212. *Metal Ions and Complexes in Organic Reactions. Part III.*[1] *Reduction of 1-Bromonaphthalene in Some Reaction Systems Containing Copper*(I).

By R. G. R. Bacon and H. A. O. Hill.

1-Bromonaphthalene in boiling pyridine solution was reduced to naphthalene by cuprous acetate, or by acetic acid, acetic anhydride, or monofluoroacetic acid in the presence of cuprous oxide. The production of deuteronaphthalene when hexadeuteroacetic anhydride was used shows that the α-carbon atom was the hydrogen donor. Monochloroacetic acid with cuprous oxide gave mainly 1-chloronaphthalene, which was also produced by the anhydrides of monochloro-, dichlorofluoro-, and trichloro-acetic acid. Formic acid, iodoacetic acid, cyanoacetic acid, and trifluoroacetic anhydride were ineffective. Reduction or halogen exchange was accompanied by different amounts of decarboxylation and tar formation; a reaction mechanism is suggested. Under similar conditions, naphthalene was produced by benzoic anhydride, while *o*-chlorobenzoic anhydride gave 1-chloronaphthalene. Other systems found to reduce 1-bromonaphthalene were cuprous chloride–pyridine *N*-oxide, Cu_2O–MeO^-–dimethylformamide, and Cu_2O–BH_4^-–pyridine or –dimethylformamide; cuprous hydride in pyridine was ineffective.

THIS Paper is concerned with reductions of the type ArHal ⟶ ArH, effected by solutions of cuprous salts of carboxylic acids and by some other copper-containing reaction systems. There are various published procedures for such reductions, generally involving metal catalysts or metal-containing reagents; in some cases nuclear coupling, 2ArHal ⟶ ArAr, occurs instead of, or together with, the reduction. Reducing agents without metal constituents, such as hydriodic acid, are sometimes effective, at least for activated halides.[2] Recommended metal-containing reagents include: palladium on calcium carbonate with hydrogen,[3] or with alkali and an alcohol;[4] nickel with hydrogen,[5] or Raney nickel alloy

[1] Part II, preceding paper.
[2] Blatt *et al.*, *J. Org. Chem.*, 1957, **22**, 1046, 1588; Mosby, *ibid.*, 1959, **24**, 421.
[3] Busch and Stöve, *Ber.*, 1916, **49**, 1063.
[4] Busch *et al.*, *J. prakt. Chem.*, 1936, **146**, 1; Mayo and Hurwitz, *J. Amer. Chem. Soc.*, 1949, **71**, 776.
[5] Grigorovskii and Federov, *Zhur. priklad. Khim.*, 1948, **21**, 529.

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with aqueous alkali;[6] magnesium with propan-2-ol;[7] triphenyltin hydride.[8] Complex metal hydrides are rarely effective.[9]

Copper promotes the reduction of aryl halides in the presence of certain hydrogen donors, such as ethanol[10] or tetralin.[11] Also, reduction sometimes occurs as a side-reaction, or even supersedes coupling, in preparations of biaryl compounds with copper by the Ullmann method,[12] and in such cases it is a portion of the halogenated aromatic compound which must furnish the hydrogen. Benzoic, caproic, and other carboxylic acids are known to reduce nitro-aryl halides at 150—200° in the presence of copper.[13] The reduction procedure to which we have given most attention involves copper(I), and was first described by Edwards and his co-workers,[14,15] who reported yields of ~60% from a mixture of the halide, acetic anhydride, and cuprous oxide in boiling pyridine. This method has been occasionally used in synthesis,[16] but has apparently not otherwise been further studied. Edwards represented the reduction[14] by an equation (a later version[15] is unbalanced) in which the carboxyl group of acetic acid was shown as the hydrogen donor; the origin of the acid was not explained:

$$2Cu^+ + RBr + MeCO_2H \longrightarrow 2Cu^{2+} + RH + Br^- + MeCO_2^-$$

We have carried out a series of reactions, with boiling pyridine as the solvent, 1-bromonaphthalene as the substrate, and cuprous oxide with various carboxylic acids (Table 1) or anhydrides (Table 2) as the reducing system. In experiments with aliphatic acids or anhydrides the cuprous oxide generally dissolved, carbon dioxide was evolved, in some cases well below the boiling point of the solvent, and a varying amount of tar formed.

