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REACTIONS OF CUPRIC HALIDES WITH ORGANIC COMPOUNDS—IV

REACTIONS OF 9-ALKOXY- AND 9-ACYLOXYANTHRACENES

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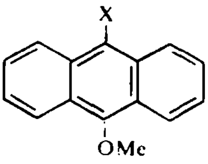
Abstract—9-Alkoxy and 9-acyloxyanthracenes react with cupric bromide and with cupric chloride to give 9-alkoxy (or acyloxy) 10-halogenoanthracenes and/or bianthron-9-yl. The formation of the former product proceeds by ligand transfer of halogen of the cupric halide whilst bianthron-9-yl results from the dimerization of 9-anthryloxy radicals. These are formed in a 4-centre transition state between the substituted anthracene and the cupric halide. The ratio of the two products and the relative rates of reaction are interpreted in terms of the above processes. The reaction of 9-methylthioanthracene with cupric halides was also studied.

CUPRIC bromide and cupric chloride effect halogenation of anthracene in the 9-position,[2] and 9-halogeno-[3], 9-alkyl,[1] and 9-arylanthracenes[1] in the 10-position under heterogeneous conditions in carbon tetrachloride benzene, or chlorobenzene as solvent. The reactions were shown to be basically homolytic in character. Electron-donating substitutents were shown to increase the rate of reaction somewhat. The present work extends the study of reactions of cupric halides with 9-substituted anthracenes to 9-alkoxy- and 9-acyloxyanthracenes to determine the effect of the substituent on the reaction.

9-Methoxyanthracene on reaction with cupric bromide and with cupric chloride gave in addition to the expected 9-halogeno-10-methoxyanthracene (**1**), bianthron-9-yl (**2**) as the principal product. The formation of the halogenated product is assumed to take place in the same way as postulated for the halogenation of other 9-substituted anthracenes, i.e. by ligand transfer of a halogen atom from the cupric halide to give



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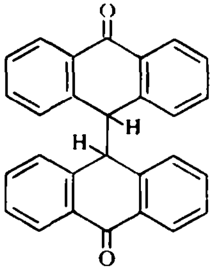

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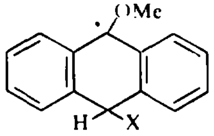
the intermediate radical (**3**).[1,3] Attack occurs at the 10-position on steric grounds. As expected from the previous studies, the effect of the methoxyl group was to increase



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the rate of reaction so much so that the reaction with cupric chloride was found to go to completion at room temperature within 24 hr.

A detailed study of this reaction was made under various conditions using different solvents, the results of which are given in Table 1. It can be seen that at lower temperatures halogenation in the 10-position occurs to a greater extent than at higher temperatures in the same solvent. Cupric bromide affords less of the halogenated product than cupric chloride under the same conditions. The nature of the solvent has an appreciable effect on the ratio of the two products obtained. Reactions in halogenated solvents give more of the 9-halogeno-10-methoxyanthracene. The reason for this is not clear.

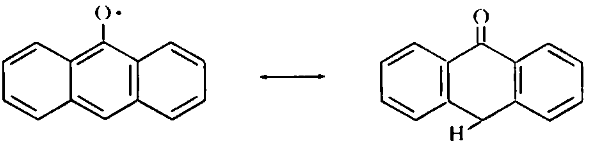
TABLE 1. REACTIONS OF 9-METHOXYANTHRACENE WITH CUPRIC BROMIDE AND CUPRIC CHLORIDE

				Products %		
Cupric halide	Solvent	Reaction conditions	Time hr.	9-MeOA	9-X-10-MeOA	Bianthron-9-yl
CuBr$_2$	CCl$_4$	R.T.*	2·4	1	13	73
CuBr$_2$	CCl$_4$	Reflux	0·5	7	3	83
CuCl$_2$	CCl$_4$	R.T.	7·5	46	10·5	42
CuCl$_2$	CCl$_4$	R.T.	24	3	25	70
CuCl$_2$	CCl$_4$	Reflux	1·5	5	15	75
CuCl$_2$	PhH	R.T.	24	7	18	72
CuCl$_2$	PhH	Reflux	0·75	11	11	76
CuCl$_2$	PhH	Reflux (with light)	0·75	8	12	76
CuCl$_2$	C$_6$H$_{12}$	R.T.	8·5	8	8	84
CuCl$_2$	Pet.	R.T.	7·5	14	8	75
CuCl$_2$	PhMe	R.T.	24	—	7	87
CuCl$_2$	PhCl	R.T.	24	—	34	64
CuCl$_2$	CH$_2$Cl·CH$_2$Cl	R.T.	6·5	27	28	43

* R.T. = Room Temperature.

