission occurred in the SCN group of *o*-nitrophenyl thiocyanate.

Effective types of aromatic donors were phenols, amines, hydrazine derivatives, nitro-compounds, carboxylic esters, quinones, and pyridine *N*-oxide; dehydrogenation products of some representatives of the first three of these types were identified. Reactivity was also observed in solvents. The possibility of hydrogen transfer proceeding by homolytic mechanisms is discussed.

We have reported[2] the preparation of diaryl ethers by a copper-promoted nucleophilic substitution process of type (1), occurring in suitably chosen organic solvents:

$$2ArHal + 2Ar'OH + Cu_2O \longrightarrow 2ArOAr' + 2CuHal + H_2O \quad (1)$$

To a varying extent, depending upon the nature of the halide and phenol, competitive reductive substitution, ArHal ⟶ ArH, frequently occurred. In one such case, the products from *p*-cresol and *o*-bromonitrobenzene included nitrobenzene and the coupled phenol (Ia) (in the form of its di-*o*-nitrophenyl ether). In another case, when benzylamine was present in a reaction mixture, conversion of 1-bromonaphthalene into 1-phenoxynaphthalene was accompanied by formation of naphthalene and of benzaldehyde.

It thus appears that reduction of a halide may be linked, *e.g.*, with the oxidative coupling of a phenol (2ArH ⟶ ArAr) or with the dehydrogenation of an amine ($RCH_2{\cdot}NH_2 \longrightarrow RCH{:}NH \longrightarrow RCHO$), and that such processes, when promoted by copper(I) oxide, may be generalised as hydrogen-transfer reactions of type (2):

$$2ArHal + \left\{\begin{matrix}4XH\\2YH_2\end{matrix}\right\} + Cu_2O \longrightarrow 2ArH + \left\{\begin{matrix}2X{\cdot}X\\2Y\end{matrix}\right\} + 2CuHal + H_2O \quad (2)$$

Having observed similar reductive effects in other studies, we have made the generalisation that an important property of copper(I) compounds, and of the metal, is the promotion of hydrogen transfer from numerous kinds of donors to certain types of acceptors, among which aryl bromides and iodides are prominent.[3-5]

This paper describes an examination of reactions between halides and selected types of aromatic compounds which might thus serve as reductants. With a high proportion of the compounds tested, reduction (2) was found to be the predominant reaction, giving compounds ArH in yields of up to ~80%. Nucleophilic substitution, exemplified by reaction (1) in the case of phenols, often occurred competitively. A further reaction (3), consistently observed to a small extent with *o*-bromonitrobenzene, was Ullmann-type coupling of the halide, in which copper(I) acted reductively, as the metal does in the conventional Ullmann process:[6]

$$2ArHal + Cu_2O \longrightarrow ArAr + CuO + CuHal_2 \quad (3)$$

This reaction will not be discussed here, since we have commented upon it elsewhere,[7] and are studying it further.

The results of copper-promoted reactions are often greatly affected by small changes in experimental method. The standard procedure used throughout these studies was to mix the halide, aromatic reductant, and commercial copper(I) oxide (or other copper species) in the molar ratio of 1 : 1 : 0·5, and to carry out the reaction under nitrogen, with stirring and refluxing, in solvents of known suitability,[2] *i.e.*, 2,4,6-collidine (b.p. 170°) or dimethylacetamide (b.p. 166°).

Series of hydrogen donors were tested against a common acceptor (Tables 1, 4, 5) and a series of acceptors against a common donor (Table 3). For the former purpose it was convenient to use a particularly easily reduced halide, and *o*-bromonitrobenzene was generally chosen. Three types of potential hydrogen donors were examined: (a) phenols, (b) aromatic amines and hydrazine derivatives, (c) aromatic compounds which are devoid of functional groups associated with reducing activity, and which therefore offer the possibility of hydrogen transfer from the nucleus being observed. The acceptors tested were mainly aryl bromides, but Table 3 demonstrates that reduction is applicable to some other types of compounds, and it is likely that future study will disclose further acceptor–donor combinations susceptible to catalysis by copper.

The most responsive aryl bromides were reduced to

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[1] Part VI, R. G. R. Bacon and Alia R. Izzat, *J. Chem. Soc.* (*C*), 1966, 791.

[2] R. G. R. Bacon and O. J. Stewart, *J. Chem. Soc.*, 1965, 4953.

[3] R. G. R. Bacon, S. C. Rennison, and O. J. Stewart, *Proc. Chem. Soc.*, 1964, 409.

[4] R. G. R. Bacon and H. A. O. Hill, *Quart. Rev.*, 1965, **19**, 95.

[5] R. G. R. Bacon and S. C. Rennison, following papers.

[6] P. E. Fanta, *Chem. Rev.*, 1946, **38**, 139; 1964, **64**, 613; *cf.* A. H. Lewin and T. Cohen, *Tetrahedron Letters*, 1965, 4531.

[7] R. G. R. Bacon, S. G. Seeterram, and O. J. Stewart, *Tetrahedron Letters*, 1967, 2003.

the extent of ~50–80% by various aromatic compounds. However, for preparative purposes, other types of reductants might be preferred as being more efficient; *e.g.*, the yield of naphthalene from 1-bromonaphthalene was 5—50% in various phenol–Cu_2O–solvent systems (this paper and ref. 2), ~80% with copper(I) acetate in pyridine,[8] and 90% or more in some alkoxide–Cu_2O–solvent systems.[5]

After chromatographic separation of products, the total recovery of identified compounds, including unchanged halide, was sometimes as high as 80—95%, but was frequently diminished, *e.g.*, by the presence of resins. Reproducibility was sometimes erratic, but this is a common feature of copper-promoted reactions,[4,7] attributable to the heterogeneity of systems employed, the occurrence of competing or consecutive reactions, changes in the copper species during the process, and effects of impurities.

