Tetrahedron. Vol. 25, pp. 5047 to 5057. Pergamon Press 1969. Printed in Great Britain

REACTIONS OF CUPRIC HALIDES WITH ORGANIC COMPOUNDS—V[1]

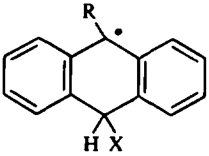
REACTIONS OF 9,10-DIALKYL- AND 9-ALKYL-10-ARYLANTHRACENES

S. GIBSON, A. D. MOSNAIM, D. C. NONHEBEL and J. A. RUSSELL
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow, C.1

(*Received in the UK* 3 *June* 1969; *Accepted for publication* 2 *July* 1969)

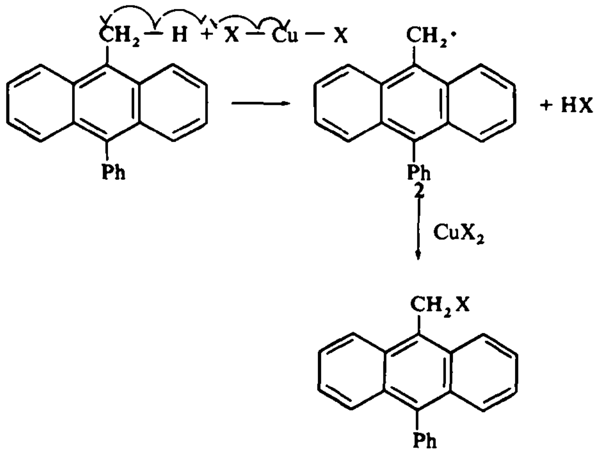
Abstract—9-Aryl-10-methylanthracenes undergo reaction with cupric halides to give the corresponding 9-aryl-10-halogenomethylanthracenes. 9-Ethyl- and 9-benzyl-10-methylanthracenes similarly undergo reaction at the Me group rather than at the Et or Bz groups to form the halogenomethyl compound. These results indicate that the 9-alkyl-10-anthrylmethyl radical is more stable than the radicals which would be formed by hydrogen abstraction from the Et or Bz groups. These reactions also gave products in which alkyl groups were replaced by halogen. A mechanistic interpretation of these results is advanced. The reactions of 9-alkyl (or aryl) 10-methylanthracenes with N-bromosuccinimide were also examined.

HALOGENATION of 9-alkyl- and 9-arylanthracenes with both cupric bromide and cupric chloride has been shown to take place exclusively in the 10-position.[1] These reactions proceed by a ligand-transfer mechanism involving transfer of the halogen of the cupric halide to the 10-position giving the radical (**1**). Reaction of this radical with cupric halide gives the resultant 9-alkyl(or aryl)-10-halogenoanthracene. The present work extends this to a study of some 9,10-disubstituted anthracenes in which ligand transfer involving attack at the 9- or 10-positions would be less probable because of steric hindrance.



1

9-Methyl-10-phenylanthracene underwent reaction with both cupric bromide and cupric chloride to give 9-halogenomethyl-10-phenylanthracene as the only product. The reaction involves attack on the methyl group by the cupric halide to give the (10-phenyl-9-anthryl)methyl radical (**2**), hydrogen halide and cuprous halide being formed as indicated in the reaction sequence shown. This radical on reaction with cupric halide gives the halogenomethyl compound (**3**) in a second ligand-transfer reaction.[2] Chromatography of 9-bromomethyl-10-phenylanthracene resulted in some hydrolysis to 9-hydroxymethyl-10-phenylanthracene (**3**, X = OH) taking place. The reaction with cupric chloride was much slower than that with cupric bromide. The difference in the rates of these reactions was appreciably greater than that observed for the difference in rates of reaction of 9-substituted anthracenes with cupric bromide and cupric chloride. In reactions of 9-methyl-10-phenylanthracene the rate-controlling step involves cleavage of a C—H bond and is likely to require a higher energy of activation than the ligand-transfer step in reaction of 9-substituted anthracenes. The reactions are thus likely to be more selective. In agreement with this, reactions of 9-methyl-10-phenylanthracene were very much slower than those of 9-alkyl(or aryl)-anthracenes.

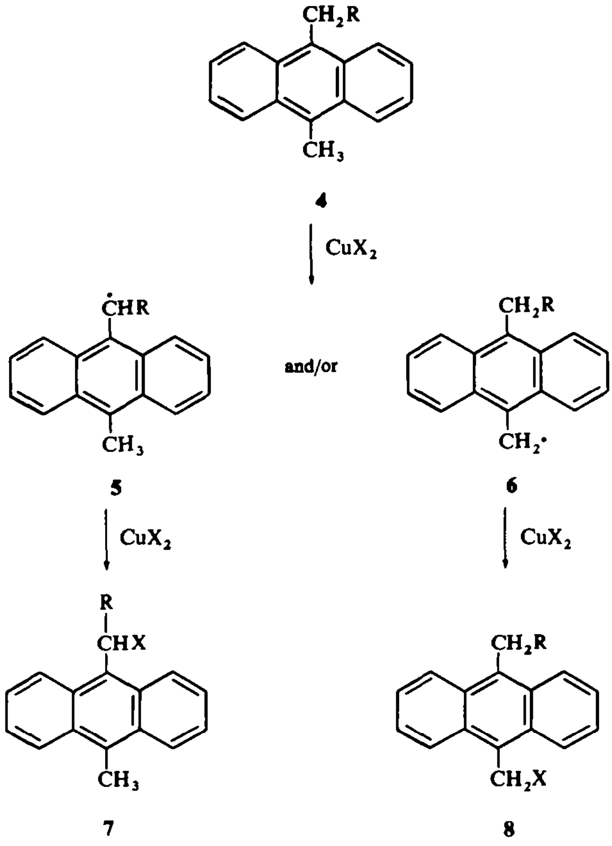


3

Consistent with the above mechanism it was found that 9-methyl-10-*p*-tolylanthracene underwent reaction with cupric chloride slightly more rapidly than 9-methyl-10-phenylanthracene. The intermediate radical should be slightly more stable.[3]