TABLE 1.

Reaction of $1\text{-}C_{10}H_7Br$ (0·5M) with $R\cdot CO_2H$ (4 mol.) and Cu_2O (2 mol.) in pyridine at 115°.

R	Time (hr.)	Unchanged $1\text{-}C_{10}H_7Br$ (%)	Product (%) (Ar = $1\text{-}C_{10}H_7$)	R	Time (hr.)	Unchanged $1\text{-}C_{10}H_7Br$ (%)	Product (%) (Ar = $1\text{-}C_{10}H_7$)
H	6	100	—	CH_2I	3	94	ArI 1
CH_3	3	46	ArH 54	$CH_2\cdot CN$	6	95	—
CH_2F	6	27	ArH 66	CCl_3	3	97	ArCl 3
CH_2Cl	3	66	ArH 3, ArCl 23				

TABLE 2.

Reaction of $1\text{-}C_{10}H_7Br$ (0·4M) with $(R\cdot CO)_2O$ (1 mol.) and Cu_2O (1 mol.) in pyridine (115°; 5 hr.).

R	Unchanged $1\text{-}C_{10}H_7Br$ (%)	Product (%) (Ar = $1\text{-}C_{10}H_7$)	R	Unchanged $1\text{-}C_{10}H_7Br$ (%)	Product (%) (Ar = $1\text{-}C_{10}H_7$)
CH_3	36	ArH 64	$CFCl_2$	71	ArCl 29
CD_3	40	ArD 43, ArH 17	CCl_3 †	67	ArCl 27
CD_3 *	14	ArD 56, ArH 30	Ph	78	ArH 22
CF_3	100	—	$o\text{-}C_6H_4Cl$	76	ArCl 24
CH_2Cl	60	ArCl 40			

* $1\text{-}C_{10}H_7Br$ (0·8M); $(R\cdot CO)_2O$ (1 mol.); Cu_2O (1 mol.). † $1\text{-}C_{10}H_7Br$ (0·4M); $(R\cdot CO)_2O$ (4 mol.); Cu_2O (4 mol.); reaction period, 3 hr.

[6] Schwenk, Papa, and Ginsberg, *Ind. Eng. Chem., Analyt.*, 1943, **15**, 376.
[7] Bryce-Smith, Wakefield, and Blues, *Proc. Chem. Soc.*, 1963, 219.
[8] Rothman and Becker, *J. Org. Chem.*, 1960, **25**, 2203.
[9] Gaylord, " Reductions with Complex Metal Hydrides," Interscience, New York, 1956.
[10] Meyer, G.P. 234,726 (1911).
[11] Hardacre and Perkin, *J.*, 1929, 180; Lesslie and Turner, *J.*, 1932, 281.
[12] Whaley, *J. Org. Chem.*, 1953, **18**, 833; Nursten, *J.*, 1955, 3081; Forrest, *J.*, 1960, 581; Bacon and Bankhead, *J.*, 1963, 839.
[13] Smith, *J. Amer. Chem. Soc.*, 1949, **71**, 2855; Smith and Campanaro, *ibid.*, 1953, **75**, 3602.
[14] Edwards and Stewart, *Chem. and Ind.*, 1953, 472.
[15] Edwards and McIndoe, *Chem. and Ind.*, 1953, 1091.
[16] Topsom and Vaughan, *J.*, 1957, 2842.

