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Reactions of Copper(II) Halides with Organic Compounds. Part VI.¹ Reactions of 9-Alkyl- and 9-Aryl-10-halogenoanthracenes

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9-Alkyl(and aryl)-10-halogenoanthracenes react with copper(II) halides to give products in which the alkyl (or aryl) group or the halogen is replaced by halogen from the copper(II) halide. When the alkyl group is methyl, the 9-halogeno-10-halogenomethylanthracene is also obtained. Products arising from halogen exchange between the copper(II) halide and the halogenomethyl group were also obtained. These results are interpreted by a radical mechanism.

COPPER(II) halides effect the halogenation in the 10position of 9-alkyl-, 9-aryl-, and 9-halogeno-anthracenes under heterogeneous conditions.^{2,3} The reactions of 9,10-dialkylanthracenes with copper(II) halides are more complex and lead principally to products in which one or other of the alkyl groups has been replaced by halogen. If one of the alkyl groups was methyl then the 9-alkyl-10-halogenomethylanthracene was also formed via the (10-alkyl-9-anthryl)methyl radical (1). No product was ever formed as a result of hydrogen abstraction from an ethyl or benzyl group indicating that the intermediate secondary radicals (2; R = Me or Ph) which could have arisen from attack on these groups, are less stable than the alternative primary radicals (1). The object of the present work was to extend this study to reactions of 9-alkyl- and 9-aryl-10-halogenoanthracenes in which the behaviour of the alkyl or aryl group could be studied

¹ Part V, S. Gibson, A. D. Mosnaim, D. C. Nonhebel, and J. A. Russell, *Tetrahedron*, 1969, **25**, 2047.

without having to consider the possibility of reaction at the 10-position.



RESULTS AND DISCUSSION

The reactions of copper(II) chloride with 9-alkyl-10-chloroanthracenes and 9-chloro-10-phenylanthracene were studied and the products of reaction were analysed by g.l.c. (Table). 9-Chloro-10-methylanthracene (3; X = Cl) afforded 9-chloro-10-chloromethylanthracene

² A. D. Mosnaim, D. C. Nonhebel, and J. A. Russell, *Tetra*hedron, 1969, **25**, 3485.

³ A. D. Mosnaim and D. C. Nonhebel, *Tetrahedron*, 1969, **25**, 1591.

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(5; X = Y = Cl) and 9,10-dichloroanthracene (7; X = Y = Cl). The former resulted from reaction of the copper(II) chloride with the methyl group to give the (10-chloro-9-anthryl)methyl radical (4; X = Cl) which on further reaction with copper(II) chloride gave 9chloro-10-chloromethylanthracene (Scheme). Ligandtransfer of chlorine to the 10-position of 9-chloro-10methylanthracene gave the radical (6; X = Y = Cl)

tion to a small extent with copper(II) chloride to give 9,10-dichloroanthracene. Replacement of a phenyl group by chlorine was also observed in the reaction of 9-benzyl-10-phenylanthracene with copper(II) chloride. These unusual reactions, involving as they do replacement of a phenyl group by chlorine, can be rationalized only by the mechanism postulated above. It is interesting to note that the extent of reaction was

Reactions of copper (II) halides with 9-alkyl(or aryl)-10-halogenoanthracenes 9 10-Disubstituted anthracenes obtained (%)

$\begin{array}{c} {\rm Reactant} \\ \textbf{9-R-10-XC_{14}H_8} \end{array}$		Copper(II) halide	9,10- Di-Br	9,10- Di-Cl	9-R-10-Br	9-R-10-Cl	9-CH ₂ Br-10-Br	9-CH ₂ Cl-10-Br	9-CH ₂ Br-10-Cl	9-CH2Cl-10-Cl
R	х									
Me	Br	CuBr ₂ ^a	4		40		9			
Me	\mathbf{Br}	CuCi ⁵	0	0	31	42	7	20	0	0
Me	C1	CuBr, °	0	0	9	60	21	10	0	0
Me	Cl	CuCl ₂ ^a		3		68				7
\mathbf{Ph}	\mathbf{Br}	CuBr, d	19		64					
\mathbf{Ph}	\mathbf{Br}	CuCl,		0	83	17				
\mathbf{Ph}	Cl	CuBr, e	0		2	79				
\mathbf{Ph}	Cl	CuCl ₂ °		2		94				
PhCH ₂	C1	$CuCl_{2}$		20		80				
Et -	C1	$CuCl_2$		2		98				

^e Unidentified compound having a greater retention time also obtained on g.l.c. ^b Inorganic residue contains bromide as well as chloride. ^c Inorganic residue contains chloride as well as bromide. ^d Six unidentified compounds having greater retention times also obtained on g.l.c. ^e Two unidentified compounds having greater retention times also obtained on g.l.c.

which after further reaction with copper(II) chloride in a second ligand-transfer reaction gave 9,10-dichloroanthracene (Scheme).