TABLE 1

Products from solutions of o-Br.C_6H_4·NO_2 (0·0166 mole; 0·4M in 2,4,6-collidine) + phenols (0·0166 mole) + Cu_2O (0·0083 mole), at b.p. for 2 hr., under N_2 (Corresponding data for solutions in dimethylacetamide are shown in parentheses)

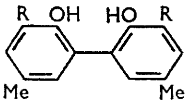
Phenol	Reduction: $PhNO_2$ (%)	Substitution: o-NO_2·C_6H_4·OAr (%)	Coupling: (o-NO_2·C_6H_4)$_2$ (%)	Oxidation: identified product from the phenol (%)	
None	(0—2)	—	(3)	—	
p-Cresol [a]	22	48	3	(Ia) [f]	3
2,4-Dimethylphenol	80	—	—	(Ib) [f]	Trace
2,6-Dimethylphenol [b,c]	70 (73)	2 (0)	3 (5)	(II)	20 (30)
2,4,6-Trimethylphenol	50 (75)	—	3 (4)	(IIIa)	9 (13)
2,6-Di-t-butyl-4-methylphenol [d]	32	—	20	(IIIb)	20
2,6-Dichlorophenol	55	3	—	—	
Catechol	71 (66)	—	—	—	
Resorcinol	31 (24)	11 (15)	—	—	
Hydroquinone [e]	53 (64)	2 (1)	2 (1)	—	
Coupled phenol (Ia) [a]	50	30	—	—	
Coupled phenol (II) [e]	75	—	3	—	

[a] Quoted from ref. 2; reaction time, 16 hr. [b] Reaction for 72 hr. in refluxing m-xylene gave 6% $PhNO_2$. [c] 2,6-Dimethylanisole in collidine gave 2% $PhNO_2$. [d] p-Br·C_6H_4·NO_2 yielded 25% $PhNO_2$ in 66 hr. in dimethylacetamide. [e] *Cf.* reduction by the corresponding quinone (Table 5). [f] Isolated as o-nitrophenyl ethers.

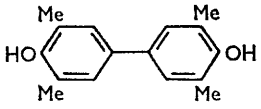
(a) *Reduction by Phenols*.—Results of reactions between o-bromonitrobenzene and eleven phenols (Table 1) showed reductive substitutions to be predominant (except in the case of p-cresol), with minor contributions from nucleophilic substitution and Ullmann coupling. However, if consideration is given to a wider range of phenols and halides, by inclusion of about twenty examples previously reported,[2] it is evident that reactions of types (1) and (2) are, on average, of roughly comparable importance; polar or steric effects of substituents presumably determine which result predominates in individual cases. Reduction seems to be favoured if NO_2, or other unsaturated substituent, is present in either the halide or phenol. For copper-promoted reactions in general,[4,6,9] available data suggest that aromatic substituent effects do not form a similar pattern to those established, *e.g.*, for conventional nucleophilic substitution processes.

The phenols used as reductants were largely converted into resins, but from five reaction mixtures (Table 1) the following crystalline phenolic oxidation products were isolated chromatographically: (Ia) and probably (Ib), due to *ortho*-coupling of the respective phenols; (II), due to *para*-coupling of the phenol; (IIIa) and (IIIb), due to coupling at an α-carbon atom of the respective phenols, (IIIb) being accompanied by the corresponding stilbenequinone (V).

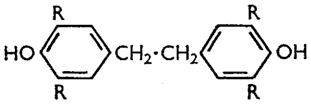
Mechanistic problems concerning reductions of the halides are thus linked with those which have arisen during the numerous studies of phenolic oxidative coupling processes which have been made in recent years.[10] So far as reduction of the halide is concerned, accession of electrons to an adsorbed ArBr molecule from the surface of a copper(I) species (or the metal) might successively produce an aryl radical Ar· or anion Ar^-;[4,6] a donor might then furnish either a hydrogen atom to the former, or a proton to the latter, giving the reduced product ArH. However, the evidence concerning phenolic coupling processes under most conditions is



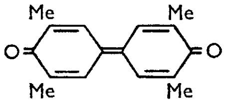
(Ia) R = H
(Ib) R = Me



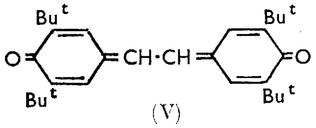
(II)



(IIIa) R = Me
(IIIb) R = Bu^t



(IV)



(V)

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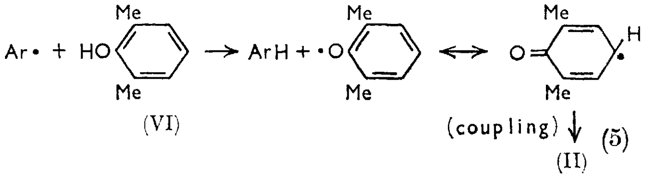
[8] R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1964, 1112.

[9] R. G. R. Bacon and H. A. O. Hill, *J. Chem. Soc.*, 1964, 1097.

[10] (*a*) A. I. Scott, *Quart. Rev.*, 1965, **19**, 1; (*b*) a bibliography for oxidations of 2,6-dimethylphenol is given in ref. 1; (*c*) *cf.* D. H. R. Barton, Pedler Lecture, *Chem. in Britain*, 1967, 330.

strongly in favour of homolytic mechanisms, featuring aryloxy radicals as intermediates.[10] Accordingly, we tentatively show a reaction sequence (4)—(10), in which 2,6-dimethylphenol exemplifies a phenolic hydrogen donor:

$$\mathrm{ArBr} + \mathrm{Cu^+} \rightleftharpoons \begin{array}{c}\text{complex on}\\ \mathrm{Cu_2O}\text{ surface}\end{array} \rightleftharpoons \mathrm{Ar\cdot} + \mathrm{Cu^{2+}} + \mathrm{Br^-} \qquad (4)$$



