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REACTION OF CUPRIC HALIDES WITH ORGANIC COMPOUNDS—II

9-HALOGENOANTHRACENES

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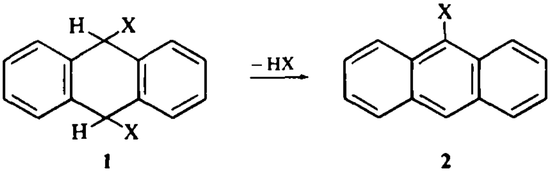
Abstract—9-Bromoanthracene and 9-chloroanthracene with cupric chloride and cupric bromide respectively give only 9-bromo-10-chloroanthracene. The reaction is postulated to proceed by a radical mechanism. Reactions of 9-halogenoanthracene with other halogenating agents were also examined.

CUPRIC bromide and cupric chloride have been shown to react with aromatic hydrocarbons under heterogeneous conditions in non-polar solvents. Thus anthracene and pyrene were shown to react very readily with both cupric bromide and cupric chloride to give respectively excellent yields of 9-halogenoanthracenes and 1-halogenopyrenes.[1,2] 9-Bromoanthracene was also shown to undergo reaction with cupric bromide to give 9,10-dibromoanthracene, and similarly with cupric chloride 9-chloroanthracene afforded 9,10-dichloroanthracene.[1] A mixture of *o*- and *p*-bromotoluene was obtained from the reaction of toluene with cupric bromide.[3] These processes have been postulated to proceed by an ionic[2,3] and by a radical mechanism.[1]

The present work involves a closer examination of the reaction of 9-bromo- and 9-chloroanthracene with both cupric bromide and cupric chloride under heterogeneous conditions in chlorobenzene with a view to establishing the mechanism of these reactions. The reaction products were analysed by GLC and were compared with those obtained from the reactions of the 9-halogenoathracenes with other halogenating agents under a variety of conditions (Tables 1 and 2).

Halogenation of anthracene is generally accepted to proceed *via* addition of halogen across the 9,10 positions to form 9,10-dihalogeno-9,10-dihydroanthracene (1) which readily undergoes dehydrohalogenation to yield the 9-halogenoanthracene (2).[4,6]



The same reaction pathway applies to the formation of 9,10-dihalogenoanthracenes from the 9-halogenoanthracene.[5] Thus in the bromination of 9-bromoanthracene 9,9,10-tribromo-9,10-dihydroanthracene is precipitated out of the reaction medium. This slowly undergoes decomposition with the evolution of hydrogen bromide yielding 9,10-dibromoanthracene. Bromination of 9-chloroanthracene similarly

TABLE 1. HALOGENATION OF 9-BROMOANTHRACENE

Halogenating Agent	Solvent	Halogenated anthracenes obtained (%)				
		9-Br	9-Cl	9,10-DiBr	9-Br-10-Cl	9,10-DiCl
Chlorine	AcOH	20	68	0	1	10
Chlorine	CCl_4	34	6	0	27	32
Phosphorus pentachloride	PhH	63	7	0	17	12
Phosphorus pentachloride	CCl_4	66	17	0	7	7
Iodobenzene dichloride + peroxide	AcOH	0	9	0	10	80
Iodobenzene dichloride	AcOH	0	12	0	21	67
Iodobenzene dichloride + peroxide	CCl_4	0	2	0	1	97
Iodobenzene dichloride	CCl_4	0	4	0	0	94
Iodobenzene dichloride + peroxide	PhCl	0	0	0	1	98
Cupric chloride[a]	PhCl	4	0	0	96	0
Bromine	AcOH	0		98		
Bromine	CCl_4	75		21		
Phosphorus pentabromide	PhH	52		46		
N-Bromosuccinimide	CCl_4	5		95		
Cupric bromide[b]	PhCl	4		96		