In contrast, 9-benzyl-10-chloroanthracene and 9chloro-10-ethylanthracene gave on reaction with copper(II) chloride 9,10-dichloroanthracene as the only product in a ligand-transfer reaction. No product was obtained as a result of attack at the methylene group of the benzyl or ethyl groups. This implies that the secondary radicals (2; R = Ph or Me), which would have been formed in such a reaction, are less stable than the primary radical (4) as a consequence of the steric impossibility of the unpaired electron in the radicals (2; R = Ph or Me) lying in the plane of the anthracene ring.

9-Chloro-10-phenylanthracene also underwent reac-

greater in the reactions of 9-benzyl-10-chloroanthracene and 9-benzyl-10-methylanthracene than in those of 9-chloro-10-ethylanthracene and 9-ethyl-10-methylanthracene suggesting that in some way a benzyl group facilitates these reactions.

Similar results were obtained from a study of the reactions of 9-bromo-10-methylanthracene and 9-bromo-10-phenylanthracene with copper(II) bromide. The extent of reaction after a given time was greater than that observed in the reactions with copper(II) chloride consistent with the Cu-Br bond being weaker than the Cu-Cl bond.

However, treatment of 9-bromo-10-phenylanthracene with bromine in acetic acid produced no 9,10-dibromoanthracene. This is consistent with the proposed mechanism since bromine in acetic acid would be more likely to be a source of Br⁺ than Br[•].

The reaction of 9-chloro-10-methylanthracene with copper(II) bromide and 9-bromo-10-methylanthracene with copper(II) chloride were also examined to see if any halogen exchange occurred. Amongst other products, the reactions gave 9-bromo-10-methylanthracene and 9-chloro-10-methylanthracene respectively consistent with reaction of the copper(II) halide with the 9-halogeno-10-methylanthracene to give the radical (8). Reaction of this radical with copper(II) bromide or chloride could afford either 9-bromo-10-methylanthracene or 9-chloro-10-methylanthracene. More halogen exchange was observed in the reaction of 9-bromo-10chloride than methylanthracene with copper(II) 9-chloro-10-methylanthracene in that between copper(II) bromide (see Table) consistent and with the greater strength of the carbon-chlorine bond than the carbon-bromine bond. Hence.

the intermediate radical (8) would be more likely to react with copper(II) halide to give 9-chloro-10-methylanthracene than to give 9-bromo-10-methylanthracene. Similarly, it was found that 9-bromo-10-phenylanthracene underwent reaction to a much greater extent



with copper(II) chloride than did 9-chloro-10-phenylanthracene with copper(II) bromide.

The reaction of 9-chloro-10-methylanthracene with copper(II) bromide also gave 9-bromomethyl-10-chloroanthracene (5; X = Cl, Y = Br) and 9-bromo-10bromomethylanthracene (5; X = Y = Br), the formation of which must have arisen from reaction of 9bromo-10-methylanthracene and/or 9-bromomethyl-10chloroanthracene with copper(II) bromide. 9-Bromo-10-methylanthracene also underwent reaction with copper(II) chloride at the methyl group to give 9-bromo-10-chloromethylanthracene. This reaction also gave 9-bromo-10-bromomethylanthracene, the formation of which can be explained only by reaction of 9-bromo-10-methylanthracene and/or 9-bromo-10-chloromethylanthracene with copper(II) bromide chloride. This latter is formed as a result of halogen exchange between 9-bromo-10-methylanthracene and copper(II) chloride.

