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REACTIONS OF CUPRIC HALIDES WITH ORGANIC COMPOUNDS—III

9-ALKYL AND 9-ARYLANTHRACENES

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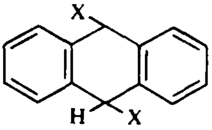
Abstract—9-Alkyl and 9-arylanthracenes have been shown to undergo halogenation with cupric halides to give good yields of their 10-halogenated derivatives. Electron-donating groups in 9-arylanthracenes were shown to increase the rate of reaction. The results are interpreted in terms of a ligand-transfer mechanism.

Cupric bromide and cupric chloride have been shown to halogenate 9-halogenoanthracenes in the 10-position.[1] The reactions have been postulated to proceed by ligand transfer of the halogen of the cupric halide to[4] the 9-halogenoanthracene giving rise to the intermediate radical (**1**). Reaction of this radical with cupric halide then leads to the 9,10-dihalogenoanthracene. The present work involves an extension of this study to 9-alkyl and 9-arylanthracenes. Halogenation of these compounds has been shown to take place in the 10-position using bromine or chlorine in carbon disulphide[2,3] though 9-Me derivatives of some substituted anthracenes afford the corresponding bromomethyl compounds.[4,5] It was thus of interest to study the products of halogenation with cupric halides. The importance of electronic effects on the rates of reaction was also examined using 9-*p*-substituted arylanthracenes.



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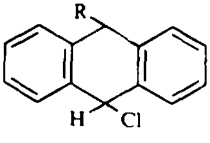
RESULTS AND DISCUSSION

9-Alkyl and 9-arylanthracenes were all synthesized by reaction of anthrone with excess of the appropriate Grignard reagent.[6,7] Table 1 records the yields of compounds not hitherto prepared by this route.

Chlorination of the range of 9-alkyl and 9-arylanthracenes with cupric chloride in refluxing chlorobenzene always proceeded exclusively in the 10-position in yields of better than 95% as estimated by GLC (Table 2). Bromination with cupric bromide similarly afforded the 9-alkyl(or aryl)-10-bromoanthracenes as the sole product except for 9-methylanthracene which gave a small amount of a polymer of dianthrylethane. This material was also isolated in the reactions of 9-methylanthracene with methyl radicals.[8] There was no evidence for the formation of any 9-bromomethylanthracene nor under the reactions conditions used (i.e. two mole of cupric bromide per mole of 9-methylanthracene) was any further reaction to 9-bromo-10-bromomethylanthracene observed. This product was obtained in addition to 9-bromo-10-methylanthracene in the bromination of 9-methylanthracene with bromine in carbon tetrachloride except when this reaction was carried out in very dilute solution. Halogenation with cupric halides was thus demonstrated to be at least as good a method of halogenation of these 9-substituted anthracenes as that involving the free halogen. It was also very free from by-products. Thus 9-allylanthracene gave exclusively 9-allyl-10-chloroanthracene. No addition of chlorine to the double bond was observed.

The rates of reaction of 9-*p*-substituted phenylanthracenes with cupric chloride, as judged from the time taken for the reactions to proceed to completion, indicate that electron-donating groups facilitate the reaction (Table 2). A more accurate assessment of relative reactivity was obtained from competitive experiments in which a mixture of one mole of 9-phenylanthracene and one mole of 9-arylanthracene was allowed to react with two moles (one equivalent) or cupric chloride. The reaction products were analysed by GLC. Table 3 records the relative reactivity of these 9-arylanthracenes. The results again show that electron-donating substitution in the *para* position of the Ph group facilitate the reaction. Chlorination of 9-arylanthracenes with iodobenzene dichloride were also examined and shown to result in chlorination in the 10-position. Iodobenzene dichloride has been shown to be a radical chlorinating agent.[9] The relative reactivities of the 9-arylanthracenes investigated towards chlorination with cupric chloride and with iodobenzene dichloride were strikingly similar suggesting that the two reactions proceed by a similar mechanism.

