226. *Copper*(II) *Halides as Halogenating Agents.*

By D. C. Nonhebel.

Copper(II) chloride and bromide have been shown to react with anthracene and pyrene to give excellent yields of 9-halogenoanthracenes and 1-halogenopyrenes. The reaction is postulated as proceeding by homolytic decomposition of a π-complex between the copper(II) halide and the aromatic hydrocarbon.

Copper(II) halides have been used as halogenating agents in homogeneous conditions for compounds containing active hydrogen atoms,[1,2] and in heterogeneous conditions in non-polar solvents for aromatic hydrocarbons,[3,4] as well as for the preparation of dialkyl phosphorochloridates from dialkyl phosphites.[5] The present work is concerned with the second type of reaction, with particular reference to its synthetic possibilities and mechanism.

Use of copper(II) chloride and bromide has been shown to afford 9-halogenoanthracenes and 1-halogenopyrenes in a variety of non-polar solvents, in all cases in good yield (see Tables 1 and 2). Large quantities of hydrogen halide were evolved and two mol. of copper(II) halide were required. The copper(II) halide was quantitatively converted into copper(I) halide. The stoicheiometry of the reaction can be written as $2CuX_2 + C_{14}H_{10} \longrightarrow 2CuX + C_{14}H_9X + HX$. This method is superior to others for the preparation of 9-halogenoanthracenes and 1-halogenopyrenes in both simplicity and yield It is particularly valuable for 9-chloroanthracene which was previously prepared by chlorination of anthracene with t-butyl hypochlorite [6] or phosphorus pentachloride.[6] The process is not, however, generally applicable for the halogenation of aromatic hydrocarbons: chrysene, phenanthrene, and fluorene were recovered unchanged after being heated with copper(II) halides for a considerable time. There was no advantage in carrying out the reactions under nitrogen.

9-Chloro- and 9,10-dichloro-anthracene were obtained after reaction of 1 mol. each of copper(II) chloride and anthracene but with an excess of anthracene 9-chloroanthracene was the sole product. In the same conditions 9-chloroanthracene was converted into 9,10-dichloroanthracene, and similarly 9-bromoanthracene with copper(II) bromide gave

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[1] Kochi, *J. Amer. Chem. Soc.*, 1955, **77**, 5274.

[2] Fort, *J. Org. Chem.*, 1961, **26**, 765; Castro, *J. Org. Chem.*, 1961, **26**, 4183.

[3] Nonhebel, *Proc. Chem. Soc.*, 1961, 307.

[4] Ware and Borchert, *J. Org. Chem.*, 1961, **26**, 2263, 2267.

[5] Smith, *J.*, 1962, 1122; Engelsma, Farenhorst, and Kooyman, *Rec. Trav. chim.*, 1954, **73**, 878.

[6] Mikhailov and Promyslov, *J. Gen. Chem.* (*U.S.S.R.*), 1950, **20**, 338.

9,10-dibromoanthracene. This indicates that in the main halogenation 9,10-dichloroanthracene is formed from 9-chloroanthracene Reaction between copper(II) chloride and anthracene in refluxing chlorobenzene was complete within one minute, whereas Ware and Borchert used a reaction time of several days.[4] The reason for this is not clear. They also stated on scanty evidence that the reaction could not be satisfactorily extended to copper(II) bromide. The results in Tables 1 and 2 show that it can be so extended if suitable conditions are used. Ware and Borchert's conditions involved refluxing nitrobenzene in which it has been shown that copper(II) bromide is partially dissociated to copper(I) bromide and bromine. A less polar, lower-boiling solvent such as carbon tetrachloride or chlorobenzene seems to be more suitable. 9-Bromoanthracene was obtained in 90% yield in nitrobenzene at 100°.