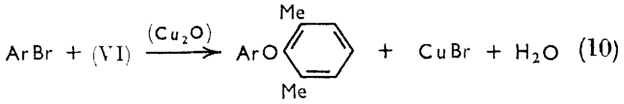
$$(?)\quad 2\mathrm{Ar\cdot} + (\mathrm{II}) \longrightarrow 2\,\mathrm{ArH} + (\mathrm{IV}) \qquad (6)$$

$$(?)\quad x\mathrm{Ar\cdot} + (\mathrm{IV}) \longrightarrow x\mathrm{ArH} + \text{products from (IV)} \qquad (7)$$

$$2\,\mathrm{Cu^{2+}} + 2\,(\mathrm{VI}) \longrightarrow 2\,\mathrm{Cu^+} + 2\,\mathrm{H^+} + (\mathrm{II}) \qquad (8)$$

(or other reductant) (or other oxidation products)

$$2\mathrm{Ar\cdot} \longrightarrow \mathrm{ArAr} \qquad (9)$$



Homolytic reactions (4) and (5), involving reduction of the halide by the phenol (VI), are shown in competition with catalysed nucleophilic substitution (10) and Ullmann coupling (9), and are followed by further halide reductions, (6) and (7). The scheme includes the latter reactions (uncertain in mechanism) in recognition, respectively, of reduction of halide by the coupled phenol (II), which is produced by oxidation of the phenol (VI) (Table 1), and reduction of halide by the diphenoquinone (IV), which is produced by oxidation of (II) (Table 5). In a related reaction sequence, both hydroquinone and its oxidation product, *p*-benzoquinone, proved to be reductants for the halide (Tables 1 and 5). Reaction (8) is included to suggest the regeneration of copper(I) by the dehydrogenating or brominating action of copper(II) bromide [4] on (VI), or on some other oxidisable compound in the system. Analysis of solutions left at the end of reactions showed the copper ions to be in the univalent state.

Phenolic reductants (Table 1) included catechol and resorcinol. Their reductive action on *o*-chloro-, *o*-bromo-, and *o*-iodo-nitrobenzene (that of catechol being superior) was previously observed by Nursten [11] when he introduced these phenols into mixtures of the halides with copper, during Ullmann coupling reactions. He suggested that a radical mechanism was involved.

When copper species were varied (Table 2), reduction occurred to a varying extent, accompanied by the oxidative coupling (VI) ⟶ (II). Metallic copper was in some cases as effective as copper(I) oxide; its effect may be accommodated in the above reaction scheme by replacing process (4) by (4a):

$$\mathrm{ArBr} + \mathrm{Cu} \rightleftharpoons \begin{array}{c}\text{complex on}\\ \text{Cu surface}\end{array} \rightleftharpoons \mathrm{Ar\cdot} + \mathrm{Cu^+} + \mathrm{Br^-} \qquad (4a)$$

TABLE 2

o-Br.C_6H_4·NO_2 + 2,6-dimethylphenol + copper species (Conditions as in Table 1; solvent, 2,4,6-collidine)

Copper species	Reduction: $PhNO_2$ (%)	Coupling: (*o*-NO_2·C_6H_4)$_2$ (%)	Oxidation: coupled phenol (II) (%)
None	0	—	0
Cu_2O	70	3	20
Cu [a]	67	4	20
CuBr	34	—	16
CuCN [b] ...	5	—	0
Cu_2S	6	—	4
CuO	34	5	19

[a] With some other halides and 2,6-dimethylphenol, Cu was not always as effective as Cu_2O. [b] The main product was *o*-NO_2·C_6H_4·CN; the solvent was dimethylacetamide.

The normal result of heating metallic copper with an aryl bromide, with or without a solvent, is the Ullmann coupling reaction, and little is known about the reductive substitution which is sometimes observed as a side-reaction when it is carried out under conventional conditions.[4,6] It now appears that reaction may be diverted from coupling to reductive substitution by hydrogen donors which may include monohydric phenols (Table 2), dihydric phenols,[11] and alkoxides.[5]

Reduction occurred to a moderate extent (Table 2) in the presence of copper(I) bromide; hence, catalysis should continue, though probably to a diminished extent, if this species is formed in a reaction system by dissolution of copper(I) oxide (or copper) during a process of type (2). Catalytic effects of copper(I) salts with aryl halides are discussed elsewhere.[5] The observed reduction of halide in the presence of copper(II) oxide (Table 2) may have followed an intermediate stage, in which copper(I) was generated through oxidation, *e.g.*, of the phenol by copper(II).

Reactivities of a selection of halides (Table 3) may be compared with that of *o*-bromonitrobenzene when they were similarly treated with 2,6-dimethylphenol (not the most efficient of phenolic reductants) in conjunction with copper(I) oxide. Oxidative coupling, (VI) ⟶ (II), regularly accompanied halide reduction, and also occurred when halide was omitted and oxygen replaced nitrogen in the reaction flask. Reduction of aryl bromides was best achieved when they contained unsaturated nuclear substituents, *p*-NO_2, and *o*- or *p*-COX, though none responded as readily as the *o*-nitro-halide; the unsubstituted aryl bromides were but feebly reactive under these conditions.

4-Nitrobenzyl bromide underwent some reduction, whilst benzhydryl bromide was efficiently coupled to tetraphenylethane, as happens with certain other transition-metal reductants.[12] We found that copper(I)

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[11] H. E. Nursten, *J. Chem. Soc.*, 1955, 3081.

[12] *E.g.*, C. E. Castro, *J. Amer. Chem. Soc.*, 1961, **83**, 3262; C. E. Castro and W. C. Kray, *ibid.*, 1963, **85**, 2768.

compounds effected this coupling, in high yield, in the absence of the phenol. A normal alkyl bromide was unaffected in the phenol–Cu$_2$O system, and only elimination resulted with an alicyclic secondary bromide. α-Halogeno-ketones underwent extensive reduction of the type: $-\text{CO}\cdot\text{CHHal}- \longrightarrow -\text{CO}\cdot\text{CH}_2-$, such as occurs with chromium(II) salts as reductants;[13] further investigation of the copper-promoted reaction is needed because of the possibility that the solvents employed may participate.[5,13b] The high reactivity shown by o-nitro-halides and α-halogeno-ketones may be due to bonding of a chelate type between the pair of neighbouring substituents and the metal atom. This idea has often been expressed in connection with reactions of *ortho*-substituted aromatic compounds involving copper, and a suggestion of a similar kind has been made concerning the ready hydrogenolysis of α-halogeno-ketones on palladium.[14]

Other substrates were briefly examined under the conditions shown in Table 3. There was no evidence of reduction of olefinic or ketonic carbonyl bonds. o-Nitrophenyl thiocyanate was tested because of the pseudohalide character of SCN groups. It underwent fission at the ArS–CN bond, giving low yields of the corresponding disulphide and monosulphide, the former of which was probably precursor to the latter. Conversion of thiocyanates into disulphides by nucleophiles is well known,[15] but the presence of both the phenol and the copper species seemed necessary in the case now described.

