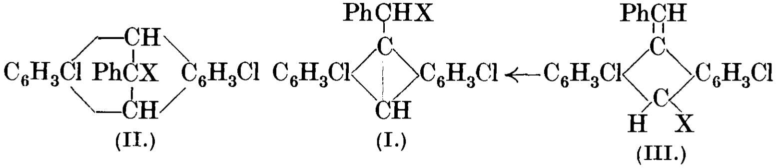
CCCLXX.—*Transannular Anionotropic Migrations.*

By James Wilfred Cook.

It has been shown (Barnett, Cook, and Matthews, *Ber.*, 1927, **60**, 2353) that the monobromo-derivative of 1 : 5-dichloro-9-benzylanthracene exhibits dual properties inasmuch as it yields two distinct series of hydroxy-, acetoxy-, methoxy-, and ethoxy-compounds by suitable treatment, *viz.*, (*a*) yellow and fluorescent compounds which are represented by formula (I) and (*b*) colourless and non-fluorescent isomeric compounds, obtained when the hydrogen bromide formed by the reaction is removed as rapidly as it is produced, which pass into their yellow isomerides under the influence of hydrogen ions. Moreover, both hydroxy-compounds are converted by hydrogen bromide into the original bromo-compound. Barnett and Matthews (*loc. cit.*) suggested tentatively that the colourless compounds have endocyclic structures (II), whereas the author (Cook, *Ber.*, 1927, **60**, 2366) regarded this as improbable and assigned a benzylidene structure (III) to the colourless compounds, postulating a migration of X to account for the interconversion of compounds of the two series :



The present communication deals with attempts to decide between structures (II) and (III); it is not claimed that the endocyclic structure (II) is definitely disproved, but there is much new evidence to substantiate structure (III) for the colourless compounds.

The analogy existing between the tautomeric system contained in a 9-alkyl derivative of anthracene (the " bridge " being regarded as equivalent to an ethylenic bond) and the simpler 3-carbon system has been established by the interconversion of 1 : 5-dichloro-10-phenyl-9-methylanthracene and the pseudo-tautomeric methylene compound (Barnett and Cook, *Ber.*, 1928, **61**, 314), and the postulated change (III)⟶(I) is then seen to be comparable with the bromine migrations in simpler conjugated systems recently studied by Farmer, Laroia, Switz, and Thorpe (J., 1927, 2937) * and Farmer, Lawrence, and Thorpe (this vol., p. 729) * and with the mobile anion tautomeric changes described by Burton and Ingold (this vol., p. 904).*

The suggestion was made tentatively (Cook, *loc. cit.*) that the rearrangement in the anthracene series is preceded by ionic dissociation, and this mechanism has been confirmed in the case of the α-phenylallyl system by the experiments of Burton (this vol., p. 1650). The order of mobility of the anions (Br>OAc> OH or OR), identical with that observed by Burton and Ingold in their compounds, is further evidence of the ionic nature of

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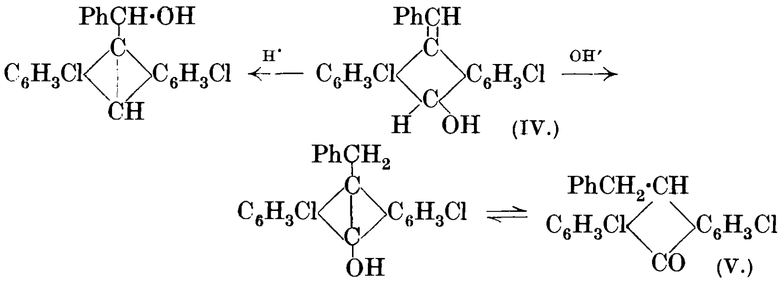
* Other examples of mobile anion tautomerism may be found from the references given in these papers.

the migrations and it is also significant that, whereas hydrogen ions promote hydroxyl migration in the colourless hydroxy-compound (IV), hydroxyl ions bring about hydrogen migration. The 1 : 5-dichloro-9-benzylanthrone (V) resulting from the latter change was identified by direct comparison with an authentic sample and also by conversion into 1 : 5-dichloro-9-benzyl-10-phenylanthracene by treatment with magnesium phenyl bromide, followed by dehydration of the resulting carbinol.



