

REACTIONS OF CUPRIC HALIDES WITH ORGANIC COMPOUNDS—VII¹

REACTIONS OF 9-ALKOXY- AND 9-ACYLOXY-10-ALKYLANTHRACENES

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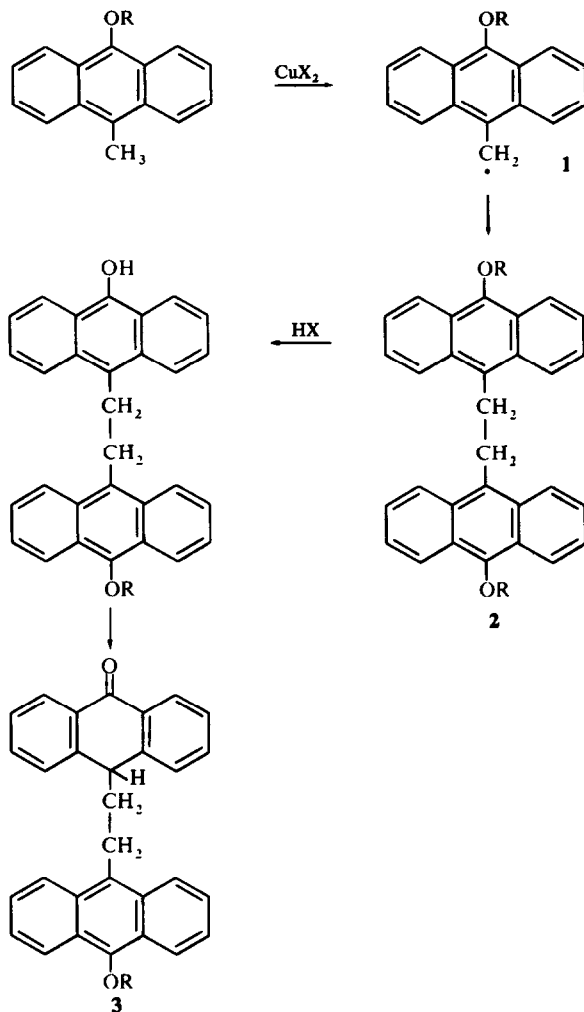
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Abstract—9-Alkoxy(or acyloxy)-10-methylanthracenes undergo reaction with cupric halides at the Me group to give coupled products, whereas 9-alkoxy(or acyloxy)-10-benzyl(or ethyl)anthracenes react at the alkoxy or acyloxy group to afford 10-benzyl- and 10-ethylideneanthrones respectively. Both types of reaction are postulated to proceed by a radical mechanism.

9-Benzyl- and 9-methyl-10-phenoxyanthracenes behave differently giving on reaction with cupric chloride 9-chloro-10-phenoxyanthracene as a result of a ligand-transfer reaction.

PRELIMINARY results have shown that 9-methoxy-10-methylanthracene undergoes reaction with cupric bromide and cupric chloride under heterogeneous conditions to give the coupled product, 1-(10-anthron-9-yl)-2-(10-methoxy-9-anthryl)ethane (3, R = Me), reaction occurring at the Me group.² A similar product (3, R = PhCO) was obtained from the reactions of 9-benzoyloxy-10-methylanthracene with cupric halides. Reaction is postulated to occur initially at the Me group to give the [10-methoxy(or benzoyloxy)-9-anthryl]methyl radical (1, R = Me or PhCO) analogous to the formation of the (10-phenyl-9-anthryl)methyl radical formed in the reaction of 9-methyl-10-phenylanthracene with cupric halides.³ This radical then dimerizes, and the dimer (2, R = Me, PhCO) is partially demethylated or debenzoylated by the hydrogen halide produced in the reaction to give after ketonization the coupled product (3). The present paper discusses the reactions of 9-alkoxy-10-methylanthracenes with cupric halides in greater detail and also the reactions of 9-alkoxy-10-alkylanthracenes in which the alkyl group is other than Me.