9-Benzyl-10-methylanthracene (**4**; R = Ph) and 9-ethyl-10-methylanthracene (**4**; R = Me) could in the same way give rise to either or both of the two alternative radicals (**5** and **6**) which would lead to the products (**7** and **8**) respectively. It is generally accepted that secondary radicals are more stable than primary[4] and hence one would predict that reaction would take place *via* the radical (**5**). In reactions of both these compounds with cupric halides, the halogenomethyl compound (**8**) was obtained albeit in low yield while none of the product involving attack at the methylene of the ethyl or benzyl group was detected. Beckwith and Waters observed that the reaction of 9-methylanthracene with methyl radicals gave amongst other products some 9,10-diethylanthracene.[5] This must have arisen by methylation of 9-ethyl-10-methylanthracene and must have proceeded via the radical (**6**; R = Me). The noteworthy feature of this reaction was the absence of any 9-isopropyl-10-methylanthracene which would have arisen from reaction of radical (**5**; R = Me) with methyl radicals.

The above results clearly suggest that the primary radical (**6**) is formed in preference to the secondary radical (**5**), i.e. that primary radical (**6**) is more stable. This can only be explained on steric grounds. The radical (**5**, R = Ph) might be expected to be particularly stable as it is benzylic in its relation to both the phenyl group and the anthryl group. Examination of a model of this radical clearly shows that coplanarity



of the anthracene system and the phenyl group necessary for maximum delocalization of the odd electron is not possible. Moreover, if the radical is in a conformation such that the unpaired electron can overlap with the anthracene system, there is still appreciable steric interaction between the phenyl group and the 1-proton of the anthracene. This becomes even more apparent if the "thickness" of the benzene ring is taken into consideration. This results in the alternative primary radical being more stable. The same reasoning can be applied to the two radicals (5 and 6, R = Me) which could be derived from 9-ethyl-10-methylanthracene. It is noteworthy that in both cases the 10-Me group is sterically more accessible to attack.

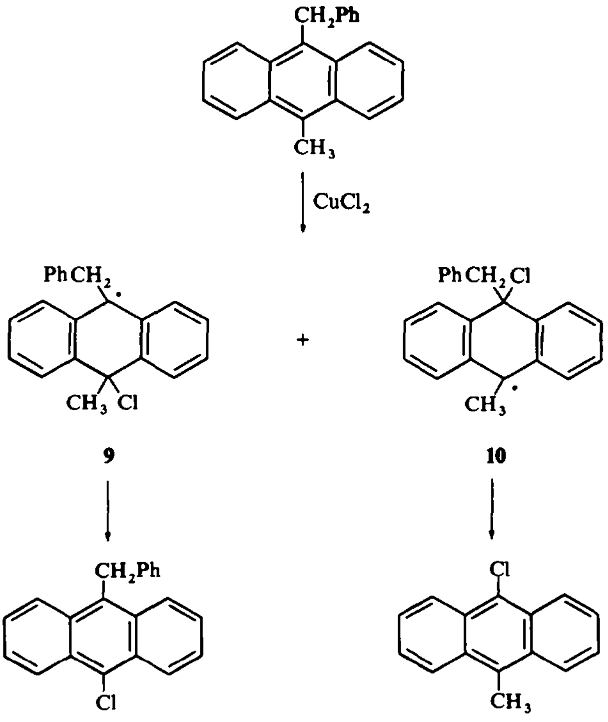
It could also be argued that the radical (5) is formed in addition to the radical (6) and being more stable has time to dissociate itself from the attendant copper species and accumulate in solution until it dimerizes.* Such compounds, being of much higher M.W., would have very much greater retention times on GLC. There was no evidence for the presence of such high M.W. compounds, though similar compounds can be eluted on GLC. In some of the reactions investigated, compounds having slightly greater retention times than the identified products were detected. The retention times of these unidentified compounds were consistent with their having arisen

---

* The authors are indebted to the referees for this suggestion.

from further halogenation of the products or the starting material probably in the side rings of the anthracene nucleus. The retention times of these compounds were definitely not great enough for these compounds to be dimeric species.