This prototropic change, effected by brief boiling with sodium hydroxide solution, is comparable with analogous changes in open-chain systems (Burton and Ingold, *loc. cit.*).

More definite evidence that the substituent group in the colourless compounds is attached to the 10-carbon atom of the anthracene ring is afforded by an experiment carried out with the 1 : 5-dichloro-10-ethoxy-9-benzylidene-9 : 10-dihydroanthracene * (VI) prepared by Barnett (unpublished work) by the action of magnesium benzyl chloride on 1 : 5-dichloroethoxyanthrone and dehydration of the resulting dihydroanthranol. This ethoxy-compound (VI) is different from the colourless ethoxy-compound previously prepared (Barnett, Cook, and Matthews, *Ber.*, 1927, **60**, 2361) and is presumably its geometrical isomeride. It has not been possible to effect its direct conversion into the ω-ethoxy-compound, the reaction with alcoholic hydrogen chloride being slow and incomplete. This difference in migratory power between the two geometrical isomerides is curious and may be compared with a similar difference observed with the 1 : 2-dibromides of the two stereoisomeric hexatrienes (Farmer, Laroia, Switz, and Thorpe, J., 1927, 2942). The desired conversion was obtained through the bromo-compound, replacement of the ethoxy-group by the more mobile bromine atom by treatment of (VI) with hydrogen bromide leading to the same monobromo-

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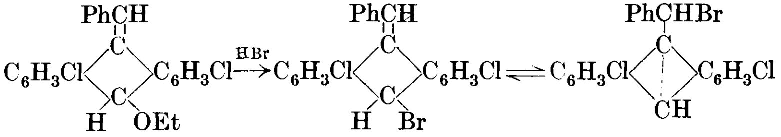
* I am indebted to Dr. E. de Barry Barnett for his kindness in giving me a few grams of this benzylidene compound.—J. W. C.

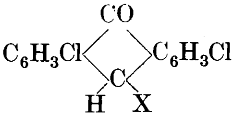
compound (VII) as was obtained by bromination of 1 : 5-dichloro-9-benzylanthracene.



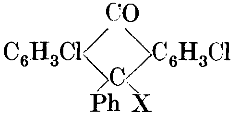
(VI.) (VII.) (VIII.)

The inversion of geometrical configuration evidently proceeds through the tautomeric phase (VIII), it having been shown already that (VIII) cannot be isolated owing to the ease with which it passes into its isomeride of the " colourless " type (Barnett, Cook, and Matthews, *loc. cit.* Compare Barnett, Cook, and Ellison, this vol., p. 889).

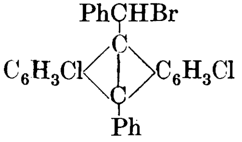
It should be possible to obtain evidence of structure (III) for the colourless compounds by oxidation to the anthrone derivative (IX).



(IX.)



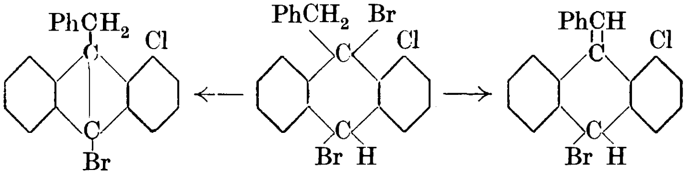
(X.)



(XI.)

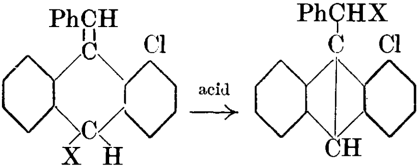
As long as there is a mobile hydrogen atom this course is not practicable on account of the ease with which the enol is oxidised. If the mobile hydrogen atom is replaced by a phenyl group, enolisation is no longer possible, so that the phenylanthrone derivative (X) should be capable of isolation from the oxidation products. With this object in view the preparation of a series of derivatives of 1 : 5-dichloro-9-benzyl-10-phenylanthracene was initiated. The substance gave a reactive *monobromo*-derivative, but the *hydroxy*- and *ethoxy*-compounds obtained from it by treatment with aqueous acetone and ethyl alcohol, respectively, in the presence of calcium carbonate were obviously of the " yellow " and fluorescent type, and this, coupled with the deep orange colour of the bromo-compound, renders it fairly certain that the latter has structure (XI). The influence of replacement of hydrogen by phenyl on the equilibrium of the anionotropic system is explicable on the electronic hypothesis of Burton and Ingold and steric influences would operate in the same direction.

