

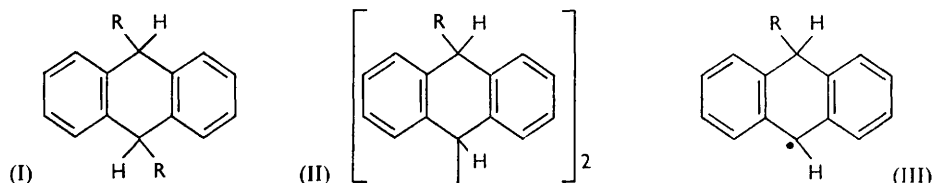
36. Free-radical Reactions of 9:10-Diphenylanthracene.

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9:10-Diphenylanthracene reacts in a terminal ring with both free benzyl and free phenyl radicals to give products which are thought to be 1:2-dibenzyl-1:2-dihydro- and 1:4-dibenzyl-1:4-dihydro-9:10-diphenylanthracene from the former, and that from the latter has been shown to be 1:4:9:10-tetraphenylanthracene. Methyl and benzyl radicals also add at the *meso*-positions, but the phenyl radical seems to be incapable of doing so, probably for steric reasons.

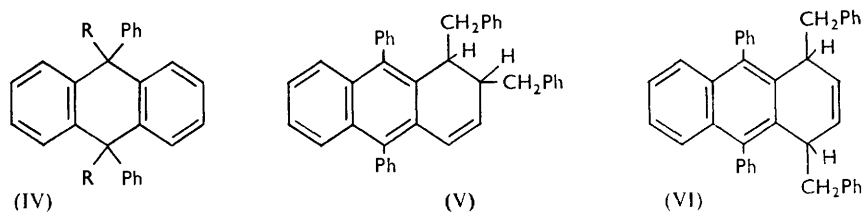
Analogies to other reactions are discussed, and synthetical work leading to the preparation of 1:6-diphenylhexa-2:4-diene is described.

PREVIOUSLY^{1,2} it was shown that benzyl radicals add to the *meso*-positions of anthracene to give the adducts (I) and (II) ($R = CH_2Ph$), hydrogen abstraction from the initial radical adduct (III; $R = CH_2Ph$) by the benzyl radical not being favoured. Phenyl and methyl radicals, in contrast, give mainly *meso*-substituted products, although the adduct (II; $R = Ph$ or Me) is also formed.^{3,4} These radicals are evidently much more effective dehydrogenating agents towards radicals of type (III) than is the benzyl radical.³



Acridine also reacts with benzyl radicals in the *meso*-positions to form the dihydro-adduct, but with 9-phenylacridine the attack of the benzyl radical is mainly transferred to the 1-position of a side ring.⁵ A similar transfer of reactivity to positions in a side ring has now been established for 9:10-diphenylanthracene.

Heating of this hydrocarbon with an excess of *tert.*-butyl peroxide in boiling toluene gives a number of products. That formed in highest yield is 9:10-dibenzyl-9:10-dihydro-9:10-diphenylanthracene (IV; $R = CH_2Ph$) which, as expected, is not fluorescent and has an ultraviolet spectrum of benzenoid type. Also formed are small amounts of two isomeric hydrocarbons which have ultraviolet spectra of naphthalene type and appear to



be 1:2-dibenzyl-1:2-dihydro-9:10-diphenyl (V) and 1:4-dibenzyl-1:4-dihydro-9:10-diphenylanthracene (VI). The former shows spectral resemblances to vinylnaphthalene⁶ and even closer similarity with the spectrum of 1:2-dihydro-1-hydroxy-2:2:9:10-tetraphenylanthracene,⁷ whilst the latter similarly resembles the maleic anhydride adduct of

¹ Norman and Waters, *J.*, 1957, 950.

² Beckwith and Waters, *J.*, 1957, 1001.

³ Norman and Waters, preceding paper.

⁴ Beckwith and Waters, *J.*, 1956, 1108.

⁵ Waters and Watson, *J.*, 1957, 253.

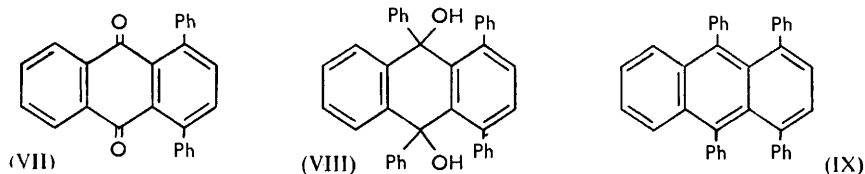
⁶ Laitinen, Miller, and Parks, *J. Amer. Chem. Soc.*, 1947, **69**, 2707.