Naphthalene was obtained in yields of up to ~85% with acetic acid, acetic anhydride, or monofluoroacetic acid; monochloroacetic acid caused a little reduction but gave mainly 1-chloronaphthalene; monochloro-, dichlorofluoro-, and trichloro-acetic anhydride gave only 1-chloronaphthalene. We considered that cuprous salts of carboxylic acids were intermediates, and found that a pyridine solution of previously prepared cuprous acetate had the same effect as a mixture of cuprous oxide with acetic acid or acetic anhydride in pyridine.

The role of the solvent needs elucidation; Edwards[15] found quinoline to be inferior to pyridine, and we observed neither reduction of the halide nor dissolution of cuprous oxide when dimethylformamide was used as solvent in conjunction with acetic anhydride. It is known that heterocyclic bases catalyse the fission of acid anhydrides, *e.g.*, by water,[17] and they may have a similar function in the formation of cuprous salts:

$$\text{Cu:O:Cu} + \text{Ac:OAc} + :B \longrightarrow \text{CuO}^- + \text{CuOAc} + \text{B}^+:\text{Ac} \longrightarrow 2\text{CuOAc} + \text{B}:$$
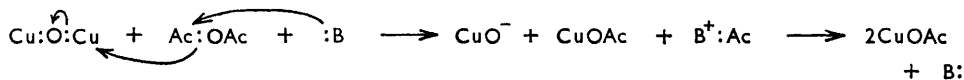
The relative proportions of reagents used were equivalent to a halide : CuOAc ratio of 1 : 4 in the case of the carboxylic acids and 1 : 2 in the case of the anhydrides. The proportions used by Edwards were equivalent to a 1 : 4 ratio, but he used twice as much anhydride as is theoretically needed to form cuprous acetate. The valency state of copper during the reaction has not been quantitatively examined. An initial green colour, indicative of copper(II), was generally observed until tar formation obscured it, but much copper(I) oxide could be precipitated from solution at the end of a reaction.

For the reactions involving cuprous salts of aliphatic carboxylic acids, it was considered that hydrogen attached to the α-carbon atom was the most likely cause of reduction, and, indeed, this centre was the only possible source of hydrogen, apart from pyridine, when carboxylic acid anhydrides were employed as reagents; when hexadeuteroacetic anhydride was used in place of acetic anhydride (Table 1), mass-spectral analysis showed that 1-deuteronaphthalene and naphthalene were produced in a ratio of about 7 : 3. The α-carbon atom must therefore be at least the main source of hydrogen for the reduction. It was shown that 1-deuteronaphthalene did not exchange deuterium for hydrogen under the conditions of the experiment. The formation of some undeuterated naphthalene could be due to some contaminant with reactive hydrogen, which perhaps exchanges with $(CD_3 \cdot CO)_2O$, or could be due to a reaction in which pyridine is the hydrogen donor. It has been reported[18] that deuterium (added in the form of $CH_3 \cdot CO_2D$) exchanges with the α-hydrogen in $(CH_3 \cdot CO)_2O$, the reaction attaining equilibrium in 24 hour at 150°.

The reactions in which acids or anhydrides with the α-groups CH_2Cl, $CFCl_2$, or CCl_3 gave 1-chloronaphthalene provide some supporting evidence for participation of atoms at the α-carbon centre. Interpretation of these experiments is complicated by the possibility that loss of chlorine in decompositions of these compounds would lead to cuprous chloride, which we have shown to convert 1-bromo- into 1-chloro-naphthalene in pyridine solution.[19] Comparison of available rate data suggests, however, that conversion of cuprous oxide into cuprous chloride would need to be rapid and complete in order to account for the observed yields of 1-chloronaphthalene. We consider that this is unlikely, and tentatively conclude that transfer of chlorine directly from the α-carbon to the aromatic nucleus is at least partly responsible for the result.

