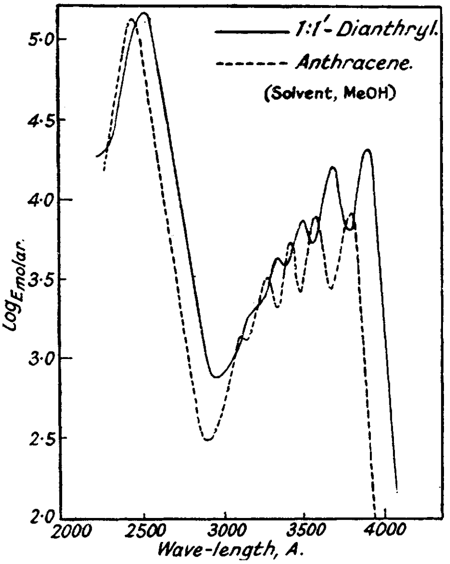
567. The Symmetrical Dianthryls. Part III.

By F. Bell and D. H. Waring.

9 : 9′-Dianthryl-3 : 3′-dicarboxylic acid has been obtained in stable optically active forms. "Intramolecular overcrowding" with consequent non-planarity has been detected in derivatives of 3 : 4 : 5 : 6-dibenzphenanthrene. Attempts to synthesise molecules with a greater degree of overcrowding by processes involving pinacol reductions or diene additions have been unsuccessful.

In Part II (this vol., p. 1579) it was shown that 1 : 1′-dianthryl can readily be obtained in optically active forms of considerable stability. This shows that the molecule is non-planar, a point which is further confirmed by the very close resemblance of the ultra-violet absorption spectrum of this hydrocarbon to that of anthracene (see figure) * (see Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127, for a discussion on ultra-violet spectra). The carbon bond in position 1 : 1′ must have a high resistance to distortion.

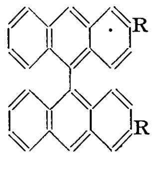


It follows that 9 : 9′-dianthryl (I) should be permanently non-planar and that any unsymmetrically substituted 9 : 9′-dianthryl should exist in enantiomorphous forms of high optical stability. A survey of the literature showed that no such appropriately substituted 9 : 9′-dianthryl had been described and, therefore, a synthesis of 9 : 9′-dianthryl-3 : 3′-dicarboxylic acid (II) was worked out. 2-Methylanthraquinone was reduced, and the resultant mixture of anthrones separated by Barnett and Goodway's method (*J.*, 1929, 1754). The 3-methylanthrone so obtained was reduced to 3 : 3′-*dimethyl*-9 : 9′-*anthrapinacol* by aluminium amalgam and the pinacol was then dehydrated to yield 3 : 3′-*dimethyl*-9 : 9′-*dianthryl.* Oxidation of this with chromic acid gave 9 : 9′-*dianthryl*-3 : 3′-*dicarboxylic acid,* which was resolved into optically active forms by crystallisation of the quinidine salt. The enantiomorphous forms, $[\alpha]_{5461}$ +129° and −132° (acetone, $c = 0{\cdot}10$) were completely unchanged in rotatory power when boiled in xylene solution for 2 hours.

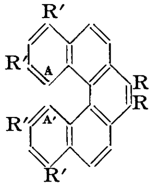
3 : 4 : 5 : 6-Dibenzphenanthrene (III) is closely related to the systems under discussion. It is impossible without either (*a*) distortion of the ring systems or (*b*) adoption of a non-planar form to accommodate the hydrogen atoms in positions 4′ and 1″ (A and A′). The second possibility envisaged, which may be conveniently termed "intramolecular overcrowding," would result in the existence of enantiomorphous forms. To test this, 3 : 4 : 5 : 6-dibenzphenanthrene-9 : 10-dicarboxylic acid (IV) was combined with various alkaloids. Only the *morphine* salt was suitable for crystallisation. This was found to exhibit marked and rapid mutarotation in solution. From this result it was expected that the acid recovered from the alkaloidal salt would be optically inactive, and this was found to be so. In order to increase the optical stability, 4′ : 4″ : 6′ : 6″-*tetramethyl*-3 : 4 : 5 : 6-*dibenzphenanthrene*-9 : 10-*dicarboxylic acid* (V) was prepared by Newman's method (*J. Amer. Chem. Soc.*, 1940, **62**, 1683). Crystallisation of the morphine salt furnished fractions of markedly different rotatory power.