The problem was attacked from another standpoint by attempting the preparation of colourless series of derivatives from 1-*chloro*-9-*benzylanthracene* and 4-*chloro*-9-*benzylanthracene*. If the endocyclic structure were correct, the molecule would be symmetrical and these two series of compounds would have identical structures (XII). Now, although 1 : 5-dichloro-9-benzylanthracene gives a reactive bromo-derivative, 9-benzylanthracene yields only the 10-bromo-derivative (Cook, J., 1926, 2161. Compare *Ber.*, 1927, **60**, 2366), so that the first possible pitfall was that a single α-chlorine atom might fail to have the necessary influence on the bromination. Actually, 1-chloro-9-benzylanthracene on bromination yielded a very unstable dibromide which decomposed into a mixture of the 10-*bromo*-compound (XIII; 30%) and the *benzylidene* compound (XIV; 70%):

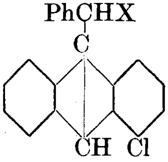


(XIII.) (XIV.)

From the reactive bromo-compound (XIV) derivatives were obtained of both "colourless" (XV) and "yellow" (XVI) types.



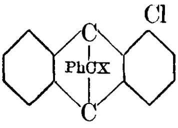
(XV.) (XVI.)



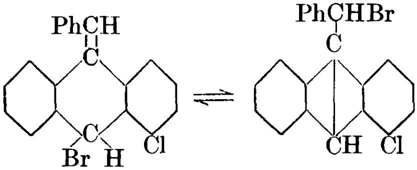
(XVII.)

(X = OH, O·COMe or OR.)

The unstable dibromide of 4-chloro-9-benzylanthracene gave only the reactive *bromo*-compound, but this passed into "yellow" substitution products (XVII) even in the presence of calcium carbonate and it seems fairly certain in this case that the ω-bromo-compound is the stable tautomeride, so that the bromo-compound has structure (XVIII).



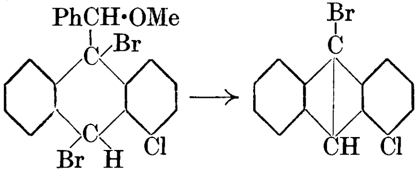
(XII.)



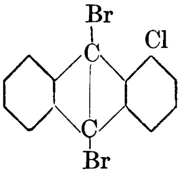
(XVIII.)

The steric effect of the α-chlorine atom can account for these differences between the 1-chloro- and the 4-chloro-derivatives of 9-benzylanthracene. The non-formation of colourless derivatives of the 4-chloro-compound has prevented definite refutation of the endocyclic structure. It is certain, however, that the endocyclic compounds were not formed as intermediate products in the preparation of the ω-derivatives of 4-chloro-9-benzylanthracene, since the latter substances were quite different from the isomeric ω-derivatives obtained from 1-chloro-9-benzylanthracene.

The proof of the structure assigned to the " yellow " compounds is similar to that previously advanced in the case of the 1 : 5-dichloro-compounds. For instance, 4-chloro-ω-methoxy-9-benzylanthracene gave an unstable dibromide which spontaneously decomposed into benzaldehyde and 4-chloro-9-bromoanthracene (XIX) :



(XIX.)



(XX.)

This new bromo-compound was identical with the substance obtained by Barnett and Matthews (*Rec. trav. chim.*, 1924, **43**, 535) by thermal decomposition of α-chloroanthracene dibromide, and the present result determines the orientation of their compound. 4-Chloro-9-bromoanthracene is stable in the presence of excess of bromine, thus resembling 1 : 5-dichloro-9-bromoanthracene (Barnett, Cook, and Matthews, *loc. cit.*), but differing from 9-bromoanthracene itself which is readily brominated. 1-Chloro-9-bromoanthracene appears to resemble 9-bromoanthracene, since it was not isolated from the decomposition products of the dibromide of 1-chloro-ω-methoxy-9-benzylanthracene, only the dibromo-compound (XX) being obtained. The bromine necessary for bromination of the monobromo-compound was evidently obtained by partial loss of bromine from the original dibromide of the methoxybenzyl compound. The difference in behaviour between the isomeric α-chloro-9-bromoanthracenes may again be attributed to the steric effect of the α-chlorine atom, provided it is assumed that bromination is preceded by 9 : 10-addition of bromine, as is certainly the case with the bromination of many other anthracene derivatives.