[a] Time for complete reaction 2·5 hr

[b] Time for complete reaction 23 hr

TABLE 2. HALOGENATION OF 9-CHLOROANTHRACENE

Halogenating agent	Solvent	Halogenated anthracenes obtained (%)				
		9-Br	9-Cl	9,10DiBr	9-Br-10-Cl	9,10-DiCl
Bromine	AcOH[c]	3	11	4	75	6
Bromine	AcOH[d]	0	0	8	92	0
Bromine	CCl_4	7	77	3	13	0
Phosphorus pentabromide	PhH	8	60	1	31	0
N-Bromosuccinimide	CCl_4	0	7	0	93	0
Cupric bromide[a]	PhCl	0	4	0	96	0
Chlorine	AcOH		73			25
Chlorine	CCl_4		34			65
Phosphorus pentachloride	PhH		84			15
Iodobenzene dichloride + peroxide	AcOH		10			66
Iodobenzene dichloride	AcOH		10			56
Iodobenzene dichloride + peroxide	CCl_4		23			65
Iodobenzene dichloride	CCl_4		22			61
Iodobenzene dichloride + peroxide	PhCl		0			77
Cupric chloride[b]	PhCl		4			96

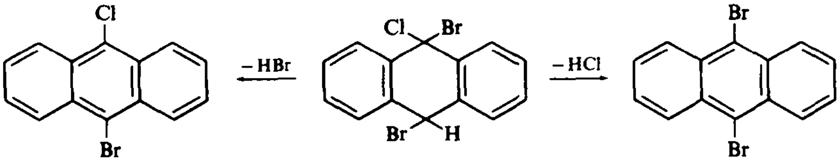
[a] Time for complete reaction 5·5 hr.

[b] Time for complete reaction 23 hr.

[c] Reaction carried out at room temp.

[d] Addition of Br_2 at room temperature and then mixture refluxed.

affords 9,10-dibromo-9-chloro-9,10-dihydroanthracene (**4**) which is said to give exclusively 9-bromo-10-chloroanthracene (**3**) by loss of hydrogen bromide.[5] Loss of hydrogen chloride would have furnished 9,10-dibromoanthracene (**5**). Similarly

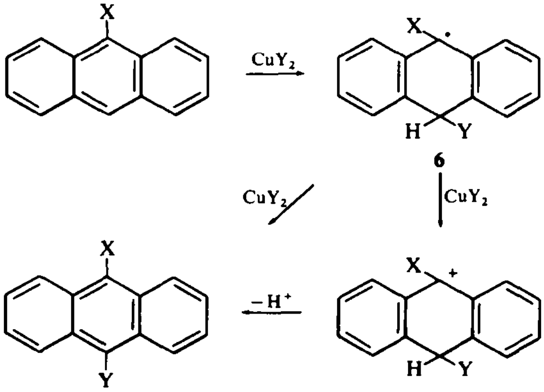


3 **4** **5**

9-bromo-9,10-dichloro-9,10-dihydroanthracene, formed in the chlorination of 9-bromoanthracene, is also said to give only 9-bromo-10-chloroanthracene.[6]

Reinvestigation of the bromination of 9-chloroanthracene under a variety of conditions gave in all cases small amounts of 9,10-dibromoanthracene as well as 9-bromo-10-chloroanthracene. In one experiment the intermediate 9,10-dibromo-9-chloro-9,10-dihydroanthracene was isolated and then allowed to decompose in acetic acid. The products obtained were substantially the same as when it was not separated off from the reaction mixture. The chlorination of 9-bromoanthracene which proceeds by the intermediate, 9-bromo-9,10-dichloro-9,10-dihydroanthracene, afforded in all cases *less* 9-bromo-10-chloroanthracene than 9,10-dichloroanthracene. These results can be rationalized on the basis that the C–Br bond is weaker than the C–Cl bond and hence loss of hydrogen bromide from the intermediate would be favoured. Stereochemical considerations would thus appear to be of lesser importance than indicated by earlier workers.[5] Similarly chlorination of 9-bromoanthracene with iodobenzene dichloride and with phosphorus pentachloride gave less 9-bromo-10-chloroanthracene than 9,10-dichloroanthracene.

In contrast to these reactions, that between 9-bromoanthracene and cupric chloride and that between 9-chloroanthracene and cupric bromide gave exclusively 9-bromo-10-chloroanthracene. This indicates that the reactions with cupric halides proceed by a different mechanism than those with halogen, phosphorus pentahalides, and iodobenzene dichloride. In the reaction with cupric halides the mechanism is postulated to involve the ligand transfer of a halogen atom to give the intermediate radical (**6**).