TABLE 3

Reduction of solutions of halides etc., by 2,6-dimethylphenol + Cu$_2$O (conditions as in Table 1, but with varying time of reaction)

Substrate RX	Time (hr.)	Solvent [a]	Reduction of substrate: RH (%)	Oxidation of phenol: (II) (%)	Other products (%)	
1-Bromonaphthalene [b]	48	C	6	10	2,6,1-Me$_2$C$_6$H$_3$·OR	10
9-Bromophenanthrene	70	D	3	—	—	
p-Br·C$_6$H$_4$·NO$_2$ [c]	22	C	65	7	(p-NO$_2$·C$_6$H$_4$)$_2$	4
p-Br·C$_6$H$_4$·COMe	66	D	23	4	2,6,1-Me$_2$C$_6$H$_3$·OR	3
o-Br·C$_6$H$_4$·CHO	18	D	17	34	—	
o-Br·C$_6$H$_4$·CO$_2$Me	24	D	33	—	—	
p-NO$_2$·C$_6$H$_4$·CH$_2$Br [d]	21	C	19	5	—	
Ph$_2$CHBr	21	C	—	7	Ph$_2$CH·CHPh$_2$	80
n-C$_{10}$H$_{21}$Br	52	D	—	—	—	
3-Bromocholestane	96	D	—	18	Cholest-2-ene	70
PhCO·CH$_2$Cl	4	D	10	7	—	
3-Bromocamphor	48	D	70	33	—	
3-Bromocamphor	16	P	73	—	—	
2-Bromocholestan-3-one	70	D	38	—	—	
o-NO$_2$·C$_6$H$_4$·SCN	11	D	—	30	(o-NO$_2$·C$_6$H$_4$·S)$_2$ (o-NO$_2$·C$_6$H$_4$)$_2$S	12 6
(o-NO$_2$·C$_6$H$_4$·S)$_2$	11	D	—	10	(o-NO$_2$·C$_6$H$_4$)$_2$S	7
O$_2$	2	C	—	25	—	

[a] C = 2,4,6-collidine, D = dimethylacetamide, P = pyridine. [b] 27% C$_{10}$H$_8$ produced with o-nitrophenol (ref. 2), 11% with o-nitroanisole. [c] *Cf.* o-isomer (Table 1). [d] 8—9% reduction to p-Me·C$_6$H$_4$·NO$_2$ occurred in collidine or dimethylacetamide in the absence of Cu$_2$O.

TABLE 4

Products from solutions of o-Br.C$_6$H$_4$·NO$_2$ (ArBr) + amines or hydrazine derivatives + Cu$_2$O (conditions as in Table 1; solvent, dimethylacetamide)

Reductant	Reduction: PhNO$_2$ (%)	Substitution: product (%)		Coupling: ArAr (%)	Oxidation: identified product (%)	
PhNH$_2$	13	ArNHPh	3	—	PhN:NPh	3
PhNMe$_2$	75	—		3	—	
Ph$_2$NH	0	ArNPh$_2$	44	—	—	
PhCH$_2$·NH$_2$	50	ArNH·CH$_2$Ph	15	5	PhCHO	2
Ph$_2$CH·NH$_2$ [a]	70	ArNH·CHPh$_2$	Trace	4	Ph$_2$C:N·CHPh$_2$	50
n-C$_8$H$_{17}$·NH$_2$	35	ArNH·C$_8$H$_{17}$-n	34	7	—	
CH$_2$Bu^t·CMe$_2$·NH$_2$	51	—		5	—	
PhNH·NHPh [b]	16	—		—	PhN:NPh	46
PhNH·NH$_2$	10	—		11	—	
2,4,1-C$_6$H$_3$(NO$_2$)$_2$·NH·NH$_2$ [c,d]	70	—		—	m-C$_6$H$_4$(NO$_2$)$_2$	43
1-C$_{10}$H$_7$·NH·NH$_2$ [e]	10	—		—	C$_{10}$H$_8$	25

[a] Reaction time, 6 hr.; 1-C$_{10}$H$_7$I gave C$_{10}$H$_8$ (19%) in 72 hr. [b] p-Br·C$_6$H$_4$·NO$_2$ gave PhNO$_2$ (21%) and PhN:NPh (40%) in 20 hr.; 1-C$_{10}$H$_7$Br gave C$_{10}$H$_8$ (8%) in 66 hr. [c] *Cf.* reduction by m-C$_6$H$_4$(NO$_2$)$_2$ (Table 5). [d] p-Br·C$_6$H$_4$·NO$_2$ gave PhNO$_2$ (6%) and m-C$_6$H$_4$(NO$_2$)$_2$ (43%) in 24 hr. [e] Solvent, collidine; the hydrazine hydrochloride, neutralised with NaOH, was used, and o-Cl·C$_6$H$_4$·NO$_2$ (17%) was one of the products.

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[13] (*a*) P. L. Julian, W. Cole, A. Magnani, and E. W. Meyer, *J. Amer. Chem. Soc.*, 1945, **67**, 1728; (*b*) G. Rosenkranz, O. Mancera, J. Gatica, and C. Djerassi, *ibid.*, 1952, **72**, 4077.

[14] D. A. Denton, F. J. McQuillan, and P. L. Simpson, *J. Chem. Soc.*, 1964, 5535.