The ω-*methoxy*-derivative of 1-chloro-9-benzylanthracene was converted by hydrogen bromide into the " colourless " bromo-compound (XIV), so that, as in the 1 : 5-dichloro-series, the " benzylidene " bromo-compound is the stable tautomeride, whereas with the hydroxy-, *acetoxy*-, and alkoxy-derivatives the ω-structure is the more stable. This curious difference, in conjunction with the fact that the ω-bromo-derivative of 4-chloro-9-benzylanthracene is the stable tautomeride, is doubtless due to steric factors. Thus, the omega structure is normally the stable type, but the presence of the chlorine atom in position 1 hinders the attachment of such a bulky group as bromine to the ω-carbon atom. It is perhaps significant that the bromine atom tends to take up a position as remote as possible from the α-chlorine atom (XIV and XVIII) and it may be that this is partly determined by polar factors.

It has been shown (Cook, J., 1926, 2161) that the action of excess of bromine on 10-bromo-9-benzylanthracene results in addition to one of the *Bz* rings with the formation of a tetrabromide. When 1-chloro-10-bromo-9-benzylanthracene (XIII) was treated with excess of bromine a tetrabromide was not obtained, the only product isolated being 4-chloro-9-bromoanthracene (XIX). At present it is not proposed to discuss this apparent replacement of a benzyl group by a hydrogen atom by means of bromine.

EXPERIMENTAL.

Prototropic Rearrangement of 1 : 5-*Dichloro*-10-*hydroxy*-9-*benzylidene*-9 : 10-*dihydroanthracene* (IV).—The hydroxy-compound (5 g.) was added to a solution of alcoholic sodium hydroxide prepared from sodium (5 g.) and 95% alcohol (125 c.c.). A deep blood-red colour was developed on boiling and the boiling was continued for ½ hour. The resinous product, obtained by dilution with water, was recrystallised twice from ethyl acetate and then formed colourless crystals (1·5 g.) which melted at 169—170° alone or when mixed with 1 : 5-dichloro-9-benzylanthrone (V). The identification was completed by treatment with magnesium phenyl bromide, dehydration of the resulting dihydroanthranol yielding 1 : 5-dichloro-9-benzyl-10-phenylanthracene, m. p. 211—212° (alone or mixed with an authentic sample).

The corresponding ethoxy-compound was recovered unchanged after boiling for 7 hours with alcoholic sodium hydroxide.

Action of Hydrogen Bromide on 1 : 5-*Dichloro*-10-*ethoxy*-9-*benzylidene*-9 : 10-*dihydroanthracene* (VI).—This ethoxy-compound (m. p. 170°; 1·5 g.), one of the products of the action of magnesium benzyl chloride on 1 : 5-dichloro-10-ethoxy-9-anthrone (see footnote on p. 2800) and shown to be different from the original colourless ethoxy-derivative of 1 : 5-dichloro-9-benzylanthracene, was dissolved in toluene (10 c.c.), and hydrogen bromide passed through the boiling solution for 20 minutes. After cooling and dilution with light petroleum, crystals separated which, after recrystallisation from benzene–light petroleum, melted at 180—182° alone or mixed with the monobromo-derivative obtained from 1 : 5-dichloro-9-benzylanthracene. The identification of the bromo-compound was completed by its conversion into the original colourless ethoxy-compound by means of alcohol in the presence of calcium carbonate. The new ethoxy-compound of Barnett was thus indirectly converted into its geometrical isomeride.