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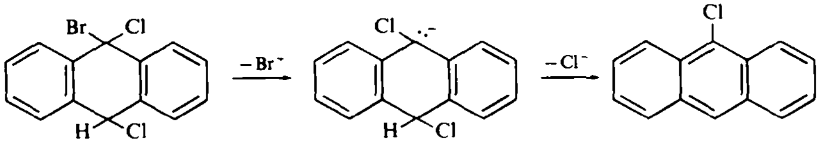
Attack takes place exclusively at the 10-position on steric considerations. The intermediate radical is then postulated to undergo reaction with a further molecule of cupric halide to give the product or more probably oxidation of the radical takes place to give the carbonium ion (7) followed by loss of a proton.[7] A second ligand transfer reaction to form a 9,9,10-trihalogeno-9,10-dihydroanthracene does not appear to occur as no 9,10-dichloroanthracene was formed in the reaction of 9-bromoanthracene with cupric chloride. The cupric halide reactions appear to take place on the surface of the halide since at no time is there any evidence of any dissolution of the halide in the solvent.

The proposed mechanism conflicts with that postulated by Kovacic and Davies[3] for the bromination of toluene with cupric bromide. It is believed that the mechanism for their reaction differs from that for the reaction between cupric halides and anthracene. It is noteworthy that for the reaction with toluene, cupric chloride was found to be ineffective whereas in reactions with anthracene and substituted anthracenes it reacts readily though somewhat less rapidly than cupric bromide. This is quite consistent with the proposed mechanism involving ligand transfer of a halogen atom as cupric bromide is a better ligand transfer reagent than cupric chloride.[8,9]

9-Bromo-10-chloroanthracene was also produced efficiently in the reaction between N-bromosuccinimide and 9-chloroanthracene.

The formation of 9-chloroanthracene from the chlorination of 9-bromanthracene in glacial acetic acid may proceed by the consecutive loss of Br^+ and Cl^- from the intermediate 9-bromo-9,10-dichloro-9,10-dihydroanthracene. Further work is necessary to confirm the mechanism of this process. Direct substitution of chlorine for bromine is considered unlikely since under comparable conditions 9-bromo-10-phenylanthracene gave no 9-chloro-10-phenylanthracene. Loss of halogen from 9,10-dihalogeno-9,10-dihydroanthracenes has been frequently observed.[6]



EXPERIMENTAL

Materials. Anhydrous cupric bromide and cupric chloride were finely ground and then dried over P_2O_5 for at least 3 days at 60° in a vacuum oven.

9-Bromo and 9-chloroanthracene were obtained by halogenation of anthracene with the appropriate cupric halide.[1,10] 9,10-Dibromo- and 9,10-dichloroanthracene were similarly obtained by halogenation of the appropriate 9-halogenoanthracene with cupric halide.[1] The compounds were purified by repeated chromatography on alumina followed by crystallization from light petroleum until analysis by GLC showed only one peak.

9-*Bromo*-10-*chloroanthracene*. A vigorously stirred mixture of cupric bromide (1·1175 g, 5 mmole) and 9-chloroanthracene (0·5313 g, 2·5 mmole) in chlorobenzene (100 ml) was heated under reflux until the evolution of HBr ceased (5½ hr).

The hot reaction mixture was filtered to remove the cuprous bromide and the filtrate evaporated to dryness. The residue, in light petroleum (b.p. 60–80°) was chromatographed on alumina. Elution with light petroleum followed by successive crystallizations from chloroform, light petroleum, pyridine and ethylmethyl ketone gave pale-yellow plates of 9-bromo-10-chloroanthracene, m.p. 210–212°. (Found: C, 57·5; H, 3·10; Br + Cl, 54·4. Calc. for $C_{14}H_8BrCl$: C, 57·7; H, 2·8; Br + Cl, 54·8%).

Analysis of reaction products. A soln of the reaction product in CS_2 was analysed using a Perkin–Elmer F11 gas–liquid chromatograph with twin columns packed with silicone Gum Rubber E-301 on AW-DMCS 80–100 mesh Chromosorb G 2·5:97·5 operating at 245°.