The feasibility of halogen exchange occurring between a halogenomethyl group and copper(II) halide was demonstrated from a study of the reactions of 9-halogenomethylanthracenes with copper(II) halides. 9-Bromomethylanthracene with copper(II) bromide and 9-chloromethylanthracene with copper(II) chloride gave excellent yields of 9-bromo-10-bromomethylanthracene and 9-chloro-10-chloromethylanthracene respectively. The reactions proceeded by a ligandtransfer reaction via the radical (9), further reaction of which gave the product. It was not possible to separate cleanly the mixtures of products obtained from the reaction of 9-bromomethylanthracene with copper(II) chloride or of 9-chloromethylanthracene with copper(II) bromide. Analysis of the inorganic residue showed the presence, in both cases, of bromide and chloride indicating that halogen exchange between the halogenomethyl group and copper(II) halide must have occurred. This is visualized as probably taking place through a fourcentre transition state (10) analogous to that proposed for the reaction between 9-alkoxyanthracenes and copper(II) halides.4

Bacon and Hill proposed a similar mechanism to the above to explain the halogen interchange observed between 1-bromonaphthalene and copper(I) chloride in

⁴ D. C. Nonhebel and J. A. Russell, Tetrahedron, 1969, 25, 3494.

polar organic solvents.⁵ That copper(II) rather than copper(I) chloride was the active species in the halogen-exchange reactions in chlorobenzene was demonstrated



from a study of the reaction of 9-bromo-10-bromomethylanthracene with copper(I) and copper(II) chlorides in this solvent. The reaction with copper(II) chloride afforded 60% of 9-bromo-10-chloromethylanthracene whilst that with copper(I) chloride gave only 6% of this compound under the same conditions. The reaction of copper(I) chloride with 9-bromo-10-phenylanthracene was also studied. No halogen exchange in the nucleus occurred demonstrating that the halogenexchange reactions in chlorobenzene involve the copper(II) halide.

Some of the reactions investigated gave products which had greater retention times on g.l.c. These were not investigated further but probably arise as a result of further halogenation in the side rings of the anthracene molecule.

9-Halogeno-10-halogenomethylanthracenes were prepared by halogenomethylation of the appropriate 9-halogenoanthracene. The mass spectra of 9-bromo-10-chloromethylanthracene and 9-bromomethyl-10chloroanthracene showed the absence of peaks due to 9-chloro-10-chloromethylanthracene and 9-bromo-10-bromomethylanthracene respectively, which could conceivably have arisen as a result of halogen interchange during their preparation. Loss of the benzylic halogen occurred more readily than loss of the nuclear halogen on electron impact.

Chromatography on alumina of 9-chloro-10-chloromethylanthracenes resulted in the formation of bis (10-chloro-9-anthryl)methyl ethers (11; X = Y = Cl).



The structure was assigned to this on mass spectral evidence. Similarly 9-bromo-10-bromomethylanthra-

⁵ R. G. R. Bacon and H. A. O. Hill, J. Chem. Soc., 1964, 1097; *Quart. Rev.*, 1965, **19**, 95.

cene gave, on chromatography, bis-(10-bromo-9-anthryl)methyl ether (11; X = Y = Br). The formation of these ethers presumably arises as a result of hydrolysis of some of the halogenomethyl compound to the corresponding hydroxymethyl compound followed by reaction between these to give the ether.

The mass spectrum of the product obtained after chromatography of 9-bromo-10-chloromethylanthracene showed peaks attributable to bis-(10-bromo-9-anthryl)methyl ether but, in addition, there were strong peaks due to the ions $C_{30}H_{20}BrClO$ at m/e 510 and 512 together with peaks at m/e 225 (C₁₅H₁₀Cl) and 241 $(C_{11}H_{10}ClO)$. These data can be explained on the basis that the sample contained in addition to bis-(10-bromo-9anthryl)methyl ether some (10-bromo-9-anthryl)methyl-(10-chloro-9-anthryl) methyl ether (10; X = Br, Y = Cl). From the intensities of the various peaks and assuming similar volatilities for both ethers, it would appear that these compounds are present in comparable amounts. The formation of the mixed ether must presumably involve, at some stage nucleophilic replacement of bromide by chloride probably facilitated by the presence of the alumina. Chloride would be generated both as a result of hydrolysis of the chloromethyl group and also in reaction of the hydroxymethyl compound with the chloromethyl compound in the formation of the ether. No evidence for the presence of any bis-(10-chloro-9anthryl)methyl ether was obtained. Some of this might have been expected had substitution taken place in the ether. Thus, it seems that the nucleophilic substitution occurred either in 9-bromo-10-hydroxymethylanthracene or in 9-bromo-10-chloromethylanthracene. The product obtained as a result of chromatography of 9-bromomethyl-10-chloroanthracene as judged from its mass spectrum consisted predominantly of bis-(10-chloro-9-anthryl)methyl (10-chloro-9-anthryl)methyl ether. The very much smaller amount of halogen interchange is consistent with the C-Cl bond being stronger than the C-Br bond.