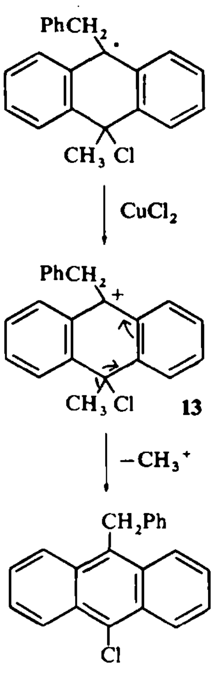
Reaction of 9-benzyl-10-methylanthracene with cupric chloride also afforded 9-chloro-10-methylanthracene, 9-chloro-10-chloromethylanthracene, and 9-benzyl-10-chloroanthracene. 9-chloro-10-methylanthracene and 9-benzyl-10-chloroanthracene arise from ligand transfer from the cupric chloride at the 9- or 10- positions in 9-benzyl-10-methylanthracene to give the intermediate radicals (**9** and **10**). These radicals, by loss of a methyl or a benzyl group, afford the products (**11** and **12**). The 9-chloro-10-methylanthracene can then undergo further chlorination in the methyl group to give 9-chloro-10-chloro-methylanthracene.[6] Three routes can be postulated for the formation of 9-benzyl-10-chloroanthracene (**11**) from the radical (**9**). The radical (**9**) could first undergo oxidation by cupric chloride to the carbonium ion (**13**) followed by loss of a methyl carbonium ion (sequence 1).[7] Alternatively loss of a methyl radical could occur directly from the radical (sequence 2). The third possibility involves attack by the cupric chloride on the Me group to give in a concerted process the product (sequence 3). The first two of these sequences do not seem energetically very feasible and the concerted process seems the most feasible. It is impossible to distinguish between these routes by study of the reaction products since they are the same in each case. The same processes can be written for conversion of the radical (**10**)



9 **10**

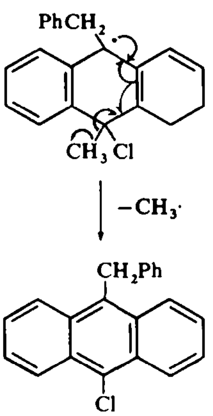
11 **12**

into 9-chloro-10-methylanthracene. From the results it would appear that reaction of cupric chloride with the 9-benzyl-10-methylanthracene takes place preferentially at the 10-position to give the radical (9), possibly on steric grounds. In contrast in the corresponding reaction with cupric bromide, no 9-benzyl-10-bromoanthracene was obtained indicating that attack took place preferentially at the 9-position. The smaller extent of reaction with cupric bromide than with cupric chloride can also be rationalized on steric grounds. In other ligand-transfer reactions of cupric halides, cupric bromide has always been found to react faster than cupric chloride. Ligand-transfer of bromine to the 9- or 10- positions of a 9,10-disubstituted anthracene would be less ready than that of the smaller chlorine.

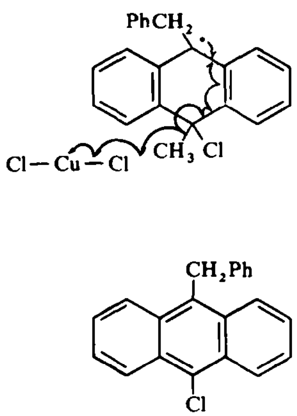


13

Sequence 1



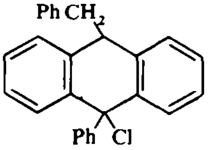
Sequence 2



Sequence 3

The same general picture emerged from the reactions of 9-ethyl-10-methylanthracene with both cupric bromide and cupric chloride. The extent of reaction of this compound was appreciably less than that of 9-benzyl-10-methylanthracene which in turn was much less than that of 9-methyl-10-phenylanthracene. The reasons for this are not at all clear at this stage.

The reaction of cupric chloride with 9-benzyl-10-phenylanthracene was also investigated with the aim of trying to detect any benzyl chloride which might be formed in this reaction. As expected this compound underwent reaction to give some 9-chloro-10-phenylanthracene, but in addition to this a significant amount of 9-benzyl-10-chloroanthracene was also obtained which could only arise as a result of loss of the phenyl group. Benzyl chloride was also detected using GLC consistent with the proposed mechanism. The formation of 9-benzyl-10-chloroanthracene was most unexpected involving as it does loss of a phenyl group. This can only be explained by a concerted attack (cf. sequence 3) by cupric chloride on the radical (**14**). 9-*p*-Methoxybenzyl-10-phenylanthracene underwent reaction appreciably more readily than 9-benzyl-10-phenylanthracene to give as the sole product 9-chloro-10-phenylanthracene. Both these compounds underwent reaction more rapidly than did 9-benzyl-10-methylanthracene and 9-ethyl-10-methylanthracene. A possible explanation for this is that the radical formed as a result of the ligand transfer of chlorine is formed reversibly and can then undergo further reaction more readily when loss of a benzyl or particularly a *p*-methoxybenzyl group is involved than when there is loss of the methyl group. Any radical or carbonium ion character in this reaction would be stabilised in the case of a *p*-methoxybenzyl or benzyl group much more than in the case of a Me group. In neither of these reactions was any product obtained from reaction at the CH_2 of the benzyl group. This underlines the difference in stability or at least ease of formation of radicals of the types (**5** and **6**, R = Ph).