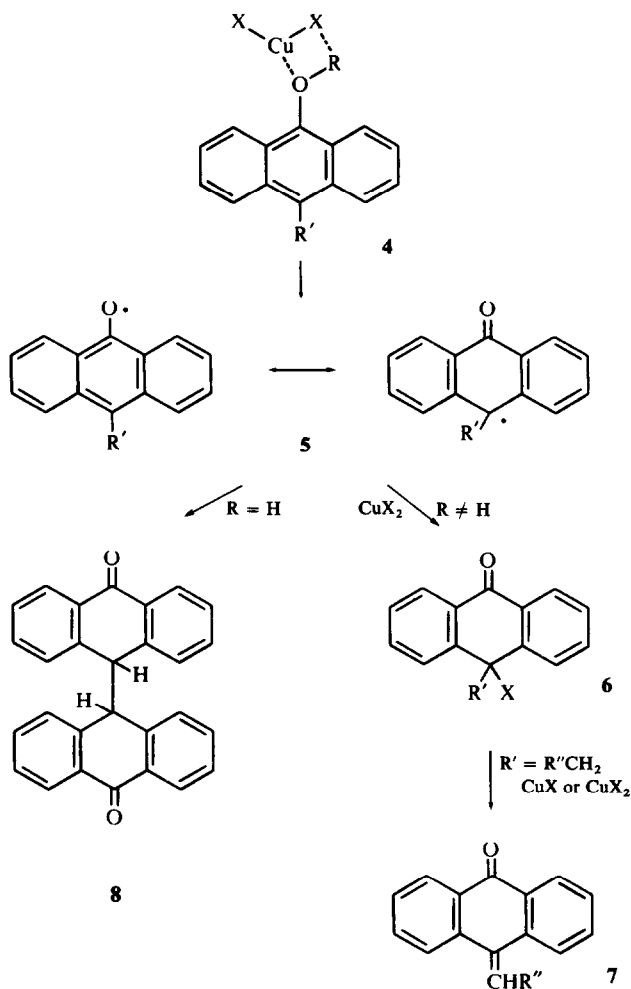
9-Ethoxy-10-ethylanthracene (4, R = R¹ = Et) and 9-benzyl-10-benzyloxyanthracene (4, R = R¹ = PhCH₂) react with cupric halides to give 10-ethylideneanthrone and 10-benzalanthrone respectively. Reaction occurs initially at the alkoxy group rather than at the alkyl group to give the mesomeric radical (5, R = Et or PhCH₂) via the 4-centre transition state (4) postulated in reactions of 9-alkoxy- and 9-acyloxyanthracenes with cupric halides.⁴ This mesomeric radical is then postulated to undergo reaction with cupric halide to give the 10-alkyl-10-halogenoanthrone (6) rather than dimerize, as it does in reactions of 9-alkoxyanthracenes, which give bianthron-9-yl (8).⁴ The reason for the difference in behaviour is undoubtedly steric. F-strain would hinder the dimerization of the 10-substituted mesomeric radicals. The 10-alkyl-10-halogenoanthrones are then postulated to undergo dehydrohalogenation to the 10-alkylideneanthrone (7). 10-Benzyl-10-chloroanthrone has been shown to undergo



facile dehydrohalogenation in refluxing carbon tetrachloride in the presence of either cuprous chloride or cupric chloride which supports the observed results.⁵

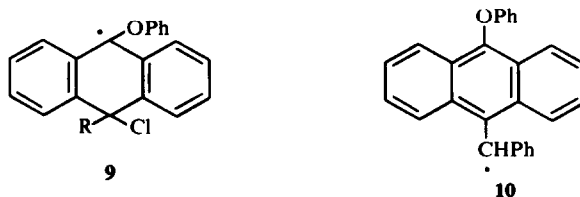
Further confirmation of this reaction pathway was obtained from examining the reaction between 9-methoxy-10-phenylanthracene and cupric chloride which led to 10-chloro-10-phenylanthrone which could not undergo dehydrohalogenation. Crystallization of this from ethanol gave 10-ethoxy-10-phenylanthrone while chromatography on alumina of the reaction product gave 10-hydroxy-10-phenylanthrone.

The rate of reaction of 9-benzyloxyanthracene was very much faster than that of 9-acetoxyanthracene.⁴ It was thus reasoned that if reaction of 9-benzyl-10-benzyloxyanthracene involves initially attack of the benzyloxy group that 9-acetoxy-10-benzylanthracene should react considerably more slowly. Consistent with this the reaction of 9-benzyl-10-benzyloxyanthracene with cupric chloride in carbon tetrachloride went to completion in less than $1\frac{1}{2}$ hr, whilst 9-acetoxy-10-benzylanthracene



had only been converted into 10-benzalanthrone to the extent of 22% after 4½ hr. The rates of reaction of 9-methoxy-10-methylantracene and 9-benzoyloxy-10-methylantracene are consistent with attack taking place at the methyl group. 9-Benzoyloxyanthracene reacts with cupric chloride very much slower than 9-methoxyanthracene as expected for reactions involving attack at the alkoxy group.⁴

