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REACTIONS OF COPPER(II) HALIDES WITH AROMATIC COMPOUNDS—XI

REACTIONS OF 9-ALKYL- AND 9-ARYLANTHRACENES IN METHANOL

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Abstract—9-Alkyl and 9-arylanthracenes react with copper(II) bromide in methanol to give 10-alkyl (or aryl)-10-methoxyanthrones as the major product. 9-Methylanthracene additionally affords 10-methoxy-10-methoxymethylanthrone. The formation of all these products can be interpreted in terms of an initial electron-transfer oxidation of the aromatic moiety to the radical cation.

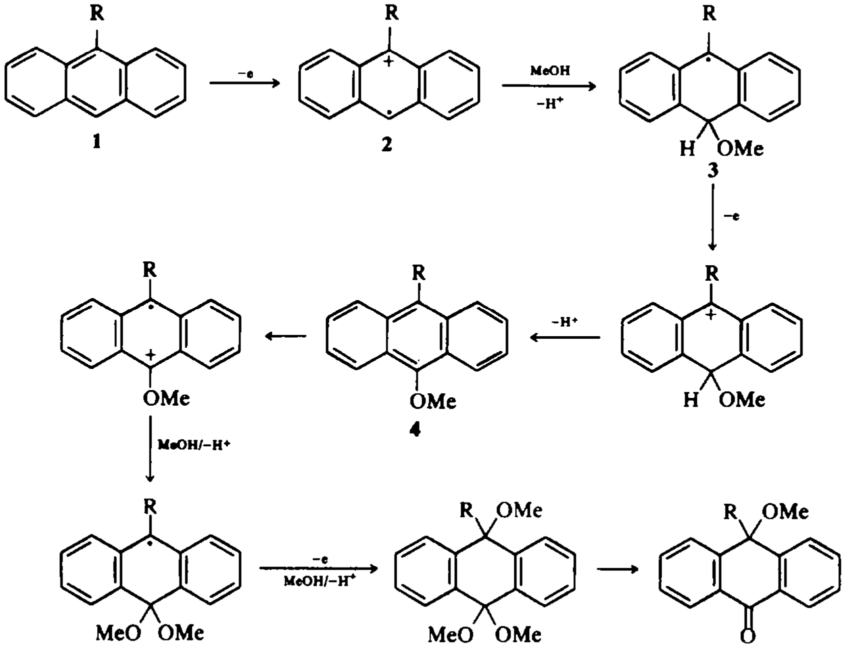
Copper(II) halides have found extensive use as halogenating agents in both heterogeneous[2,3] and homogeneous conditions.[4-6] In heterogeneous conditions, the preferred mechanism involves ligand-transfer of a halogen atom from the copper(II) halide followed by oxidation of the resultant radical to the halogenated product. On occasion the reaction products are more consistent with initial electron-transfer oxidation of the substrate to a radical cation.[7,8] In homogeneous conditions copper(II) halides will be solvated and hence it is improbable that they would effect halogenation by a ligand-transfer mechanism. An electron-transfer mechanism is, however, feasible and it was to investigate the possibility of this type of mechanism that the present study involving reaction of 9-alkylanthracenes with copper halides in methanol was undertaken.

Reaction of 9-phenylanthracene (**1a**) with copper(II) bromide in methanol gave as the sole product 10 - methoxy - 10 - phenylanthrone (**5a**). The same product was also obtained in the anodic oxidation of 9-phenylanthracene.[9] This latter process undoubtedly involves electron transfer to 9-phenylanthracene with the formation of the radical cation (**2a**). It seems probable that the same sequence of events takes place in the reaction with copper(II) bromide in methanol. We suggest that the initial radical cation reacts with the solvent, methanol, at the 10-position to give the radical (**3a**). Oxidation of **3a** with copper(II) bromide followed by loss of a proton would yield 9 - methoxy - 10 - phenylanthracene (**4a**). Subsequent oxidation of this and reaction of the derived radical cation with methanol leads eventually to 10 - methoxy - 10 - phenylanthrone (**5a**) (Scheme 1). Support for this scheme comes from the observation that 9 - methoxy - 10 - phenylanthracene itself is oxidized under the same reaction conditions to 10 - methoxy - 10 - phenylanthrone. This latter process occurs very much faster than oxidation of 9 - phenylanthracene and accounts for the fact that 9 - methoxy - 10 - phenylanthracene cannot be detected in the reaction product.