* Since 1 : 1′-dianthryl is racemised above 120°, the molecule must then be able to assume a planar form and the ultra-violet absorption spectrum might be expected to show new features.

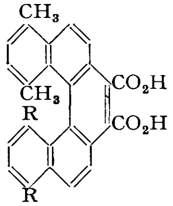
The fraction of $[\alpha]_{5461}$ $-182°$ on decomposition with cold hydrochloric acid gave the free acid with an initial $[\alpha]_{5461}$ $-47{\cdot}2°$ in acetone solution. This rotation rapidly fell and was zero after 5 hours. The alkaloidal salt from the mother-liquor, treated in the same way, gave the free acid with an initial $[\alpha]_{5461}$ $+18°$ in acetone solution.



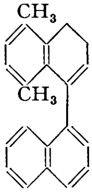
(I; R = H.)
(II; R = CO_2H.)



(III; R = H, R′ = H.)
(IV; R = CO_2H, R′ = H.)
(V; R = CO_2H, R′ = CH_3.)



(VI; R = H.)
(VII; R = CH_3.)



(VIII.)

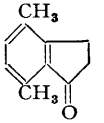
To increase still further the overcrowding in positions A and A′, we attempted the synthesis of (VI) and (VII). 5 : 8-*Dimethyl*-3 : 4-*dihydro*-1 : 1′-*dinaphthyl* (VIII) was prepared by dehydration of the alcohol obtained by the interaction of 5 : 8-dimethyl-1-tetralone with α-naphthylmagnesium bromide. This diene failed to interact with maleic anhydride under the usual conditions.

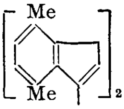
Next, 5 : 8-dimethyl-1-tetralone was submittted to reduction under conditions which give an excellent yield of the pinacol of 5 : 7-dimethyl-1-tetralone, but no pinacol was obtained, the bulk of the tetralone being recovered unchanged and the residue being resinous.

This lack of success emphasizes the difficulty of preparing molecules which might be expected to be strained and distorted by overcrowding of the component atoms. The pinacol synthesis, which probably involves a preliminary union of the oxygen atoms of two ketone molecules with a metallic atom, would require for its successful completion an almost planar structure in which the two uniting carbon atoms encounter a minimum of resistance to close approach (compare Barnett, *Ber.*, 1932, **65**, 1563). Similarly, all the available evidence (for summary, see " Organic Reactions," Vol. IV, p. 35, Wiley, 1948) points to the necessity for an almost planar diene for the successful addition of the dienophil.

The literature reveals descriptions of five compounds (excluding complex dyes) in which overcrowding is present or might be expected. Four of these, namely, picene-12 : 13-dicarboxylic acid (Waldmann and Pitschak, *Annalen*, 1937, **527**, 183), 6 : 7-dimethylchrysene (Newman, *J. Amer. Chem. Soc.*, 1940, **62**, 2295), 4 : 5 : 8-trimethyl-1-phenanthrylacetic acid (Newman and Husey, *ibid.*, 1947, **69**, 978, 3023), and 4-methyl-5 : 6-benz-1-phenanthrylacetic acid (Newman and Wheatley, *ibid.*, 1948, **70**, 1913), have been prepared by ring closures remote from the conflicting groups. The fifth, 5-formylphenanthrene-4-carboxylic acid, has been prepared by the rupture of a carbon–carbon bond in pyrene by ozonolysis (Vollmann, Becker, Corell, and Streeck, *Annalen*, 1937, **531**, 149). Reactions of the pinacol and diene addition types appear to be possible only if the resistance to planarity is slight (although sufficient to be detectable by mutarotation and the much less descriminating method of ultra-violet absorption spectroscopy). To obtain further evidence on this point we next studied 4 : 7-dimethylindan-1-one (IX) (Plattner and Wyss, *Helv. Chim. Acta*, 1941, **24**, 483). This was reduced to the pinacol and the latter dehydrated by boiling it with acetic acid to yield a 4 : 4′ : 7 : 7′-*tetramethyldi-indenyl*, the overall yield being 50%. The product formed colourless needles, m. p. 178°. Straus, Kuhnel, and Haensel (*Ber.*, 1933, **66**, 1847) obtained 3 : 3′-di-indenyl by an indirect process and describe it as yellow prisms, m. p. 130·5—131·5°. It may be, therefore, that the above tetramethyldi-indenyl, which does not undergo reaction with maleic anhydride, is a 1 : 1′-di-indenyl and not the expected tetramethyl-3 : 3′-di-indenyl (X), although the compound underwent no change on warming with sodium methoxide, an agent which converts 1 : 1′-di-indenyl into the presumably more stable 3 : 3′-di-indenyl.

