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KEKULÉ STRUCTURES AND THE BENZYLIC COUPLING OF *o*-DIMETHYL-DERIVATIVES

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Abstract—The benzylic coupling of a number of symmetric *o*-dimethyl derivatives of aromatic hydrocarbons and quinones has been measured. The results do not support the assumption of Kekulé structures but rather point to the existence of one true double bond in each ring besides circular delocalized π-electrons. 6,7-Dimethyl-1,2:3,4-dibenzanthracene, its 9,10-quinone, 9,10-dimethyl-3,4-benzotetraphene, 2'-methyl-1,2:6,7-dibenzopyrene and 2',3'-dimethyl-1,2:6,7-dibenzopyrene have been synthesized.

NUMEROUS ATTEMPTS have been made to prove the existence of Kekulé structures using *o*-disubstituted compounds. When chemical reactions are applied in these efforts the inherent difficulty is. that an excited state. not the ground state of the molecule. may participate. However. NMR spectra offer a better prospect for observing the electronic ground state. Thus the presence of a true double bond can be demonstrated by the splitting of the Me NMR signal.[1] A fixed double bond like the one in the middle ring of 9-methylphenanthrene produces a Me doublet with a separation of 1·0 Hz.

There is no indication of any splitting in the Me signal of *o*-xylene. Decoupling of the aromatic protons has very little effect as shown by the black area in Fig. 1. I. A true double bond could only be located in the position 3.4.5.6. This non-adjacent double bond in *o*-xylene becomes apparent in 4.5-dibromo-*o*-xylene (Fig. 1. II). The Me signal is a doublet with a separation of 0·3 Hz.

The Me signal of durene is a doublet with a separation of 0·25–0·3 Hz (Fig. 1. III). Since this results from 2 three center bonds (marked by dashed lines) the total degree of localization must be rather high.

The Me signal of 2.3-dimethylnaphthalene (Fig. 1. IV) is a rather clear doublet with a separation of 0·5 Hz. Substitution of H_1 by Br increases the separation to 0·9 Hz.[2] This example shows the additivity of true double bond character which is the result of the repulsion of part of one true double bond by the large electron cloud of Br. This cannot be explained by Kekulé structures.[2]

2.3.6.7-Tetramethylnaphthalene[3] has a Me doublet with a separation of 0·45 Hz. This is certainly less than in 2.3-dimethylnaphthalene (Fig. 1. V). It is reasonable to assume that those circular delocalized π-electrons which can migrate between the 2-rings are to some extent pushed into the non-substituted ring in 2.3-dimethylnaphthalene thus making the ring with the Me groups less benzenoid and more reactive. This cannot be the case in 2,3,6,7-tetramethylnaphthalene and one must conclude that these circular delocalized π-electrons have a slight counteracting effect to the tendency to localize the true double bond adjacent to the β-Me groups.

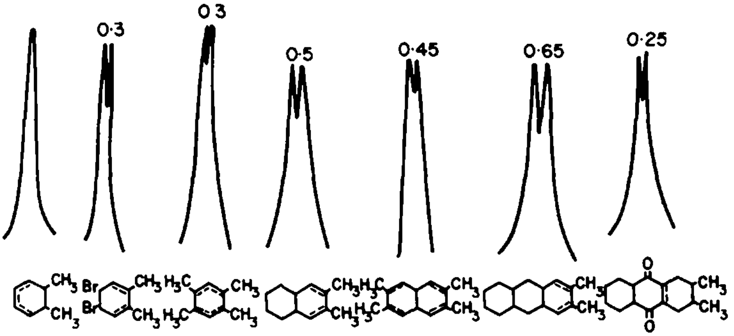


FIG 1. Comparison of Me signal in the NMR spectra of symmetric di- and tetramethyl derivatives.

This being the case their influence must be further reduced in 2.3-dimethylanthracene[4] which has in fact a Me doublet with an increased separation of 0·65 Hz. (Fig. 1. VI). In passing from benzene to naphthalene and anthracene derivatives a distinct annellation effect is thus observed.

An effect which is contrary to the effect of Br can be observed in 2.3-dimethylanthraquinone.[4] The electronic deficiency of the CO groups attracts the double bond partly away from the Me groups as indicated by the dotted line in Fig. 1, VII. The Me doublet separation of 0·65 Hz in the hydrocarbon is therefore reduced to 0·25 Hz in 2.3-dimethylanthraquinone.