9-Methoxyanthracene is readily dealkylated by acids to anthrone.[4] It was conceivable that the hydrogen chloride produced in the reaction could have resulted in the formation of anthrone which in the presence of cupric halide could have afforded bianthron-9-yl. That this was not so, was demonstrated by passing hydrogen chloride into a solution of 9-methoxyanthracene both in the absence of and in the presence of cuprous chloride when no reaction took place.

The formation of bianthron-9-yl is postulated to proceed by dimerization of the mesomeric radical (**4**), the formation of which is visualized to occur *via* a 4-centre transition state (**5**). This latter then breaks down homolytically or heterolytically to



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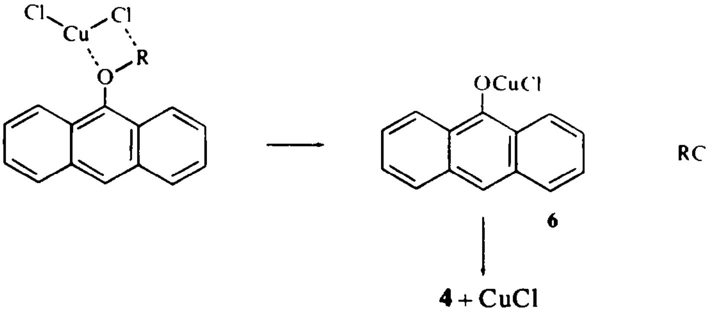
give the chlorocupric salt of 9-anthranol (**6**). This then dissociates homolytically to the radical (**4**) and cuprous chloride. Definitive evidence cannot be adduced in favour of either homolytic or heterolytic breakdown of the 4-centre transition state. Changes in



the nature of the group R would have qualitatively but not quantitatively the same effects on the ease of homolytic and of heterolytic cleavage of the O—R bond. There are precedent for both types of cleavage.[5,6]

Benzyl ethers are much more readily cleaved both homolytically and heterolytically than methyl ethers. Hence it would be expected that 9-benzyloxyanthracene would be more reactive in its reaction with cupric halides than 9-methoxyanthracene and that dealkylation and dimerization would occur rather than substitution in the 10-position. Accordingly 9-benzyloxyanthracene was prepared by reaction of anthrone with benzyl toluene-*p*-sulphonate. It was found to be rather unstable and elementary analysis was not possible. The methylene protons in its NMR spectrum appeared at τ 4·8 (2H). The NMR spectrum of 9-benzyl-10-benzyloxyanthracene has signals due to methylene protons at τ 4·74 and τ 5·02; that at τ 5·02 being ascribed to the methylene protons of the benzyl group by analogy with the methylene proton signal in 9-benzylanthracene (τ 5·02). Reaction of 9-benzyloxyanthracene with cupric chloride proceeded very rapidly giving bianthron-9-yl as the sole product.

In contrast to this, 9-phenoxyanthracene gave on reaction with both cupric bromide and with cupric chloride only 9-halogeno-10-phenoxyanthracene with no bianthron-9-yl. The O—Ph bond is not readily cleaved and the competing reaction of cupric halide involving attack at the 10-position takes precedence. The relative reactivities at the 10-position of 9-methoxy-, 9-benzyloxy-, and 9-phenoxyanthracenes would be expected to be much the same. That 9-benzyloxyanthracene reacts exclusively at the benzyloxy group is due to the ease of cleavage of the O—CH_2Ph bond. 9-Bromo-10-phenoxyanthracene was also obtained by bromination of 9-phenoxyanthracene. 9-

Chloro-10-phenoxyanthracene was identified on the basis of elemental analysis and on the close similarity of its IR spectrum with that of 9-bromo-10-phenoxyanthracene.