(IX.)





(X.)

EXPERIMENTAL.

(Analyses and ultra-violet absorption spectra are by Drs. Weiler and Strauss, Oxford. M. p.s are uncorrected.)

3-*Methyl*-9-*anthrone*.—A solution of 2-methylanthraquinone (200 g.) in 90% sulphuric acid (4000 g.) was treated gradually with fine aluminium powder (36 g.), with stirring, during 4 hours. The solution became greenish-yellow when the reaction was completed, and the product was poured on crushed ice. The precipitated mixture of anthrones was washed free from acid and air-dried while protected from light. The crude dried product was treated according to Barnett and Goodway (*loc. cit.*) and yielded 23 g. of 3-methyl-9-anthrone, m. p. 102° (overall yield from the methylanthraquinone, 12%).

3 : 3′-*Dimethyl*-9 : 9′-*anthrapinacol*.—A solution of 3-methyl-9-anthrone (23 g.) in absolute ethyl alcohol (120 c.c.) and sulphur-free benzene (80 c.c.) was treated according to Newman (*J. Amer. Chem. Soc.*, 1940, **62**, 1683) with aluminium foil (5 g., freshly scratched) and mercuric chloride (0·3 g.). A further 100 c.c. of absolute alcohol were added to the thick reaction mass after 3 hours, and the mixture was heated under reflux for a further 3 hours. After decomposition with water and hydrochloric acid the solvents were removed in steam. The residual solid, when crystallised from methyl alcohol, yielded 3 : 3′-*dimethyl*-9 : 9′-*anthrapinacol* (20 g.) as fine colourless needles, m. p. 166° (88% yield) (Found : C, 86·2; H, 6·1. $C_{30}H_{26}O_2$ requires C, 86·0; H, 6·2%).

3 : 3′-*Dimethyl*-9 : 9′-*dianthryl*.—A solution of the above pinacol (18 g.) in glacial acetic acid (200 c.c.) was treated with 180 c.c. of 70% sulphuric acid, and heated on a water-bath for 5 hours. The crude product, obtained by precipitation with water, was crystallised from benzene–light petroleum, and yielded 3 : 3′-*dimethyl*-9 : 9′ *dianthryl* (9·8 g.) as colourless plates, m. p. 268° (60% yield) (Found : C, 94·2; H, 5·9. $C_{30}H_{22}$ requires C, 94·2; H, 5·8%).

9 : 9′-*Dianthryl*-3 : 3′-*dicarboxylic Acid*.—A solution of the above dianthryl (18 g.) in glacial acetic acid (500 c.c.) was treated gradually with chromic acid (32 g.). The deep red solution was heated under reflux for 5 hours and poured into water, and the precipitate extracted with sodium carbonate solution. The unchanged insoluble material (about 6 g.) was reoxidised by the above method. The combined aqueous alkali extracts on acidification yielded a flocculent yellow precipitate which was filtered off and dried. Crystallisation from glacial acetic acid gave 9·8 g. (47%) of 9 : 9′-*dianthryl*-3 : 3′-*dicarboxylic acid* as a pale yellow crystalline powder, m. p. 198—200° (Found : equiv., 222·2. $C_{30}H_{18}O_4$ requires equiv., 221), smoothly converted by excess of chromic acid into anthraquinone-2-carboxylic acid, m. p. 291° (Found : equiv., 254. Calc. : equiv., 252).

Resolution. The finely powdered acid (9·2 g.) was added slowly to a solution of quinidine (15 g.) in alcohol (250 c.c.). The clear solution was allowed to cool overnight, and the fine crystalline powder which separated weighed 9·5 g.; $[\alpha]^{21}_{5461}$ was −127° (chloroform, $c = 0{\cdot}09$). Three subsequent crystallisations from alcohol brought the salt to the constant rotatory power of $[\alpha]^{21}_{5461}$ −153°. The salt (5·2 g.) on decomposition yielded 1·9 g. of acid which when crystallised from acetic acid gave fine needles, m. p. 146—150°, $[\alpha]^{21}_{5461}$ −132° (acetone, $c = 0{\cdot}10$). The rotation and m. p. were unchanged by a further crystallisation.