⁷ Étienne and Weill-Raynal, *Bull. Soc. chim. France*, 1953, **20**, 1136.

9:10-diphenylanthracene, which is known to be a 1:4- and not a 9:10-adduct.⁸ Attempted synthesis of the 1:4-dibenzyl adduct by the route effective for 1:4:9:10-tetraphenylanthracene (IX) was unsuccessful. Some new compounds related to 1:6-diphenylhexadiene have been synthesised.

Methyl radicals, generated by the decomposition of *tert.*-butyl peroxide in chlorobenzene, give only in poor yield the *meso*-adduct 9:10-dihydro-9:10-dimethyl-9:10-diphenylanthracene (IV; R = Me) together with products derived from attack on the solvent.⁹

Phenyl radicals, made by the action of zinc powder in acetone on benzenediazonium zincchloride, $(\text{PhN}_2)_2\text{ZnCl}_4$, do not add to the *meso*-positions of 9:10-diphenylanthracene but give a 3% yield of 1:4:9:10-tetraphenylanthracene (IX), identified by the following synthesis. 1:4-Diphenylbutadiene was condensed with 1:4-naphthaquinone to give the quinone (VII) which was converted into the diphenyl-diol (VIII) with phenylmagnesium bromide and thence into 1:4:9:10-tetraphenylanthracene.¹⁰



The proof of this reactivity in the side ring of 9:10-diphenylanthracene towards phenyl radicals lends strong support for the formulations, as side-ring adducts, of the two naphthalenic products (V) and (VI) of the reaction between 9:10-diphenylanthracene and benzyl radicals. It may be noted that phenyl-radical attack involves hydrogen removal from the initial radical adduct to re-form a stable, aromatic product in which the substituent phenyl groups are conjugated with the rest of the molecule.

Two points of theoretical interest are evident. First, the isolation of 9:10-dibenzyl-9:10-dihydro-9:10-diphenylanthracene and the corresponding dimethyl compound shows that phenyl substituents are not large enough to block the *meso*-carbon atoms from direct attack by both benzyl and methyl radicals. This accords with the observation¹¹ that 9:10-diphenylanthracene is as efficient an inhibiting agent towards the benzoyl peroxide-catalysed autoxidation of benzaldehyde as anthracene itself. Clearly this free-radical attack at the *meso*-positions of 9:10-diphenylanthracene must take place at an angle to the plane of the anthracene ring, and would be consistent with benzyl addition to the activated triplet state of the molecule, first postulated by Ingold and Marshall.¹² The failure of the phenyl radical to add to the *meso*-positions of 9:10-diphenylanthracene can be attributed to steric effects, for it is impossible to construct a scale model of the corresponding adduct (IV; R = Ph).

Secondly, arylation of the *meso*-positions of anthracene and of acridine must enhance the reactivity towards free radicals of the carbon centres in the side ring, particularly at the *ortho*-carbon atoms. Enhanced side-ring reactivity is exhibited also in the Diels-Alder reactions of these *meso*-arylated compounds^{8,13} but from this analogy one need not infer that the Diels-Alder addition proceeds by a homolytic mechanism.

This demonstration of side-ring reactivity in the anthracene series brought about by the blocking of the *meso*-positions is also of interest in connection with the clear evidence of

⁸ Cook and Hunter, *J.*, 1953, 4109.

⁹ Beckwith and Waters, *J.*, 1957, 1665.

¹⁰ Weizmann, Haskelberg, and Bergmann, *J.*, 1939, 391.

¹¹ Turner and Waters, *J.*, 1956, 879.

¹² Ingold and Marshall, *J.*, 1926, 3080.

¹³ Gillet, *Bull. Soc. chim. France*, 1950, 17, 1141.

side-ring metabolic attack on anthracene and related carcinogenic hydrocarbons,^{14,15} and further investigation is intended.

EXPERIMENTAL

9 : 10-Diphenylanthracene.—Anthraquinone (25 g.) was gradually added to a stirred solution of phenyl-lithium [from bromobenzene (52 g.) and lithium (4.5 g.) in ether (20 ml.)] and after 30 minutes' refluxing the mixture was decomposed with aqueous ammonium chloride.¹⁶ The precipitated 9 : 10-dihydroxy-9 : 10-diphenyl-dihydroanthracenes (m. p. *ca.* 180°; 80%) were dried and dissolved in acetic acid (200 ml.), and the solution cautiously treated with phenylhydrazine (20 g.) and refluxed for 30 min. On cooling 9 : 10-diphenylanthracene (m. p. 248° from benzene) was deposited.