Derivatives of 1 : 5-*Dichloro*-9-*benzyl*-10-*phenylanthracene.*

(a) ω-*Bromo-derivative* (XI).—A solution of 1 : 5-dichloro-9-benzyl-10-phenylanthracene (16 g.) in carbon disulphide (100 c.c.) was treated slowly at the ordinary temperature with bromine (2 c.c.). After 3 hours the solvent was removed by distillation; the residual resin, when treated with ether, became solid. The product crystallised from benzene–ether in orange crystals, m. p. 179—180° (Found : Cl + Br, 30·6. $C_{27}H_{17}Cl_2Br$ requires Cl + Br, 30·7%).

(b) ω-*Hydroxy-derivative.*—The bromo-compound (XI; 5 g.) was heated on the water-bath for 4 hours with calcium carbonate (1 g.) and acetone (60 c.c.) diluted with water (15 c.c.). The product was recrystallised twice from benzene–light petroleum and twice from benzene–alcohol and then formed canary-yellow nodules, m. p. 189—191° (Found : C, 75·1; H, 4·3. $C_{27}H_{18}OCl_2$ requires C, 75·5; H, 4·2%). Solutions of the substance had a blue fluorescence.

(c) ω-*Ethoxy-derivative.*—The bromo-compound (XI; 5 g.) was heated on the water-bath for 2 hours with ethyl alcohol (50 c.c.). The crude product, m. p. 150—155°, was repeatedly crystallised from benzene–alcohol until it melted constantly at 173—174° (Found : C, 75·9; H, 4·85. $C_{29}H_{22}OCl_2$ requires C, 76·1; H, 4·8%). This *ethoxy*-compound formed glistening yellow leaflets, fluorescent in solution, and the same result was obtained when the reaction was carried out in the presence of calcium carbonate.

α-*Chloro*-9-*benzylanthracenes.*

1-*Chloro*-9-*benzylanthracene.*—1-Chloro-9-anthrone (30 g.), obtained by reducing α-chloroanthraquinone with aluminium and sulphuric acid (Eckert and Tomaschek, *Monatsh.*, 1918, **39**, 839; compare Barnett and Matthews, J., 1923, **123**, 2550), was added slowly to a Grignard solution prepared from benzyl chloride (42 c.c.) and magnesium powder (9 g.), the solution being cooled in a freezing mixture. After 4 hours the suspension was poured on ice and ammonium chloride, the ethereal solution washed, and the ether removed by distillation. The viscous residue was treated with light petroleum, and the resulting solid (40 g.) twice recrystallised from benzene–light petroleum (Found : C, 78·6; H, 5·4. $C_{21}H_{17}OCl$ requires C, 78·6; H, 5·3%). 1-*Chloro*-9-*hydroxy*-9-*benzyl*-9 : 10-*dihydroanthracene* forms a colourless crystalline powder, m. p. 126—127°. It was dehydrated by allowing its solution in acetic acid containing hydrochloric acid to stand over-night at the ordinary temperature. The resulting 1-*chloro*-9-*benzylanthracene*, recrystallised from benzene–alcohol, formed pale yellow nodules, m. p. 119—120° (Found : C, 83·5; H, 5·05. $C_{21}H_{15}Cl$ requires C, 83·3; H, 5·0%).

4-*Chloro*-9-*benzylanthracene* was obtained in good yield in exactly the same way from 4-chloro-9-anthrone, prepared by reducing α-chloroanthraquinone with tin and hydrochloric acid (Barnett and Matthews, J., 1923, **123**, 2550). The crude dihydroanthranol was not purified but was converted into the chlorobenzylanthracene, pale yellow needles from ethyl acetate–alcohol, m. p. 120° (Found : Cl, 11·8. $C_{21}H_{15}Cl$ requires Cl, 11·7%).

Bromination. Each α-chloro-9-benzylanthracene (15 g.) was dissolved in carbon disulphide (50 c.c.) and the solution, cooled in a freezing mixture, was treated with bromine (2·5 c.c.). The bromine was taken up without evolution of hydrogen bromide and in each case a solid additive compound separated, which passed into solution with liberation of hydrogen bromide on warming to the ordinary temperature. After an hour the solvent was removed by distillation, the residual oil treated with light petroleum, and the resulting yellow solid collected and dried. The crude product from 1-chloro-9-benzylanthracene was obviously a mixture. A little was dissolved in boiling pyridine, alcohol added to the solution, and the resulting 1-*chloro*-10-*bromo*-9-*benzylanthracene* (XIII) recrystallised from ethyl acetate; it then formed yellow silky needles, m. p. 160° (Found : C, 66·0; H, 3·8. $C_{21}H_{14}ClBr$ requires C, 66·1; H, 3·7%). The constitution assigned to this bromo-compound depends upon its inert character, the substance being recovered unchanged after boiling for an hour with acetic anhydride containing sodium acetate or with alcoholic potassium hydroxide solution.