14

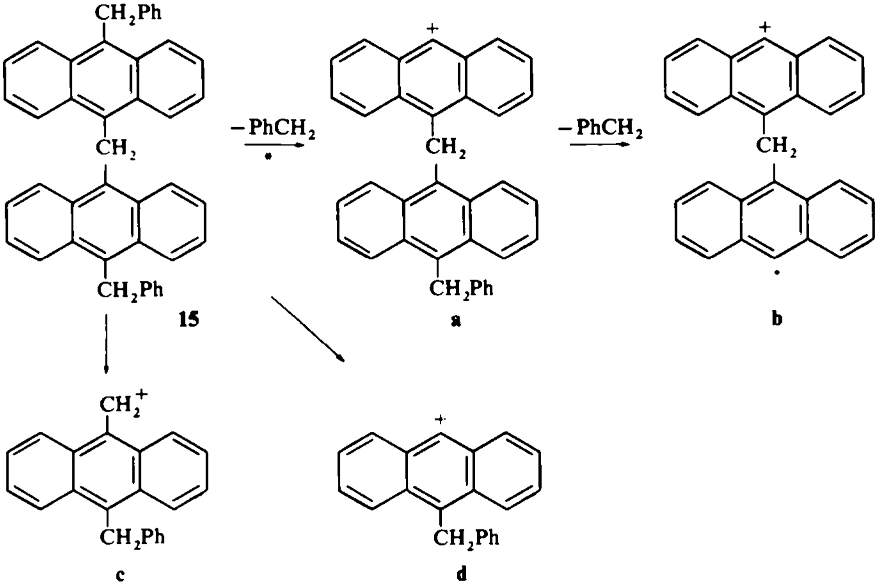
The reactions of 9-methyl-10-phenylanthracene, 9-ethyl-10-methylanthracene, and 9-benzyl-10-methylanthracene with N-bromosuccinimide in presence of peroxide were also examined and found in all cases to give the bromomethyl compound together with products involving loss of an alkyl group. These results essentially confirm those obtained with cupric halides with respect to the contention that a methyl group rather than an ethyl or a benzyl group undergoes attack to form an intermediate radical.

9-Benzyl-10-methylanthracene, 9-ethyl-10-methylanthracene, and 9-methyl-10-*p*-tolylanthracene were obtained in excellent yield by the Huang-Minlon reduction of the corresponding formyl compounds. The Huang-Minlon reduction of 9-benzoyl-10-phenylanthracene failed probably on steric grounds and 9-benzyl-10-phenylanthracene was prepared by the Grignard reaction between benzylmagnesium chloride and 10-phenylanthrone.[8] 9-*p*-Methoxybenzyl-10-phenylanthracene was obtained by a Grignard coupling reaction between 9-bromomethyl-10-phenylanthracene and *p*-methoxyphenylmagnesium bromide in excellent yield. This is probably the most convenient route to compounds of this type.

The halogenomethyl compounds were very easily obtained by bromomethylation and chloromethylation of the appropriate 9-substituted anthracene.[10] Yields were frequently excellent. Zinc halides were not found to be necessary to promote these reactions.

A by-product obtained in the chloromethylation of 9-benzylanthracene was bis-(10-benzyl-9-anthryl)methane (15). Its structure was assigned on the basis of mass spectral data. The molecular formula was shown to be $C_{43}H_{32}$. This was also the base peak. Prominent fragments **a** and **b** result from the loss of one and two benzyl groups from the molecular ion. Metastable transitions from the parent to fragment

a, and from fragment **a** to fragment **b** were observed. Other prominent peaks observed arise from cleavage of the bond between the central methylene group and one of the anthracene nuclei to give fragments **c** and **d**. All these assignments were supported by accurate mass measurements on the fragments. This compound must have arisen from attack on 9-benzylanthracene by the intermediate 9-benzyl-10-anthrylmethyl carbonium ion which would be formed in the chloromethylation reaction. There are other examples in the literature of this type of product being formed in the chloromethylation of activated aromatic compounds.[11]



15 **a** **b** c **d**

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. NMR spectra in deuteriochloroform were recorded on a Perkin Elmer R10 spectrometer at 60 MHz using TMS as an internal standard, GLC analysis was carried out as in previous work. Cupric bromide and cupric chloride were ground and dried as previously described. Mass spectra were recorded on an A.E.I. MS9 mass spectrometer.

Preparation of starting materials

9-*Methyl*-10-*phenylanthracene*. This was prepared by the Huang-Minlon reduction of 9-formyl-10-phenylanthracene.[12] It was crystallised from light petroleum as pale yellow plates (88%), m.p. 112–113° (lit.[12] 113°).

9-*Formyl*-10-p-*tolylanthracene*. A mixture of 9-*p*-tolylanthracene (9·9 g), N-methylformanilide (10 g), phosphorus oxychloride (10 g) and *o*-dichlorobenzene (6 ml) was heated on a steam bath for 1½ hr.[10] The mixture was then poured into a soln of NaOAc (40 g) in 10 ml) and the whole steam distilled. The solid residue was filtered off, and dissolved in CH_2Cl_2. The CH_2Cl_2 layer was washed twice with 20% HCl, and then with $NaHCO_3$aq and dried. The solvent was distilled off and the residue in benzene chromatographed on alumina. Elution with benzene gave 9-*formyl*-10-p-*tolylanthracene* (9·52 g, 87%) which crystallized from CH_2Cl_2-light petroleum as yellow prisms, m.p. 177–178° (Found: C, 88·8; H, 5·6. $C_{22}H_{16}O$ requires: C, 89·2; H, 5·4%); NMR τ – 1·57 (1H; CHO), 7·48 (3H :Me).

9-Methyl-10-p-tolyanthracene. A stirred soln of 9-formyl-10-*p-tolyanthracene* (8·8 g) and hydrazine hydrate (9 ml) in EtOH (100 ml) was refluxed for 1 hr.[13] EtOH was distilled off and KOH (6 g) in ethylene glycol (70 ml) was added. The mixture was distilled until the temp of the soln reached 210°. It was then refluxed for 4 hr. After cooling, the mixture was poured into water (250 ml) and the whole extracted twice with benzene. The benzene extracts were washed with water and dried. After evaporation of the solvent the residue in light petroleum was chromatographed on alumina. Elution with light petroleum afforded *9-methyl-10-p-tolylanthracene* (7·37 g, 88%) as very pale yellow needles from light petroleum m.p. 147·5–148·5°. (Found: C, 93·2; H, 6·6. $C_{22}H_{18}$ requires: C, 93·6; H, 6·40%); NMR τ 6·88 (3H; 9-Me), 7·51 (3H; Me of MeC_6H_4).