Further information on the effect of the group R was obtained from a study of the reactions of 9-acyloxyanthracenes with cupric halides. The ether oxygen would have a slight positive charge due to mesomeric release of electrons from the ether oxygen to the CO group. The postulated 4-centre transition state would thus be formed less readily and consequently 9-acyloxyanthracenes would be expected to react less readily than 9-methoxyanthracene. Reaction at the 10-position would also be expected to proceed somewhat less readily than with 9-methoxyanthracene on the basis that a OMe group is more strongly electron releasing than an OAc group. It was shown that 9-acetoxyanthracene behaved similarly to 9-methoxyanthracene in its reactions with cupric halides giving bianthron-9-yl as the sole product. Consistent with the proposed mechanism 9-acetoxyanthracene was less reactive than 9-methoxyanthracene.

The influence of electronic effects on the rate of reaction and on the products obtained could in principle be studied by successive replacement of hydrogen by chlorine. Unfortunately attempts to prepare 9-chloroacetoxy- and 9-trichloroacetoxyanthracenes failed. It was, however, possible to make a fairly systematic study of electronic effects by examining the reactions of *p*-substituted 9-benzoyloxyanthracenes with cupric chloride. The substituent had no significant effect on the products of reaction: in all cases 2–3% of the 10-halogeno product was obtained. Electron-attracting substituents did significantly increase the rate of reaction. An electron-attracting group in the *para* position of a benzoyl group decreases the degree of polarization of the carbonyl group and hence the mesomeric electron release from the ether oxygen will be less, leading to the easier formation of the 4-centre transition state. The position of the carbonyl peak in the IR spectra of 9-acyloxyanthracenes is in accord with this postulate. The absorption frequency is greatest (1748 cm^{-1}) in 9-*p*-nitrobenzoyloxyanthracene indicating that polarization of the CO group is least in this compound, and lowest (1735 cm^{-1}) in 9-*p*-methylbenzoyloxyanthracene. The lower reactivity of 9-benzoyloxyanthracene as compared with 9-acetoxyanthracene can be similarly explained. In these reactions an approximate estimate of the amount of 9-(*p*-substituted benzoyloxy)-10-chloroanthracene was made from an analysis of the UV spectrum of the mixture of this product with unreacted starting material. Attempts to synthesize these compounds from the 9-aroyloxyanthracene with phosphorus pentachloride or sulphuryl chloride failed. In the reactions of 9-benzoyloxy-, 9-*p*-methylbenzoyloxy- and 9-*p*-chlorobenzoyloxyanthracenes with cupric chloride it was also possible to isolate the appropriate substituted benzoyl chloride from the reaction mixture as its *p*-nitroanilide consistent with the proposed mechanism.

Further information on the mechanism of these reactions was obtained by examining the reactions of 9-methylthioanthracene with cupric halides. Unlike 9-methoxyanthracene the only reaction product with both cupric bromide and cupric chloride was the 9-halogeno-10-methylthioanthracene. Sulphur forms very much weaker complexes than oxygen and hence reaction at the 10-position is much more feasible than reaction a *via* 4-centre transition state. 9-Chloro-10-methylthioanthracene was synthesized from 9-chloro-10-anthracenethiol. 9-Bromo-10-methylthioanthracene was identified by comparison of its IR and NMR spectra with the spectra of the analogous chloro compound and by elemental analysis.

Anthrone was also shown to react readily with both cupric bromide and cupric chloride in carbon tetrachloride to give bianthron-9-yl. Tautomerization of anthrone to anthranol is slow in non-polar solvents even at their b.p.[7] and hence it seemed probable that reaction proceeded by abstraction of a H-atom to give the mesomeric radical (**4**) rather than through 9-anthranol to give first the chlorocupric salt of 9-anthranol (**6**) which would then decompose to give the radical (**4**). Reaction by this route might have been expected by analogy to the ready reaction of β-naphthol with cupric halides under similar conditions.[8] It was also shown that 9-anthranol did not react as readily as anthrone under the same reaction conditions.

EXPERIMENTAL

IR spectra were recorded as Nujol mulls on a Perkin–Elmer 237 grating spectrometer; NMR spectra in $CDCl_3$ on a Perkin-Elmer R10 spectrometer at 40 MHz using TMS as an internal standard. Light petroleum refers to the fraction b.p. 60–80° unless otherwise stated. Chromatographies were carried out using Spence Grade H alumina.

Materials. Cupric bromide and cupric chloride were dried and ground as described previously.[1]

9-Methoxyanthracene,[4] 9-phenoxyanthracene,[9] 9-acetoxyanthracene,[10] 9-benzoyloxyanthracene[19] and 9-methylthioanthracene[11] were prepared by literature procedures and purified by chromatography on alumina eluting with light petroleum.