EXPERIMENTAL

Light petroleum refers to the fraction of b.p. 60-80°. M.p.s were taken on a Kofler hot stage and are uncorrected. Chromatographies were carried out with Spence Grade H alumina. G.l.c. analysis was carried out as described in previous papers.³ Copper(II) bromide and copper(II) chloride were dried and ground as previously described. Mass spectra were determined on an A.E.I. MS9 mass spectrometer.

Materials.--9-Alkyl-10-halogenoanthracenes and 9-halogeno-10-phenylanthracenes were prepared as described previously by halogenation of the 9-substituted anthracene with the appropriate copper(11) halide.² 9-Bromomethylanthracene and 9-chloromethylanthracene were prepared by reaction of 9-hydroxymethylanthracene with phosphorus tribromide 6 and thionyl chloride respectively.7 9-Bromomethyl-10-phenylanthracene and 9-chloromethyl-

⁶ J. Romo and A. Romo de Vivar, Bol. Inst. Quim. Univ. nac. auton. Mexico, 1956, **3**, 15. ⁷ F. H. C. Stewart, Austral. J. Chem., 1960, **13**, 478.

10-phenylanthracene were obtained by halogenomethylation of 9-phenylanthracene. All these compounds were purified until analysis by g.l.c. showed only one peak.

9-Bromo-10-bromomethylanthracene. -- Bromomethylation of 9-bromoanthracene was carried out as previously described for the bromomethylation of 9-alkylanthracenes.¹ 9-Bromo-10-bromomethylanthracene crystallized as yellow needles, from benzene-light petroleum (43%), m.p. 198-200° (lit.,⁸ 200°)

A portion of the product was chromatographed on alumina. Elution with benzene gave bis-(10-bromo-9anthryl)methyl ether, which crystallized as yellow needles from benzene (28%), m.p. 260-263° (Found: C, 64.5; H, 3.7; Br, 28.7%. C₃₀H₂₀Br₂O requires C, 64.8; H, 3.6; Br, 28.7%); mass spectrum: M^+ 555.98622 (35%) (C₃₀- ${\rm H_{20}}^{79}{\rm Br}^{81}{\rm BrO}$ requires 555.98622); prominent ions at m/e $\begin{array}{l} & \mathbf{120} \\ 557\cdot98407 \quad (20\%, \ \mathbf{C_{30}H_{20}^{81}Br_2O^+}), \ 553\cdot98788 \quad (19\%, \ \mathbf{C_{30^-}} \\ \mathbf{H_{20}^{79}Br_2O^+}), \ 287 \quad (12\%), \ 285\cdot99834 \quad (9\%, \ \mathbf{C_{15}H_{11}^{79}BrO^+}), \end{array}$ 285.98119 (18%, $C_{15}H_{9}^{81}BrO^{+}$), 284.99044 (12%, $C_{15}H_{10}^{-}$ ⁷⁹BrO⁺), 284.97355 (12%, $C_{15}H_{8}^{81}BrO^{+}$), 273 (14%), 272.00175 $C_{15}H_{11}^{81}Br^+$), 270.99437 (100%, $C_{15}H_{10}^{81}Br^+$), (87%, 270.00337 (92%, $C_{15}H_{11}^{79}Br^+$), 268.99652 (92%, $C_{15}H_{10}^{-1}$ ⁷⁹Br⁺), 206 (29%), 191 (32%), and 189 (62%); metastable peak at 242.1 (556 -> 269).

9-Bromo-10-chloromethylanthracene.--This compound was similarly obtained by chloromethylation of 9-bromoanthracene, and crystallized as yellow needles from light petroleum (31%), m.p. 198-200° (lit.,⁹ 198-199.5°); mass spectrum: M^+ 303.96531 (22%) (C₁₅H₁₀⁷⁹Br³⁵Cl requires 303.96545; prominent ions at m/e 306 (28%), 272 (18%), 271 (99%), 270 (19%), 268.99652 (100%, $C_{15}H_{10}^{79}Br^+$), 227 (18%), 226 (10%), 225.04714 (56%), $C_{15}H_{10}^{35}Cl^+$, 190(21%), and 189.07051 (91%, $C_{15}H_{9}^+$); metastable peaks at 238.0 (304 -> 269), 158.8 (225 -> 189), and 132.7 (269 --- 189).