[15] R. G. R. Bacon, 'Organic Sulphur Compounds,' vol. 1, ed. N. Kharasch, Pergamon, 1961, p. 306; for conversion of a nitro-disulphide into the nitro-sulphide see, *e.g.*, E. R. Cole, *Chem. and Ind.*, 1957, 1511.

Deuteriated camphor was obtained by treatment of 3-bromocamphor with 2,6-dimethylphenol which had been labelled with deuterium in its hydroxy-group or nucleus, but the interpretation of these experiments was complicated by the high mobility of deuterium in the reaction system.

(b) *Reduction by Amines and Hydrazino-compounds.*—Results of reactions of *o*-bromonitrobenzene with these types of nitrogenous compounds (in Table 4, which includes two aliphatic examples) showed a broadly similar pattern to that obtained with phenols (Table 1). Reduction to nitrobenzene predominated (except with diphenylamine), in competition with nucleophilic substitution and Ullmann-type coupling; and the donors in some cases yielded identified oxidation products, which could be considered to arise from oxidative coupling or from dehydrogenation.

As in the case of phenolic hydrogen donors, these products are also obtainable from reactions, generally considered to be homolytic in mechanism, occurring between the amino- or hydrazino-compounds and conventional metal-containing oxidants.[16-20] The location of transferred hydrogen in the donor may vary; *e.g.*, it may be nuclear- or methyl-H in dimethylaniline,[21] N–H or α-C–H in an aliphatic amine.[22] Some preliminary experiments involving reduction of *o*-bromonitrobenzene by *N*-deuteriated benzylamine were inconclusive.

(c) *Reduction by Nitro-compounds, Esters, Quinones, etc.*—Although compounds of these types (Table 5) contain no hydrogen atoms of obvious lability, the reduction of *o*-bromonitrobenzene to nitrobenzene readily occurred, and varied in extent over a range fairly similar to that resulting from the use of phenols or amines. Apart from the methyl groups present in some of the examples, it is the aromatic nucleus which must be considered as a source of hydrogen for the reduction. Possibly the oxygen-containing groups present in all the examples (nitro, carboxylate, *N*-oxide, or quinonoid) serve both to activate nuclear hydrogen and to associate with copper in a transition state of the reaction.

TABLE 5

Reduction of *o*-Br.$C_6H_4{\cdot}NO_2$ by aromatic nitro-compounds, esters, etc. + Cu_2O (conditions as in Table 1; solvent, dimethylacetamide)

Reductant	Reduction: $PhNO_2$ (%)	Coupling (*o*-$NO_2{\cdot}C_6H_4)_2$ (%)
1-$C_{10}H_7{\cdot}NO_2$	5	7
m-$C_6H_4(NO_2)_2$	32	—
1,2,4-$C_6H_3Me(NO_2)_2$	50	4
1,3,5-$C_6H_3(NO_2)_3$	47	—
m-$NO_2{\cdot}C_6H_4{\cdot}CO_2Me$	66	—
m-$C_6H_4(CO_2Me)_2$	10	—
Pyridine *N*-oxide	30	4
p-Benzoquinone	75	—
3,3′,5,5′-Tetramethyl-4,4′-diphenoquinone (IV) [a]	44	—

[a] (II) (27%) was also formed.

Observations of a similar nature, previously reported, include the reduction of 1-bromonaphthalene to naphthalene by Cu_2O–benzoic anhydride–pyridine[8] or by CuCl–pyridine *N*-oxide,[9] and certain cases of reduction occurring as a side-reaction, in the absence of solvents, during the Ullmann coupling of some nuclear substituted aryl halides, one portion of which therefore appears to furnish hydrogen for another portion. Forrest[23] observed various side-reactions in Ullmann coupling processes, one of which was displacement of hydrogen by an aryl group at the 2-position of 1,3-dinitrobenzene when this compound was introduced into reaction systems.

It is tempting to find significance in the fact that nitro-compounds and quinones, like phenols and amines, are well known inhibitors of radical-initiated polymerisations, but these effects have been attributed to interactions of radicals with nitro- or quinonoid groups rather than to hydrogen abstraction.[24] Likewise, effects of nitro-compounds in the homolytic decomposition of benzoyl peroxide have been considered to involve participation of NO_2 groups.[25]

A feature of the reaction in which the diphenoquinone (IV) was employed as a reductant was the appearance of its own reduction product, the dihydroxybiphenyl (II) (Table 5). We suggest that (unless reduction by the solvent is involved) this may be due to hydrogen transfer in a disproportionation of the general type:

$$\begin{matrix}\text{Quinone} \\ \text{(or dipheno-} \\ \text{quinone)}\end{matrix} \longrightarrow \begin{matrix}\text{hydroquinone} \\ \text{(or dihydroxy-} \\ \text{biphenyl)}\end{matrix} + \begin{matrix}\text{resinous dehydrogen-} \\ \text{ation products of} \\ \text{the quinone} \\ \text{(or diphenoquinone)}\end{matrix}$$

It has long been on record that *p*-benzoquinone is converted into hydroquinone and resins on heating, either alone, or in the presence of water or organic solvents.[26] We carried out some control experiments with *p*-benzoquinone or 3,3′,5,5′-tetramethyldiphenoquinone (IV) in refluxing solvents (collidine, dimethylacetamide, xylene) and observed their conversion into hydroquinone or the dihydroxybiphenyl (II) respectively, together with extensive formation of resins. There was no indication of catalysis by copper(I) oxide. We have reported elsewhere[27] that (IV) is efficiently reduced to (II) by a phenolic hydrogen donor.

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(d) *Possible Contribution of Solvents.*—Under standard conditions (Tables 1, 4, 5) the extent of reduction of *o*-bromonitrobenzene, which was the most reactive halide employed, varied from 0 to 80%, depending upon the reductant tested. This suggests that the solvents, 2,4,6-collidine and dimethylacetamide, were not significantly contributing to the reduction, and indeed, control experiments without reductants produced only 0—2% nitrobenzene. If however the period of reaction was prolonged in these control experiments, the production of nitrobenzene tended to rise fairly steeply but erratically; in boiling dimethylacetamide, 15—40% yields resulted after 4—8 hr., and likewise high yields of camphor were obtained from bromocamphor (cf. ref. 5).