9-*Benzyloxyanthracene*. To a soln of anthrone (20 g, 0·103 mole) in MeOH (140 ml), were added alternately a few drops of a methanolic soln of benzyl toluene *p*-sulphonate[12] (in all, 50 g in 60 ml) and a few drops of a 30% NaoH aq (40 ml in all). After the addition was complete, the mixture was heated under reflux for 40 min, filtered and a large excess of water was added to the filtrate. The ppt was filtered off, and dissolved in CH_2Cl_2. The CH_2Cl_2 soln was washed with water, and dried (Na_2SO_4). The residue, after evaporation of the CH_2Cl_2, in light petroleum (b.p. 40–60°) was chromatographed on alumina. Elution with light petroleum (b.p. 40–60°) gave pale yellow needles of 9-*benzyloxyanthracene*, m.p. 74–75° (from MeOH).

9-p-*Methylbenzoyloxyanthracene*. Anthrone (10 g) in pyridine (70 ml) was treated with *p*-toluoyl chloride (12 g) and the mixture heated on a steam bath for 15 min. It was then poured into excess cold water. The ppt was dissolved in CH_2Cl_2 and the Ch_2Cl_2 soln washed with water. The dried soln was evaporated and the residue crystallized from benzene–light petroleum as yellow needles of 9-p-*methylbenzoyloxyanthracene*, m.p. 170–172°. (Found: C, 83·9; H, 5·1. $C_{22}H_{16}O_2$ requires: C, 84·6; H, 5·1%), IR 1735 cm^{-1}.

9-p-*Chlorobenzoyloxyanthracene*. This was similarly prepared from anthrone and *p*-chlorobenzoyl-chloride. Crystallization from benzene–light petroleum gave pale yellow needles of 9-p-*chlorobenzoyloxyanthracene*, m.p. 190–192°. (Found: C, 76·4; H, 4·2; Cl, 10·4. $C_{21}H_{13}ClO_2$ requires C, 75·8; H, 3·9; Cl, 10·6%), IR 1743 cm^{-1}.

9-p-*Nitrobenzoyloxyanthracene*. This was similarly prepared from anthrone and *p*-nitrobenzoyl chloride. Crystallization from benzene gave red needles of 9-p-*nitrobenzoyloxyanthracene*, m.p. 219–220°. (Found: C, 73·6; H, 3·9; N, 4·1. $C_{21}H_{13}NO_4$ requires: C, 73·5; H, 3·7; N, 4·1%). IR 1748 cm^{-1}.

Reaction of 9-*methoxyanthracene with cupric bromide in carbon tetrachloride*

(a) A stirred mixture of 9- methoxyanthracene (2g, 9·62 mole) and cupric bromide (2·149 g, 9·62 mmole) in CCl_4 was heated under reflux until evolution of HCl ceased (1 hr). The ppt was filtered off and washed with a little light petroleum (b.p. 40–60°). The filtrate was evaporated to dryness and chromatographed on alumina. 5% Benzene in light petroleum eluted 9-bromo-10-methoxyanthracene which crystallized from light petroleum as yellow needles, m.p. and mixed m.p. 143–144°. Continued elution with 5% benzene in light petroleum gave mixtures of 9-methoxyanthracene and 9-bromo-10-methoxyanthracene. The mixture was analysed by UV absorption spectroscopy. The ppt was washed with hot $CHCl_3$ giving bianthron-9-yl as white needles from benzene, m.p. and mixed m.p. 245–249° dec. The total yields of products were 9-bromo-10-methoxyanthracene (0·0848 g, 3%), 9-methoxyanthracene (0·152 g, 7%), bianthron-9-yl (1·552 g, 83%).

(b) The reaction was carried out at room temp for 24 hr. The products were obtained as above. The total yields were 9-methoxyanthracene (1%), 9-bromo-10-methoxyanthracene (13%), bianthron-9-yl

(73%). 9-Bromo-10-methoxyanthraceme was synthesized by bromination of 9-methoxyanthracene in CCl_4 as yellow needles from EtOH, m.p. 144–145° (lit,[13] 145°).