There is a Me signal with a separation of 0·4 Hz in 2.3-dimethyltriphenylene[5] (Fig. 2. VIII). This value is lower than in 2,3-dimethylnaphthalene (0·5 Hz) and in 2.3.6.7-tetramethylnaphthalene (0·45 Hz) and slightly higher than in dibromo *o*-xylene and durene (0·3 Hz). Triphenylene is best formulated with 3 aromatic sextets in the external rings. There is a lower electronic density in the central ring which amounts to about half an aromatic ring.[6] It is therefore understandable that the Me splitting of the Me doublet is between the above mentioned benzene and naphthalene derivatives.

No splitting can be observed in the Me signal of 8,9-dimethylfluoranthene[7] (Fig. 2. IX). Decoupling of the adjacent aromatic protons has very little effect as shown by

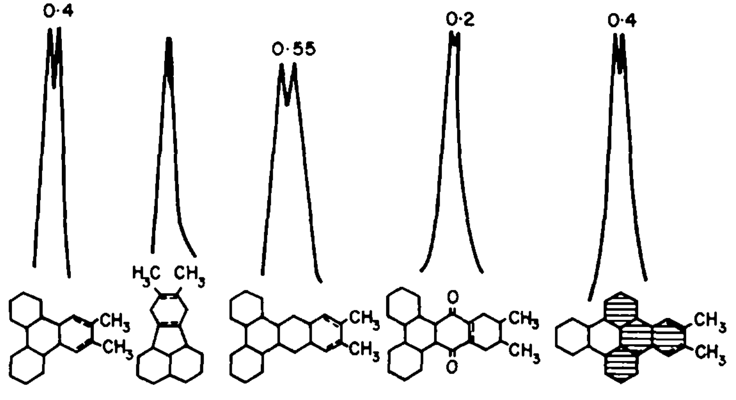
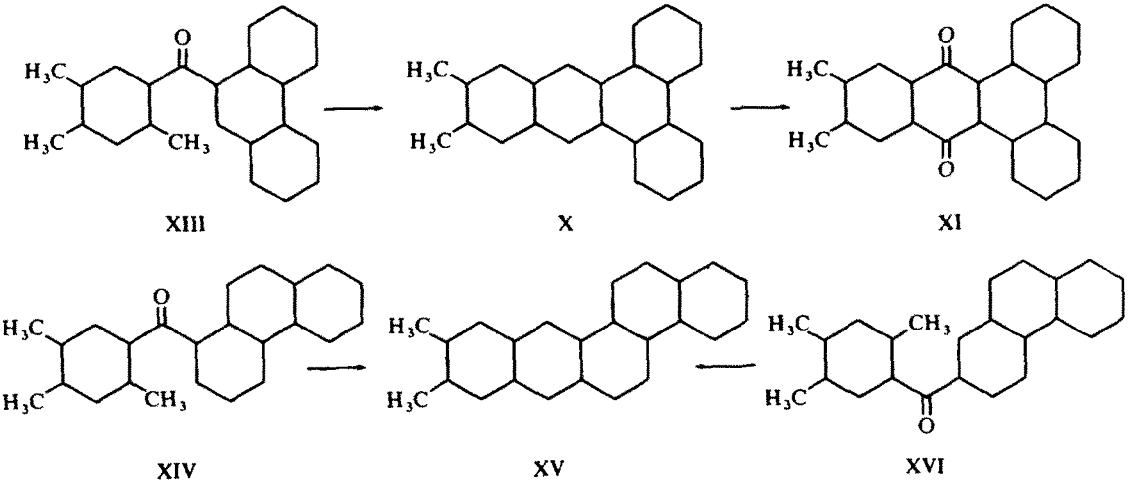
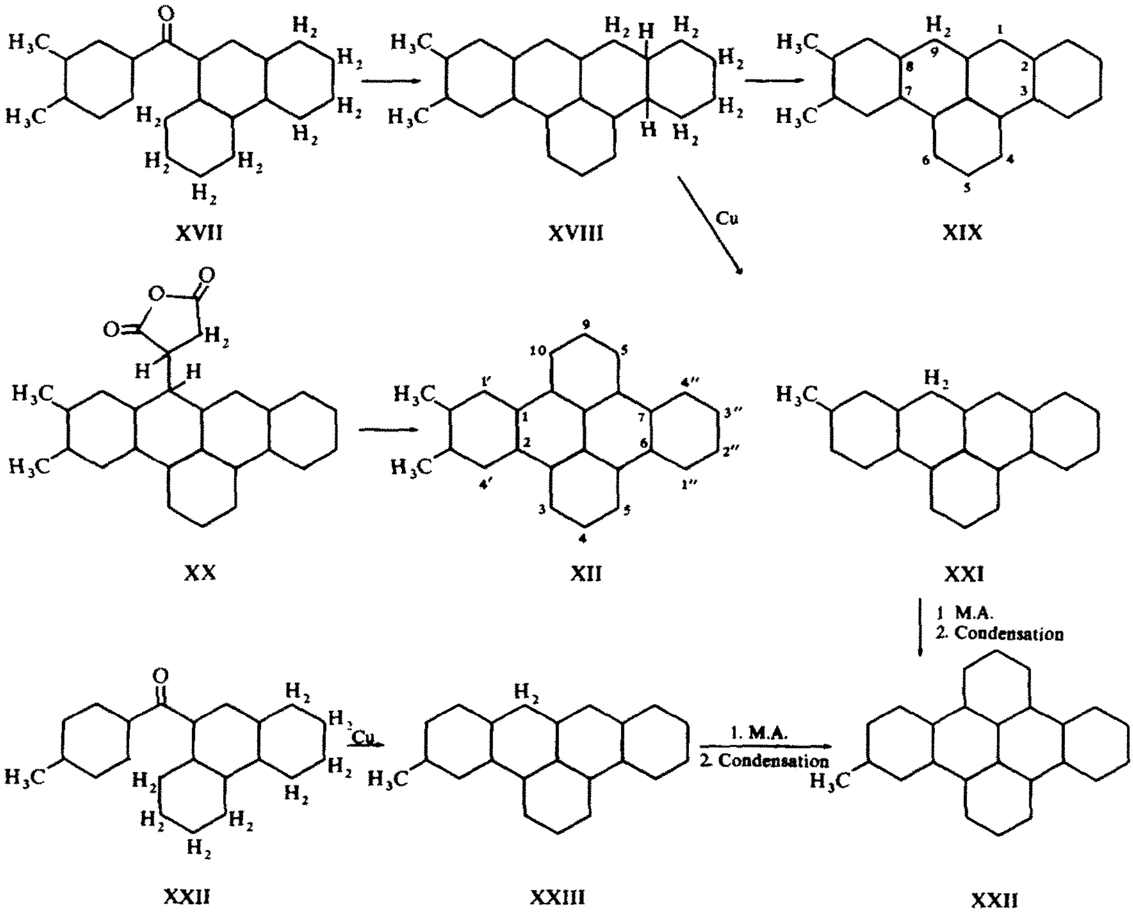