Reaction with Methyl Radicals.—9 : 10-Diphenylanthracene (8.7 g.), *tert.*-butyl peroxide (5.5 g.), and chlorobenzene (150 ml.) were refluxed under nitrogen for 50 hr., then concentrated to about 30 ml. and cooled. Impure 9 : 10-diphenylanthracene and a small quantity (0.14 g.) of 9 : 10-dihydro-9 : 10-dimethyl-9 : 10-diphenylanthracene separated. The latter had m. p. 324°, after separation with methanol and crystallisation from much benzene, and was identical with synthetic material (see below). Chromatography of the residue gave more diphenylanthracene (total recovery, 4.3 g.), a little 3 : 3'-dichloro-4 : 4'-dimethyldiphenyl⁹ (0.2 g.), and coloured resin containing chlorine.

Reaction with Benzyl Radicals.—9 : 10-Diphenylanthracene (6 g.), *tert.*-butyl peroxide (10 g.), and toluene (150 ml.) were refluxed under nitrogen for 7 days. On cooling, white crystals (0.85 g.) were deposited. These formed minute rhombs, m. p. 312° (from xylene) of 9 : 10-dibenzyl-9 : 10-dihydro-9 : 10-diphenylanthracene, identical with authentic material (see below). The filtrate from separation of this material was evaporated to dryness and extracted with hot methanol (3 × 40 ml.) which removed dibenzyl (5.0 g.). The portion insoluble in cold methanol was dried and then treated with hot light petroleum (100 ml.; b. p. 60–80°). There remained undissolved a mixture of 9 : 10-dibenzyl-9 : 10-dihydro-9 : 10-diphenylanthracene (0.3 g.) and 9 : 10-diphenylanthracene (1.8 g.). Chromatography of the petroleum solution through activated alumina gave successively dibenzyl (0.7 g.), 9 : 10-diphenylanthracene (0.22 g.), crystals (m. p. 176°, from methyl acetate) probably of 1 : 2-dibenzyl-1 : 2-dihydro-9 : 10-diphenylanthracene (0.28 g.) (see below), and needles (m. p. 228°, from methyl acetate) probably of 1 : 4-dibenzyl-1 : 4-dihydro-9 : 10-diphenylanthracene (0.23 g.) (Found: C, 93.6; H, 6.3. C₄₀H₃₂ requires C, 93.7; H, 6.3%). The ultraviolet spectrum [max. at 2360 (ε 65,800) and 2950 Å (ε 9500)] of the last compound was similar to that reported for 1 : 4-dihydro-9 : 10-diphenyl-1 : 4-*endo*-αβ-succinic anhydride.⁸ On attempted dehydrogenation with sulphur at 240° extensive decomposition occurred.

Reaction with Sodium and Benzyl Chloride.—9 : 10-Diphenylanthracene (4.7 g.), sodium (4 g.), and broken glass (10 g.) were shaken in ether (60 ml.) under nitrogen for 3 days. The dark blue solution was then filtered (glass wool) under nitrogen, and the filtrate was treated dropwise with freshly distilled benzyl chloride until the solution became yellow. Excess of dilute acid was added cautiously. Treatment of the solid product with benzene gave a residue (0.23 g.) of 9 : 10-dibenzyl-9 : 10-dihydro-9 : 10-diphenylanthracene, m. p. and mixed m. p. 312°, and 9 : 10-diphenylanthracene (2.1 g.). Chromatography of the more soluble remainder gave dibenzyl (0.9 g.), more 9 : 10-diphenylanthracene, and an amorphous product (0.6 g.) which slowly crystallised from ether-methanol. Further crystallisation from methyl acetate gave rods, m. p. 178°, probably of 1 : 2-dibenzyl-1 : 2-dihydro-9 : 10-diphenylanthracene (Found: C, 93.5; H, 6.4. C₄₀H₃₂ requires C, 93.7; H, 6.3%); light absorption in chloroform, maxima at 2570 (ε 41,200), 2640 (ε 38,700), 2770 (ε 31,000), 2930 (ε 13,600), 3030 (ε 16,750), and 3130 Å (ε 14,850). This absorption is similar to that of vinylnaphthalene⁶ and almost identical with that of 1 : 2-dihydro-1-hydroxy-2 : 2 : 9 : 10-tetraphenylanthracene.⁷ Finally, 1 : 4-dibenzyl-1 : 4-dihydro-9 : 10-diphenylanthracene (0.07 g.), m. p. 228°, was obtained. The preceding 1 : 2-dihydro-compound was not affected by sulphur at 240° for 2 hr. Treatment with chloranil in boiling xylene gave a 30% yield of an *isomer*, m. p. 164° (Found: C, 93.9; H, 6.3. C₄₀H₃₂

¹⁴ Boyland and Levi, *Biochem. J.*, 1935, **29**, 2679.