Reduction of the halide appears to be intimately connected with the observed decarboxylation, but the latter process also occurs in the absence of the halide. There are many recommended procedures for catalysing the decarboxylation of acids, *e.g.*, with copper, copper

[17] Banfa and Gold, *J.*, 1953, 1406; Gold and Jefferson, *J.*, 1953, 1409.
[18] Miklukin and Rekasheva, *Doklady Akad. Nauk S.S.S.R.*, 1955, **101**, 881.
[19] Bacon and Hill, *J.*, 1964, 1097.

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sulphate, or copper chromite,[20] or with cuprous halides,[21] or with some pre-formed cupric salt of the acid under examination;[22] refluxing quinoline is the usual medium, and a tertiary base may itself catalyse the decomposition. Ready decarboxylation was observed when a mixture of cuprous oxide, acetic anhydride, and pyridine was heated. Reduction was unsuccessful with formic, cyanoacetic, and trichloroacetic acid (Table 1), but their decarboxylation occurred vigorously, even at room temperature, and they had probably all decomposed when the boiling point of the solvent was reached. With cyanoacetic acid, cuprous oxide partly dissolved to give a red solution (cf. Part II [1]), and formic acid reduced the oxide to copper. Decarboxylation was not vigorous with iodoacetic acid, but a solid complex appeared, and there was little reaction apart from tar formation. Among the anhydrides examined (Table 2), the trifluoro-compound underwent ready decarboxylation, but, as expected from its lack of hydrogen or chlorine, it did not affect the bromonaphthalene. Decarboxylation was faster with the acids than with the anhydrides and resulted in less tar formation. The ease of decarboxylation was approximately in the order $CCl_3 \cdot CO_2H > HCO_2H > CN \cdot CH_2 \cdot CO_2H > CH_2I \cdot CO_2H > CH_2Cl \cdot CO_2H > CH_2F \cdot CO_2H > CH_3 \cdot CO_2H$, and $(CFCl_2 \cdot CO)_2O > (CCl_3 \cdot CO)_2O > (CF_3 \cdot CO)_2O > (CH_2Cl \cdot CO)_2O > (CH_3 \cdot CO)_2O$. Products from trichloroacetic anhydride included chloroform, detected by gas chromatography, and those from trifluoroacetic anhydride included fluoroform. Reasons for the relative reactivity of trihalogeno-acetic acids have been discussed by Hine.[23]

A common feature of mechanisms proposed for decarboxylation reactions [24] is the accession of a pair of electrons to the α-carbon atom, a process which is aided by electron-attracting substituents, and which may be followed by the resulting or incipient carbanion acquiring a proton (1) or becoming a carbene [25] by loss of an anion (2). It is known, for silver at least, that the latter process can be aided by a metal cation.[26] For the replacements effected by cuprous salts of aliphatic acids, we assume, as for other cuprous-salt reactions,[19] the formation of a halide-copper complex, and we tentatively suggest that its breakdown may occur by a cyclic mechanism (3), involving transfer of a hydride (or perhaps chloride) ion from the α-carbon atom to the aromatic nucleus in place of the expelled bromide ion:
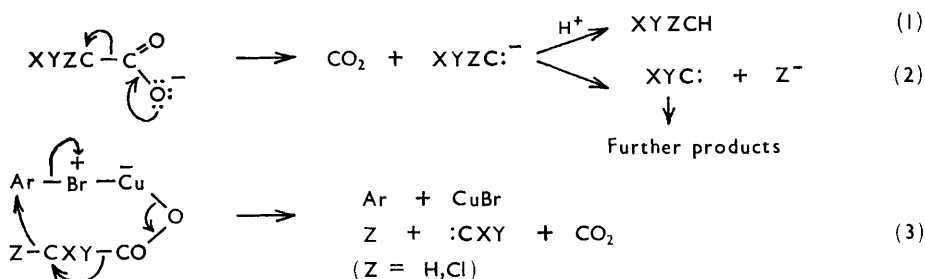
We have no experimental evidence for intermediate carbenes, but the tarry products of the reaction are perhaps thus derived.