FIG 2. Comparison of Me signals in the NMR spectra of symmetric dimethyl derivatives.

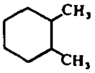
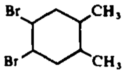
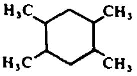
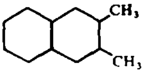
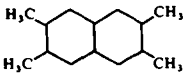
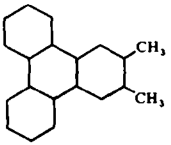
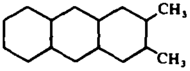
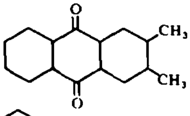
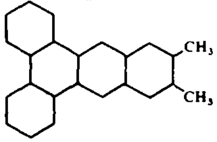
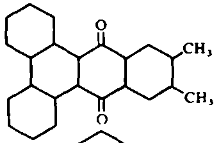
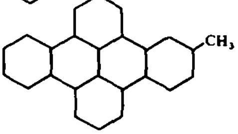
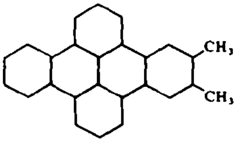


All Hexagon symbolize aromatic rings



All Hexagons symbolize aromatic rings

TABLE 1 NMR SPECTRA CHEMICAL SHIFT IN τ

Compound	Aromatic	Me
	$H_{3,4,5,6}$ 3·05 (s. sharp)	7·89 (s)
	$H_{3,6}$ 2·82 (s. broad)	7·89 (d)
	$H_{3,6}$ 3·40 (s. broad)	7·93 (d)
	$H_{1,4}$ 2·67 (s. broad); $H_{5,8}$ 2·50 (nα); $H_{6,7}$ 2·84 (nβ)	7·75 (d)
	$H_{1,4,5,8}$ 2·69 (s. broad)	7·69 (d)
	$H_{1,4}$ 1·87 (s. broad); $H_{6,7,10,11}$ 2·57 (nβ); $H_{5,8,9,12}$ 1·60 (nα)	7·57 (d)
	$H_{1,4}$ 2·40 (s. broad); $H_{6,7}$ 2·74 (nβ); $H_{5,8}$ 2·19 (nα); $H_{9,10}$ 1·90 (s)	7·57 (d)
	$H_{6,7}$ 2·69 (nβ); $H_{1,4}$ 2·12 (s); $H_{5,8}$ 1·87 (nα)	7·57 (d)
	$H_{2',3',2'',3''}$ 2·50 (nβ); $H_{5,8}$ 2·35 (s. broad); $H_{1'',4'}$ 1·61 (nα); $H_{1',4''}$ 1·48 (nα); $H_{9,10}$ 1·30 (s)	7·57 (d)
	$H_{2',3',2'',3''}$, 2·38 (nα); $H_{5,8}$ 2·22 (s); $H_{1'',4'}$ 1·44 (nα); $H_{1',4''}$ 0·67 (nα)	7·62 (d)
	$H_{3'}$ 2·55 (m); $H_{1'}$ 1·53 (s. broad); $H_{4'}$ 1·50 (m); $H_{1'',4''}$ 1·36 (nα); $H_{2'',3''}$ 2·37 (nβ); $H_{3,5,8,10}$ 1·26 (d); $H_{4,9}$ 2·08 (t)	7·36 (m)
	$H_{1',4'}$ 1·42 (n α); $H_{2',3'}$ 2·3 (nβ); $H_{1'',4''}$ 1·68 (s. broad); $H_{4,9}$ 2·14 (t); $H_{3,5,8,10}$ 1·22 (d)	7·5 (d)

s = singlet. d = doublet. t = triplet. m = multiplet. nα = naphthalene type. nβ = naphthalene type.

the black area. One must therefore assume a similar electronic structure for the ring attached to the Me groups as in *o*-xylene. This appears reasonable, since 7,10-dimethylfluoranthene also shows no Me doublet but a rather sharp singlet. In this case the ring attached to the Me groups must be closely related to *p*-xylene.[2]

6,7-Dimethyl-1,2:3,4-dibenzanthracene has a Me doublet with a separation of 0·55 Hz (Fig. 2, X). This value is lower than in 2,3-dibenzanthracene. In passing to 6,7-dimethyl-1,2:3,4-dibenzanthraquinone (Fig. 2, XI) a reduction of the Me splitting from 0·55 Hz in the case of the hydrocarbon to 0·2 Hz in the quinone is recorded. This change is quite similar as in going from 2,3-dimethylanthracene to 2,3-dimethylanthraquinone and must also be related to the attraction of the double bond into the positions between the electronic deficient CO groups (dotted line in Fig. 2, XI).

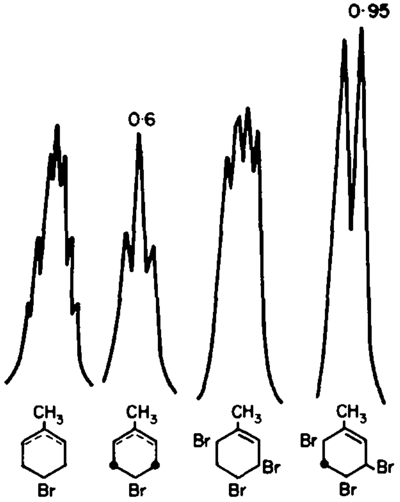


FIG 3. Comparison of Me signals in the NMR spectra of toluene and its bromine derivatives.