9-Benzyl-10-methylanthracene. 9-Benzyl-10-formylanthracene[10] (22 g) was reduced as described in the previous experiment, and the product in light petroleum chromatographed on alumina giving 9-benzyl-10-methyl anthracene (19 g, 90%) which crystallized from light petroleum as yellow needles, m.p. 167–168° (lit[14] .168°); NMR τ 5·04 (2H; CH_2Ph), 6·93 (3H; Me).

9-Ethyl-10-methylanthracene. 9-Ethyl-10-formylanthracene[15] (9 g) was reduced as described above, and the product chromatographed on alumina giving 9-ethyl-10-methylanthracene (7·5 g, 87%), which crystallized from petrol as pale yellow needles, m.p. 143–144° (lit[14], 143–144°); NMR τ 6·39 (s; 2H; CH_2Me protons); 6·71 (s; 3H; Me protons); 8·60 (t; 3H; Me protons of Et group).

9-Benzoyl-10-phenylanthracene. A soln of the Perrier complex of benzoyl chloride was prepared by stirring a soln of the chloride (2·81 g, 0·02 mole) in 1,z-dichloroethane (25 ml) with excess freshly ground $AlCl_3$ for 1 hr. The mixture was filtered and the filtrate added to a stirred soln of 9-phenylanthracene (5·08 g, 0·02 mole) in 1,1-dichloroethane (100 ml) at 0°. The soln was stirred at 0° for 1½ hr and the ice-bath was then removed and stirring was continued for a further 2½ hr. The soln was then poured into 6 N HCl (200 ml). The organic layer after washing with water and $NaHCO_3$ aq was dried and the solvent evaporated. The residue in 3 :1 light petroleum: benzene was chromatographed on alumina. Unchanged 9-phenylanthracene (1·165 g, 21% recovery) was first eluted followed by *9-benzoyl-10-phenylanthracene* (4·2 g, 73%), which crystallized from light petroleum CH_2Cl_2 as yellow prisms, m.p. 217–219°. (Found: C, 90·8; H, 5·1. $C_{27}H_{18}O$ requires: C, 90·5; H, 5·1%); IR, ν_{max} (CCl_4) 166·9 mm^{-1}.

9-Benzyl-10-phenylanthracene. (a) Attempted reduction of 9-benzoyl-10-phenylanthracene using the Huang–Minlon procedure used above afforded only unchanged starting material.

(b) 10-Phenylanthrone[16] (1·512 g, 5·6 mmole) was added to a soln of benzylmagnesium chloride (from 2·125 g, 16·8 mmole benzyl chloride) in ether. The product was chromatographed on alumina. Elution with light petroleum gave 9-benzyl-10-phenylanthracene (0·69 g, 36%), which crystallized in pale yellow plates from AcOH m.p. 154–155 (lit[8]. 155°).

9-p-*Methoxybenzyl-10-phenylanthracene.* An ethereal solution of *p*-methoxyphenylmagnesium bromide was prepared from *p*-bromoanisole (4·68 g, 25 mmole) and added dropwise to a soln of 9-phenyl-bromomethyl-10-phenylanthracene (1·87 g, 5 mmole) in ether (100 ml). Stirring was continued for a further 20 min. Excess Grignard reagent was decomposed by dropwise addition of 6 N HCl. The ethereal layer was separated off, washed with water, and $NaHCO_3$aq, and dried (Na_2SO_4). The ether was evaporated off, and the residue in 9 :1 light petroleum :benzene was chromatographed on alumina. Elution with this solvent gave 9-p-*methoxybenzyl-10-phenylanthracene* which crystallized from light petroleum—CH_2Cl_2 as pale yellow needles (1·55 g, 83%), m.p. 147°. (Found: C, 89·7; H, 5·9. $C_{28}H_{22}O$ requires: C, 89·8; H, 5·6%); NMR, τ 4·99 (2H: CH_2Ph), 6·30 (3H; OMe).

9-Bromomethyl-10-phenylanthracene. A mixture of paraformaldehyde (0·69 g, 23 mmole), AcOH (7 ml), and a 45% HBr in AcOH (9 ml) was stirred for 20 min until dissolution was complete. This solon was added to a stirred suspension of 9-phenylanthracene (2·29 g, 9 mmole) in AcOH (11 ml). Stirring was continued for 3¼ hr at 55°. After cooling, the ppt was filtered off. The ppt was dissolved in benzene, and the benzene solon washed with $NaHCO_3$aq, dried and evaporated. The residue was crystallized from light petroleum as yellow plates of 9-bromomethyl-10-phenylanthracene, (0·44 g, 14%), m.p. 170–176° dec (lit.[17] 177°).

9-Benzyl-10-bromomethylanthracene. Bromomethylation of 9-benzylanthracene (2·41 g, 9 mmole) as described previously gave *9-benzyl-10-bromomethylanthracene* as yellow needles from light petroleum (3·1 g, 96%) m.p. 157–162° dec. (Found: C, 72·2; H, 5·0; Br, 22·85. $C_{22}H_{17}Br$ requires: C, 72·2; H, 4·9; Br, 22·9%); NMR τ 4·50 (2H; CH_2Br), 5·05 (2H; CH_2Ph).