The reaction of 9-benzyl-10-phenoxyanthracene (4; R = Ph, R' = PhCH₂) with cupric chloride was investigated in the hope that reaction might occur at the benzyl group since reaction at the phenoxy group would seem to be precluded.⁴ The only



product obtained was 9-chloro-10-phenoxyanthracene indicating that a ligand-transfer reaction with cupric chloride to give the radical (9, R = PhCH₂) must have occurred. Further reaction with cupric chloride would lead to the observed product. The behaviour of 9-benzyl-10-phenoxyanthracene with cupric chloride is thus analogous to that of 9-benzyl-10-chloroanthracene and 9-benzyl-10-phenylanthracene which gave 9,10-dichloroanthracene and 9-chloro-10-phenylanthracene respectively.^{1, 3} That the radical (10) was not formed is attributed, as in the other reactions, to steric effects which would seem to preclude the p-orbital containing the single electron lying in the same plane as the anthracene system. The facility with which 9-methoxy-10-methylanthracene and 9-benzoyloxy-10-methylanthracene undergo reaction at the methyl group compared to the reluctance of 9-benzoyloxy-10-benzylanthracene or 9-ethoxy-10-ethylanthracene to react in the alkyl group can also be explained on the basis of the stabilities of the radicals which would be formed.

Cleavage of the O—Ph bond in diaryl ethers is generally very difficult. Hence the reaction of 9-methyl-10-phenoxyanthracene with cupric chloride was investigated with the expectation that the dimer (2, R = Ph) would be formed and would be stable under the reaction conditions thereby confirming the mechanistic pathway for the reactions of 9-alkoxy-10-methylanthracenes with cupric halides. In the event, the only product from the reaction was 9-chloro-10-phenoxyanthracene arising from a ligand-transfer reaction of chlorine from the cupric chloride to give the radical (9, R = Me). Attack at this position would be favoured compared to attack at the 10-position on steric grounds. It is not clear at this stage why 9-methoxy-10-methylanthracene, and 9-methyl-10-phenylanthracene undergo reaction with cupric halides to form the (10-substituted-9-anthryl)methyl radical whilst 9-methyl-10-phenoxyanthracene reacts by a ligand-transfer at the 9-position nor why the (10-methoxy-9-anthryl)methyl radical dimerizes whilst the (10-phenyl-9-anthryl)methyl radical reacts with cupric halides to give 9-halogenomethyl-10-phenylanthracene.

9-Benzoyloxy-10-methylanthracene was synthesised by reaction of 10-methylanthrone with benzoyl chloride. It was characterized on the basis of its NMR and IR spectra and from its mass spectrum. The base peak in the latter was of the [C₆H₅CO]⁺ ion.

9-Methyl-10-phenoxyanthracene and 9-benzyl-10-phenoxyanthracene were prepared following the procedure of Theilacker *et al.*⁶ for the preparation of 9-phenoxyanthracene, from the reaction of 9-alkyl-10-bromoanthracene with phenol in the presence of potassium hydroxide and copper powder. Both these reactions gave, in addition to the desired products, the 9-alkylanthracenes. The NMR and mass spectra of these compounds were consistent with their structures.

EXPERIMENTAL

Light petroleum refers to the fraction b.p. 60–80°. NMR spectra were recorded in CDCl₃ on a Perkin-Elmer R10 spectrometer at 40 MHz using TMS as an internal standard; mass spectra on an A.E.I. MS9 spectrometer; and UV spectra in ethanol on a Perkin-Elmer 202 spectrophotometer. GLC was carried out as described in previous papers.⁷ Chromatographies were carried out using Spence Grade H alumina. Cupric bromide and cupric chloride were dried and ground as described previously.⁷

Preparation of starting materials

9-Methoxy-10-methylanthracene. This was prepared by treatment of anthrone with MeI and KOH.⁸ The crude product was chromatographed on alumina. Elution with 10% benzene in light petroleum b.p. 40–60°

gave 9-methoxy-10-methylanthracene, which was crystallized from light petroleum as pale yellow pyramids, m.p. 143–144° (lit.⁸ 144–145°); NMR τ 5.93 (3H; OMe), 7.04 (3H; Me). UV λ_{\max} 255 sh (log ϵ 4.99), 260 (5.10), 328 (2.89), 345 (3.33), 360 (3.66), 379 (3.85), 401 (3.78) nm; mass spectrum: M^+ 222; base peak m/e 207.