The reduction of 1-bromonaphthalene by benzoic anhydride and cuprous oxide (Table 2) raises a new problem. Unlike the procedure described by Smith and his co-workers,[13]

[20] Shepard, Winslow, and Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 2083; Walling and Wolfstirn, *ibid.*, 1947, **69**, 852; Rydon and Tweddle, *J.*, 1955, 3499.
[21] Uhle, *J. Amer. Chem. Soc.*, 1949, **71**, 761; Plieninger, Suehiro, Suhr, and Decker, *Chem. Ber.*, 1955, **88**, 370.
[22] Dougherty, *J. Amer. Chem. Soc.*, 1928, **50**, 571; Piers and Brown, *Canad. J. Chem.*, 1962, **40**, 559.
[23] J. Hine, Burske, M. Hine, and Langford, *J. Amer. Chem. Soc.*, 1957, **79**, 1406.
[24] Brown, *Quart. Rev.*, 1951, **5**, 131.
[25] Kirmse, *Angew. Chem.*, 1961, **73**, 161.
[26] Nenitzescu *et al.*, *Angew. Chem.*, 1960, **72**, 415, 416.

this reaction does not involve the presence of free carboxyl groups, and, unless an adventitious donor is responsible, the hydrogen source is presumably the aromatic nucleus of cuprous benzoate. In this connection, it may be relevant to cite the thermal decarboxylation of cupric benzoate, a complicated reaction for which it has been suggested [27] that intramolecular transfer of hydride ion from the *ortho*-position may occur. An analogous but intermolecular hydride-ion transfer may be involved in the halide reduction. Use of *o*-chlorobenzoic anhydride led to 1-chloronaphthalene (Table 2). However, caution is needed, as in the case of chloro-substituted acetic acids, in ascribing this result to a transfer of chloride ion directly from one aromatic nucleus to another; halogen atoms in *o*-halogeno-benzoic acids are fairly labile,[28] and the same result would be observed if some reaction involving the chloro-anhydride and cuprous oxide produced cuprous chloride. In the working-up of the products from this reaction, analysis showed the presence of equal parts ($\sim$17%) of benzoic and salicyclic acids. This could mean that separate replacements of chlorine by hydrogen and by a hydroxyl group had occurred, or, perhaps more likely, that a reaction product was a copper salt of *o*-carboxyphenyl benzoate, which has also been considered as an intermediate in the thermal decomposition of cupric benzoate.[27] Reactions with both of the aromatic anhydrides resulted in green solutions, little gas evolution, and formation of relatively little tar, which was acidic, whereas tars in other cases had been basic.

We have been concerned with four other types of reducing system containing copper(I). One reaction, already reported,[19] was the reduction (up to $\sim$40%) which accompanied halide exchange in the system 2-bromonaphthalene–cuprous chloride–pyridine *N*-oxide. The heterocyclic nucleus of the solvent may be involved as hydrogen donor, like the aromatic nucleus of benzoic anhydride, and the course of the reaction is similarly obscure. The other three reducing systems, containing cuprous hydride, sodium borohydride, and sodium methoxide, respectively, are all capable of hydride-ion donation. Cuprous hydride, an unstable solid, was prepared as described by Wiberg and Henle: [29] $4\text{CuI} + \text{LiAlH}_4 \longrightarrow 4\text{CuH} + \text{LiI} + \text{AlI}_3$. It was desirable to examine its reducing activity towards the halide, particularly in view of the hydride-like species which are postulated as intermediates in copper(I)-catalysed homogeneous hydrogenations.[30] It failed to reduce 1-bromo-naphthalene during its decomposition to copper in pyridine at 80°, but with a more reactive halide, 2-iodocyclohexyl benzoate (involved in a different investigation), cuprous iodide and cyclohexyl benzoate were produced in pyridine at 50°.