2′,3′-Dimethyl-1,2:6,7-dibenzopyrene shows a Me doublet with a separation of 0·4 Hz. (Fig. 2, XII) which is exactly the same value as in 2,3-dimethyltriphenylene. This leads to the assumption that the aromatic conjugation of the triphenylene complex (marked with shadow) and an empty ring "E" dominate the electronic structure of the former hydrocarbons. If the two Me groups were connected with the phenylene ring adjacent to the empty ring "E" then no splitting of the Me signal should be observed as in *o*-xylene. In the case of the electronic structure resonating between these two structures the Me splitting should be about halfway between 0 and 0·4 Hz, which is obviously not the case. An asymmetric electronic structure for 1,2:6,7-dibenzopyrene and its higher benzologues has already been deduced from the electronic spectra.[8]

The Me signal in toluene is a broad unresolved multiplet.[9] It is simplified in 4-bromotoluene, to a septet produced by an overlapping triplet of triplet. (Fig. 3). That the double bond is located as a three center bond adjacent to Me is shown by decoupling of the *m*-protons (marked with points). Then the septet is simplified to a clear triplet with a separation of 0·6 Hz. In 2.4.5-tribromotoluene[10] the Me signal is a double doublet. Decoupling of the proton H_3 produces a Me doublet with a separation of 0·95 Hz. This is the highest value observed in toluene derivatives and not much different from the doublet in 9-methylphenanthrene (1·0 Hz). This shows that the electronic structure of the benzene ring is not principally different from any other benzenoid ring, only the mobility of the only true double bond is greater. If the double bond in 2.4.5-tribromotoluene is almost completely fixed then this cannot be the case to the same extent in 2.3.4.5-tetrachlorotoluene which has a Me doublet with a separation of only 0·63 ± 0·02 Hz. The Cl atoms are obviously not so effective in double bond localization as the Br atoms.

The above results can obviously not be explained by the assumption of Kekulé structures with 3 double bonds but can easily be caused by the existence of only one true mobile double bond in any benzenoid ring. This would be placed in the lowest orbital of the three π-orbitals and could be repelled by the influence of Br or attracted by the CO groups in quinones.

The synthesis of the new compounds

The condensation of 2.4.5-trimethylbenzoyl chloride with phenanthrene and $AlCl_3$ gives as main product the ketone XIII. However, smaller amounts of isomeric ketones XIV and XVI were also formed. This was shown by the pyrolysis of the crude ketone mixture. The main product was 6,7-dimethyl-1.2:3.4-dibenzanthracene (X). Its constitution could easily be established by UV and NMR spectra. Oxidation gave quinone XI. Another isomeric hydrocarbon formed by this pyrolysis was 8.9-dimethyl-3.4-dibenzotetraphene (XV) which could have originated from ketones XIV and XVI. There was also a small amount of a yellow hydrocarbon formed from ketone XVI. It has the structure of an 8.9-dimethyl-1.2-benzotetracene and could be readily removed by its high reactivity with maleic anhydride.

The condensation of 3.4-dimethylbenzoyl chloride with octahydrophenanthrene and $AlCl_3$ gave ketone XVII. Pyrolysis yielded mainly the $2^{11}.3^{11}$-dimethyl-2.3:7.8-dibenzophenalene (XIX). Its NMR spectrum showed that it consisted of two isomers formed by the migration of the CH_2 group between positions 1 and 9. It shows therefore 4 sharp Me signals originating from 6 protons. The CH_2 signal is a broad multiplet. A by-product of the pyrolysis was the hexahydro-derivative XVIII. In accordance with its structure it showed the UV spectrum of an alkylphenanthrene.

In order to promote the dehydrogenation during the pyrolysis of ketone XVII Cu powder was added. Under these conditions one Me group was lost and monomethyl-derivative XXI was formed as shown by the NMR spectrum. This was not identical with hydrocarbon XXIII which was obtained by pyrolysis of ketone XXII with Cu powder. In this case no loss of Me group was observed. When heated with maleic anhydride hydrocarbon XIX formed the succinic anhydride derivative (XX). If anhydride XX or the free acid was submitted to a melt with NaCl–$ZnCl_2$, dimethyl-dibenzopyrene (XII) was formed. When this treatment with maleic anhydride and cyclization with NaCl–$ZnCl_2$ was applied to the different hydrocarbons XXI and XXIII, both yielded the same 2'-methyl-1,2:6.7-dibenzopyrene (XXIV). This was established beyond doubt from the NMR spectra.

EXPERIMENTAL[*]

2.4.5-*Trimethylbenzoyl chloride* was prepared from the acid with $SOCl_2$ and distilled. b.p. 180–185°/12 mm.