9-Ethoxy-10-ethylantracene. This was similarly obtained from the reaction between anthrone, EtI and KOH,⁹ and was crystallized from light petroleum, m.p. 84° (lit.⁹ 84°).

9-Benzyl-10-benzoyloxanthracene. This was similarly obtained starting with benzyl chloride, and was crystallized from light petroleum m.p. 137° (lit.¹⁰ 137°); NMR τ 4.74 (2H; OCH₂Ph), 5.02 (2H; CH₂Ph); UV λ_{\max} 254 sh (log ϵ 4.50), 261 (4.73), 330 (2.88), 345 (3.31), 361 (3.71), 380 (3.93), 402 (3.91) nm.

9-Benzoyloxy-10-methylanthracene. A mixture of benzoyl chloride (12 ml; 0.086 mole), 10-methylanthrone¹¹ (18 g, 0.086 mole) in pyridine (144 ml) containing piperidine (1 ml) was heated on a steam bath for 15 min. A little water was added to the mixture which was allowed to cool. The cooled mixture was filtered and the crystals obtained were recrystallized from 3:1 EtOH-pyridine and then from light petroleum giving pale yellow needles of 9-benzoyloxy-10-methylanthracene (15 g, 56%) m.p. 183–185°. (Found: C, 84.6; H, 5.15; M^+ 312. C₂₂H₁₆O₂ requires: C, 84.6; 5.1%; M^+ 312, NMR τ 7.0 (3H, Me); IR ν_{\max} (CCl₄) 1752 cm⁻¹ (C=O).

9-Acetoxy-10-benzylantracene. This was synthesized from the reaction between 10-benzalanthrone and Ac₂O in the presence of Zn dust, and was crystallized from benzene-light petroleum, m.p. 209–211° (lit.¹² 210–211°); NMR τ 5.09 (2H; CH₂Ph), 7.46 (3H; OCOMe).

9-Methoxy-10-phenylantracene. This was prepared from 10-phenylantrone¹³ and methyl *p*-toluene-sulphonate and was crystallized from EtOH/butan-2-one as pale yellow needles, m.p. 162–163° (lit.¹² 161–163°).

9-Benzyl-10-phenoxyanthracene. A vigorously stirred intimate mixture of finely ground 9-benzyl-10-bromoanthracene (10.41 g, 0.03 mole), phenol (4.23 g, 0.045 mole), powdered KOH (2.52 g, 0.045 mole), and Cu powder (0.127 g, 0.002 mole) was heated to 220° within 30 min, kept at 220° for a further 30 min, then for 1 hr at 240°, and finally for 1 hr at 250°.⁶ Ether was added to the cooled mixture and the whole left overnight. The mixture was then extracted successively with benzene, light petroleum and EtOH. The combined extracts were evaporated to dryness and the residue dissolved in benzene. The benzene soln was washed with KOH aq and then water before drying (Na₂SO₄). The dried soln was chromatographed on alumina. Elution with benzene gave a reddish-yellow solid. This material, in light petroleum, was rechromatographed on alumina. Elution with light petroleum gave 9-benzylantracene (0.95 g, 12%), m.p. and mixed m.p. 136°. Further elution with light petroleum gave 9-benzyl-10-phenoxyanthracene, which was crystallized from EtOH as yellow needles (2.2 g, 20%), m.p. 222–223°. (Found: C, 90.2; H, 5.6. M^+ , 360.1518. C₂₇H₂₀O requires: C, 90.0; H, 5.6%, M^+ , 360.1514).

9-Methyl-10-phenoxyanthracene. Following the procedure described in the preceding experiment, 9-bromo-10-methylanthracene (8.11 g, 0.03 mole) was converted to 9-methyl-10-phenoxyanthracene (1.5 g, 17%), which was crystallized from EtOH as yellow needles, m.p. 193–195°. (Found: C, 89.0; H, 5.4. M^+ , 284.12034. C₂₁H₁₆O requires: C, 88.7; H, 5.7%, M^+ , 284.12011).