These results are in complete accord with the postulated ligand-transfer mechanism giving the intermediate radical (2). This then undergoes oxidation with cupric chloride to the carbonium ion (3) which loses a proton to give the 9-aryl-10-chloroanthracene (4). An alternative route from the radical (2) to the product involving cupric chloride acting as a H-atom acceptor can also be envisaged (see sequence). It is not possible to say which of these routes is likely to be preferred. Reaction with iodobenzene dichloride also proceeds by way of the radical (2) but this then gives the 9-aryl-9,10-dichloro-9,10-dihydroanthracene from which the product is obtained by elimination of hydrogen chloride.[1] Both reactions proceed through the same intermediate radical, the formation of which is believed to be the rate-determining step and hence it is reasonable that the relative reactivities of the substrates studies would be similar.



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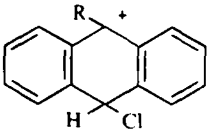

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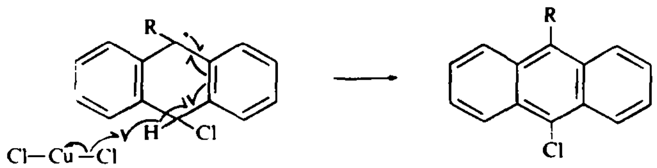

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The observed influence of substituents on the rate is in line with the known electrophilic nature of atomic halogen.[10]

The rates of reaction of 9-alkylanthracenes with both cupric chloride and with iodobenzene dichloride were similarly studied. The results (Table 3) indicate no clear trend for the effect of the alkyl group on the rate of reaction. There is again a close correlation between the relative reactivity towards the two chlorinating agents. It is noteworthy that 9-t-butylanthracene is relatively reactive. The conversion of the radical (**2**) into the product, 9-t-butyl-10-chloroanthracene results in a considerable increase in steric congestion due to the interaction between the t-butyl group and the protons at the 1 and 8 positions on the anthracene nucleus. If the second stage in the reaction i.e. the transformation of the radical (**2**) into the product, were rate-determining, 9-t-butylanthracene would be expected to show considerably diminished reactivity. It is relevant to note that in the preparations of 9-alkylanthracenes by the reaction of alkyl magneisum halides with anthrone which proceeds by the 9-alkyl-9,10-dihydro-9-anthranol that this product is only isolated when the alkyl group is t-butyl. In all other instances the dihydroanthranol undergoes spontaneous dehydration to the 9-alkylanthracene.

9-*o*-Tolylanthracene was much less reactive than 9-*p*-tolylanthracene. This is attributed to steric influences which inhibit the approach of the reagent so reaction may occur. In reaction with cupric chloride the ease of formation of a π-complex between the aromatic system and the cupric halide would be decreased. This has been postulated as a stage prior to the ligand-transfer reaction to account for the fact that only polycyclic aromatic compounds react readily with cupric halides. The methyl signals in the NMR spectra of 9-*o*-tolyl- and 9-*p*-tolyl-anthracene appear at τ 8·21 and 7·62 respectively. The abnormally high position of the methyl signal of *o*-tolylanthracene indicates that the methyl group in this compound lies above the anthracene ring system and is shielded by it. Models of 9-*o*-tolylanthracene indicate that the *o*-tolyl group and the anthracene system cannot be coplanar, rather that they will be perpendicular to each other with the methyl group lying above the anthracene system.

The effect of solvents on the rates of reaction of 9-methyl and 9-phenylanthracene were also examined (Table 4). The results indicate that for aromatic solvents reaction is fastest in benzene and slowest in fluorobenzene with reaction in chlorobenzene

TABLE 1. PREPARATION OF 9-ALKYLANTHRACENES

Compound	m.p.	Lit. m.p.	Yield %
9-Allylanthracene[a]	49–51°	—	43
9-*o*-Tolylanthracene	125°	125–126°[b]	14
9-*p*-Tolylanthracene	145°	145–145·5°[c]	29
9-*p*-Methoxyphenylanthracene	166–167°	168–168·5°[d]	24
9-*p*-Chlorophenylanthracene	179–180°	179–180°[c]	34

[a] Analysis: Found C, 93–6; H, 6·5. $C_{17}H_{14}$ requires: C, 93·5; H, 6·5%.