9-Bromo-10-methoxyanthracene was also obtained by heating under reflux a mixture of 9-methoxyanthracene (1 g, 4·81 mmole), N-bromosuccinimide (0·856 g, 4·81 mmole) and a trace of dibenzoyl peroxide in CCl_4 (50 ml) for 20 min. The mixture was filtered to remove succinimide and the filtrate evaporated to dryness. Crystallization of the residue from light petroleum gave pale yellow needles of 9-bromo-10-methoxyanthracene, m.p. 144–145° (1·3 g, 95%).

Reaction of 9-*methoxyanthracene with cupric bromide in methanol*

A soln of 9-methoxyanthracene (1 g, 4·8 mmole) and cupric bromide (2·15 g, 9·6 mmole) in anhydrous MeOH (80 ml) was heated under reflux in an atmosphere of argon until reaction was complete (15 min). The mixture was filtered and the filtrate diluted with excess water, and then extracted with CH_2Cl_2. The CH_2Cl_2 extracts were dried and evaporated to dryness. The residue in light petroleum was chromatographed on alumina. Elution with 5% benzene in light petroleum gave 9-bromo-10-methoxyanthracene, m.p. 144–145° (0·13 g, 9%). The ppt was washed several times with hot $CHCl_3$. The washings were evaporated to dryness and the residue was fractionally crystallized from benzene–light petroleum giving anthraquinone, m.p. and mixed m.p. 285° (0·365 g, 36%), and bianthron-9-yl, m.p. and mixed m.p. 245–249° dec, (0·326 g, 35%)

Reaction of 9-*Methoxyanthracene with cupric chloride*

A stirred mixture of 9-methoxyanthracene (2 g, 9·6 mmole) and cupric chloride (1·294 g, 9·6 mmole) in solvent (90 ml) was either kept at room temp or heated under reflux (see Table for solvents and times of reaction). The mixture was worked up as in the reaction with cupric bromide. Chromatography on alumina gave 9-chloro-10-methoxyanthracene as yellow needles from light petroleum, m.p. and mixed m.p. 153–154° (Lit,[13] 154°). Later fractions consisted of mixtures of 9-chloro-10-methoxyanthracene with unreached 9-methoxyanthracene. Analysis of the mixtures was made by UV absorption spectroscopy. Bianthron-9-yl was isolated as before by washing the precipitate with $CHCl_3$.

Reaction of 9-*benzyloxyanthracene with cupric chloride*

The reaction of 9-benzyloxyanthracene (0·295 g, 1·04 mmole) with cupric chloride (0·14 g, 1·04 mmole) in refluxing CCl_4 was carried out as above. the time for complete reaction was less than 5 min. The mixture was worked up as for the reactions of 9-methoxyanthracene and gave bianthron-9-yl (0·153 g, 77%) and a trace of unreacted 9-benzyloxyanthracene.

Reaction of 9-*phenoxyanthracene with cupric bromide*

A mixture of 9-phenoxyanthracene (0·5 g, 1·85 mmole), cupric bromide (0·826 g, 3·7 mmole) in CCl_4 (20 ml) was refluxed for 8 hr until no more HCl was evolved. The mixture was filtered and the filtrate evaporated to dryness. The IR spectrum of the crude product showed no CO absorption showing the absence of bianthron-9-yl. The residue in 5% benzene in light petroleum was chromatographed on alumina. Elution with this solvent gave 9-*bromo*-10-*phenoxyanthracene* which crystallized from light petroleum as pale yellow needles, m.p. 139–140° (Found: C, 68·8; H, 3·8. $C_{20}H_{13}BrO$ requires: C, 68·75; H, 3·7%).

9-Bromo-10-phenoxyanthracene was synthesized by the addition of Br_2 (0·0687 g, 0·43 mmole) in CCl_4 (5 ml) to a soln of 9-phenoxyanthracene (0·116 g, 0·43 mmole) in CCl_4 (5 ml). HBr was evolved. The mixture was washed with $Na_2S_2O_3$aq and then with water. The dried soln was evaporated and the product crystallized from light petroleum, m.p. and mixed m.p. 139–140°.

Reactions of 9-*phenoxyanthracene with cupric chloride*

The reaction was carried out as above using cupric chloride (0·497 g, 3·7 mmole). The reaction time was 10·5 hr. The product was chromatographed on alumina. Elution with 5% benzene in light petroleum gave 9-*chloro*-10-*phenoxyanthracene* which crystallized from light petroleum in yellow needles, m.p. 132–133°, (Found: C, 78·9; H, 4·4. $C_{20}H_{13}ClO$ requires: C, 78·75; H, 4·3%).