Reactions with cupric halide. These were carried out as described in the preparation of 9-bromo-10-chloroanthracene, and the reaction products analysed by GLC.

Reactions with chlorine. A slow stream of Cl_2 was bubbled through a soln of the 9-halogenoanthracene (5 mmole) in AcOH or CCl_4 (150 ml) for 1 hr. The solvent was distilled off and the residue analysed by GLC.

Reaction with bromine. (a) Bromine (0·4 g, 2·5 mmoles) was added to a soln of the 9-halogenoanthracene (2·5 mmoles) in AcOH or CCl_4 (100 ml). A yellow solid was precipitated out of the reaction medium. The mixture was stirred for 1 hr at room temperature during which time the solid dissolved and hydrogen halide was evolved. After evaporation of the solvent, the residue was analysed by GLC.

(b) Br_2 (0·8 g, 5 mmole) was added dropwise during 30 min to a soln of 9-chloroanthracene (0·5313 g, 2·5 mmole) in AcOH (100 ml). The mixture was stirred for a further 30 min at room temp and was then heated under reflux for 1 hr. The product was analysed by GLC.

(c) Br_2 (0·4 g, 2·5 mmole) was added to a soln of 9-chloroanthracene (0·5313 g, 2·5 mmole) in AcOH (100 ml) at room temp. After 5 min, the yellow ppt of 9,10-dibromo-9-chloro-9,10-dihydroanthracene (0·2805 g) was filtered off, m.p. 140–142° dec and then 200–210°. A soln of this compound (0·1 g) in AcOH (20 ml) was stirred for 1 hr at room temp during which time hydrogen halide was evolved. The AcOH was distilled off. GLC analysis of the residue showed it to contain 9-bromoanthracene (6%), 9-chloroanthracene (8%), 9,10-dibromoanthracene (3%), 9-bromo-10-chloroanthracene (81%) and 9,10-dichloroanthracene (traces).

Reactions with iodobenzene dichloride. To a refluxing soln of the 9-halogenoanthracene (2·5 mmole) in AcOH, CCl_4, or chlorobenzene (100 ml), was added iodobenzene dichloride[11] (1·375 g, 5 mmole) and in some experiments (Tables 1 and 2) dibenzoyl peroxide (0·006 g). The mixture was heated under reflux for 1 hr, and then worked up in the usual way.

Reactions with phosphorus pentahalide. Phosphorus pentahalide (5 mmole) was added to a stirred soln of 9-halogenoanthracene (2·5 mmole) in benzene or CCl_4 (100 ml) and the mixture heated under reflux or 1 hr. The solvent was distilled off and the residue analysed by GLC.

Reactions with N-*bromosuccinimide.* 9-Halogenoanthracene (2·5 mmole), N-bromosuccinimide (2·5 mmole), dibenzoyl peroxide (0·012 g) in CCl_4 (100 ml) was heated under reflux for 1 hr. The cooled mixture was filtered and the filtrate evaporated to dryness and the residue analysed by GLC.

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REFERENCES

[1] D. C. Nonhebel, *J. Chem. Soc.* 1216 (1963) is to be considered Part I of a series.

[2] J. C. Ware and E. E. Borchert, *J. Org. Chem.* **26**, 2263, 2267 (1961).

[3] P. Kovacic and K. E. Davies, *J. Am. Chem. Soc.* **86**, 427 (1964).

[4] Cf. E. Clar, *Polycyclic Hydrocarbons* Vol. I, p. 292. Academic Press, London (1964).

[5] E. de B. Barnett and J. W. Cook, *J. Chem. Soc.* **125**, 1084 (1924).

[6] E. de B. Barnett and M. A. Matthews, *Rec. Trav. Chim.* **43**, 530 (1924).

[7] J. K. Kochi and A. Bemis, *J. Am. Chem. Soc.* **90**, 4038 (1968).

[8] J. K. Kochi and R. B. Subramanian, *Ibid.* **87**, 1508 (1965).

[9] W. I. Bengough, unpublished studies.

[10] D. C. Nonhebel, *Organic Syntheses*, Vol. 43, p. 27. Wiley, New York (1963).

[11] H. J. Lucas and E. R. Kennedy *Organic Syntheses* Col. Vol. III, p. 482, Wiley, New York (1955).