When the bromo-compound (XIII) was treated with excess of bromine (2 mols.) in carbon disulphide solution the bromine was slowly taken up with liberation of hydrogen bromide. After 12 hours the solvent was distilled off and the viscous residue triturated with a little ether. A solid remained which, recrystallised from ethyl acetate–alcohol, melted at 149—150° alone or mixed with 4-chloro-9-bromoanthracene (XIX) (Found : C, 57·3; H, 2·9. Calc. : C, 57·6; H, 2·75%).

1-*Chloro*-10-*bromo*-9-*benzylidene*-9 : 10-*dihydroanthracene* (XIV).—This was the chief product of the bromination of 1-chloro-9-benzylanthracene, but could not be isolated from the crude mixture on account of its reactive nature. It was obtained, however, when hydrogen bromide was conducted through a boiling solution of 1-chloro-ω-methoxy-9-benzylanthracene (see below; 4 g.) in benzene (10 c.c.) for 15 minutes. The *bromo*-compound was obtained by adding light petroleum to the cooled solution and after recrystallisation from benzene–light petroleum formed almost colourless needles, m. p. 151—153° (Found: C, 66·1; H, 3·9. $C_{21}H_{14}ClBr$ requires C, 66·1; H, 3·7%). There can be no doubt that this compound was identical with the reactive bromo-compound present in the crude bromination mixture of 1-chloro-9-benzylanthracene, since by heating with methyl alcohol and calcium carbonate it was converted into the same colourless methoxy-compound as was obtained from the original bromination mixture. This mode of preparation of the pure bromo-compound (XIV) lends support to the hypothesis that in solution it is in tautomeric equilibrium with 1-chloro-ω-bromo-9-benzylanthracene (compare the equilibrium VII $\rightleftharpoons$ VIII).

4-*Chloro-ω-bromo*-9-*benzylanthracene* (XVIII) appeared to be the only isomeride formed by brominating 4-chloro-9-benzylanthracene. After recrystallisation from benzene–light petroleum it formed deep yellow nodules, m. p. 165—166° (Found: C, 66·2; H, 3·8. $C_{21}H_{14}ClBr$ requires C, 66·1; H, 3·7%).

"Colourless" Derivatives of 1-*Chloro*-9-*benzylanthracene.*

In all experiments with the bromo-compound (XIV) the crude mixture of isomerides obtained by brominating 1-chloro-9-benzylanthracene was used. The products (XV and XVI) obtained from (XIV) were usually very soluble in most solvents and remained in solution, the sparingly soluble 10-bromo-compound (XIII) being filtered off. The proportion of the latter compound isolated was consistently 30% of the crude mixture.

1 - *Chloro* - 10 - *hydroxy* - 9 - *benzylidene* - 9 : 10 - *dihydroanthracene* (XV; X = OH).—The mixed bromo-compounds (5 g.) were heated on the water-bath for 4 hours with acetone (60 c.c.), water (15 c.c.), and calcium carbonate (1 g.). After cooling, the 10-bromo-compound (XIII) was filtered off, the acetone distilled from the filtrate, and the resinous product recrystallised twice from benzene–light petroleum and once from toluene. The substance then formed a colourless crystalline powder, m. p. 185°, which, like the analogous 1 : 5-dichloro-compound (IV), gave an intense orange-red colour with boiling alcoholic potassium hydroxide solution (Found: C, 79·3; H, 4·8. $C_{21}H_{15}OCl$ requires C, 79·1; H, 4·7%).

The corresponding *acetoxy*-compound (XV; X = O·COMe) was obtained when a solution of this hydroxy-compound (3 g.) in pyridine (10 c.c.) was treated for 6 hours at the ordinary temperature with acetic anhydride (5 c.c.). It formed colourless glistening crystals, m. p. 151—153°, from ethyl acetate–alcohol (Found : C, 76·3; H, 4·8. $C_{23}H_{17}O_2Cl$ requires C, 76·6; H, 4·7%).