Reductive effects are not unexpected for these solvents. Substantial reduction, observed in certain Ullmann coupling processes,[28] was attributed to solvent dimethylformamide (a commoner medium for the reaction than dimethylacetamide). Reduction of the type $-CO{\cdot}CHI \longrightarrow -CO{\cdot}CH_2-$ was reported to occur, without a catalyst, in 2,4,6-collidine, and a mechanism involving the methyl groups was suggested.[13b]

Our observed reduction of *o*-bromonitrobenzene may however have two explanations. (*i*) Since some nitro-compounds are reductants (Table 5), self-reduction, by disproportionation, cannot be excluded. (*ii*) Reduction may be due to the solvent, or to impurities in it, or to an intermediate produced from it. The suggestion of an intermediate is included here because *p*-nitrodimethylaniline, a potential reductant (cf. Table 4) was an observed product from *p*-bromonitrobenzene (less responsive to reduction than the *ortho*-isomer) as a result of long heating in dimethylacetamide with cuprous oxide. Substantial conversion of *p*-chloronitrobenzene into the dimethylamino-compound was recently reported to occur, without the aid of catalyst, in boiling dimethylformamide.[29]

Further study of these problems is needed, but the practical point to be noted is that control experiments are necessary to check whether an observed reductive effect is indeed due essentially to a solute under test rather than to the solvent employed.

EXPERIMENTAL

Procedures used for reactions, and for isolation of products, were as previously described;[2] conditions and results are summarised in the Tables. Solutions usually darkened, becoming almost black by the end of the reaction period. Copper(I) oxide, or copper, dissolved to a varying extent, corresponding to the reactivity of the halides and reductants; dissolution was in some cases complete. Crude isolated products varied from yellow to red-brown in colour and were separated chromatographically on alumina columns (Spence type H), as indicated below.

Products Obtained with Phenols.—(*a*) After reaction of *o*-bromonitrobenzene with various phenols (Table 1), nitrobenzene was eluted with 9 : 1 light petroleum (b.p. 60—80°)–ether. Since it was difficult to separate nitrobenzene from unchanged *o*-bromonitrobenzene, chromatographic fractions containing the two compounds were combined and analysed by gas chromatography on trixylyl phosphate–Celite columns. 2,2′-Dinitrobiphenyl was eluted with ether.

The products from reaction with 2,4-dimethylphenol included mixtures, eluted by ether, which, when repeatedly recrystallised yielded small amounts of almost colourless needles, m.p. 161—163°. This material showed a hydroxy-group peak in its infrared spectrum and was possibly the mono-*o*-nitrophenyl ether (cf. ref. 2) of 2,2′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl (Ib) (Found: C, 72·5; H, 5·9. $C_{22}H_{21}NO_4$ requires C, 72·7; H, 5·8%). In the case of products from reaction with 2,6-dimethylphenol, nitrobenzene was followed, in the same eluting solvent mixture, by 2,6-*dimethyl*-1-2′-*nitrophenoxybenzene*, obtained as pale yellow needles (from ethanol), m.p. 73—74° (Found: C, 69·4; H, 5·5; N, 5·9. $C_{14}H_{13}NO_3$ requires C, 69·1; H, 5·4; N, 5·8%). Subsequent elution with chloroform, or with ether–methylene chloride, gave 4,4′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl (II), which, after vacuum-sublimation and recrystallisation from xylene, was obtained as pale yellow needles, m.p. and mixed m.p. 223°, identical with an authentic sample.[1]

Products from reaction with 2,4,6-trimethylphenol included 4,4′-dihydroxy-3,3′,5,5′-tetramethylbibenzyl (IIIb), which was eluted with chloroform and purified as pale yellow needles, m.p. 168—170° (from benzene) (lit.,[30] 168°). It was identical with an authentic sample, prepared [30] *via* the stilbenequinone, and was further characterised as the diacetate, which formed dimorphic crystals, m.p. 136—139° and 146—148° (lit.,[30] 148°) (Found: C, 74·2; H, 7·6. Calc. for $C_{22}H_{26}O_4$: C, 74·55; H, 7·4%). Products from reaction with 2,6-di-t-butyl-4-methylphenol included mixtures of 3,3′,5,5′-tetra-t-butyl-4,4′-dihydroxybibenzyl (IIIb) and 3,3′,5,5′-tetra-t-butylstilbenequinone (V), which followed nitrobenzene in 9 : 1 light petroleum–ether chromatographic fractions. The more soluble dihydroxy-compound was separated from the quinone by extraction with ethanol and was obtained as pale yellow needles, m.p. 171—172° (from ethanol) (lit.,[31] 169—170°) (Found: C, 82·4; H, 10·9. Calc. for $C_{30}H_{46}O_2$: C, 82·1; H, 10·6%). These products were identical with authentic samples [31] of the quinone and the dihydroxy-compound. Only the latter was obtained by oxidising 2,6-di-t-butyl-4-methylphenol with silver(I) oxide.[32] Extension of the time of the copper-promoted halide reduction from 2 to 16 hr. resulted in exclusive production of the dihydroxy-compound (IIIb), possibly because of disproportionation of the quinone (V).

Products of the reaction with 2,6-dichlorophenol contained an exceptional amount of resin; 2,6-*dichloro*-1-2′-*nitrophenoxybenzene* followed nitrobenzene on elution with 9 : 1 light petroleum–ether and was purified as yellow needles, m.p. 112—114° (from ethanol) (Found: C, 50·5; H, 2·6; N, 5·1. $C_{12}H_7Cl_2NO_3$ requires C, 50·7; H, 2·5; N, 4·9%). Products of the reaction with resorcinol gave 1,3-*di*-2′-*nitrophenoxybenzene*, eluted with 9 : 1 ether–methylene chloride and obtained as yellow needles, m.p. 90° (from ethanol) (Found: C, 61·3; H, 3·5; N, 7·8.