¹⁵ Berenblum, Crowfoot, Holiday, and Schoental, *Cancer Res.*, 1943, **3**, 151.

¹⁶ Cf. Willemart, *Bull. Soc. chim. France*, 1942, **9**, 83.

requires C, 93.7; H, 6.3%). This had a different infrared spectrum from the compound of m. p. 178°, and its ultraviolet spectrum in chloroform had maxima at 2570 (ϵ 46,500), 2640 (ϵ 45,500), 2760 (ϵ 37,700), 2900 (ϵ 19,600), 3020 (ϵ 21,100), and 3130 Å (ϵ 17,050).

Reaction with Phenyl Radicals (cf. ref. 3).—Benzenediazonium zincchloride (28 g.; 4 mol.) was suspended in dry acetone (200 ml.) in which was dissolved 9 : 10-diphenylanthracene (5.5 g.; 1 mol.). A small quantity of chalk was added, and a stream of dry nitrogen was passed over the system. Zinc powder ("AnalaR") (5 g.) was added in small portions. After the initial reaction was over, the mixture was refluxed for 1 hr. and filtered. The solvent was evaporated and the resulting material was extracted in hot light petroleum. This solution was concentrated to 500 ml. and chromatographed. Elution with light petroleum gave diphenyl (25 mg.) and then 9 : 10-diphenylanthracene (4.41 g.; 80% recovery). Elution with light petroleum-benzene gave 1 : 4 : 9 : 10-tetraphenylanthracene (0.24 g.; 3%), m. p. and mixed m. p. 203—204°, identical with an authentic specimen synthesised as described below.

Preparations of Reference Compounds.—9 : 10-Dibenzyl-9 : 10-dihydro-9 : 10-diphenylanthracene. 9 : 10-Dihydro-9 : 10-dihydroxy-9 : 10-diphenylanthracene (see p. 173) (4 g.) in hot dry chloroform (30 ml.) was treated with gaseous hydrogen chloride; acetic acid (60 ml.) then precipitated 9 : 10-dichloro-9 : 10-dihydro-9 : 10-diphenylanthracene, m. p. 186° (4.8 g.). A mixture of this compound (2.2 g.) in hot benzene and the Grignard reagent from benzyl chloride (10 g.) and magnesium (2 g.) in ether (50 ml.) was refluxed for 4 hr. After decomposition with hydrochloric acid the organic solution was evaporated to dryness and the residue extracted with hot benzene. There remained 9 : 10-dibenzyl-9 : 10-dihydro-9 : 10-diphenylanthracene (40 mg.), rhombs (from toluene), m. p. 312° (Found: C, 93.6; H, 6.4. $C_{40}H_{32}$ requires C, 93.7; H, 6.3%); absorption maximum (in alcohol) at 2650 Å (ϵ 4450). The remaining benzene solution yielded 9 : 10-diphenylanthracene (0.7 g.) and dibenzyl (1.1 g.).

9 : 10-Dihydro-9 : 10-dimethyl-9 : 10-diphenylanthracene. This was prepared similarly from the above dichloro-compound and methylmagnesium iodide, and formed minute rhombs, m. p. 324° (from benzene) (Found: C, 93.5; H, 6.7. $C_{28}H_{24}$ requires C, 93.3; H, 6.7%); absorption maxima (in chloroform) at 2590 (ϵ 1450), 2650 (ϵ 1730), and 2730 Å (ϵ 1350).