The rate of reaction of copper(II) halides with 9 - *p* - substituted phenylanthracenes under heterogeneous conditions is only slightly affected by the nature of the *para*-substituent consistent with the reaction being a ligand-transfer reaction.[3] If the analogous reaction in methanol is an electron-transfer process a much greater sensitivity to the electronic nature of the substituent would be expected.[10] It was thus not surprising when it was found that 9 - *p* - methoxyphenylanthracene reacted very much more rapidly than 9 - phenylanthracene. The product of the reaction was 10 - methoxy - 10 - *p* - methoxyphenylanthrone (**5b**).

In order to assess further the influence of the substituent in the 9-position, the behaviour of a series of 9-alkylanthracenes was examined under the same conditions. 9-Methylanthracene gave in addition to the normal product, i.e. 10 - methoxy - 10 - methylanthrone (**5c**), two further products 10 - methoxy - 10 - methoxymethylanthracene (**5d**) and 1,2 - di - 9 - anthrylethane (**13a**). Reaction of 10 - methoxy - 10 - methylanthrone with copper(II) bromide in methanol failed to afford any 10 - methoxy - 10 - methoxymethylanthrone indicating that this latter must be formed by some other route. Another possible route to this product involves reaction of 9 - methoxymethylanthracene (**1d**) with copper(II) bromide in methanol. This does indeed form 10 - methoxy - 10 - methoxymethylanthrone but other products are also obtained in lesser quantities as indicated by GLC. These minor products were not formed in the reaction of 9-methylanthracene indicating that another route should be considered. A third possibility is that 10 - methoxy - 10 - methoxymethylanthrone is formed via 9 - methoxy - 10 - methylanthracene (**4c**). Reaction of this under the same conditions did afford both the anthrones (**5c** and **5d**). Scheme 2 outlines possible routes from 9 - methoxy - 10 - methylanthracene to these products. The essential feature is that the radical cation (**6a**) derived from this latter can either react with methanol as in Scheme 1 to afford 10 - methoxy - 10 - methylanthrone, or it can lose a proton to form the radical (**7a**). Oxidation of this to the carbonium ion (**8a**) and reaction with methanol would yield 9 - methoxy - 10 - methoxymethylanthracene (**9a**), reaction of which as indicated by Scheme 1 would lead to 10 - methoxy - 10 - methoxymethylanthrone. Oxidation of the radical (**7a**) to the carbonium ion (**8a**) would be expected to be rapid as the latter would be stabilized by the 10-OMe group. It is thus not surprising that no 1,2 - di(10 - methoxy - 9 - anthryl) ethane was obtained.

Scheme 3 outlines a plausible route to 1,2 - di - 9 - anthrylethane (**13a**). Loss of a proton from the radical cation (**11a**) would yield the 9-anthrylmethyl radical (**12a**), dimerization of which gives **13a**. Oxidation of the radical (**12a**) to the carbonium ion (**14a**) would be expected to proceed very much less readily than oxidation of **7a** to **8a**. This process may occur to some extent and would result



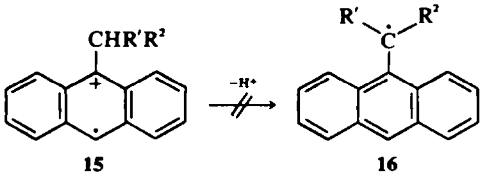
a: R = Ph
b: R = p-MeOC$_6$H$_4$
c: R = Me
d: R = CH$_2$OMe
e: R = Et
f: R = Pr^i
g: R = PhCH$_2$

Scheme 1.

in the formation of 9 - methoxymethylanthracene, which as has been discussed could lead to 10 - methoxy - 10 - methoxymethylanthrone. It is not, however, likely to be the principal route to this compound.