9-(2.4.5-*Trimethylbenzoyl*)-*phenanthrene* (XIII). The acid chloride (75 g) and phenanthrene (66 g) were dissolved in C_6H_6 (100 ml). Powdered $AlCl_3$ (75 g) was added in two portions with stirring. After the evolution of HCL ceased. the dark orange red mixture was decomposed with ice and HCl. Xylene was added. and the organic layer washed with hot water and then with NH_4OH. In order to remove water. some of the solvent was distilled off. and the soln. filtered. On standing crystals (19 g) separated. Recrystallization from EtOH yielded long pale yellow prisms. m.p. 192–194° which dissolved in conc H_2SO_4 to form a yellow soln. (Found: C. 88·3; H. 6·4 $C_{24}H_{20}O$ requires: C. 88·85; H. 6·21%).

6.7-*Dimethyl*-1.2:3.4-*dibenzanthracene* (X). The above xylene soln of the ketones was boiled to remove solvents. After further heating at 420° for 30 min evolution of water ceased. On cooling the dark brown glass was dissolved in xylene. traces of water removed by boiling and the soln. chromatographed over alumina (500 g. Grade 1). Eluting with xylene gave first a colourless soln with a blue fluorescence which showed the UV spectrum of a 1.2:3.4-dibenzanthracene derivative. All fractions showing this spectrum were united and concentrated. Pale yellow leaflets were obtained which after recrystallization from xylene had m.p. 219–220° and dissolved in conc H_2SO_4 to give a blue-green soln. (Found: C. 94·0; H. 6·0. $C_{24}H_{18}$ requires: C. 94·1; H. 5·9%) UV (cyclohexane): α. 3770 (2·77: *P*. 3510 (3·48). 3360 (3·92). 3240 (4·02); β 2890 (5·19). 2785 (5·04). 2680 (4·79). 2500 (4·62). 2440 (4·56); β'2200 (4·58).

9.10-*Dimethyl*-3.4-*tetraphene* (XV). The later fractions from the column showing the UV spectrum of a 3,4-benzotetraphene derivative were united. Concentration yielded yellow crystals (3 g). The UV spectrum indicated that they contained an isomer. 8·9-dimethyl-1.2-benzotetracene with *P*-bands at 4540 and 4250 Å. This could be removed by treating a dil. boiling xylene solution of the hydrocarbon (1·3 g) with small amounts of maleic anhydride until these bands disappeared. On cooling pale yellow plates crystallized which after recrystallization from xylene had m.p. 308–309° and dissolved in conc H_2SO_4 to give a magenta soln. (Found: C. 93·8; H. 6·0. $C_{24}H_{18}$ requires: C. 94·1; H. 5·9%). UV (benzene): α. 3950 (3.50) 3840 (3·71);. *P* 3680 (3·86). 3490 (3·80). 3340 (3·66); *β* 3075 (4·60). 2880 (5·20). 2850 (4·81).

6.7-*Dimethyl*-1.2:3.4-*dibenzanthraquinone* (XI). 6.7-Dimethyl-1.2:3.4-dibenzanthracene (0·5 g) was suspended in AcOH (10 ml) and refluxed with a slight excess of CrO_3 (0·2 gms) for 30 min. The purple soln. rapidly became green. Water was added and the ppt filtered. washed with water and dried (0·4 g). Recrystallization twice from EtOH yielded small thin orange-yellow needles. m.p. 237–238° which dissolved in conc sulphuric acid to give an emerald green colour. (Found: C. 85·5; H. 4·9. $C_{24}H_{16}O_2$ requires: C. 85·7; H. 4·8%). UV (ethanol): *α* 4030 (3·76); *P* 3050 (4·40); *β* 2885 (4·57). 2690 (4·69). 2480 (4·78).

9(3.4-*Dimethylbenzoyl*)-1.2.3.4.5.6.7.8-*octahydrophenanthrene* (XVII). 3.4-Dimethylbenzoyl chloride (210 g) and octahydrophenanthrene (220 g) were dissolved in benzene (900 ml). Powdered $AlCl_3$ (250 g) was added with stirring. The mixture which was stirred for 2 hrs at room temperature was firstly orange red. but became dark reddish-brown. Decomposition with ice and dil. HCl gave an organic layer which was washed with water and NH_4OH filtered and dried (Na_2SO_4). Concentration yielded a thick brown oil. When titurated with ether colourless crystals were obtained which. after repeated crystallization from EtOH had m.p. 107–109° and dissolved in conc H_2SO_4 to give a yellow soln. (Found: C. 86·4; H. 8·2. $C_{23}H_{26}O$ requires: C. 86·8; H. 8·2%).