The reactions occur at temperatures well below those at which copper(II) halides dissociate to copper(I) halides and halogen,[7] indicating that participation of halogen atoms is improbable. This is particularly so in the dehydrogenation of 9,10-dihydroanthracene with copper(II) halides with the evolution of hydrogen halides, reactions which are complete at room temperature in 24 hours. No dissociation could be envisaged under these conditions. It seems feasible that a π-complex is formed between the copper(II) halide and the aromatic hydrocarbon. [The solubility of copper(II) tetrafluoroborate in benzene has been explained by the formation of a π-complex.[8]] Consistently with this, copper(II) halides appear to react only with aromatic compounds which might be expected to form π-complexes fairly readily. It was also found that the reactions were considerably retarded by traces of glycerol, ethylene glycol, ethanol, or water, all of which could solvate the copper(II) chloride, preventing formation of the π-complex. Copper(II) halides reacted with toluene, to give bibenzyl, and in the reaction with copper(II) bromide some benzyl bromide was also obtained. The formation of bibenzyl is strongly indicative of the participation of benzyl radicals: $CuX_2 + Ph{\cdot}CH_3 \longrightarrow Ph{\cdot}CH_2{\cdot} + CuX + HX$; $2Ph{\cdot}CH_2{\cdot} \longrightarrow (CH_2Ph)_2$. Copper(II) bromide dissociates very slowly in refluxing toluene, to give copper(I) bromide and bromine, and the latter bromine then reacts with benzyl radicals to give benzyl bromide. It thus seems possible that the reaction of copper(II) halides with aromatic hydrocarbons proceeds by homolytic decomposition of a π-complex formed between the copper(II) halide and the aromatic hydrocarbon rather than by a polar mechanism favoured by Ware and Borchert.[4]

The reaction possesses similarities to the use of *N*-bromosuccinimide for bromination of aromatic hydrocarbons, though the latter reagent brominates chrysene, phenanthrene, and fluorene as well as anthracene and pyrene.[9] Moreover, copper(II) bromide was found by us to be ineffective in the dehydrogenation of tetralin to naphthalene and in the bromination of methyl crotonate to methyl γ-bromocrotonate (in the latter case after three weeks' refluxing methyl $\alpha\beta$-dibromobutyrate was obtained). The active intermediate in bromination by *N*-bromosuccinimide is atomic bromine,[10] and the fact that reactions with copper(II) bromide are different is consistent with their proceeding by a somewhat different course.

Table 1 shows that the reaction of copper(II) chloride and anthracene is much faster in chlorobenzene and tetrachloroethane than in xylene Xylene is rather more acidic than either chlorobenzene or tetrachloroethane and thus might be expected to compete with anthracene for the formation of a π-complex with copper(II) chloride, thus retarding the reaction. The reaction in diethylene glycol was also somewhat slower than that in chlorobenzene, in spite of the fact that copper(II) chloride is significantly soluble in it; this indicates that the reaction is not dependent on the solubility of the copper(II) halide in

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[7] Shchukarev and Oranskaya, *J. Gen. Chem.* (*U.S.S.R.*), 1954, **24**, 1889; Barret and Guenebaut-Thevenot, *Bull. Soc. chim. France*, 1957, 409.

[8] D. W. A. Sharp, personal communication.

[9] Djerassi, *Chem. Rev.*, 1948, **43**, 271.

[10] McGrath and Tedder, *Proc. Chem. Soc.*, 1961, 80.

the solvent. It was found that copper(II) chloride is not detectably soluble in refluxing chlorobenzene. All this points to the fact that the reaction proceeds between anthracene and solid copper(II) halide and not between anthracene and dissolved copper(II) halide with dissolution of the halide as the slow step.

A cursory examination was made of the possibility of halogenation by other metal halides which can undergo a one-electron transfer, similar to that of copper(II) halides. Mercury(II) chloride and bromide were both without effect on anthracene or 9,10-dihydroanthracene. Iron(III) chloride reacted slowly with anthracene in carbon tetrachloride to give 1% of 9-chloroanthracene with a variety of unidentified products This was sufficient to indicate that the reaction followed a somewhat different course from that for copper(II) halides. The difference may lie in the fact that copper(II) halides are more ionic than iron(III) halides.

The reaction also seems to be different from that under homogeneous conditions. Thus anthracene was not brominated by copper(II) bromide in methanol, nor did acetone react with copper(II) chloride under heterogeneous conditions in carbon tetrachloride. Halogenations under homogeneous conditions may well be polar, as postulated by Kochi.[1]

The ultraviolet spectra of 9-halogeno- and 9,10-dihalogeno-anthracenes and 1-halogenopyrenes are recorded in Table 3.

EXPERIMENTAL

Identities were confirmed by mixed m. p. determinations, and infrared and ultraviolet comparison. Ultraviolet spectra were determined for cyclohexane solutions.