The validity of the above schemes for the behaviour of 9-methylanthracene has been further tested by consideration of 2-substituted 9-methylanthracenes. Thus 2 - chloro - 9 - methylanthracene reacted much less rapidly than 9 - methylanthracene and gave only 3 - chloro - 10 - methoxy - 10 - methylanthrone. The absence of **10c** and **13c** indicates that loss of a proton from the radical cations (**6c** and **11c**) occurs less readily than from **6a** and **11a**. The electron-withdrawing effect of chlorine would increase the positive charge density on the two radical cations thereby favouring their reaction with methanol. The lesser overall reactivity of 2 - chloro - 9 - methylanthracene is consistent with the initial step of the reaction involving electron transfer.

9-Ethyl-, 9-isopropyl- and 9-benzylanthracenes all underwent reaction with copper(II) bromide in methanol to give the corresponding 10 - alkyl - 10 - methoxyanthrone. In no case was either a dimer or a 10 - methoxy - 10 - α - methoxyalkylanthrone obtained. At first sight this is somewhat unusual in that loss of a proton from the radical cation (**15**) of one of these 9-alkylanthracenes would lead to a secondary α-9-anthrylalkyl radical (**16**).

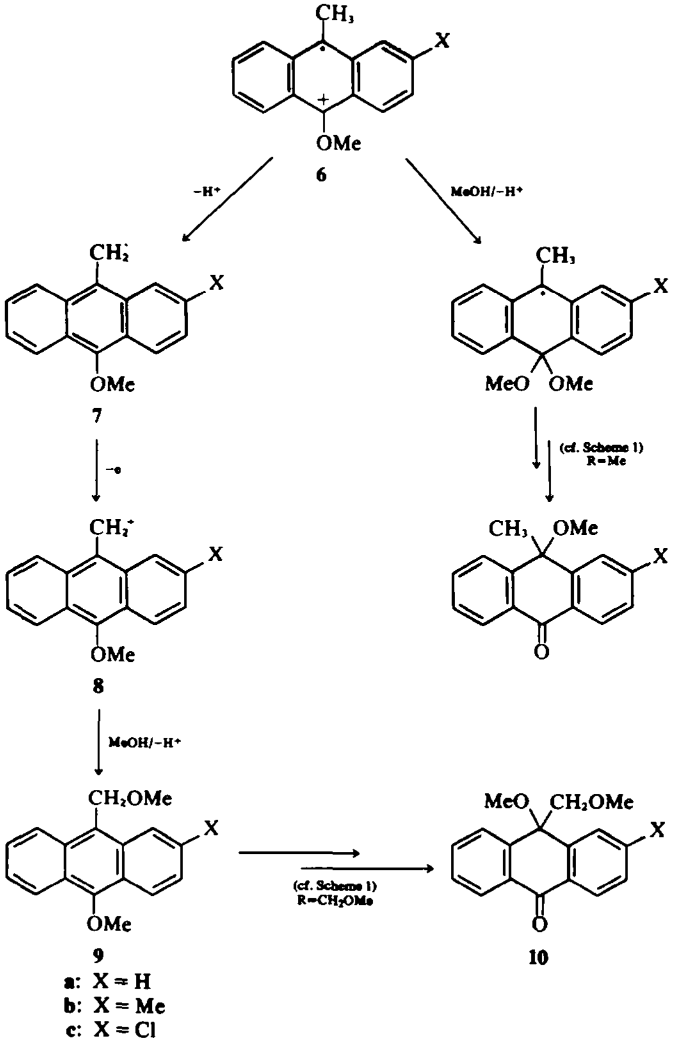


15 **16**

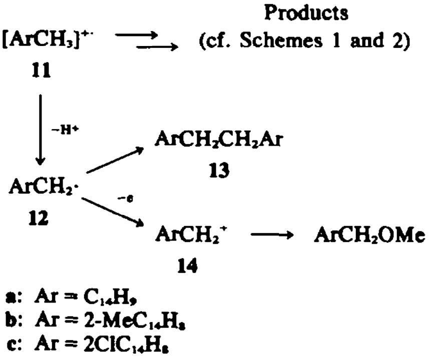
This might be expected to be more stable than the primary 9-anthrylmethyl radical. Investigation of models reveals that if the p-orbital containing the unpaired electron is in the plane of the aromatic system, then there would be severe steric interaction between the groups R^1 and R^2 and the hydrogens on C_1 and C_8. This effect had been noted earlier in reactions of 9 - alkyl - 10 - methylanthracenes with copper(II) halides under heterogeneous conditions where it was shown that reaction occurred exclusively at the methyl group.[11] Rüchardt *et al.* have likewise shown that the stability of α,α'-dialkylbenzyl radicals is substantially reduced if coplanarity cannot be attained.[12] These considerations account for the absence of products which would be derived from the radical **16**. It is noteworthy that 9 - ethoxy - 10 - ethylanthracene under the same conditions also only gave 10 - ethyl - 10 - methoxyanthrone.

The rates of reaction of 9-ethyl and 9-isopropylanthracenes were significantly greater than that for 9 - methylanthracene as would be expected. 9 - Benzylanthracene was however, very substantially less reactive. This can be attributed to the electron-withdrawing influence of the phenyl group with respect to hydrogen.