Reactions with cupric halides—reaction of 9-methoxy-10-methylanthracene

(a) *With cupric bromide.* A vigorously stirred mixture of 9-methoxy-10-methylanthracene (1 g, 4.5 mmole) and cupric bromide (2.011 g, 9 mmole) in CCl₄ (45 ml) was refluxed for 1½ hr when evolution HBr had ceased. The cuprous bromide was filtered off and the filtrate evaporated. The residue in 10:1 light petroleum:benzene was chromatographed on alumina. Elution with this solvent mixture gave 9-methoxy-10-methylanthracene (0.0369, 3%) m.p. 143–144°. Elution with benzene gave 1-(10-anthron-9-yl)-2-(10-methoxy-9-anthryl)ethane, which was crystallized from light petroleum as a yellow plates (0.622 g, 65%), m.p. 212–214° (melts and solidifies) and 228–230°; NMR τ 1.4–3.2. (Found: C, 87.2; H, 5.4. M.W. 429. C₃₁H₂₄O₂ requires: C, 86.9; H, 5.6%, M.W. 428); NMR τ 1.4–3.2 (m; 16H; aromatic protons), 5.8 (s; 4H; OMe + H_a), 6.55 (t; 2H; CH₂Ar; J = 6Hz), 7.7 (t; 2H; CH₂; J = 6Hz); IR ν_{\max} (CCl₄), 2820 (OMe), 1668 (C=O), 1262 (C—O—C), 1020 (C—O—C) cm⁻¹; UV λ_{\max} 254 (log ϵ 5.13), 266 (5.12), 336 (3.08), 352 (3.48), 368 (3.78), 388 (3.99), 411 (3.96), 444 (3.08) nm.

(b) *With cupric chloride.* This was carried out as above using cupric chloride (1.21 g, 9 mmole). The reaction time was 2 hr. The reaction mixture gave, after chromatography, 1-(10-anthron-9-yl)-2-(10-methoxy-9-anthryl)ethane (0.74 g, 77%), and unreacted 9-methoxy-10-methylanthracene (0.047 g, 4%).

Reaction of 9-benzoyloxy-10-methylanthracene

(a) *With cupric bromide.* A vigorously stirred mixture of 9-benzoyloxy-10-methylanthracene (3 g, 9.6

mmole) and cupric bromide (4.29 g, 19.2 mmole) in CCl_4 (100 ml) was refluxed for 6 hr when evolution of HBr had ceased. The reaction product in 5:1 light petroleum:benzene was chromatographed on alumina. Elution with benzene gave 1-(10-anthron-9-yl)-2-(10-benzoyloxy-9-anthryl)ethane (1.62 g, 65%), which was crystallized from MeOH as a yellow powder, m.p. 171–173°. (Found: C, 85.6; H, 5.2. $\text{C}_{37}\text{H}_{26}\text{O}_3$ requires: C, 85.7; H, 5.05%); NMR τ 1.3–3.2 (m; 21H; aromatic protons), 4.8 (s; 1H; H_4), 6.5 (t; 2H; CH_2Ar ; $J = 6\text{Hz}$), 7.6 (t; 2H; CH_2 ; $J = 6\text{Hz}$); IR ν_{max} (CCl_4) 1744 (PhCOO), 1662 (anthrone carbonyl) cm^{-1} ; UV λ_{max} 264 (log ϵ 4.54), 347 (3.35), 364 (3.65), 384 (3.88), 406 (3.88), 440 (3.40) nm.

(b) *With cupric chloride.* This was carried out as above using cupric chloride (2.583 g, 19.2 mmole) in chlorobenzene (100 ml). The reaction time was 15 min. Chromatography of the reaction product gave initially 9-benzoyloxy-10-methylanthracene (0.586 g, 19%) followed by 1-(10-anthron-9-yl)-2-(10-benzoyloxy-9-anthryl)ethane, m.p. and mixed m.p. 171–173°.

Reaction of 9-benzyl-10-benzoyloxyanthracene

(a) *With cupric bromide.* A vigorously stirred mixture of 9-benzyl-10-benzoyloxyanthracene (0.5 g, 1.34 mmole) and cupric bromide (0.598 g, 2.68 mmole) in CCl_4 (14 ml) was refluxed for $\frac{1}{2}$ hr. The reaction product was chromatographed on alumina. Elution with 10% benzene in light petroleum b.p. 40–60° gave unreacted 9-benzyl-10-benzoyloxyanthracene (0.02 g, 4%). Elution with benzene gave 10-benzalanthrone¹² (0.30 g, 83%), which was crystallized from light petroleum as yellow needles, m.p. and mixed m.p. 128–130°.

(b) *With cupric chloride.* (i) The reaction was carried out as above using cupric chloride (0.36 g, 2.68 mmole) for 1 hr. Chromatography of the crude product gave unreacted 9-benzyl-10-benzoyloxyanthracene (0.03 g, 6%) and 10-benzalanthrone (0.31 g, 85%).