The original mother-liquor when concentrated to 100 c.c. and kept overnight deposited 4·3 g. of a white amorphous powder. The filtrate was evaporated to dryness, and the salt when decomposed gave 3·4 g. of acid, m. p. 141—146°, $[\alpha]^{21}_{5461}$ +123° (acetone, $c = 0{\cdot}09$). Two crystallisations from acetic acid gave material of $[\alpha]^{21}_{5461}$ +129°, m. p. 145—146°. The rotation of the (+)-acid in xylene was unchanged after it had been heated under reflux (b. p. 139°) for 2 hours on an oil-bath.

3 : 4 : 5 : 6-*Dibenzphenanthrene*-9 : 10-*dicarboxylic Acid*.—The anhydride of this acid (15 g.; Weidlich, *Ber.*, 1938, **71**, 1203) was suspended in 10% potassium hydroxide solution (100 c.c.) and heated under reflux for 15 minutes. A white crystalline deposit of the potassium salt separated, which was dissolved by addition of 400 c.c. of water and boiling. The clear solution was poured into excess of dilute hydrochloric acid, and the pale yellow precipitate of 3 : 4 : 5 : 6-*dibenzphenanthrene*-9 : 10-*dicarboxylic acid* filtered off and air-dried (15·5 g., 98%), m. p. indefinite (shrinkage and decomposition with conversion into the anhydride) (Found : equiv., 184·5. $C_{24}H_{14}O_4$ requires equiv., 183).

Attempted resolution. Quinine, quinidine, brucine, cinchonine, cinchonidine, and strychnine all failed to give satisfactory salt formation. The acid (6·5 g.) in alcohol (150 c.c.) was treated at the boil with finely powdered morphine (11·8 g.). When dissolution was complete the mixture was cooled and a white crystalline solid was obtained after seeding and vigorous scratching. After being kept overnight in a refrigerator, this was filtered off and washed with a little alcohol; 12·5 g., $[\alpha]^{21}_{5461}$ −165° (chloroform, $c = 1{\cdot}0$). Recrystallisation from alcohol yielded 8·4 g. of the *morphine* salt, $[\alpha]^{20}_{5461}$ −182° (chloroform, $c = 1{\cdot}0$) (Found : N, 2·16. $C_{41}H_{33}O_7N$ requires N, 2·15%). A small quantity of the salt when crystallised further showed a decrease in optical activity ($[\alpha]^{20}_{5461}$ −174°). The original mother-liquor was evaporated to crystallising point and yielded 4·3 g. of salt, $[\alpha]_{5461}$ −149° (chloroform, $c = 1{\cdot}0$), the rotation being unchanged by further recrystallisation. The acid obtained by decomposition of either fraction of the morphine salt was found to be inactive. A sample of the salt having the highest activity obtained, $[\alpha]_{5461}$ −182° in chloroform solution ($c = 2{\cdot}0$), was placed in a polarimeter tube at room temperature, and the rotation observed at intervals as shown below. Finally, the solution was kept for 24 hours, but no further change could be observed.

Time (hours)	0	1	2	4	6	8	24
α_{5461}	−7·28°	−6·96°	−6·68°	−6·48°	−6·20°	−6·12°	−6·0°
$[\alpha]^{20-22}_{5461}$	−182°	−174°	−167°	−162°	−155°	−153°	−150°

Tetramethyl-3 : 4 : 3′ : 4′-*tetrahydro*-1 : 1′-*dinaphthyl*.—Reduction of 5 : 7-dimethyl-1-tetralone (20 g.) in the usual way and treatment of the resulting pinacol with glacial acetic acid yielded 5 : 7 : 5′ : 7′-*tetramethyl*-3 : 4 : 3′ : 4′-*tetrahydro*-1 : 1′-*dinaphthyl* (16 g.), which crystallised in stout colourless needles, m. p. 135—136°, from acetic acid (Found : C, 91·8; H, 8·3. $C_{24}H_{36}$ requires C, 91·7; H, 8·3%).