Materials.—Anthracene was B.D.H.'s blue-fluorescent grade. Anhydrous copper(II) chloride and bromide were finely ground, dried at 120° and stored *in vacuo* over phosphorus pentoxide.

Reactions of Aromatic Hydrocarbons with Copper(II) *Halides.*—A stirred mixture of copper(II) halide (0·050 mole) and aromatic hydrocarbon (0·025 mole) in solvent (100 ml.) was heated under reflux until all the halide was converted into copper(I) halide and evolution of hydrogen halide ceased. The copper(I) halide was filtered off from the hot mixture and the filtrate evaporated to dryness. The residue in light petroleum (b. p. 40—60°) was chromatographed on alumina. Elution with light petroleum gave the products (see Tables 1 and 2).

TABLE 1.

Reactions of copper(II) halides and anthracene.

CuX_2	$CuX_2 : C_{14}H_{10}$	Solvent *	Reaction time	Products	Yield (%)
$CuCl_2$	2 : 1	CCl_4	7 hr.	9-Chloroanthracene	98
$CuCl_2$	2 : 1	C_6H_6	20 min.	9-Chloroanthracene	98
$CuCl_2$	2 : 1	$CHMeCl·CHCl_2$	45 min.	9-Chloroanthracene	83
$CuCl_2$	2 : 1	" Iso-octane "	7 min.	9-Chloroanthracene	87
$CuCl_2$	2 : 1	PhMe	3 min.	9-Chloroanthracene	85
				9,10-Dichloroanthracene	4 †
$CuCl_2$	2 : 1	Xylene	2 hr.	9-Chloroanthracene	81
				9,10-Dichloroanthracene	3 †
$CuCl_2$	2 : 1	PhCl	1 min.	9-Chloroanthracene	79
				9,10-Dichloroanthracene	7 †
$CuCl_2$	1 : 1	PhCl	1 min.	9-Chloroanthracene	60
$CuCl_2$	2 : 1	PhCl + 1% of EtOH	15 min.	9-Chloroanthracene	87
$CuCl_2$	2 : 1	$(CHCl_2)_2$	1 min.	9-Chloroanthracene	77
				9,10-Dichloroanthracene	7 †
$CuCl_2$	2 : 1	$(HO·CH_2·CH_2)_2O$	5 min.	9-Chloroanthracene	62
$CuBr_2$	2 : 1	CCl_4	4 hr.	9-Bromoanthracene	99
$CuBr_2$	2 : 1	PhCl	1 min.	9-Bromoanthracene	99
$CuBr_2$	2 : 1	$PhNO_2$	30 min.	9-Bromoanthracene	90
$CuBr_2$	2 : 1	MeOH	8 hr.	No reaction	

* Reactions carried out at the temperature of the refluxing solvent, except that in nitrobenzene which was carried out at 100°.

† 9,10-Dichloroanthracene was separated from 9-chloroanthracene by fractional crystallization after chromatography on alumina.

Table 2.

Reactions of aromatic compounds with copper(II) halides.

Aromatic compound	CuX_2 *	Solvent †	Reaction time	Products	Yield (%)
9-Chloroanthracene	$CuCl_2$	PhCl	5 hr.	9,10-Dichloroanthracene	99
9-Bromoanthracene	$CuBr_2$	PhCl	30 min.	9,10-Dibromoanthracene	92
Pyrene	$CuCl_2$	CCl_4	7 hr.	1-Chloropyrene	90
Pyrene	$CuCl_2$	PhCl	1 min.	1-Chloropyrene	95
Pyrene	$CuBr_2$	CCl_4	4 hr.	1-Bromopyrene	94
Pyrene	$CuBr_2$	PhCl	1 min.	1-Bromopyrene	95
Chrysene	$CuCl_2$	PhCl	6 hr.	No reaction	
Phenanthrene	$CuCl_2$	CCl_4	168 hr.	No reaction	
Phenanthrene	$CuCl_2$	PhCl	6 hr.	No reaction	
Fluorene	$CuCl_2$	CCl_4	168 hr.	No reaction	
Tetralin	$CuCl_2$	CCl_4	72 hr.	No reaction	
9,10-Dihydroanthracene	$CuCl_2$	CCl_4	24 hr.	Anthracene	99
9,10-Dihydroanthracene	$CuCl_2$	C_6H_6	24 hr.	Anthracene	99
9,10-Dihydroanthracene	$CuBr_2$	CCl_4	24 hr.	Anthracene	99

* Molar ratios of CuX_2 : aromatic hydrocarbon of 2 : 1 used in all experiments.