A light petroleum solution of 9-bromo-10-chloromethylanthracene was chromatographed on alumina. Elution with benzene gave a yellow solid which crystallized from benzene as yellow needles, m.p. 250-257°; mass spectrum: M⁺ 555.98838 (13%), (C₃₀H₂₀⁷¹Br⁸¹BrO requires 555.98799) and 510.04031 (10%) (C₃₀H₂₀⁷⁹Br³⁵ClO requires 510.03865); prominent peaks at m/e 553.98838 (6%, C₃₀H₂₀⁷⁹Br₂O), 512 (12%) 287 (10%), 286 (18%), 285 (19%), 284 (11%),273 (11%), 272 (85%), 271 (97%), 270 (85%), 269 (91%), 241 (13%), 240 (3%), 239 (12%), 228 (23%), 227 (35%), 226 (79%), 225 (82%), 206 (36%), 191 (57%), and 189 (100%). This was consistent with the product being a mixture of bis-(10-bromo-9-anthryl)methyl ether and (10-bromo-9anthryl)methyl (10-chloro-9-anthryl)methyl ether.

9-Bromomethyl-10-chloroanthracene. — Bromomethylation of 9-chloroanthracene by the standard procedure gave 9-bromomethyl-10-chloranthacene as yellow needles from light petroleum (32%), m.p. 170-176° (Found: C, 58.3; H, 3.5. C₁₅H₁₀BrCl requires C, 58.9; H, 3.3%); mass spectrum: M^+ 303.96425 (6%) (C₁₅H₁₀⁷⁹Br³⁵Cl requires 303.96545); prominent peaks at m/e 306 (7%), 270.99411 $(3\%, C_{15}H_{10}^{81}Br^{+}), 268.99652 (3\%, C_{15}H_{10}^{79}Br^{+}), 228 (7\%),$ 227 (35%), 226 (22%), 225.04675 (100%, $C_{15}H_{10}^{35}Cl$), and 189.07015 (37%, and $C_{15}H_9^+$); metastable peaks at 166.5 and (304 -> 225), and 158.8 (225 -> 189).

A light petroleum solution of this was chromatographed

⁸ E. de B. Barnett and M. A. Matthews, Chem. Ber., 1926, 59, 1429. ⁹ D. E. Applequist, M. A. Lintner, and R. Searle, J. Org. Chem.,

1968, 33, 254.

on alumina. Elution with benzene gave a yellow solid, which crystallized from benzene-light petroleum as yellow needles, m.p. 262—265°; mass spectrum: M^+ 466·08900 (14%) ($C_{30}H_{20}^{35}Cl_2O$ requires 466·08912) and M^+ 510·04018 (0·5%) ($C_{30}H_{20}^{79}Br^{35}ClO$ requires 510·03865); prominent peaks at m/e 468 (10%), 242 (14%), 241 (16%), 240·03452 (25%, $C_{15}H_{9}^{35}ClO^+$), 239 (18%), 228 (28%), 227 (43%), 226·05491 (83%, $C_{15}H_{11}^{35}Cl^+$), 225·04714 (100%, $C_{15} H_{10}^{35}Cl^+$), 206 (15%), 191 (23%), and 189 (42%). This was consistent with the product being predominantly bis-(10-chloro-9-anthryl)methyl ether with a little (10-bromo-9-anthryl)methyl (10-chloro-9-anthryl)methyl ether.

9-Chloro-10-chloromethylanthracene.— Chloromethylation of 9-chloroanthracene gave 9-chloro-10-chloromethylanthracene which crystallized as yellow needles from light petroleum (10%), m.p. 159—165° (Found: C, 69.0; H, 4.0. $C_{15}H_{10}Cl_2$ requires C, 69.0; H, 3.9%).