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TABLE 2. HALOGENATION OF 9-ALKYL AND 9-ARYLANTHRACENES (9-$RC_{14}H_9$)

R	Halogenating Agent	Rxn. time (min)	Product (9-X—10-$RC_{14}H_8$) X	R	M.P.	Lit m.p.	Ref Found (%) C	H	X	Formulae	Calc (%) C	H	X
Me	$CuCl_2$	35	Cl	Me	180–181°	179–180°							
Me	$CuBr_2$	30	Br	Me	170–172	173							
Et	$CuCl_2$	35	Cl	Et	111–113	111							
Pr^n	$CuCl_2$	65	Cl	Pr^n	93–94		79·9	5·9	13·9	$C_{17}H_{15}Cl$	80·1	5·9	13·95
Pr^i	$CuCl_2$	20	Cl	Pr^i	65–66		79·9	5·9		$C_{17}H_{15}Cl$	80·1	5·9	
Bu^t	$CuCl_2$	30	Cl	Bu^t	98–100		80·1	6·5	13·3	$C_{18}H_{17}Cl$	80·4	6·4	13·2
C_6H_{11}*	$CuCl_2$	35	Cl	C_6H_{11}	138–139		81·2	6·45		$C_{20}H_{19}Cl$	81·5	6·5	
$CH_2{=}CH{-}CH_2$	$CuCl_2$	330	Cl	C_3H_5	94		80·4	5·2		$C_{17}H_{13}Cl$	80·8	5·2	
$PhCH_2$	$CuCl_2$	20	Cl	$PhCH_2$	127–128	128–129							
Ph	$CuCl_2$	60	Cl	Ph	173–174	175							
Ph	$PhI{\cdot}Cl_2$	60	Cl	Ph	173–174	175							
Ph	$CuBr_2$	50	Br	Ph	154–155	154–155							
o-MeC_6H_4	$CuCl_2$	100	Cl	o-MeC_6H_4	96		82·85	4·9	11·35	$C_{21}H_{15}Cl$	83·3	5·0	11·7
p-MeC_6H_4	$CuCl_2$	45	Cl	p-MeC_6H_4	199		83·3	5·3	11·8	$C_{21}H_{15}Cl$	83·3	5·0	11·7
p-MeC_6H_4	$PhI{\cdot}Cl_2$	50	Cl	p-MeC_6H_4	199								
p-MeC_6H_4	$CuBr_2$	40	Br	p-MeC_6H_4	196		72·4	4·1		$C_{21}H_{15}Br$	72·6	4·35	
p-$MeOC_6H_4$	$CuCl_2$	45	Cl	p-$MeOC_6H_4$	199–201		78·6	4·8	11·0	$C_{21}H_{15}ClO$	79·1	4·7	11·1
p-ClC_6H_4	$CuCl_2$	60	Cl	p-ClC_6H_4	208–209		74·7	3·9	21·75	$C_{20}H_{12}Cl_2$	74·3	3·7	21·9

* C_6H_{11} = Cyclohexyl.

TABLE 3. RELATIVE RATES OF HALOGENATION OF 9-ALKYL- AND 9-ARYLANTHRACENES (9-$RC_{14}H_9$)

	Halogenating agent		
R	$CuCl_2$	$PhI{\cdot}Cl_2$	$CuBr_2$
Me	5·9	12·8	2·8
Et	2·8	1·6	—
Pr^n	1·4	1·7	—
Pr^i	1·7	1·5	—
Bu^t	5·6	—	—
Cyclohexyl	1·5	1·4	—
$CH_2{=}CH{-}CH_2$	3·9	8·8	—
$PhCH_2$	1·3	2·9	—
Ph	1·0	1·0	1·0
o-MeC_6H_4	0·6	0·7	—
p-MeC_6H_4	1·3	1·2	1·1
p-$MeOC_6H_4$	1·9	1·8	—
p-ClC_6H_4	0·7	0·5	—