† Reactions carried out at the temperature of the refluxing solvent except those with 9,10-dihydroanthracene which were at room temperature.

Reaction of Anthracene and Copper(II) *Bromide in Nitrobenzene.*—After filtration from the copper(I) chloride, the nitrobenzene layer was steam-distilled. The involatile residue was extracted with methylene chloride, dried (Na_2SO_4), and evaporated to dryness. The residue, in light petroleum (b. p. 40—60°), was chromatographed on alumina. Elution with light petroleum (b. p. 40—60°) gave 9-bromoanthracene.

Reaction of Toluene and Copper(II) *Bromide.*—A stirred suspension of copper(II) bromide (22 g., 0·1 mole) in dry toluene (500 ml.) was refluxed for 72 hr. The copper(II) bromide was filtered off and the filtrate washed with sodium thiosulphate, and dried (Na_2SO_4). The solution was concentrated. Analysis of the residue by gas-chromatography showed the presence of bibenzyl (48%) and benzyl bromide (2·5%) by comparison with known mixtures of toluene, bibenzyl, and benzyl bromine. The hydrogen bromide evolved (75% of the theoretical amount) was estimated by absorption in standard sodium hydroxide solution and back-titration with hydrochloric acid.

Reaction of Toluene and Copper(II) *Chloride.*—A stirred suspension of copper(II) chloride (13·5 g.) in toluene (200 ml.) was refluxed for 7 days, at the end of which reaction was not complete. Gas-chromatography of the product showed the presence of bibenzyl and absence of benzyl chloride.

Reaction of Methyl Crotonate with Copper(II) *Bromide.*—A stirred suspension of copper(II) bromide (45 g.) in methyl crotonate (20 g.) and carbon tetrachloride (100 ml.) was refluxed for 3 weeks. The copper(I) bromide was filtered off and the filtrate distilled. The fraction of b. p. 110—120/13 mm. was shown by gas-chromatography and infrared comparison to be methyl αβ-dibromobutyrate obtained by the addition of bromine to methyl crotonate. Gas-chromatography showed the complete absence of methyl γ-bromocrotonate.

Table 3.

Ultraviolet spectra (mμ) (ε in parentheses).

9-Chloro-anthracene	9-Bromo-anthracene	9,10-Dichloro-anthracene	9,10-Dibromo-anthracene	1-Chloro-pyrene	1-Bromo-pyrene
249sh (86,000)	250sh (100,000)	252 (85,700)	256sh (83,500)	243 (59,400)	242 (53,600)
256 (177,000)	256 (158,000)	260 (177,000)	260 (161,000)	265 (22,600)	265 (19,800)
318sh (1250)	318sh (1250)	342 (3030)	344 (3050)	276 (39,600)	276 (31,000)
332 (2800)	334 (2700)	360 (6720)	361 (7350)	313 (10,900)	314 (9900)
348 (5700)	350 (5800)	379 (11,700)	381 (13,400)	326 (25,300)	326 (21,900)
367 (8500)	368 (8800)	401 (10,800)	402 (13,400)	342 (38,600)	343 (31,800)
385 (7200)	387 (7500)				

Reaction of Anthracene and Iron(III) *Chloride.*—A stirred mixture of iron(III) chloride (16·2 g.) and anthracene (8·9 g.) in carbon tetrachloride was refluxed for 8 hr. The inorganic material was filtered off and the filtrate evaporated to dryness. The residue was extracted with light petroleum (b. p. 40—60°) and chromatographed on alumina. Elution with light petroleum (b. p. 40—60°) gave 9-chloroanthracene.

Reactions with Mercury(II) *Chloride and Bromide*.—A solution of mercury(II) halide (10 g.) and anthracene (5 g.) in benzene (200 ml.) was refluxed for 72 hr. Unchanged anthracene was recovered.

A solution of 9,10-dihydroanthracene (5 g.) and mercury(II) bromide (10 g.) in benzene was refluxed for 72 hr. Unchanged 9,10-dihydroanthracene was recovered.

Ultraviolet Spectra (*Table* 3).—These were recorded with a Unicam S.P. 500 spectrophotometer for solutions in cyclohexane.

CHEMISTRY DEPARTMENT, ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY,
GLASGOW, C.1.

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