In the presence of cuprous oxide, borohydride ion caused $\sim$25% reduction of 1-bromo-naphthalene, in pyridine at 60° or in boiling dimethylformamide; copper was formed in the first case and an amine in the second. This reduction could be classified among the substitutions of an aryl halide by nucleophiles promoted by cuprous oxide.[1] The reduction (50%) of 1-bromonaphthalene, which accompanied substitution by methoxide ion,[1] may be regarded as a hydride-ion transfer catalysed by cuprous oxide: $\text{ArBr} + \text{CH}_3 \cdot \text{O}^- \longrightarrow \text{ArH} + \text{Br}^- + \text{CH}_2\text{O}$. There is an old observation [31] that a little reduction accompanies substitution in the reaction of bromobenzene with sodium methoxide in methanol at 220°, and there are better-known reduction processes for nitro-groups by methoxide,[32] and for diazonium salts by methanol or ethanol.[33] Deuterium- or tritium-labelled alcohols have been used [34] to prove that C–H and not O–H in $>$CH·OH groups is concerned in the diazonium-salt reductions. The various types of halide-reducing systems described in the present paper are under further investigation.

[27] Toland, *J. Amer. Chem. Soc.*, 1961, **83**, 2507.
[28] Grundy, *Chem. and Ind.*, 1954, 23, and references therein.
[29] Wiberg and Henle, *Z. Naturforsch.*, 1952, **7b**, 250.
[30] Halpern, *Quart. Rev.*, 1956, **10**, 463.
[31] Blau, *Monatsh.*, 1886, **7**, 621.
[32] Ogata and Mibae, *J. Org. Chem.*, 1962, **27**, 2048.
[33] Kornblum, *Org. Reactions*, 1944, **2**, 264.
[34] Melander, *Arkiv Kemi*, 1951, **3**, 525; Miklukin and Rekashava, *Zhur. obshchei Khim.*, 1954, **24**, 96.

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EXPERIMENTAL

Naphthalene from 1-Bromonaphthalene.—(a) 1-Bromonaphthalene (0·01 mole), acetic anhydride (0·01 mole), vacuum-dried cuprous oxide (0·01 mole), and purified pyridine [19] (25 ml.) were heated under reflux (115°), with stirring, in a nitrogen atmosphere. The cuprous oxide dissolved and the solution became green and then darkened. Evolved gas (100 ml.) was collected in a gas burette and was found by mass-spectral analysis to contain only carbon dioxide and nitrogen. The reaction mixture was added to 6N-hydrochloric acid, which dissolved the tar. After ether extraction, washing with 6N-hydrochloric acid and 10% sodium hydrogen carbonate, distillation, and sublimation, naphthalene, m. p. 79—80° (picrate, m. p. 150°), was isolated (Table 2) together with unchanged 1-bromonaphthalene. Analysis of the product was best made by gas chromatography.[19] At 120°, with dimethylformamide as solvent, the cuprous oxide did not dissolve, no gas was evolved, unchanged 1-bromonaphthalene was recovered (90%) by distillation, and gas chromatography revealed no naphthalene in it. With pyridine and the omission of bromonaphthalene, the initially yellow solution darkened, carbon dioxide was evolved, and the mixture became black and viscous.

(b) Reaction was carried out similarly with 1-bromonaphthalene (0·025 mole), acetic acid (0·1 mole), cuprous oxide (0·05 mole), and pyridine (50 ml.). Some of the oxide was undissolved; the mixture became very dark green and carbon dioxide was evolved; naphthalene was isolated (Table 1).

(c) A preparation [35] of cuprous acetate yielded almost colourless flakes (54%). This salt (0·1 mole) and 1-bromonaphthalene (0·05 mole) were dissolved in purified pyridine (40 ml.) and allowed to react under the usual conditions for 3 hr. The solution darkened, carbon dioxide was evolved, and naphthalene (50%) was isolated.

(d) The reaction with fluoroacetic acid (Table 1) in pyridine (25 ml.) resulted in much gas evolution and a tarry product. Naphthalene was determined by gas chromatography.