(ii) A vigorously stirred mixture of 9-benzyl-10-benzoyloxyanthracene (0.4676 g, 1.25 mmole) and cupric chloride (0.336 g, 2.5 mmole) in CCl_4 (100 ml) was refluxed for $1\frac{1}{2}$ hr. GLC of the crude product showed it to contain only 10-benzalanthrone.

Reaction of 9-acetoxy-10-benzylanthracene with cupric chloride

The reaction was carried out as above using 9-acetoxy-10-benzylanthracene (0.4075 g, 1.25 mmole) for $4\frac{1}{2}$ hr. The product was analysed by GLC and shown to contain 10-benzalanthrone (22%) and 9-acetoxy-10-benzylanthracene (78%).

Reaction of 9-ethoxy-10-ethylanthracene

(a) *With cupric bromide.* A vigorously stirred mixture of 9-ethoxy-10-ethylanthracene (0.50 g, 2 mmole) and cupric bromide (0.894 g, 4 mmole) in CCl_4 (14 ml) was refluxed for 20 min. The crude product was chromatographed on alumina. Elution with benzene gave 10-ethylideneanthrone (0.395 g, 85%) as a red oil. This was identified by comparison of its IR and NMR spectra with that of an authentic sample of 10-ethylideneanthrone;¹⁴ IR ν_{max} (CCl_4) 1670 cm^{-1} (C=O); NMR τ 3.4 (q; 1H; =CHMe) and 7.8 (d; 3H; =CHCH₃).

(b) *With cupric chloride.* The reaction was carried out as above but with cupric chloride (0.538 g, 4 mmole) with a reaction time of 20 min. Chromatography of the crude reaction product gave 10-ethylideneanthrone (0.395 g, 90%).

Reaction of 9-methoxy-10-phenylanthracene

(a) *With cupric bromide.* A vigorously stirred mixture of 9-methoxy-10-phenylanthracene (1 g, 3.5 mmole) and cupric bromide (1.57 g, 7 mmole) in chlorobenzene (45 ml) was refluxed for 7 hr. The crude product in 1:1 benzene:light petroleum was chromatographed on alumina. Elution with this solvent gave unreacted 9-methoxy-10-phenylanthracene (0.37 g, 37%). Elution with 10% chloroform in benzene gave 10-hydroxy-10-phenylanthrone¹⁵ (0.60 g, 61%) as white needles from benzene, m.p. and mixed m.p. 208°; IR ν_{max} (CCl_4) 3600 (OH) and 1674 cm^{-1} (C=O).

(b) *With cupric chloride.* (i) The reaction was carried out as above but with cupric chloride (0.947 g, 7 mmole) for $8\frac{1}{2}$ hr. Chromatography of the crude product gave unchanged 9-methoxy-10-phenylanthracene (0.175 g, 17%) and 10-hydroxy-10-phenylanthrone (0.75 g, 79%).

(ii) The reaction was repeated and a portion of the crude product crystallized from benzene–light petroleum when white needles of 10-chloro-10-phenylanthrone crystallized out, m.p. 162–163° (lit.¹⁶ 164°); IR ν_{max} (CCl_4) 1674 cm^{-1} (C=O). A further portion of the crude product was crystallized from EtOH when white needles of 10-ethoxy-10-phenylanthrone were obtained, m.p. 155–157° (lit.¹⁴ 158°); IR ν_{max} (CCl_4) 1672 cm^{-1} (C=O); NMR τ 6.9 (q; 2H; CH_2CH_3) and 8.85 (t; 3H; CH_2CH_3).

Reaction of 9-benzyl-10-phenoxyanthracene with cupric chloride

A vigorously stirred mixture of 9-benzyl-10-phenoxyanthracene (0.90 g, 2.5 mmole) and cupric chloride (0.6725 g, 5 mmole) in CCl_4 (100 ml) was refluxed for 4½ hr. The crude reaction product was analysed by GLC and shown to contain 9-chloro-10-phenoxyanthracene (48%) and unreacted 9-benzyl-10-phenoxyanthracene (52%).

Reaction of 9-methyl-10-phenoxyanthracene with cupric chloride

The reaction was carried out as above for 4½ hr. The crude product was analysed by GLC and shown to contain 9-chloro-10-phenoxyanthracene⁴ (62%) and unreacted 9-methyl-10-phenoxyanthracene (38%).

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