TABLE 4. EFFECT OF SOLVENTS ON RATES OF REACTION WITH CUPRIC CHLORIDE

Compound	Solvent	Temp°	Rxn. Time hr	Product (%)
9-Methylanthracene	CCl_4	77°	11	>95
9-Methylanthracene	C_6H_{12}	83	8	>95
9-Methylanthracene	C_6H_6	80	0·67	>95
9-Methylanthracene	C_6H_5Cl	80	0·75	>95
9-Methylanthracene	C_6H_5F	85	16	>95
9-Phenylanthracene	CCl_4	77	16	80
9-Phenylanthracene	C_6H_{12}	83	15	>95
9-Phenylanthracene	C_6H_6	80	12	>95
9-Phenylanthracene	C_6H_5Cl	80	16	85
9-Phenylanthracene	C_6H_5F	85	16	30

TABLE 5. UV SPECTRA OF 9-SUBSTITUTED ANTHRACENES (9-$RC_{14}H_9$)

Substituent	λ_{max}(nm)* in ethanol					
Methyl	253 sh (4·96)	258 (5·21)	333 (3·39)	349 (3·72)	367 (3·94)	387 (3·93)
Ethyl	249 sh (5·00)	255 (5·27)	332 (3·46)	347 (3·74)	365 (3·93)	385 (3·91)
Propyl	249 sh (4·96)	255 (5·26)	332 (3·47)	347 (3·78)	365 (3·98)	386 (3·97)
Isopropyl	249 sh (4·97)	255 (5·25)	333 (3·52)	348 (3·81)	366 (3·98)	385 (3·95)
t-Butyl	250 sh (4·43)	256 (5·12)	338 (3·19)	355 (3·31)	372 (3·46)	390 (3·37)
Cyclohexyl	251 sh (5·09)	255 (5·20)	333 (3·54)	349 (3·81)	366 (3·95)	386 (3·94)
Allyl	252 sh (4·93)	255 (4·99)	333 (3·41)	347 (3·62)	365 (3·76)	385 (3·74)
Benzyl	250 sh (4·73)	256 (4·85)	333 (3·54)	343 (3·83)	367 (4·03)	386 (4·02)
Phenyl	250 sh (4·90)	256 (5·09)	331 (3·44)	347 (3·77)	365 (3·97)	385 (3·94)
o-Tolyl	245 sh (4·86)	254 (5·11)	331 (3·52)	346 (3·84)	364 (4·03)	383 (4·02)
p-Tolyl	247 sh (4·90)	255 (5·12)	331 (3·54)	346 (3·84)	364 (4·00)	383 (3·97)
p-Methoxyphenyl	247 sh (4·98)	255 (5·21)	332 (3·54)	346 (3·83)	364 (4·01)	383 (3·99)
p-Chlorophenyl	247 sh (4·93)	254 (5·13)	331 (3·57)	346 (3·84)	364 (4·02)	383 (4·00)

* log. ε_{max} in parentheses.