(e) Reaction with benzoic anhydride (Table 2), in pyridine (50 ml.), resulted in a green solution and very little gas evolution; some of the cuprous oxide was undissolved. After addition of the product to 6N-hydrochloric acid and extraction with benzene, the extract was separated into neutral and acidic fractions. The former contained naphthalene and 1-bromonaphthalene, and the latter only benzoic acid.

Deuteronaphthalene.—Hexadeuteroacetic anhydride (Nichem Inc.) was found by mass-spectral analysis to contain 1% of hydrogen relative to its deuterium content. Reactions were carried out in purified pyridine (25 ml.) under the conditions shown in Table 2 and described above for acetic anhydride. The products were analysed by gas chromatography. Naphthalene was isolated, purified by sublimation, and analysed for deuterium by mass spectroscopy. In the infrared spectrum of the deuteronaphthalene, peaks attributed to C–D were found at 4·4m, 12·6s, 12·8vs, and 13·3m μ. Peaks at 12·3m (doublet), 13·1m, and 13·25m μ (may have been due to a small amount of the 2-deutero-isomer, since the 1-bromo-naphthalene used contained ∼2% of its 2-isomer. No deuterated pyridine was detected by mass-spectral analysis of recovered solvent. A sample of the deuteronaphthalene was kept in a mixture of acetic anhydride, pyridine, and cuprous oxide, under the conditions used in the reaction; no change was found in its deuterium content.

1-Chloronaphthalene.—(a) Reaction with monochloroacetic anhydride (Table 2) in pyridine (25 ml.) resulted in evolution of gas (200 ml.) containing carbon dioxide, and formation of a very tarry product. Halides were isolated as a liquid fraction (1·7 g.), b. p. 50—62°/0·05 mm., which was analysed by gas chromatography. The corresponding reaction with monochloroacetic acid (Table 1) proceeded similarly, but a little naphthalene accompanied the isolated halides.

(b) The mixture containing dichlorofluoroacetic anhydride (Table 2) was made in pyridine (25 ml.) below 0° and the temperature slowly raised to the b. p. Cuprous oxide began to dissolve and carbon dioxide was evolved, even below 50°. The total gas amounted to 400 ml. and the tarry product yielded a halide fraction (2·0 g.), b. p. 52—62°/0·05 mm., which was analysed by gas chromatography.

(c) Trichloroacetic anhydride, b. p. 60°/0·5 mm., was prepared [36] (30%) and used (Table 2) in the manner described under (b). Evolution of gas occurred even below 30° but the mixture was eventually taken to the b. p. and the product examined in the usual way. Attempts to

[35] Calvin and Wilmarth, *J. Amer. Chem. Soc.*, 1956, **78**, 1301.
[36] I.G. Farbenindustrie A.-G., F.P. 703,816 (1931).

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detect dichlorocarbene by addition of cyclohexene [37] or 1-methoxynaphthalene [38] to the reaction mixture were unsuccessful.   Use of trichloroacetic acid (Table 1) led to a violent reaction in the cold, but the mixture was cautiously brought to the b. p. and a little chloronaphthalene was isolated.

(*d*) *o*-Chlorobenzoic anhydride, m. p. 79°, was prepared [39] from *o*-chlorobenzoic acid and *o*-chlorobenzoyl chloride, and was used in pyridine (25 ml.) under the conditions stated (Table 2). The mixture became green, deposited an acidic tar, and evolved only ~10 ml. of gas.   After addition of the product to 6N-hydrochloric acid and extraction with benzene, the extract was shaken with 20% aqueous sodium hydroxide to remove organic acids, which, after precipitation, were converted into their methyl esters; gas chromatography showed methyl *o*-chlorobenzoate (65%), methyl benzoate (17%), and methyl salicylate (18%).   An artificial mixture of this composition showed the same infrared absorption spectrum as that from the reaction.   The neutral portion of the reaction product was isolated as a liquid (1·9 g.), b. p. 50—62°/0·05 mm., which was analysed for 1-chloronaphthalene (18—24%) and unchanged 1-bromonaphthalene by gas chromatography.