2''.3''-*Dimethyl*-2.3:7.8-*dibenzophenalene* (XIX). The above crude ketone (370 g) was heated to 390–400° in a distillation apparatus. The liquid darkened much less than during other Elbs reactions. After 30 min. no more water was evolved and the amount of water in the receiver flask measured 19 ml. almost theoretical. The residue in the distillation flask was a slight brown glass which crystallized when titurated with light petrol (100–120°). The ppt (40 g) was filtered and washed with light petrol. Chromatography of a sample with light petrol on alumina (Grade 1) gave a soln with a blue fluorescence. Concentration yielded colourless needles. m.p. 148–150°. which dissolved in conc H_2SO_4 with a deep red colour and an orange fluorescence. (Found: C. 93·6; H. 6·3. $C_{23}H_{18}$ requires: C. 93·8: H. 6·2%).

2'',3''-*Dimethyl*-2,3:7,8-*dibenzophenalyl*-(9)-*succinic anhydride* (XX). The above crystallized non-chromatographed hydrocarbon (10 g) and maleic anhydride (10 g) were refluxed in xylene (75 ml) for 5 hr. On cooling. light brown crystals (2 g) precipitated. After filtration the mother liquor was steam distilled and the residue dissolved in dil NaOH. The soln was filtered from an insoluble product and the hot mother liquor acidified with conc HCl. After boiling for ½ hour the resinous ppt crystallized (11 g). Recrystallization from C_6H_6 yielded colourless prisms. m.p. 213–214°. which dissolved in conc H_2SO_4 to give a deep magenta soln. (Found: C. 79·2; H. 5·5. $C_{27}H_{22}O_4$ requires: C. 79·0 H. 5·4%).

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[*] M.ps are uncorrected and were taken in evacuated capillaries.

1′.2′.3′.4′.2.3-Hexahydro-2″.3″-dimethyl-2.3:7.8-*dibenzphenalene* (XVIII). The residue (0·14 g) from the above extraction with dil NaOH was dissolved in hot xylene, boiled to remove water and chromatographed on alumina. Elution first with light petrol (40–60°) then with benzene and concentrating the benzene soln gave colourless crystals (70 mgs). Recrystallization from light petrol (100–120°) yielded colourless prisms, m.p. 169–171°, which gave no colour with conc H_2SO_4. (Found: C, 92·0; H, 8·0. $C_{23}H_{24}$ requires: C, 92·0; H, 8·0%). UV (phenanthrene type): *α*, 3570, 3390, 3220; *P*, 3070, 2950, 2840, 2750; *β*, 3610; *β*′ 2180 Å (cyclohexane). The NMR spectrum at 60 MHz in CS_2 shows two Me groups at τ 7·58 and 7·64 which must be attached to the aromatic part of the molecule. The other part of the spectrum fits exactly to structure XVIII.

2′.3′-Dimethyl-1.2:6.7-*dibenzopyrene* (XII). The above acid or anhydride (5 g) $ZnCl_2$ (35 g) and NaCl (8 g) were powdered together and the mixture heated to 310° for 10 min. The melt separated into two layers, a wine red organic and a colourless inorganic. The cooled melt was powdered and repeatedly extracted with hot xylene. The soln was boiled to remove water and chromatographed over alumina (Grade 1). Elution gave first dimethyldibenzophenalene (XIX) and then dimethyl-dibenzopyrene (XII) which according to UV spectral examination also contained some of the isomeric dimethylbenzoperylene. Concentration gave a mixture of these two hydrocarbons (0·7 g) which was refluxed with excess maleic anhydride and a crystal of I_2 in order to remove the perylene derivative. The melt was poured into water and extracted with dil NaOH to remove the acidic condensation product of the perylene derivative and maleic anhydride. The residue (0·4 g) was filtered and repeatedly recrystallized from xylene. *2′.3′-dimethyl*-1.2:6.7-*dibenzopyrene* formed almost colourless needles, m.p. 249–250°, which did not dissolve in conc sulphuric acid. UV (benzene): *α*, 3830, 3650, 3570, 3460; *P*, 3310, 3180, *β*, 2920, 2790. (Found: C, 94·8; H, 5·4. $C_{26}H_{18}$ requires: C, 94·5; H, 5·5%).