9-Bromomethyl-10-ethylanthracene. This was obtained similarly from 9-ethylanthracene (1·85 g, 9 mmole). Crystallization of the crude product from benzene gave yellow needles of *9-bromomethyl-10-ethylanthracene* (22 g, 83%), m.p. 165–178° dec. (Found: C, 68·5; H, 5·4; Br, 26·35. $C_{17}H_{15}Br$ requires: C, 68·3; H, 5·05; Br, 26·7%); NMR τ 4·50 (H; CH_2Br), 6·39 (q; 2H; CH_2 of Et), 8·60 (t; 3H; Me).

9-Chloromethyl-10-phenylanthracene. To a suspension of 9-phenylanthracene (2·29 g, 9 mmole) in AcOH (11 ml), was added a soln prepared by saturating a suspension of paraformaldehyde (0·69 g, 23 mmole) in AcOH (9 ml) with HCl.[10] The stirred mixture was kept at 55° for 3½ hr. After allowing to stand for a further ½ hr, the mixture was filtered. The ppt was dissolved in benzene and the benzene soln washed with Na_2CO_3 aq and then with water. After drying, the solvent was removed and the residue crystallized from light petroleum as yellow plates of *9-chloromethyl-10-phenylanthracene* (0·95 g, 35%), m.p. 171–173°. (Found: C, 82·8; H, 5·0; Cl, 11·7. $C_{21}H_{15}Cl$, requires: C, 83·3; H, 5·0; Cl, 11·7%).

9-Chloromethyl-10-p-tolylanthracene. This was similarly obtained from 9-*p*-tolylanthracene (2·39 g, 9 mmole) as *yellow plates* from light petroleum (0·86 g, 30%), m.p. 163°. (Found: C, 83·7; H, 5·5; Cl, 10·7. $C_{21}H_{17}Cl$ requires: C, 83·4; H, 5·4; Cl, 11·2%); NMR τ 4·37 (2H, CH_2Cl); 7·50 (3H, Me).

9-Benzyl-10-chloromethylanthracene. Chloromethylation of 9-benzylanthracene (2·39 g, 9 mmole), carried out as described in the previous experiments, gave *9-benzyl-10-chloromethylanthracene* as yellow needles from light petroleum (0·83 g, 29%), m.p. 140–145°. (Found: C, 83·5; H, 5·2; Cl, 10·85. $C_{22}H_{17}Cl$ requires: C, 83·4; H, 5·4; Cl, 11·2%); NMR (CS_2) 4·56 (2H; CH_2Cl), 5·12 (2H; CH_2Ph).

Some of the crude reaction product was insoluble in benzene. Crystallization of this material from xylene gave yellow needles of *bis-(9-benzyl-10-anthryl) methane* (0·2 g, 8%) m.p. 320–321°. (Found: C, 94·2; H, 6·1. M^+ 548·25085. $C_{43}H_{32}$ requires: C, 94·1; H, 5·9% M^+ 548·25038). Prominent peaks at *m/e* 457·19612 (91%, $C_{36}H_{25}^+$), 366·13860 (27%, $C_{29}H_{18}^+$), 281·13227 (17%, $C_{22}H_{15}^+$), 189 (22%, $C_{15}H_9^+$); metastable peaks at 381·1 (548 → 457), 293·1 (457 → 366).

9-Chloromethyl-10-ethylanthracene. This was obtained by the chloromethylation of 9-ethylanthracene. Crystallization of the crude product from benzene gave yellow needles of *9-chloromethyl-10-ethylanthracene* (85%), m.p. 162–180° dec. (Found: C, 79·8; H, 6·15; Cl, 14·0. $C_{17}H_{15}Cl$ requires: C, 80·1; H, 5·9; Cl, 13·9%); NMR τ 4·46 (2H; CH_2Cl), 6·39 (q; 2H; CH_2 of Et), 8·60 (t; 3H; Me).

9-Benzoyl-10-methylanthracene. A mixture of $AlCl_3$ (10·95 g) and benzoyl chloride (17·25 g) in ethylene chloride (150 ml) was stirred at room temp for 20 min and then cooled to 0°.[18] 9-Methylanthracene (14·25 g) was added to this soln and the whole stirred at 0° for 1½ hr. The soln was then poured into 6N HCl and the organic layer separated off. This was washed with $NaHCO_3$ aq, and then with water, and then dried (Na_2SO_4). The residue, after removal of the solvent, was dissolved in 2:1 light petroleum:benzene and chromatographed on alumina. Elution with this solvent gave unchanged 9-methylanthracene. Elution with 1:1 light petroleum: benzene gave 9-benzoyl-10-methylanthracene, which crystallized from benzene-light petroleum as yellow prisms (19·5 g, 88%), m.p. 174–174·5°. (Found: C, 89·0; H, 5·1. $C_{22}H_{16}O$ requires: C, 89·15; H, 5·4%); IR ν_{max} (CCl_4) 166·8 mm^{-1}; NMR, τ 6·86 (3H, Me).

Reduction of 9-benzoyl-10-methylanthracene

(a) *With sodium borohydride.* A soln of 9-benzoyl-10-methylanthracene (3 g) in MeOH (300 ml) was added to a soln of $NaBH_4$ (0·3 g) in MeOH (20 ml) and water (2 ml) and the whole refluxed for ½ hr. TLC indicated that no reduction had taken place, and 9-benzoyl-10-methylanthracene was recovered unchanged on concentrating the solution.