Ineffective Acids or Anhydrides.—With formic acid (Table 1) there was an instantaneous evolution of carbon dioxide in the cold, and the mixture, after refluxing, contained copper metal and black material; gas chromatography showed only unchanged 1-bromonaphthalene.   With iodoacetic acid (Table 1) the disappearance of the cuprous oxide was succeeded by the appearance of a bulky yellow precipitate, and, after heating, the mixture was black and viscous; gas chromatography showed a trace of 1-iodonaphthalene.   With cyanoacetic acid (Table 1) carbon dioxide was evolved vigorously at 30° and the solution turned red.   With trifluoroacetic anhydride (Table 2) in pyridine (25 ml.), 125 ml. of gas were evolved during refluxing; mass-spectral analysis of the gas showed carbon dioxide and trifluoromethane, and the very tarry product yielded only unchanged 1-bromonaphthalene.

Cuprous Hydride.—The following is an amplified account of a published method.[29]   A solution of cuprous iodide (0·5 mole) in pyridine (500 ml.) was stirred under nitrogen while lithium aluminium hydride (0·165 mole) in a mixture of diethyl ether (50 ml.) and pyridine (10 ml.) was slowly added, with sufficient cooling to keep the temperature below 20°.   The colour changed from yellow to blood red, and then to black.   After a further 4 hr. the mixture was centrifuged (filtration being very difficult) and the solution decanted from the precipitate into ether (500 ml.).   The resulting red-brown precipitate of cuprous hydride was twice purified by centrifugation, dissolving in pyridine (250 ml.) and reprecipitating with ether (250 ml.).   It was finally washed with ether, dried briefly in a vacuum, and used immediately, since it decomposed during about 2 days at room temperature.

1-Bromonaphthalene (0·02 mole) and cuprous hydride (0·04 mole) in pyridine (25 ml.) formed a deep red solution, which, when kept at 80° for 2 hr., had deposited copper; it yielded only unchanged 1-bromonaphthalene.   A similar result was obtained by using an equivalent mixture of cuprous iodide and lithium aluminium hydride in place of cuprous hydride.   When a solution of 2-iodocyclohexyl benzoate (0·0025 mole) and cuprous hydride (0·0125 mole) in pyridine (25 ml.) was kept for 8 hr. at 50° the colour changed from deep red to light green; cuprous iodide was precipitated when the solution was added to 2N-hydrochloric aicd.   Cyclo-hexyl benzoate was isolated and examined by gas chromatography.

Reduction by Borohydride.—(*a*) Reaction between 1-bromonaphthalene (0·02 mole), sodium borohydride (0·04 mole), and cuprous oxide (0·01 mole) in refluxing dimethylformamide (50 ml.) occurred with darkening and evolution of amine vapours.   The product was poured into 6N-hydrochloric acid and extracted with benzene; analysis by gas chromatography showed naphthalene (25%) and 1-bromonaphthalene (70%).

(*b*) The reaction was repeated in pyridine.   When the temperature reached 60° there was a rapid reaction, resulting in deposition of a copper mirror on the walls of the vessel.   The temperature was raised to the boiling point and the product isolated after 16 hr.; gas chromatography showed naphthalene (25%) and 1-bromonaphthalene (75%).

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[37] Doering and Hoffmann, *J. Amer. Chem. Soc.*, 1954, **76**, 6162.
[38] Parham, Bolon, and Schweizer, *J. Amer. Chem. Soc.*, 1961, **83**, 603.
[39] Vogel, " Practical Organic Chemistry," 3rd edn., Longmans, London, 1957, p. 374.

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DEPARTMENT OF ORGANIC CHEMISTRY,
QUEEN'S UNIVERSITY, BELFAST.