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$C_{18}H_{12}N_2O_6$ requires C, 61·4; H, 3·4; N, 8·0%). Reaction with hydroquinone gave a little of the isomeric 1,4-*di*-2′-*nitrophenoxybenzene*, as yellow needles, m.p. 156° (from ethanol) (Found: C, 61·3; H, 3·5; N, 8·3%); this followed 2,2′-dinitrobiphenyl in fractions eluted with ether.

(*b*) In the series of reactions with varying copper species (Table 2), copper bronze dissolved and analysis[33] of the resulting solution showed that copper(I) was present. Copper(I) bromide and cyanide were soluble in the reaction medium, and the latter afforded *o*-nitrobenzonitrile, m.p. and mixed m.p. 108—109°, eluted with ether. Use of silver oxide in place of a copper compound did not cause reduction of the halide (95% recovery), but a silver mirror formed and the phenol was oxidised to 4,4′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl (II) (30—50% in 16 hr.).

(*c*) In the series of reactions with 2,6-dimethylphenol and varying halides (Table 3) it was sometimes difficult to separate reduced products from unchanged halides by chromatography on alumina, and such fractions were analysed by gas chromatography. Only in one case (see footnote to Table) was reduction observed in the absence of copper(I) oxide. Mixtures of naphthalene with 1-bromonaphthalene were eluted by light petroleum, and were followed by 1-2′,6′-*dimethylphenoxynaphthalene*, which was eluted by 4 : 1 light petroleum–ether and obtained as cream-coloured crystals (from ethanol) (Found: C, 87·4; H, 6·6. $C_{18}H_{16}O$ requires C, 87·1; H, 6·5%). Elution with light petroleum–ether produced mixtures of phenanthrene with unchanged 9-bromophenanthrene, of nitrobenzene with unchanged *p*-bromonitrobenzene, and of acetophenone with unchanged *p*-bromoacetophenone, in the respective preparations. A further product in the second case was 4,4′-dinitrobiphenyl, m.p. 246°, which was eluted with benzene and shown to be identical with an authentic sample prepared by the Ullmann method. In the third case acetophenone was followed by 2,6-*dimethyl*-1-4′-*acetylphenoxybenzene*, which was eluted with ether and obtained as yellow crystals, m.p. 215° (from ethanol) (Found: C, 80·0; H, 7·0. $C_{16}H_{16}O_2$ requires C, 80·0; H, 6·7%). Benzaldehyde, produced from *o*-bromobenzaldehyde, was estimated by oxidation to benzoic acid. *p*-Nitrotoluene, from *p*-nitrobenzyl bromide, was eluted with petroleum and gave colourless needles, m.p. and mixed m.p. 51°. Benzhydryl bromide gave 1,1,2,2-tetraphenylethane, m.p. 209—210°, eluted by benzene.

3-Bromocholestane gave cholest-2-ene, m.p. 67—70°, eluted by 3 : 2 light petroleum-ether, and converted into cholestane, m.p. 80°, by hydrogenation with platinum catalyst. Phenacyl chloride gave acetophenone, which was estimated by gas chromatography of fractions from an alumina column. 3-Bromocamphor gave camphor, eluted by 7 : 3 light petroleum–ether and characterised as its 2,4-dinitrophenylhydrazone, m.p. 177°. 2-Bromocholestan-3-one,[34] m.p. 167°, gave cholestan-3-one, which was eluted by 1 : 4 light petroleum–ether and obtained as colourless needles, m.p. 129° (from ethanol) (lit.,[35] 129—129·5°) (Found: C, 83·6; H, 11·9. Calc. for $C_{27}H_{46}O$: C, 83·9; H, 12·0%).

Products from *o*-nitrophenyl thiocyanate[36] were chromatographed on alumina which had been deactivated with acetic acid to avoid the possibility of decomposition of thiocyanate on an alkaline column. Elution with light petroleum–ether mixtures of increasing ether content, followed by recrystallisation, successively yielded unchanged thiocyanate, analytically pure samples of di-*o*-nitrophenyl disulphide, m.p. and mixed m.p. 198—200°, and of di-*o*-nitrophenyl sulphide, m.p. 122°, and then unidentified liquid fractions.

Products Obtained with Amines and Hydrazine Derivatives.—Nitrobenzene, unchanged halide, and 2,2′-dinitrobiphenyl, which resulted from reactions with *o*-bromonitrobenzene (Table 4) were separated as described above. Other products were separated as follows. Aniline gave azobenzene, m.p. and mixed m.p. 68°, eluted with light petroleum, followed by *o*-nitrodiphenylamine, which was eluted by 2 : 3 light petroleum–ether and obtained as red leaflets, m.p. 74° (from ethanol) (lit.,[37] 75°). Reactions with dimethylaniline and diphenylamine resulted in purple and dark green solutions respectively. The only product in the latter case was *o*-nitrotriphenylamine, eluted by ether and obtained as orange crystals, m.p. 100—101° (from light petroleum) (lit.,[23] 102—103°).