1-*Chloro*-10-*methoxy*-9-*benzylidene*-9 : 10-*dihydroanthracene* (XV; X = OMe).—The mixed bromo-compounds (3·5 g.) were heated on the water-bath for an hour with methyl alcohol (100 c.c.) in the presence of calcium carbonate (1 g.). After cooling, the filtered solution was concentrated and diluted with water. The resinous product was dried and recrystallised twice from benzene–light petroleum and then formed colourless glistening needles, m. p. 129—130°. Its solutions were non-fluorescent (Found : C, 79·3; H, 5·2. $C_{22}H_{17}OCl$ requires C, 79·4; H, 5·1%).

The corresponding ethoxy-compound could not be obtained solid.

"*Yellow*" *Derivatives of* 1-*Chloro*-9-*benzylanthracene*.

1-*Chloro*-ω-*methoxy*-9-*benzylanthracene* (XVI; X = OMe).—The colourless methoxy-compound (above; 0·8 g.) was heated on the water-bath for 1½ hours with methyl alcohol (15 c.c.) containing concentrated hydrochloric acid (1 c.c.). After cooling, the solid was collected and recrystallised from alcohol; it then formed pale yellow needles, m. p. 135—136°. The solutions had a strong violet fluorescence and the m. p. was depressed by admixture with the original colourless methoxy-compound (XV) or with the methoxy-derivative obtained from 4-chloro-9-benzylanthracene (XVII) (Found : C, 79·4; H, 5·2. $C_{22}H_{17}OCl$ requires C, 79·4; H, 5·1%).

Bromine (0·3 c.c.) was added to a solution of this methoxy-compound (1·85 g.) in carbon disulphide (5 c.c.), cooled in a freezing mixture. The bromine was taken up but no hydrogen bromide was evolved. The addition of light petroleum resulted in the separation of a colourless solid, which was collected and, without purification, dissolved in boiling benzene. The solution became yellow and hydrogen bromide was evolved. After boiling for ½ hour, the solution was treated with alcohol and cooled, and the resulting crystals were recrystallised from ethyl acetate (Found : C, 45·3; H, 2·1. $C_{14}H_7ClBr_2$ requires C, 45·3; H, 1·9%). 1-*Chloro*-9 : 10-*dibromoanthracene* (XX) forms slender orange-yellow needles, m. p. 159—161°.

1-*Chloro*-ω-*acetoxy*-9-*benzylanthracene* (XVI; X = O·COMe).—(*a*) A solution of the mixed bromo-compounds (5 g.) and sodium acetate (3 g.) in glacial acetic acid (35 c.c.) was boiled for an hour, cooled, and filtered from the 10-bromo-compound (XIII), and the filtrate poured into water. The precipitate was collected, dried, and recrystallised from benzene–light petroleum and then from alcohol. The *acetoxy*-compound formed yellow prisms, m. p. 157—158°, and the m. p. was depressed by admixture with the isomeric colourless acetoxy-compound (XV) or with the acetoxy-derivative of 4-chloro-9-benzylanthracene (XVII) (Found : C, 76·4; H, 4·8. $C_{23}H_{17}O_2Cl$ requires C, 76·6; H, 4·7%).

(*b*) A solution of the colourless hydroxy-compound (XV; X = OH) (0·5 g.) in acetic acid (2 c.c.) and acetic anhydride (2 c.c.) was boiled for an hour, cooled, and diluted with alcohol. The yellow crystalline product melted at 157—158° alone or mixed with a sample of the acetoxy-compound prepared as described under (*a*).

This acetoxy-compound appeared to be readily hydrolysed by alcoholic potassium hydroxide, but the resulting hydroxy-compound could not be obtained crystalline on account of its excessive solubility.

Derivatives of 4-*Chloro*-9-*benzylanthracene*.