Attempted preparation of 1 : 4-dibenzyl-1 : 4-dihydro-9 : 10-diphenylanthracene. The route envisaged was condensation of 1 : 4-naphthaquinone with 1 : 6-diphenylhexa-2 : 4-diene, but the isomers of the latter which we prepared did not condense with the quinone. The product, m. p. 79°, from reduction of 1 : 6-diphenylhexa-1 : 3 : 5-triene, m. p. 205°,¹⁷ was obtained in very small yield. An isomer was prepared by reduction of 1 : 6-diphenylhex-3-yne-2 : 5-diol as follows: purified acetylene was passed into a solution of the Grignard reagent, from ethyl bromide (30 g.) and magnesium (6.6 g.), in tetrahydrofuran (150 ml.) until the mixture became too viscous to be stirred. Phenylacetaldehyde (25 g.) in tetrahydrofuran (50 ml.) was then added dropwise and the whole was refluxed for 1 hr. and then decomposed with aqueous ammonium chloride. The product, after chromatography, gave a mixture of stereoisomeric 1 : 6-diphenylhex-3-yne-2 : 5-diols (19 g.), m. p. 90°, which were separated by fractional crystallisation from ether-light petroleum (b. p. 40—60°). The less soluble (? meso-)1 : 6-diphenylhex-3-yne-2 : 5-diol had m. p. 105—106° and absorption maxima (in ethanol) at 2130 (ϵ 11,300), 2480 (ϵ 221), 2530 (ϵ 303), 2580 (ϵ 339), 2640 (ϵ 303), and 2680 Å (ϵ 224) (Found: C, 81.3; H, 7.1. $C_{18}H_{18}O_2$ requires C, 81.2; H, 6.8%). The other (? racemic) isomer formed needles, m. p. 102—103°, absorption maxima at 2130 (ϵ 11,500), 2480 (ϵ 201), 2550 (ϵ 294), 2580 (ϵ 374), 2640 (ϵ 206), and 2680 Å (ϵ 206), and had a different infrared spectrum (Found: C, 81.0; H, 7.0%). Reduction of the mixture (3 g.) of diols described above with lithium aluminium hydride (1.8 g.) in ether (80 ml.) gave a mixture of 1 : 6-diphenylhex-3-ene-2 : 5-diols (1.9 g.) which was also separated by fractional crystallisation from ether-light petroleum. One (? meso-trans) formed plates, m. p. 103—104° (Found: C, 80.5; H, 7.7. $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%); absorption maxima (in ethanol) at 2130 (ϵ 13,100), 2480 (ϵ 263), 2530 (ϵ 359), 2590 (ϵ 434), 2640 (ϵ 332), and 2680 Å (ϵ 286); the other (? racemic-trans) had m. p. 98—100° (Found: C, 80.7; H, 7.65%) and absorption maxima at 2140 (ϵ 11,400), 2480 (ϵ 238), 2530 (ϵ 355), 2590 (ϵ 428), 2640 (ϵ 346), and 2680 Å (ϵ 292). Dehydration of this mixture with 5% sulphuric acid in acetic acid gave authentic 1 : 6-diphenylhexa-1 : 3 : 5-triene.

Reduction of the mixed acetylene diols (5 g.) in diethylaniline (140 ml.) under nitrogen with lithium aluminium hydride (2 g.) in ether (40 ml.) at 60—70°¹⁸ gave a crystalline mixture

¹⁷ Kuhn and Winterstein, *Helv. Chim. Acta*, 1928, **11**, 123.

¹⁸ Isler, Montavon, Ruegg, and Zeller, *ibid.*, 1956, **39**, 454.

(1.8 g.) of isomeric ethylenic diols and a solution which, after chromatography, gave a (? trans-trans)-1 : 6-diphenylhexa-2 : 4-diene, needles (from methanol), m. p. 75° (Found: C, 92.0; H 7.7. C₁₈H₁₈ requires C, 92.3; H, 7.7%) and, in ethanol, had absorption maxima at 2110 (ϵ 19,000), 2420 (ϵ 31,300) and 2690 Å (ϵ 1950). It was not identical with the reduction product of 1 : 6-diphenylhexa-1 : 3 : 5-triene. (The tentative geometric structures for these compounds are based on examination of infrared spectra but are uncertain because their absorptions overlap those of the phenyl groups.)

1 : 4 : 9 : 10-Tetraphenylanthracene. The Diels-Alder reaction between 1 : 4-diphenylbutadiene¹⁹ and 1 : 4-naphthaquinone in nitrobenzene gave 1 : 4-diphenylanthraquinone.²⁰ The quinone was converted into 9 : 10-dihydro-9 : 10-dihydroxy-1 : 4 : 9 : 10-tetraphenylanthracene with phenylmagnesium bromide, and this was reduced with potassium iodide and sodium hypophosphite in glacial acetic acid to 1 : 4 : 9 : 10-tetraphenylanthracene,¹⁰ m. p. 204—205°.

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¹⁹ "Organic Syntheses," Collective Volume II, p. 229.

²⁰ Bergmann, Haskelberg, and Bergmann, *J. Org. Chem.*, 1942, 7, 303.