The reactions with benzylamine gave benzaldehyde, estimated by conversion into benzoic acid, and benzyl-*o*-nitrophenylamine, eluted with 1 : 1 light petroleum–ether and obtained as orange crystals, m.p. 74° (from ethanol) (lit.,[38] 74·5°). The reaction product from benzhydrylamine was poured into N-hydrochloric acid, rapidly extracted with ether, and the extract chromatographed on alumina. Elution with 9 : 1 light petroleum–ether furnished mixtures of nitrobenzene and *N*-diphenylmethylene benzhydrylimine, from which, by trituration with ethanol and recrystallisation from the same solvent, the imine was separated as colourless crystals, m.p. 152—153°, identical with a sample obtained by permanganate oxidation of benzhydrylamine.[39] It was rapidly hydrolysed to benzophenone at 20° by 6N-hydrochloric acid. Accordingly, the crude reaction product from benzhydrylamine and the halide yielded benzophenone and nitrobenzene if poured into 6N-hydrochloric acid during the isolation procedure. Continuation of chromatography on alumina gave *benzhydryl*-o-*nitrophenylamine*, eluted with 3 : 7 light petroleum–ether and obtained as orange crystals, m.p. 102·5—104° (from ethanol) (Found: C, 75·2; H, 5·1; N, 9·1. $C_{19}H_{16}N_2O_2$ requires C, 75·0; H, 5·3; N, 9·2%). A product from n-octylamine was *n-octyl*-o-*nitrophenylamine*, eluted with 9 : 1 light petroleum–ether and purified by distillation at 180°/30 mm. (Found: C, 67·2; H, 9·0; N, 11·3. $C_{14}H_{22}N_2O_2$ requires C, 67·2; H, 8·9; N, 11·2%). This was followed by *N*-n-octylacetamide, b.p. 168—170°/14 mm., resulting from interaction of n-octylamine with the solvent, and identical with an authentic sample[40] (Found: C, 70·4; H, 12·4; N, 8·4. Calc. for $C_{10}H_{21}NO$: C, 70·1; H, 12·4; N, 8·2%). "t-Octylamine" afforded unidentified nitrogen-containing liquid fractions. Hydrazobenzene gave azobenzene, m.p. and mixed m.p. 68°, eluted by light petroleum. 2,4-Dinitrophenylhydrazine gave *m*-dinitrobenzene, m.p. and mixed m.p. 89°, eluted by ether. 1-Naphthylhydrazine gave

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naphthalene, m.p. and mixed m.p. 80°, eluted by light petroleum.

In the absence of copper(I) oxide, uncatalysed nucleophilic substitution of *o*-bromonitrobenzene by amines proceeded, and a slight amount of reduction of *o*- or *p*-bromonitrobenzene (~4%) was observed with hydrazobenzene or benzhydrylamine as reductants.

Products Obtained with Nitro-compounds, Quinones, etc.; Decomposition of Quinones.—From reactions with *o*-bromonitrobenzene (Table 5), the amounts of nitrobenzene, unchanged halide, and 2,2′-dinitrobiphenyl were ascertained as described above, but no crystalline products derived from the reductants were isolated, except in the case of products from the tetramethyldiphenoquinone (IV) which yielded the dihydroxybiphenyl (II) under the usual chromatographic conditions.

Solutions (0·4M) of quinones in organic solvents were heated under nitrogen. The products were isolated by evaporation of solvent, or by addition of solutions to dilute acid, and were purified by chromatography on alumina. Copper(I) oxide, if added, appeared to have no significant effect on the reactions. *p*-Benzoquinone gave much black resin, and hydroquinone (~18%), after 2 hr. in boiling collidine or dimethylacetamide. *p*-Chloranil gave resins exclusively under these conditions. 3,3′,5,5′-Tetramethyldiphenoquinone (IV) was recovered unchanged from boiling benzene, but in boiling *o*-xylene it yielded much resin and small amounts of 4,4′-dihydroxy-3,3′,5,5′-tetramethylbiphenyl (II). Heating the diphenoquinone for 2—16 hr. in boiling collidine or dimethylacetamide gave the dihydroxy-compound (II) in yields of 40—50%, together with resins.

Use of Deuteriated Compounds.—(*a*) *O*-Deuteriated 2,6-dimethylphenol (50% $C_6H_3Me_2{\cdot}OD$ by n.m.r. spectral analysis) was prepared, as described[41] for other phenols by exchange between EtOD (prepared[42] from aluminium ethoxide) and $C_6H_3Me_2{\cdot}OH$. (*i*) The labelled phenol, 3-bromocamphor, and cuprous oxide (1·66 mmoles of each) were heated for 16 hr. under nitrogen in refluxing pyridine (6 ml.). The isolated camphor (70%) was shown by mass-spectral analysis to contain 26% [$^2H_1$]camphor. (*ii*) When camphor was used under the same conditions, in place of bromocamphor, it was recovered with 13% [$^2H_1$]content. (*iii*) When, under similar conditions, neither camphor nor bromocamphor was present, the recovered phenol was 14%[$^2H_1$]$C_6H_3Me_2{\cdot}OH$ (7% *O*-^{2}H, 7% *para*-^{2}H).

(*b*) The experiments described in (*a*) were repeated with a sample of 2,6-dimethylphenol which, after nuclear deuteriation,[43] had 79% [$^2H_1$]content (55% *para*-^{2}H, 24% *meta*-^{2}H, by n.m.r. spectral analysis). (*i*) Bromocamphor yielded camphor samples with [$^2H_1$]content of 11—21%, by mass-spectral analysis, after reaction periods of 16—24 hr. (*ii*) Camphor was isolated with 6% [$^2H_1$]content. (*iii*) Phenol was recovered with 72% [$^2H_1$]content (35% *para*-^{2}H, 20% *meta*-^{2}H, 17% *O*-^{2}H).

(*c*) *N*-Deuteriated benzylamine was prepared as reported[44] for a related amine, and showed 90% [$^2H_1$]content by n.m.r. spectral analysis. The labelled amine (3·3 mmoles), *o*-bromonitrobenzene (3·3 mmoles), and copper(I) oxide (1·66 mmoles) reacted for 2 hr. in refluxing dimethylacetamide. Chromatography of the product on alumina gave nitrobenzene (33%), benzyl-*o*-nitrophenylamine (18%), and 2,2′-dinitrobiphenyl (5%). The nitrobenzene, from duplicate runs, showed 13% and 18% content of [$^2H_1$]$C_6H_5{\cdot}NO_2$ by mass-spectral analysis, and the n.m.r. spectrum showed most of the deuterium to be in the *ortho*-position. Repetition of the reaction in collidine gave nitrobenzene with 7% [$^2H_1$]content. When nitrobenzene was used in place of *o*-bromonitrobenzene, in either solvent, mass-spectral analysis showed a [$^2H_1$]content of not more than 1%.

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