Reaction of 9-*acetoxyanthracene with cupric bromide*

A mixture of 9-acetoxyanthracene (2 g, 8·4 mmole) and cupric bromide (1·878 g, 8·4 mmole) in CCl_4

(90 ml) was refluxed for 2 hr. The mixure was worked up in the usual way to give 9-acetoxyanthracene (0·102 g, 5%) and bianthron-9-yl (1·28 g, 78%).

Reaction of 9-acetoxyanthracene with cupric chloride

The reaction was carried out as above using cupric chloride (1·129 g, 8·4 mmole) giving bianthron-9-yl (1·34 g, 82%) and unchanged 9-acetoxyanthracene (0·375 g, 16%). The reaction time was 3 hr.

Reaction of 9-benzoylaxyanthracene with cupric bromide

A mixture of 9-benzoyloxyanthracene (2 g, 6·7 mmole) and cupric bromide (1·5 g, 6·7 mmole) in chlorobenzene (90 ml) was refluxed for 30 min. The mixture was filtered and the filtrate evaporated to dryness. The residue was chromatographed on alumina. Elution with 20% benzene in light petroleum gave 9-benzoyloxy-10-bromoanthracene (0·083 g, 3%), which crystallized from light petroleum as yellow needles, m.p. and mixed m.p. 208–210°. Further elution gave unreacted 9-benzoyloxyanthracene (0·25 g, 12%). Bianthron-9-yl (0·966 g, 74%) was obtained from washing the ppt from the mixture with hot $CHCl_3$.

9-Benzoyloxy-10-bromoanthracene was synthesized by the bromination of 9-benzoyloxyanthracene in CCl_4 as yellow needles, m.p. 208–210° (lit.[14] 214–215°).

Reaction of 9-benzoyloxyanthracene and cupric chloride

The reaction was carried out as above using cupric chloride (0·903 g, 6·7 mmole). The reaction time was 3·5 hr. The mixture was worked up as above. Chromatography on alumina gave *9-benzoyloxy-10-chloroanthracene* (0·04 g, 2%) as yellow needles from light petroleum, m.p. 198–200°, (Found: C, 75·6; H, 3·7; CL, 10·6. $C_{21}H_{13}ClO_2$ requires: C, 75·8; H, 3·9; Cl, 10·6%), IR 1730 cm^{-1}. Unreacted 9-benzoyloxyanthracene (0·06 g, 3%) and bianthron-9-yl (1·2 g, 91%) were also isolated.

The reaction was repeated and the mixture filtered as before. The filtrate was carefully fractionally distilled through a short column. The later fractions were treated with *p*-nitroaniline when benz-*p*-nitroanilide was obtained, m.p. and mixed m.p. 198–199°.

Reaction of 9-p-methylbenzoyloxyanthracene with cupric chloride

The reaction was carried out as before using 9-*p*-methylbenzoyloxyanthracene (2·09 g, 6·7 mmole). The reaction time was 3·75 hr. Bianthron-9-yl (1·17 g, 90%) was isolated as before. The filtrate from the mixture was evaporated and the residue analysed by UV absorption spectroscopy from which it was estimated that the yield of 9-chloro-10-*p*-methylbenzoyloxyanthracene was 2–3%. UV spectroscopic analysis also indicated the presence of unreacted 9-*p*-methylbenzoyloxyanthracene (3%).

The reaction was repeated and the filtrate carefully distilled as before. Treatment of the later fractions with *p*-nitroaniline afforded *p*-methylbenz-*p*-nitroanilide, m.p. and mixed m.p. 199–200°.

Reaction of 9-p-chlorobenzoyloxyanthracene with cupric chloride

The reaction was carried out as above using 9-*p*-chlorobenzoyloxyanthracene (2·235 g, 6·7 mmole) The reaction time was 1 hr. The mixture was worked up as before giving bianthron-9-yl (1·19 g, 90%) and approximately 2% of 9-chloro-10-*p*-chlorobenzoyloxyanthraceme and 3% of unreacted 9-*p*-chlorobenzoyloxyanthracene. *p*-Chlorobenz-*p*-nitroanilide, m.p. and mixed m.p. 218–220°, was obtained by treatment of the filtrate with *p*-nitroaniline.