(b) *With lithium aluminium hydride.* A soln of 9-benzoyl-10-methylanthracene (3 g) in anhyd ether (450 ml) was added to a refluxing mixture of LAH (1·5 g) in ether (150 ml) and the whole refluxed for 4 hr. Excess LAH was destroyed by the careful addition of EtOAc and the mixture filtered. The filtrate was washed with dil HCl, and with water before drying (Na_2SO_4). The residue, after removal of the solvent, was dissolved in the minimum of benzene. Petroleum ether was added to this to precipitate out *9-α-hydroxybenzyl-10-methylanthracene* (2·65 g, 89%), m.p. 155–156·5°. (Found: C, 88·45, H, 5·8. $C_{22}H_{18}O$ requires: C, 88·6; H, 6·1%); IR, ν_{max} (CS_2) 360·0 mm^{-1} (OH); NMR τ 6·94 (3H, Me), 7·26 (1H, OH)—this peak disappeared on treatment with D_2O.

9-α-Chlorobenzyl-10-methylanthracene. A mixture of 9-α-hydroxybenzyl-10-methylanthracene (1 g) and $SOCl_2$ (0·25 ml) in benzene (30 ml) was refluxed for 3 hr. The solvent was distilled off and the residue crystallized as a yellow amorphous powder from light petroleum-CH_2Cl_2 of 9-α-chlorobenzyl-10-methylanthracene, m.p. 115–120 dec. (Satisfactory elemental analysis could not be obtained). The retention time was different from that of 9-chloromethyl-10-benzylanthracene.

Reactions with cupric halides

Reaction of 9-methyl-10-phenylanthracene with cupric bromide. A stirred mixture of 9-methyl-10-phenylanthracene (0·268 g, 1 mmole) and cupric bromide (0·447 g, 2 mmole) in chlorobenzene (100 ml) was refluxed for 23 hr. The mixture was filtered and the filtrate evaporated to dryness. GLC analysis of the residue showed the presence of 9-bromomethyl-10-phenylanthracene (>95%). The residue was crystallized from light petroleum giving yellow needles of 9-bromomethyl-10-phenylanthracene (2·88 g, 83%) m.p. and mixed m.p. 170–176°.

In a second experiment the product was chromatographed on alumina. Elution with 50:1 light petroleum: benzene gave yellow needles of 9-bromomethyl-10-phenylanthracene, m.p. and mixed m.p. 170–176°. Elution with 10:1 benzene:MeOH gave 9-hydroxymethyl-10-phenylanthracene as white needles from MeOH, m.p. 164–165° (lit.[19] 166–167°); NMR τ 4·33 (2H, CH$_2$); 8·00 (1H, OH).

Reaction of 9-methyl-10-phenylanthracene with cupric chloride. The reaction was carried out as above using cupric chloride (0·269 g, 2 mmole). GLC analysis of the crude product showed that it contained 9-chloromethyl-10-phenylanthracene (51%) and unreacted 9-methyl-10-phenylanthracene (48%). The reaction product in light petroleum was chromatographed on alumina. Elution with 50:1 light petroleum: benzene gave initially 9-chloromethyl-10-phenylanthracene (0·1270 42%) which crystallized as yellow plates from light petroleum m.p. and mixed m.p. 171–173°. Further elution gave mixture of this and 9-methyl-10-phenylanthracene.

Reaction of 9-methyl-10-p-tolylanthracene with cupric chloride. The reaction was carried out as above using 9-methyl-10-*p*-tolylanthracene (0·282 g, 1 mmole) and cupric chloride (0·269 g, 2 mmole). GLC analysis of the crude product showed to contain 9-chloromethyl-10-phenylanthracene (54%) along with unreacted 9-methyl-10-phenylanthracene (46%).

A stirred mixture of 9-methyl-10-phenylanthracene (0·335 g, 1·25 mmole), 9-methyl-10-*p*-tolylanthracene (0·3525 g, 1·25 mmole) and cupric chloride (0·3363 g, 2·5 mmole) in chlorobenzene (100 ml) was refluxed for 23 hr. GLC analysis of the crude product showed it to contain 9-chloromethyl-10-phenylanthracene, 9-chloromethyl-10-*p*-tolylanthracene (the amounts of these could not be quantitatively estimated), 9-methyl-10-phenylanthracene (27%), and 9-methyl-10-*p*-tolylanthracene (23%) from which it was possible to calculate that 9-methyl-10-*p*-tolylanthracene reacts 1·2 times as fast as 9-methyl-10-phenylanthracene.

Reaction of 9-benzyl-10-methylanthracene with cupric bromide. A stirred mixture of 9-benzyl-10-methylanthracene (0·282 g, 1 mmole) and cupric bromide (0·447 g, 2 mmole) in chlorobenzene (100 ml) was refluxed for 23 hr. GLC analysis of the product showed that it contained 9-benzyl-10-bromomethylanthracene (6%), 9-bromo-10-bromomethylanthracene (6%), 9-bromo-10-methylanthracene (4%), and unreacted 9-benzyl-10-methylanthracene (82%).

Reaction of 9-benzyl-10-methylanthracene with cupric chloride. This was carried out as above using cupric chloride (0·269 g, 2 mmole). GLC analysis of the product showed the presence of 9-benzyl-10-chloromethylanthracene (7%), 9-benzyl-10-chloroanthracene (25%), 9-chloro-10-methylanthracene (4%), 9-chloro-10-chloromethylanthracene (6%), and unreacted 9-benzyl-10-methylanthracene (57%).