Anthracene reacted rather slowly with copper(II) bromide in methanol to give anthraquinone as the only product. Anthraquinone is also formed in the anodic oxidation of anthracene.[9] This can be formulated as proceeding by the same mechanism as described for 9 - alkylanthracenes and would thus proceed via 9 - methoxyanthracene. However, reaction of 9 - methoxyanthracene under the same conditions yielded bianthron - 9 - yl and 9 - bromo - 10 - methoxyanthracene in addition to the expected anthraquinone. The formation of bian-



Scheme 2.



Scheme 3.

thron - 9 - yl can possibly be explained as arising from dimerization of the initial 9 - methoxyanthracene radical cations, which would be present in very much higher concentration in the more rapid reaction of 9 - methoxyanthracene. The 9 - bromo - 10 - methoxyanthracene probably arises from the competing ligand-transfer reaction. This same product was obtained from the analogous reaction under heterogeneous conditions.

The identities of the 10-alkyl (or aryl) - 10 - methoxyanthrones were established by IR, NMR and mass spectrometry. In addition 10 - methoxy - 10 - phenylanthrone and 10 - methoxy - 10 - *p* - methoxyphenylanthrone were synthesized. The IR spectra of these anthrones were characterized by absorption at *ca.* 2850 and 1660 cm^{-1} characteristic of a methoxyl group and an anthrone carbonyl group respectively. Their NMR spectra all had a signal at τ 6·95–7·15 due to the protons of the OMe group. This signal is anomalously high presumably because the OMe group lies over the aromatic system and hence is very appreciably shielded. Similarly the signals due to the α-protons of the alkyl groups at the 10-position are at unusually high field, again for the same reason. The mass spectra are characterized by a fairly weak molecular ion. The base peaks arose from loss of the OMe group or the alkyl group. The 10 - methoxy - 10 - methoxymethylanthrones had similar IR spectra to the above series of compounds. Their NMR spectra were characterized by peaks at τ 6·46 (2H) and 7·00 (6H) due to the protons of the methylene and the two OMe groups respectively. The base peak in their mass spectra arose from loss of the CH_2OMe group.

EXPERIMENTAL

Preparation of starting and reference materials

9-Alkyl and arylanthracenes and 9 - alkoxy - 10 - alkyl (or aryl)anthracenes were prepared as described previously.

9 - *Methoxymethylanthracene.* 9 - Hydroxymethylanthracene.[13] (2·08 g, 0·01 mol) was dissolved in MeOH (50 ml) containing conc HCl (0·5 ml). The soln was refluxed for 20 min, cooled and neutralized by addition of $KHCO_3$ (0·5 g). The filtered soln was concentrated giving 9 - methoxymethylanthracene (1·87 g, 90%), m.p. (lit.[13] 90–91°).