Reaction of 9-p-nitrobenzoyloxyanthracene with cupric chloride

The reaction was carried out as above using 9-*p*-nitrobenzoyloxyanthracene (2·302 g, 6·7 mmole). The reaction time was 40 min. The mixture was worked up in the usual way giving bianthron-9-yl (1·11 g, 86%) and approximately 2% of 9-chloro-10-*p*-nitrobenzoyloxyanthracene and 3% of unreacted 9-*p*-nitrobenzoyloxyanthracene.

Reaction of anthrone with cupric bromide

A mixture of anthrone (9·7 g, 50 mmole) and cupric bromide (11·2 g, 50 mmole) in CCl_4 (100 ml) was refluxed for 4 hr until the evolution of HBr ceased. The mixture was filtered. The ppt was washed well with $CHCl_3$ to dissolve any bianthron-9-yl. The $CHCl_3$ washings were concentrated and the soln allowed to crystallize giving bianthron-9-yl (5·8 g, 61%), m.p. and mixed m.p. 245–249° dec.

Reaction of anthrone with cupric chloride

The reaction was carried out as above using cupric chloride (6·73 g, 50 mmole) The reaction time was 6 hr. Bianthron-9-yl (6·6 g, 69%) was obtained from the mixture.

Reaction of 9-methylthioanthracene with cupric bromide

A mixture of 9-methylthioanthracene (0·5 g, 2·23 mmole) and cupric bromide (1·28 g, 4·46 mmole) in chlorobenzene (20 ml) was refluxed for 1 hr. The mixture was filtered and the filtrate evaporated. The residue was crystallized from light petroleum to give orange yellow needles of 9-bromo-10-methylthioanthracene (0·502 g, 75%), m.p. 136–138°. (Found: C, 60·6; H, 3·8. $C_{15}H_{11}BrS$ requires: C, 59·4; H, 3·6%). NMR τ 7·7 (s; 3H; CH_3—S).

Reaction of 9-methylthioanthracene with cupric chloride

The reaction was carried out as above using cupric chloride (0·60 g, 4·46 mmole). The reaction time was 1·5 hr. The crude product was crystallized several times from light petroleum to afford orange-yellow needles of *9-chloro-10-methylthioanthracene* (0·51 g, 88%), m.p. 125–127° (Found: C, 69·1; H, 4·3; Cl, 13·6; S, 12·25. $C_{15}H_{11}ClS$ requires: C, 69·6; H, 4·25; Cl, 13·75; S, 12·4%); NMR τ 7·65 (s; 3H; CH_3—S).

9-Chloro-10-methylthioanthracene[15] was synthesized by treating 9-chloro-10-anthracenethiol, in 20% NaOH aq with Me_2SO_4, m.p. 125–127°.

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REFERENCES

[1] Part III, A. D. Mosnaim, D. C. Nonhebel and J. A. Russell, *Tetrahedron* submitted for publication.
[2] D. C. Nonhebel, *J. Chem. Soc.* 1216 (1963).
[3] A. D. Mosnaim and D. C. Nonhebel, **25**, 1591 (1969).
[4] E. de B. Barnet, J. W. Cook and M. A. Matthews, *J. Chem. Soc.* **123**, 1994 (1923).
[5] F. M. Elkobaisi and W. J. Hickinbotton, *Ibid.* 1286 (1960).
[6] N. M. Cullinane, R. A. Woolhouse and G. B. Carter, *Ibid.* 2995 (1962).
[7] K. H. Meyer, *Liebigs. Ann.* **379**, 37 (1911).
[8] D. C. Nonhebel, unpublished results.
[9] W. Theilacker, V. Berger-Rose and K. H. Beyer, *Chem. Ber.* **93**, 1658 (1960).
[10] E. de B. Barnett and M. A. Matthews, *J. Chem. Soc.* **123**, 389 (1923).
[11] W. Conway and D. S. Tarbell, *J. Am. Chem. Soc.* **78**, 2228 (1956).
[12] F. L. Hahn and H. Walter, *Dtsch. Chem. Ber.* **54**, 1531 (1921).
[13] K. H. Meyer and H. Schlosser, *Liebigs Ann.* **420**, 126 (1920).
[14] K. Zahn, *Dtsch. Chem. Ber.* **67**, 2063 (1934).
[15] Z. S. Ariyan and L. A. Wiles, *J. Chem. Soc.* 1725 (1962).