TABLE 6. UV SPECTRA OF 9-ALKYL (OR ARYL)-10-HALOGENOANTHRACENES

Alkyl or Aryl group	Halogen	λ_{max} (nm)* in ethanol					
Methyl	Br	252 sh (4·89)	260 (5·09)	343 (3·53)	360 (3·80)	378 (3·98)	399 (3·93)
Methyl	Cl	253 sh (4·86)	260 (5·17)	342 (3·36)	359 (3·71)	378 (3·94)	400 (3·92)
Ethyl	Cl	253 sh (4·90)	258 (5·19)	341 (3·51)	358 (3·81)	377 (4·02)	398 (4·00)
Propyl	Cl	253 sh (4·90)	260 (5·22)	342 (3·53)	358 (3·84)	377 (4·04)	399 (4·02)
Isopropyl	Cl	253 sh (4·84)	259 (4·11)	341 (3·44)	358 (3·71)	376 (3·96)	397 (3·94)
Cyclohexyl	Cl	253 sh (4·91)	259 (5·17)	342 (3·52)	359 (3·84)	378 (4·04)	399 (4·02)
Allyl	Cl	252 sh (4·91)	260 (5·15)	342 (3·51)	358 (3·84)	377 (4·04)	399 (4·01)
Benzyl	Cl	251 sh (4·85)	258 (5·07)	341 (3·52)	358 (3·84)	377 (4·06)	398 (4·05)
Phenyl	Br	—	260 (5·01)	342 (3·52)	358 (3·86)	377 (4·08)	399 (4·05)
Phenyl	Cl	—	260 (5·06)	341 (3·54)	357 (3·89)	377 (4·01)	398 (4·10)
o-Tolyl	Cl	253 sh (4·76)	260 (4·93)	340 (3·45)	357 (3·77)	376 (3·98)	396 (3·96)
p-Tolyl	Cl	250 sh (4·84)	259 (5·08)	342 (3·60)	357 (3·86)	376 (4·05)	397 (4·01)
p-Methoxyphenyl	Cl	253 sh (4·94)	261 (5·23)	342 (3·53)	358 (3·87)	376 (4·08)	399 (4·06)
p-Chlorophenyl	Cl	250 sh (4·94)	258 (5·14)	340 (3·54)	356 (3·86)	374 (4·07)	395 (4·05)

* log ε_{max} in parentheses.

being slightly slower than that in benzene. Reactions in cyclohexane were slower than in benzene whilst those in carbon tetrachloride were even slower. These results are in line with results obtained earlier with anthracene and cupric chloride.[11] In all cases the 10-halogenated product was obtained. Russell has shown that chlorine atoms are solvated in aromatic solvents.[12, 13] It is possible that the greater reactivity of cupric chloride in benzene as compared to the reaction in carbon tetrachloride is due to the radical (2) being solvated in the former solvent and hence being somewhat more stable. Russell also found that solvation was less in chlorobenzene and fluorobenzene than in benzene which is again consistent with our results.

The UV spectra have been recorded for most of the 9-alkyl and 9-arylanthracene and also for their 10-halogenated derivatives (Table 5). The results show that the spectra of all 9-substituted anthracenes are similar. The spectra of 9,10-disubstituted anthracenes are also similar to each other (Table 6) but different from the spectra of the 9-substituted anthracenes.

EXPERIMENTAL

Light petroleum refers to the fraction b.p. 60–80°. M.p's were taken on a Kofler hot stage and are uncorrected. Chromatographies were carried out using Spence Grade H alumina. UV spectra were recorded on a Perkin–Elmer 137 spectrophotometer and NMR spectra in carbon disulphide on a Perkin–Elmer R10 spectrometer at 40 MHz using TMS as an internal standard. GLC was carried out on carbon disulphide solutions 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°. Cupric bromide and cupric chloride were ground and dried as previously described.[1]

9-Alkyl- and 9-arylanthracenes. Anthrone (1 mole) in warm benzene was added dropwise to a stirred soln of the appropriate Grignard reagent (3 moles) in ether. After the addition was complete, the mixture was refluxed for a further 30 min and the ether was then removed by distillation through a short column. The Grignard complex was decomposed by cautious addition of 6M HCl. The organic layer was washed with water, $NaHCO_3$aq, and water. The dried soln was evaporated, and the residue in light petroleum chromatographed on alumina. The products were crystallized from light petroleum (Table 1).