10 - *Methoxy* - 10 - p - *methoxyphenylanthrone.* A suspension of 9 - *p* - methoxyphenylanthracene (2·84 g), 0·01 mol) in AcOH (25 ml) was treated with sodium dichromate (2·62 g, 0·01 mol) in hot water (2·5 ml).[14] The stirred mixture was heated on a steam bath until the mixture turned green. After cooling 10 - hydroxy - 10 - *p* - methoxyphenylanthrone was filtered off and was crystallized from MeOH as needles (2·2 g, 80%), m.p. 206° (lit.[15] 206–207°). Treatment of this anthrone (0·63 g) in MeOH with 10% methanolic HCl (10 ml) as above gave 10 - methoxy - 10 - *p* - methoxyphenylanthrone (0·59 g, 89%) which crystallized as colourless needles from MeOH, m.p. 138–139° (Found: C, 80·0; H, 5·5. $C_{22}H_{18}O_3$ requires: C, 80·0; H, 5·7%); τ 1·67 (2H, d, *J* 7 Hz, H_1 and H_8), 2·50–2·83 (8H, m, Ar), 3·27 (2H, d, *J* 9 Hz, H_4 and H_5), 6·30 (3H, s, $C_6H_4OCH_3$), 7·0 (3H, s, C_{10}-OCH_3); *m/e* M^+ 330·1263 (63%) ($C_{22}H_{18}O_3$ requires M^+ 330·1256) M^+-OCH_3 299·1056 (100%) and $M^+-C_6H_4OCH_3$ 223·0766 (33%); ν_{max} ($CHCl_3$) 2850 (OCH_3) and 1660 (CO) cm^{-1}.

10 - *Methoxy* - 10 - *phenylanthrone.* This was prepared similarly from 10 - hydroxy - 10 - phenylanthrone, m.p. 208° which was in turn synthesized by oxidation of 9 - phenylanthracene with sodium dichromate.[14] 10 - Methoxy - 10 - phenylanthrone crystallized from MeOH as colourless needles, m.p. 171–172° (lit.[16] 173–174°).

Reactions with copper(II) bromide in methanol

Reaction of 9 - *phenylanthracene.* A soln of 9 - phenylanthracene (6·35 g, 0·025 mol) in MeOH (100 ml) was added to a stirred refluxing suspension of copper(II) bromide (22·34 g, 0·1 mol) in MeOH (200 ml). The mixture was refluxed for 7 days, then filtered. TLC analysis of the crude material showed two spots, the less polar corresponding to starting material. This material in 30% benzene in light petroleum was chromatographed on alumina. Elution with this solvent gave unchanged 9 - phenylanthracene (2·0 g, 31%) followed by 10 - methoxy - 10 - phenylanthrone (4·58 g, 61%), which was crystallized from MeOH as colourless needles, m.p. and m.m.p. 171–172°.

Reaction of 9 - p - *methoxyphenylanthracene.* The reaction was carried out as above but for 2 days. GLC analysis of the crude product showed the presence of unreacted 9 - *p* - methoxyphenylanthracene (35%) and 10 - methoxy - 10 - *p* - methoxyphenylanthrone (65%). Column chromatography on alumina in 30% benzene in light petroleum gave pure samples of both compounds.

Reaction of 9 - *methylanthracene.* A soln of 9 - methylanthracene (2 g, 0·0104 mol) in MeOH (100 ml) was added to a stirred refluxing suspension of copper(II) bromide (4·8 g, 0·0208 mol) in MeOH (50 ml). The mixture was refluxed for 4 hr, and worked up in the usual way. The crude product was extracted with 10% benzene in light petroleum. A white crystalline material remained insoluble and was identified as 1,2 - di(9,9′ - anthryl)ethane (42 mg, 2%), m.p. and m.m.p. 309–310°, *m/e* M^+ 382·16867 (100%) ($C_{30}H_{22}$ requires 382·17214). The organic extract was chromatographed on alumina. Elution with this solvent gave unreacted 9 - methylanthracene (2·30 g, 48%), m.p. 78–79°. Elution with 20% benzene in light petroleum gave 10 - methoxy - 10 - methylanthrone (1·24 g, 25%) as white needles from MeOH, m.p. 111–112° (Found: C, 80·9; H, 6·0. $C_{16}H_{14}O_2$ requires: C, 80·6; H, 5·9%); τ 1·62–2·62 (8H, m, Ar), 7·12 (3H, s, OCH_3) and 8·30 (3H, s, CH_3); *m/e* M^+ 238·10085 (9%) ($C_{16}H_{14}O_2$ requires: 238·09937), M^+-CH_3 223·7732 (56%) and M^+-OCH_3 207·08119 (100%); ν_{max} 2850 (OCH_3) and 1660 (CO) cm^{-1}. Elution with 30% benzene in light petroleum gave 10 - methoxy - 10 - methoxymethylanthrone (0·45 g, 80%) as yellow crystals from methanol, m.p. 85–86° (Found: C, 76·3; H, 6·2 $C_{17}H_{16}O_3$ requires: C, 76·1; H, 6·0%); τ 1·62–2·60 (8H, m, Ar), 6·46 (2H, s, CH_2) and 7·10 (6H, s, OCH_3); *m/e* M^+ 268·11069 (21%) ($C_{17}H_{16}O_3$ requires: 268·10994) and $M^+-CH_2OCH_3$ (100%); ν_{max} 2850 (OCH_3) and 1660 (CO) cm^{-1}.