Reaction of 9-ethyl-10-methylanthracene with cupric bromide. The reaction was carried out as described previously using 9-ethyl-10-methylanthracene (0·220 g, 1 mmole). GLC analysis of the crude product showed it to contain unreacted 9-ethyl-10-methylanthracene (>95%) and traces of 9-bromomethyl-10-ethylanthracene and 9-bromo-10-ethylanthracene.

Reaction of 9-ethyl-10-methylanthracene with cupric chloride. This was carried out as above using cupric chloride (0·269 g, 2 mmole). GLC analysis of the product showed it to contain unreacted 9-ethyl-10-methylantracene (>95%) and a trace of 9-chloromethyl-10-ethylanthracene.

Reaction of 9-benzyl-10-phenylanthracene with cupric chloride. This was carried out as above with 9-benzyl-10-phenylanthracene (0·344 g, 1 mmole). The filtrate from the reaction was concentrated and examined by GLC operating at 90°. GLC showed the presence of benzyl chloride. The filtrate was then evaporated in the usual way and the residue analysed by GLC which showed it to contain 9-chloro-10-phenylanthracene (19%) and 9-benzyl-10-chloroanthracene (10%) and unreacted 9-benzyl-10-phenylanthracene (44%) together with 2 unidentified compounds which had longer retention times.

Reaction of 9-p-methoxybenzyl-10-phenylanthracene with cupric chloride. This reaction was carried out as above using 9-*p*-methoxybenzyl-10-phenylanthracene (0·374 g, 1 mmole). GLC analysis of the product showed that it contained 9-chloro-10-phenylanthracene (77%) and unreacted 9-*p*-methoxybenzyl-10-phenylanthracene (23%).

Reactions with N-bromosuccinimide

Reaction of 9-methyl-10-phenylanthracene. A stirred mixture of 9-methyl-10-phenylanthracene (0·268 g, 1 mmole), N-bromosuccinimide (0·178 g, 1 mmole), and dry dibenzoyl peroxide (0·0242 g, 0·1 mmole) in CCl$_4$ (100 ml) was refluxed for 1½ hr. The cooled mixture was filtered and the filtrate evaporated. The residue was analysed by GLC and was found to contain 9-bromomethyl-10-phenylanthracene (44%), 9-bromo-10-phenyl-anthracene (29%) and unreacted 9-methyl-10-phenylanthracene (27%).

Reaction with 9-benzyl-10-methylanthracene. This was carried out as described above using 9-benzyl-10-methylanthracene (0·282 g, 1 mmole). GLC analysis of the product showed it to contain 9-benzyl-10-bromomethylanthracene (50%), 9-benzyl-10-bromoanthracene (20%), 9-bromo-10-bromo-methylanthracene (7%), and unreacted 9-benzyl-10-methyl-anthracene (22%). The residue in light petroleum :benzene was chromatographed on alumina. Elution with this solvent gave 9-benzyl-10-bromomethylanthracene (0·126 g, 35%), which crystallized from light petroleum as yellow needles, m.p. and mixed m.p. 157–162°.

Reaction with 9-ethyl-10-methylanthracene. This was carried out as described above using 9-ethyl-10-methylanthracene (0·220 g, 1 mmole). GLC analysis of the product showed it to contain 9-bromomethyl-10-ethylanthracene (28%), 9-bromo-10-methylanthracene (13%), and unreacted 9-ethyl-10-methylanthracene (59%).

Acknowledgements—The authors thank Drs. P. Bladon and G. R. Proctor and their staffs for spectra and microanalyses, Miss M. T. Campbell for technical assistance. One of us (A.D.M.) thanks the Ministry of Overseas Development for a maintenance grant, and the University of Chile for leave of absence.

REFERENCES

[1] Part IV, D. C. Nonhebel and J. A. Russell, *Tetrahedron* **25**, 3493 (1969).
[2] A. D. Mosnaim, D. C. Nonhebel and J. A. Russell, *Ibid.* **25**, 3485 (1969).
[3] R. Pearson and J. Martin, *J. Am. Chem. Soc.* **85**, 354 (1963).
[4] Cf. J. D. Roberts and M. C. Caserio, *Basic Principles of Organic Chemistry* p. 189. Benjamin, New York (1965).
[5] A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.* 1108 (1956).
[6] A. D. Mosnaim and D. C. Nonhebel, unpublished work.
[7] D. Mosnaim and D. C. Nonhebel, *Tetrahedron* **25**, 1591 (1969).
[8] E. de B. Barnett, J. W. Cook and J. L. Wiltshire, *J. Chem. Soc.* 1724 (1927).
[9] Cf. R. O. C. Norman, *Principles of Organic Synthesis* p. 206. Methuen, London (1968).
[10] Cf. G. M. Badger and R. S. Pearse, *J. Chem. Soc.* 2314 (1950).
[11] Ref. 9 p. 373.
[12] R. O. C. Norman and W. A. Waters, *J. Chem. Soc.* 167 (1958).
[13] P. F. Southern and W. A. Waters, *Ibid.* 4340 (1960).
[14] E. Berliner, *Ibid.* **66**, 533 (1944).
[15] R. H. Martin and L. van Hove, *Bull. Soc Chim. Belges* **61**, 504 (1952).
[16] R. Brisson, *Ann. Chim. Paris* 7, 311 (1952).
[17] E. de B. Barnett and M. A. Matthews. *Chem. Ber.* **59**, 1429 (1926).
[18] P. H. Gore and J. A. Hoskins, *J. Chem. Soc.* 5666 (1964).