Reactions of 9-alkyl- and 9-arylanthracenes with cupric halides

A vigorously stirred mixture of 9-alkyl (or aryl)-anthracene (2·5 mmole) and cupric halide (5 mmole) in chlorobenzene (100 ml) was heated under reflux until the evolution of hydrogen halide ceased. The reaction mixture was filtered and the filtrate evaporated. The residue was analysed by GLC. It was then purified by chromatography on alumina eluting with light petroleum. The 9-alkyl (or aryl)-10-chloroanthrancene was finally crystallized from light petroleum (Table 2).

In the reaction between 9-methylanthracene and cupric bromide continued elution with benzene gave a white crystalline compound, m.p. 310–312°, which was shown to be the polymer of 1,2-di-9'-anthrylethane.[8]

Competitive reactions of 9-alkyl(or 9-aryl) anthracenes and 9-phenylanthracene with cupric halides

A vigorously stirred mixture of the 9-alkyl(or aryl) anthracene (1·25 mmole), 9-phenylanthracene (1·25 mmole), and cupric halide (2·5 mmole) in chlorobenzene (100 ml) was refluxed until the evolution of hydrogen halide ceased. The reaction was worked up as above and the residue analysed by GLC.

Reactions with iodobenzene dichloride

A mixture of 9-phenylanthracene (or 9-*p*-tolylanthracene) (2·5 mmole) and iodobenzene dichloride (2·5 mmole) in chlorobenzene (100 ml) was refluxed until evolution of HCl ceased. The solvent was distilled off, and a trace of the residue was analysed by GLC. The remainder of the residue in light petroleum was chromatographed on alumina to give the 9-aryl-10-chloroanthracene.

Competitive reactions were carried out as above using 9-phenylanthracene (1·25 mmole), 9-alkyl(or aryl) anthracene (1·25 mmole), and iodobenzene dichloride (1·25 mmole) in chlorobenzene (50 ml). The product was analysed by GLC.

Reactions of 9-methyl- and of 9-phenylanthracene with cupric chloride in different solvents

A vigorously stirred mixture of 9-methyl(or phenyl) anthracene (1·25 mmole) and cupric chloride (2·5 mmole) in CCl_4, cyclohexane, benzene, or fluorobenzene (50 ml) was heated under reflux until reaction was complete except for very slow reactions (Table 4). A similar reaction in chlorobenzene was carried out maintaining the temp at 80°. The reaction mixture was worked up as described before and the product analysed by GLC.

Reaction of 9-methylanthracene with N-*bromosuccinimide*

To a stirred soln of 9-methylanthracene (0·48 g, 2·5 mmole) in CCl_4 (100 ml), were added N-bromosuccinimide (0·445 g, 2·5 mmole) and dibenzoyl peroxide (0·055 g, 0·25 mmole). The mixture was refluxed for 1 hr and then allowed to cool. Succinimide was filtered off and the filtrate evaporated. The product was shown by GLC analysis to contain 9-bromo-10-methyl-anthracene (44%) together with unreacted 9-methylanthracene.

Bromination of 9-methylanthracene with bromine in carbon tetrachloride

(a) A soln of Br_2 (0·05 g, 0·3125 mmole) in CCl_4 (20 ml) was added dropwise during 2 hr to a soln of 9-methylanthracene (0·0597 g, 0·3125 mmole) in CCl_4 (80 ml) at room temp. The mixture was stirred for a further 2 hr. The soln was then washed successively with water, $Na_2S_2O_3$aq, and water. The dried soln was evaporated to give 9-bromo-10-methylanthracene which crystallized from light petroleum as yellow needles, m.p. 170–172°. GLC analysis of the crude product showed the absence of any 9-bromo-10-bromomethylanthracene.

(b) Br_2 (0·05 g, 0·3125 mmole) in CCl_4 (5 ml) was added to a soln of 9-methylanthracene (0·0597 g, 0·3125 mmole) in CCl_4 (20 ml). The mixture was worked up as before. GLC analysis of the crude product showed it contained 9-bromo-10-methylanthracene (83%), 9-bromo-10-bromomethylanthracene (9%), and unreacted 9-methylanthracene (8%).

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