Reaction of 9 - *methoxymethylanthracene.* Reaction of 9 - methoxymethylanthracene (0·11 g, 5 mmol) and copper(II) bromide (0·22 g, 1 mmol) in MeOH (25 ml) was carried out for 3·5 hr. GLC analysis of crude product showed three peaks corresponding to an unknown compound (22%), 10 - methoxy - 10 - methoxymethylanthrone (6%) and unreacted 9 - methoxymethylanthracene (74%).

Reaction of 9 - *methoxy* - 10 - *methylanthracene.* The reaction of 9 - methoxy - 10 - methylanthracene (2·22 g, 0·01 mol) and copper(II) bromide (4·47 g, 0·02 mol) in MeOH (200 ml) was carried out as above for 2·5 hr. Analysis of the crude product by GLC showed the presence of 10 - methoxy - 10 - methylanthrone (10%) and 10 - methoxy - 10 - methoxymethylanthrone (90%).

Reaction of 9 - *ethylanthracene.* A mixture of 9 - ethylanthracene (8·24 g, 0·04 mol) and copper(II) bromide (17·9 g, 0·08 mol) in MeOH (400 ml) was refluxed for 6 hr and then worked up as above. The crude product was chromatographed on alumina. Elution with 10% benzene in light petroleum gave unchanged 9 - ethylanthracene (1·69 g, 20%), m.p. 55–57°. Elution with 30% benzene in light petroleum gave 10 - *ethyl* - 10 - *methoxyanthrone* (6·05 g, 60%) which was crystallized from MeOH as white crystals, m.p. 72° (Found: C, 81·1; H, 6·5. $C_{17}H_{16}O_2$ requires: C, 80·9; H, 6·4%); τ 1·67–2·63 (8H, m, Ar), 7·10 (3H, s, OMe) 7·9 (2H, q, CH_2) and 9·71 (3H, t, CH_3); *m/e* M^+ 252·1152 (3%) ($C_{17}H_{16}O_2$ requires: 252·1150), $M^+-C_2H_5$ 223·0735 (100%) and M^+-OCH_3 221·0966 (5%). Elution with 30% methylene chloride in benzene gave anthraquinone (0·312 g, 4%), m.p. and m.m.p. 285°.

Reaction of 9 - *ethoxy* - 10 - *ethylanthracene.* The product from the reaction of 9 - ethoxy - 10 - ethylanthracene (1·25 g, 0·005 mol) and copper(II) bromide (2·23 g, 0·01 mol) in MeOH (150 ml) for 2 hr gave unreacted 9 - ethoxy - 10 - ethylanthracene (33%), 10 - ethyl - 10 - methoxyanthrone (62%) and an unknown compound (5%).