4′ : 6′ : 4″ : 6″-*Tetramethyl*-1 : 2 : 7 : 8 : 9 : 10 : 11 : 14-*octahydro*-3 : 4 : 5 : 6-*dibenzphenanthrene*-9 : 10-*dicarboxylic Anhydride*.—(a) *With use of xylene as solvent.* A solution of the above diene (3 g.) and an equal weight of maleic anhydride in dry xylene (20 c.c.) was heated under reflux on an oil-bath for 3 hours. The solvent was removed by steam, and the residue separated by fractional crystallisation from acetic acid into two components : (i) the unchanged diene which was the more soluble (1·2 g.), and (ii) the *adduct*, which crystallised in thick prisms, m. p. 210—212° (0·8 g.) (Found : C, 81·7; H, 6·7. $C_{28}H_{28}O_3$ requires C, 81·5; H, 6·8%).

(b) *With use of nitrobenzene as solvent.* A mixture of 14 g. each of maleic anhydride and the diene was heated under reflux in 100 c.c. of dry nitrobenzene for 3 hours, and the solvent removed as above; the material was dried and on crystallisation from acetic acid yielded a fine crystalline powder (8·5 g.), m. p. 198—225°. Close examination showed it to be a mixture of yellow and colourless crystals which could not be separated by further crystallisation. Since this material (which was presumed to be partly dehydrogenated) and the pure adduct from the xylene condensation yielded the same product on treatment with lead tetra-acetate, no further purification was attempted.

4′ : 6′ : 4″ : 6″-*Tetramethyl*-1 : 2 : 7 : 8-*tetrahydro*-3 : 4 : 5 : 6-*dibenzphenanthrene*-9 : 10-*dicarboxylic Anhydride*.—A solution of the above adduct (7·5 g.) and lead tetra-acetate (13·5 g.) in a mixture of glacial acetic acid and acetic anhydride (20 c.c. of each) was heated at 100° for 1 hour with stirring. The solution on cooling deposited 3·1 g. of yellow crystalline needles, m. p. 245—246°. Recrystallisation from acetic acid yielded the *anhydride* (2·5 g.) as yellow needles, m. p. 247° (Found : C, 82·1; H, 5·7. $C_{28}H_{24}O_3$ requires C, 82·3; H, 5·9%).

4′ : 6′ : 4″ : 6″-*Tetramethyl*-3 : 4 : 5 : 6-*dibenzphenanthrene*-9 : 10-*dicarboxylic Anhydride*.—An intimate mixture of the above tetrahydro-compound (2·4 g.) and palladium–charcoal catalyst (0·20 g.) contained in a hard-glass test-tube was heated at 340—350° for 2 hours. There was a brisk evolution of hydrogen, and, after being cooled, the product was ground to a fine powder in a mortar. The organic material was extracted with a little hot benzene. The solvent was removed by vacuum, and the crystalline residue digested with a little sodium carbonate solution, filtered off, and dried. Four crystallisations from xylene yielded 0·53 g. of 4′ : 6′ : 4″ : 6″-*tetramethyl*-3 : 4 : 5 : 6-*dibenzphenanthrene*-9 : 10-*dicarboxylic anhydride* as orange needles, m. p. 297—298° (Found : C, 83·4; H, 4·8. $C_{28}H_{20}O_3$ requires C, 83·2; H, 4·9%).

4′ : 6′ : 4″ : 6″-*Tetramethyl*-3 : 4 : 5 : 6-*dibenzphenanthrene*-9 : 10-*dicarboxylic Acid*.—The anhydride (0·52 g.) was hydrolysed as above with 10% potassium hydroxide. The dried product was crystallised from acetic acid and yielded the *acid* as a fine yellow crystalline powder which sintered above 300° (Found : equiv., 212. $C_{28}H_{22}O_4$ requires equiv., 211).

Resolution. Finely powdered morphine (0·71 g.) in alcohol (25 c.c.) was treated at the boil with 0·493 g. of the acid. The resulting solution was left overnight after being well cooled and scratched vigorously. The fine white powdery salt which separated was dried in a vacuum, desiccator; yield 0·92 g., $[\alpha]^{20}_{5461}$ −123°. Crystallisation from alcohol (18 c.c.) gave 0·54 g. of salt, $[\alpha]^{20}_{5461}$ −173°, this value being increased to $[\alpha]^{20}_{5461}$ −182° (chloroform, $c = 0{\cdot}95$) by a further crystallisation from alcohol (12 c.c.). The salt was decomposed by shaking it with cold dilute hydrochloric acid, and the yellow flocculent precipitate was dissolved in cold sodium hydroxide, reprecipitated, filtered off, washed, and sucked as dry as possible on the pump. The slightly damp acid was shaken with cold acetone until dissolved; the filtered solution (20 c.c.) showed a rotation of −0·52° decreasing to −0·32° after one hour, −0·20° after 3 hours, and after 5 hours was too small to be observed with accuracy. The acetone solution and the washings of the polarimeter tube were evaporated to dryness, whereupon the weight of the acid in solution was found to be 0·11 g., giving an initial specific rotation of $[\alpha]^{20}_{5461}$ −47·2°. The original mother-liquor of the salt was diluted with water, decomposed as above, and the slightly damp acid gave an observed rotation of +0·18°, corresponding to a specific rotation of approximately +18°.