Chromatography on alumina of 9-chloro-10-chloromethylanthracene and elution with benzene gave bis-(10-chloro-9-anthryl)methyl ether as yellow needles from benzene (31%), m.p. 261-270° (Found: C, 77·7; H, 4·3; Cl, 14·7. $C_{30}H_{20}Cl_2O$ requires C, 77·1; H, 4·3; Cl, 15·1%); mass spectrum: M^+ 466·08818 (14%) ($C_{30}H_{20}^{35}Cl_2O$ requires 466·08912); prominent peaks at m/e 468 (10%), 242 (16%), 241 (16%), 240 (31%), 239 (20%), 228 (33%), 227 (40%), 226 (100%), 225 (82%), 206 (16%), 191 (27%), and 189 (42%).

Reactions of 9-Alkyl(or Aryl)-10-halogenoanthracenes with Copper(II) Halides.—A stirred mixture of the 9-alkyl-(or aryl)-10-halogenoanthracene (2.5 mmoles) and copper(II) halide (5 mmoles) in chlorobenzene (100 ml.) was heated under reflux for 23 hr. The mixture was filtered and the filtrate was evaporated to dryness. The residue was analysed by g.l.c. (see Table).

The residue from the reaction of 9-bromo-10-phenylanthracene was also chromatographed on alumina. Elution with light petroleum gave 9-bromo-10-phenylanthracene (0.36 g., 43%) followed by 9,10-dibromoanthracene (0.08 g., 10%), m.p. and mixed m.p. 226°.

Reaction of 9-Bromo-10-phenylanthracene with Bromine. Bromine (0.4 g., 2.5 mmoles) in glacial acetic acid (20 ml.) was added dropwise during 30 min. to a stirred solution of 9-bromo-10-phenylanthracene (0.8362 g., 2.5 mmoles) in acetic acid (80 ml.). Stirring was continued for a further 30 min. The solution was then diluted with an excess of carbon tetrachloride, washed successively with sodium thiosulphate solution, sodium hydrogen carbonate solution (several times), and water before being dried (Na₂SO₄). The residue, after evaporation of the solvent, was analysed by g.l.c. and was shown to contain only 9-bromo-10-phenylanthracene.

Reaction of 9-Bromomethylanthracene with Copper(II) Bromide.—A stirred mixture of 9-bromomethylanthracene (0·3388 g., 1·25 mmoles) and copper(II) bromide (0·5586 g., 2·5 mmoles) in chlorobenzene (100 ml.) was heated under reflux for 23 hr. The organic product was crystallized from benzene-light petroleum to give 9-bromo-10-bromomethlyanthracene as yellow needles (0·3624 g., 83%), m.p. and mixed m.p. 198—200°.

Reaction of 9-Chloromethylanthracene with Copper(II) Chloride.—A stirred mixture of 9-chloromethylanthracene (0·2831 g., 1·25 mmoles) and copper(II) chloride (0·3361 g., 2·5 mmoles) in chlorobenzene (100 ml.) was heated under reflux for 23 hr. The organic product was crystallized from benzene-light petroleum to give yellow needles of 9-chloro-10-chloromethylanthracene (0·286 g., 87%), m.p. and mixed m.p. 159—165°.

Reactions of 9-Bromomethylanthracene with Copper(II) Chloride and of 9-Chloromethylanthracene with Copper(II) Bromide.—A stirred mixture of 9-halogenomethylanthracene (1.25 mmoles) and copper(II) halide (2.5 mmoles) in chlorobenzene (100 ml.) was heated under reflux for 23 hr. The inorganic residue from both reactions was shown to contain both bromide and chloride.

Reactions of 9-Bromo-10-bromomethylanthracene with Copper(II) Chloride.—A stirred mixture of 9-bromo-10-bromomethylanthracene (0.117 g., 0.33 mmole) and copper(II) chloride (0.0888 g., 0.66 mole) in chlorobenzene (100 ml.) was heated under reflux for 23 hr. The crude product was analysed by g.l.c. and shown to contain 9-bromo-10chloromethylanthracene (60%).

Reaction of 9-Bromo-10-Bromomethylanthracene with Copper(1) Chloride.—The reaction was carried out as with copper(11) chloride but with copper(1) chloride (0.066 g., 0.66 mmole). G.l.c. analysis of the crude product showed the presence of 6% of 9-bromo-10-chloromethylanthracene.

Reaction of 9-Bromo-10-phenylanthracene with Copper(I) Chloride.—The reaction was carried out as above but with 9-bromo-10-phenylanthracene (0.111 g., 0.33 mmole). G.l.c. analysis of the crude product showed it contained only 9-bromo-10-phenylanthracene.

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