Reaction of 2,9 - *dimethylanthracene.* 2,9 - Dimethylanthracene (2·06 g, 0·01 mol), copper(II) bromide (4·47 g, 0·02 mol) in MeOH 150 ml were refluxed for 2 hr and worked up as before. The crude product was extracted with 10% benzene in light petroleum leaving a white crystalline residue of 1,2 - bis(2 - *methyl* - 9 - *anthryl*)*ethane* (0·073 g, 4%), m.p. 280° dec, *m/e* M^+ 410·2029 (9%) ($C_{32}H_{26}$ requires: 410·2034) and $M^+/2$ 205·1019 (100%). The extract was chromatographed on alumina giving initially unreacted 2,9 - dimethylanthracene (0·602 g, 29%). Elution with 20% benzene in light petroleum gave 10 - *methoxy* - 3,10 - *dimethylanthrone* (0·887 g, 39%) as yellow crystals from MeOH, m.p. 111° (Found: C, 81·1; H, 6·6. $C_{17}H_{16}O_2$ requires: C, 80·9; H, 6·4%), τ 1·66–2·76 (7H, m, ArH), 7·12 (3H, s, OMe), 7·50 (3H, s, Me), 8·30 (3H, s, Me); *m/e* M^+ 252·1158 (13%) ($C_{17}H_{16}O_2$ requires: 252·1150), M^+–OMe 221·0960 (100%) and M^+–Me 237·0919 (65%), ν_{max} 2850 (OMe) and 1660 (CO) cm^{-1}. Elution with 30% light petroleum in benzene gave yellow crystals of 10 - *methoxy* - 10 - *methoxymethyl* - 3 - *methylanthrone* (0·271 g, 10%) from MeOH, m.p. 122–123° (Found: C, 76·7; H, 6·7. $C_{18}H_{18}O_3$ requires: C, 76·6; H, 6·4%); τ 1·68–2·78 (7H, m, ArH), 6·45 (2H, s, CH_2), 7·00 (6H, s, OMe) and 7·50 (3H, s, CH_2); *m/e* M^+ 282·1257 (15%) ($C_{18}H_{18}O_3$ requires: 282·1256) and $M^+-CH_2OCH_3$ 237·0915.

Reaction of 2 - *chloro* - 9 - *methylanthracene.* This was carried out as for above using 2 - chloro - 9 - methylanthracene (2·27 g, 0·01 mol) for 8·5 hr. Chromatography of the crude product, which was shown by GLC to contain only two components, on alumina with 5% benzene in light petroleum gave unreacted 2 - chloro - 9 - methylanthracene (1·05 g, 46%). Elution with 10% benzene in light petroleum gave 3 - *chloro* - 10 - *methoxy* - 10 - *methylanthrone* (0·85 g, 31%) as yellow crystals from MeOH, m.p. 103–104°. (Found: C, 70·4; H, 4·7. $C_{16}H_{13}ClO_2$ requires: C, 70·5; H, 4·8%); τ 1·71–2·80 (7H, m, ArH), 7·14 (3H, s, CH_3) and 8·34 (3H, s, Me); *m/e* M^+ 272·0604 (14%) ($C_{16}H_{13}^{35}ClO_2$ requires: 272·0604), M^+–Me (71%) 257·0373 and M^+–OMe 241·0389 (100%); ν_{max} 2850 and 1660 cm^{-1}.

Reaction of anthracene. A mixture of anthracene (3·56 g, 0·02 mol), copper(II) bromide (8·9 g, 0·04 mol) in MeOH (300 ml) was refluxed for 6 days and after the usual work up afforded anthraquinone (3·68 g, 89%), m.p. and m.m.p. 283–285°.

Reaction of 9 - *methoxyanthracene.* A mixture of 9 - methoxyanthracene (1 g, 4·8 mmol), copper(II) bromide (2·15 g, 9·5 mmol) in MeOH (80 ml) was refluxed for 15 min. The crude organic product was extracted with 10:1 light petroleum (b.p.

60–80°): benzene and the extract chromatographed on alumina. Elution with this solvent gave 9 - bromo - 10 - methoxyanthracene (0·13 g, 9%), m.p. 145° (lit.[17] 145°). The insoluble portion of the product was fractionally crystallized from 1:1 benzene: light petroleum to give bianthron - 9 - yl (0·326 g, 35%), m.p. and m.m.p. 245–249° (lit.[18] 246–250°), and anthraquinone (0·356 g, 35%), m.p. and m.m.p. 285°.

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