3″-Methyl-2.3:7.8-*dibenzophenalene* (XXI). The crude ketone (150 g) was heated to 320°. Cu powder (8 g) added and the temp raised to 400–420°. Water and then hydrogen were evolved. After 5 hr the dehydrogenation was 80% complete. The mixture was allowed to cool and the dark liquid distilled at 270–340°/3 mm. The distillate was triturated with ether to give a yellow solid (8 g). This was chromatographed in light petrol (60–80°). Recrystallization from light petrol gave colourless needles m.p. 175–177° which dissolved in conc. sulphuric acid to give a red solution. The hydrocarbon is rather quickly oxidized in air. (Found: C, 94·1; H, 5·9. $C_{22}H_{16}$ requires: C, 94·3; H, 5·8%). The NMR spectrum in (CS_2, 60 MHz) shows two Me signals at τ 7·50 and 7·66 originating from 3 protons due to the two isomers resulting from the shifting of the CH_2 between the two middle positions giving a broad CH_2 signal at τ 5·58.

3″-Methyl-2,3:7,8-*dibenzophenalenyl*-1-(9)-*succinic acid*. This was prepared as XX. Recrystallization from C_6H_6 gave colourless prisms, m.p. 214–217°, which dissolved in conc H_2SO_4 to give a red solution. (Found: 78·9; H, 5·3. $C_{26}H_{20}O_4$ requires: C, 78·8; H, 5·1%).

9-(*4-Methylbenzoyl*)-1.2.3.4.5.6.7.8-*octahydrophenanthrene* (XXII). This was obtained from *p*-toluyl chloride (110 g), octahydrophenanthrene (124 g) and $AlCl_3$ (110 g) in C_5H_6 (600 ml) as described for XVII (yield 145 g).

2″-Methyl-2.3:7.8-*dibenzophenalene* (XXIII) was prepared from the above ketone as described for XXXI (yield 28 g). Recrystallization from light petrol (100–120°) gave needles, m.p. 154–176°, which dissolved in conc H_2SO_4 to give a red solution. The hydrocarbon oxidizes quickly in air. (Found: C, 94·1; H, 5·7. $C_{22}H_{16}$ requires C, 94·3; H, 5·7%). The NMR spectrum (CS_2, 60 MHz) is different from that of XXI. It shows the two Me signals at τ 7·42 and 7·62 originating from 3 protons. The CH_2 signal at 5·5 is broad. The spectrum proves that the CH_2 group migrates between the two middle positions.

2″-Methyl-2,3:7,8-*dibenzophenalyl*-(9)-*succinic anhydride*. This was prepared analogously to XX. Recrystallization from cyclohexane gave needles, m.p. 113°–126°, which dissolved in conc H_2SO_4 to form a deep red soln. The free dicarboxylic acid crystallized from dil. AcOH as needles m.p. 216–217°. (Found: C, 82·3; H, 4·9. $C_{26}H_{18}O_3$ requires: C, 82·5; H, 4·8%).

2′-Methyl-1.2:6.7-*dibenzopyrene* (XXIII). This hydrocarbon was prepared from 2″ and 3″-methyl-2.3:7.8-dibenzophenalyl-(9)-succinic acid, as described for 2′.3′-dimethyl-1.2:6.7-dibenzopyrene (XII). Both succinic acids gave the same 2′-methyl-1.2:6.7-dibenzopyrene. It formed yellow prisms, m.p. 263–265°, which did not dissolve in conc. H_2SO_4. (Found: C, 95·2; H, 5·1. $C_{25}H_{16}$ requires C, 94·9; H, 5·1%). UV (benzene): *α*, 3740 (2·37); *P*, 3290 (3·95), 3160 (4·05); *β*, 2900 (4·55); (cyclohexane): 2750 (4·50). The NMR spectrum (CS_2), 100 MHz shows one Me signal at τ 7·37 which is coupled to H_1 (~0·5 Hz) and less to H_3 (~ 0·2).

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