4-*Chloro*-9-*benzylanthracene*-ω-*pyridinium Bromide* (XVII; X = C_5H_5NBr).—A solution of the ω-bromo-compound (XVIII) in pyridine was heated on the water-bath for a few minutes and cooled and the solid in suspension was collected, washed with pyridine and with ether, dried, and recrystallised from alcohol–ether. The *salt* formed a yellowish crystalline powder, m. p. 220—225° (decomp.) after sintering and darkening at 215° (Found : Cl + Br, 25·2. $C_{26}H_{19}NClBr$ requires Cl + Br, 25·1%).

4-*Chloro*-ω-*hydroxy*-9-*benzylanthracene* (XVII; X = OH).—(*a*) The ω-bromo-compound (XVIII) was hydrolysed by heating with aqueous acetone in the presence of calcium carbonate in the same way as the isomeric 1-chloro-compound (p. 2807). The *hydroxy*-compound, thrice recrystallised from benzene–light petroleum, formed a yellowish crystalline powder, m. p. 98—100° (Found : C, 79·5; H, 5·1. $C_{21}H_{15}OCl$ requires C, 79·1; H, 4·7%).

(*b*) A solution of the ω-bromo-compound (XVIII; 3 g.) and sodium acetate (3 g.) in glacial acetic acid (25 c.c.) was boiled for ½ hour, and the cooled solution poured into water. The precipitated acetate, which could not be obtained crystalline, was hydrolysed with potassium hydroxide (5 g.) in alcoholic solution at the ordinary temperature. The product, twice recrystallised from benzene–light petroleum, melted at 98—100° alone or mixed with the hydroxy-compound prepared as described under (*a*). This second method of preparation suggests that the hydroxy-compound is the ω-hydroxy-compound, a hypothesis which is supported by the fluorescence and yellow colour of the substance and also by the fact that it gave no red colour with boiling alcoholic potassium hydroxide solution (compare p. 2807). Methylation with methyl-alcoholic hydrochloric acid yielded the methoxy-compound described below.

4-*Chloro-ω-acetoxy*-9-*benzylanthracene* (XVII; X = O·COMe).—The hydroxy-compound described in the preceding paragraph was acetylated in the usual manner with pyridine–acetic anhydride at 100°, and after recrystallisation from benzene–light petroleum and from methyl alcohol the product formed pale yellow nodules, m. p. 129—130° (Found: C, 76·5; H, 4·8. $C_{23}H_{17}O_2Cl$ requires C, 76·6; H, 4·7%).

4-*Chloro-ω-methoxy*-9-*benzylanthracene* (XVII; X = OMe).—The ω-bromo-compound (XVIII; 3 g.) was heated on the water-bath for 1½ hours with methyl alcohol (100 c.c.) and calcium carbonate (2 g.). The product, recrystallised from methyl ethyl ketone–alcohol, formed pale yellow crystals, m. p. 144°, fluorescent in solution (Found: C, 79·2; H, 5·2. $C_{22}H_{17}OCl$ requires C, 79·2; H, 5·1%). This *methoxy*-compound was not changed when its solution in methyl alcohol containing hydrochloric or sulphuric acid was submitted to prolonged boiling.

A solution of the methoxy-compound (2·6 g.) in carbon disulphide (15 c.c.) was cooled in a freezing mixture and treated with bromine (0·4 c.c.). The additive compound was not isolated, the carbon disulphide being distilled off and the residue, which had a strong odour of benzaldehyde, treated with a little boiling alcohol. The resulting solid was recrystallised from acetic acid and from methyl ethyl ketone–alcohol and then formed straw-coloured needles; these melted at 152—153°, alone or mixed with the monobromo-derivative of α-chloroanthracene prepared by Barnett and Matthews (*Rec. trav. chim.*, 1924, **43**, 535), so that their compound must have structure (XIX) (Found: Cl + Br, 39·6. Calc.: Cl + Br, 39·6%).

4-*Chloro-ω-ethoxy*-9-*benzylanthracene* (XVII; X = OEt).—This was prepared from the bromo-compound (XVIII) by treatment with ethyl alcohol in the presence of calcium carbonate and formed yellowish nodules, m. p. 135—137°, from alcohol (Found: C, 79·5; H, 5·6. $C_{23}H_{19}OCl$ requires C, 79·7; H, 5·5%). This *ethoxy*-compound was fluorescent in solution and was not changed by heating with an alcoholic solution of hydrogen chloride.

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