5 : 8-*Dimethyl*-3 : 4-*dihydro*-1 : 1′-*dinaphthyl*.—The Grignard reagent prepared in the usual way from 1-bromonaphthalene (20 g.) in anhydrous ether (100 c.c.) was treated slowly with a solution of 5 : 8-dimethyl-1-tetralone (16 g.) in anhydrous ether (50 c.c.). After the initial vigorous reaction had subsided the mixture was heated under reflux for one hour and worked up in the usual way. The naphthalene was steam-distilled, and the semi-solid residue extracted with benzene. After removal of the solvent, the residue was heated under reflux for 2 hours with acetic acid and, on cooling, the solution deposited colourless plates of 5 : 8-*dimethyl*-3 : 4-*dihydro*-1 : 1′-*dinaphthyl* (5·3 g.), m. p. 112° unchanged by recrystallisation from alcohol (Found : C, 93·0; H, 7·0. $C_{22}H_{20}$ requires C, 92·9; H, 7·1%).

Treatment of 5 : 8-*Dimethyl*-3 : 4-*dihydro*-1 : 1′-*dinaphthyl with Maleic Anhydride*.—A solution of the above diene (4·4 g.) and maleic anhydride (3·0 g.) in dry xylene (40 c.c.) was heated under reflux for 3 hours. The solvent was removed by steam, and the diene recovered unchanged.

Attempted Pinacolic Reduction of 5 : 8-*Dimethyl*-1-*tetralone*.—A solution of 5 : 8-dimethyl-1-tetralone (28 g.) in absolute alcohol (200 c.c.) and sulphur-free benzene (133 c.c.) was treated in the usual way with aluminium foil (freshly cleaned; 8 g.) and mercuric chloride (0·5 g.). After being heated under reflux for 6 hours the ketone (21 g.) was recovered unchanged. The small quantity of residue was boiled for 2 hours with glacial acetic acid (10 c.c.) and gave 3 g. of a viscous oil, b. p. 215—220°/10 mm., which set to a resinous solid and did not yield an adduct with maleic anhydride.

4 : 7-*Dimethylindanone* (cf. Plattner and Wyss, *loc. cit.*).—2 : 5-Dimethylbenzyl chloride, b. p. 93°/12 mm., reacted immediately with ethyl sodiomalonate (5-hours' heating is unnecessary). The derived 2 : 5-dimethylbenzylmalonic acid was obtained as a white crystalline solid. Cyclisation of β-2 : 5-dimethylphenylpropionic acid yielded at once the pure indanone, m. p. 79° (yields as in literature).

4 : 7 : 4′ : 7′-*Tetramethyldi-indenyl*.—A solution of 4 : 7-dimethylindanone (30 g.) in absolute alcohol (225 c.c.) and sulphur-free benzene (150 c.c.) was reduced in the usual way with amalgamated aluminium foil (9 g.). The product was boiled with glacial acetic acid (100 c.c.) for 2 hours, and the white powder which separated on cooling was crystallised several times from acetic anhydride, yielding the *di-indenyl* as fine colourless needles, m. p. 178° (12·5 g., 50%) (Found : C, 91·9; H, 7·5. $C_{22}H_{22}$ requires C, 92·3; H, 7·7%). A similar experiment with indan-1-one yielded only an orange-coloured complex material which could not be obtained crystalline from any of the usual solvents.

The above diene was recovered unchanged after being boiled for 2 hours with 2 moles of maleic anhydride in xylene.

One of the authors (D. H. W.) is in receipt of a grant from the Department of Scientific and Industrial Research for which he wishes to express his indebtedness.

College of Technology, Belfast.

[*Received, June* 13*th*, 1949.]