569. *Benzocyclobutenes. Part I. Attempted Syntheses of 1,2-Diphenylbenzocyclobutene.*

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o-Dibenzoylbenzene has been used as the starting point in attempted syntheses of 1,2-diphenylbenzocyclobutene (I). Pinacol reduction led to 1,3-diphenylisobenzofuran (VI), the *meso*- and racemic diols (IV), and 9,9′,10,10′-tetrahydro-10,10′-diphenyl-9,9′-bianthryl. The more accessible of the diols could not be converted into the related dibromo-derivative (XI); instead, cyclisation occurred to give 9-phenylanthracene. The diketone (V) was reduced with sodium in propan-2-ol to *o*-dibenzylbenzene (IX), which with *N*-bromosuccinimide gave either the α-bromo- or the αα′-dibromo-derivative (XI). Neither of these bromo-derivatives could be cyclised to benzocyclobutenes; instead they readily yielded derivatives of 9-phenylanthracene.

Derivatives of benzocyclobutene were first made by Finkelstein [1] in 1910 and the parent compound was prepared by Cava and Napier [2] in 1956. So far all attempts to prepare benzocyclobutadiene or its derivatives have failed, although the transient existence of benzocyclobutadiene has been demonstrated by the formation of dimers [1,3] of this compound when attempting to prepare it, and also by trapping the benzocyclobutadiene with cyclopentadiene [4] and with furan.[5] The objectives of the experiments now described were the preparation of 1,2-diphenylbenzocyclobutene (I) and of the related butadiene in the hope that the latter might be stabilised by conjugation and be prevented from polymerising by steric hindrance. The experiments described in the present paper were not successful, but in retrospect this is not surprising since 1,2-diphenylbenzocyclobutene [6,7] is now known to be highly reactive and probably would not have survived under many of the experimental conditions which were used.

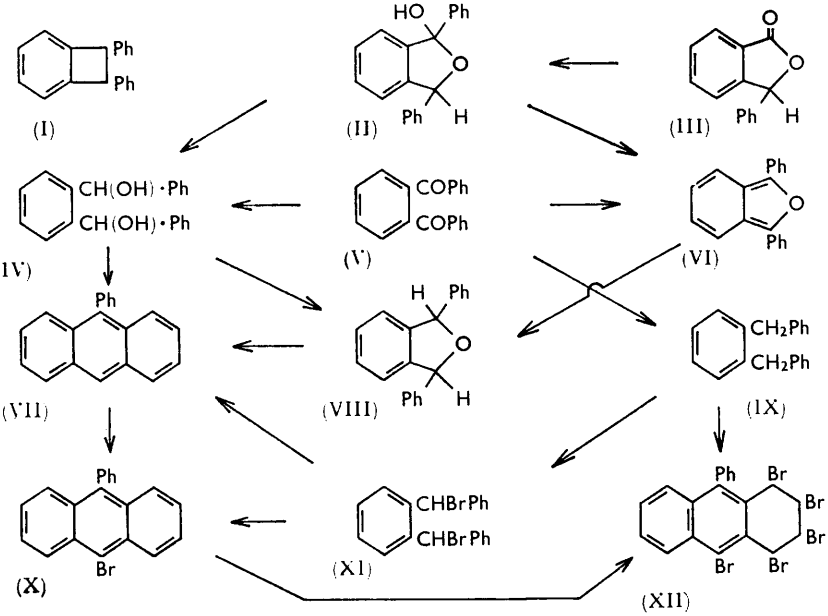
o-Dibenzoylbenzene (V), which was required for the present work, is not readily prepared by any of the previously described methods.[8] The most convenient starting-point for its preparation was 9,10-dihydro-9,10-dihydroxy-9,10-diphenylanthracene, prepared from anthraquinone and phenyl-lithium,[9] and this gave a high yield of *o*-dibenzoylbenzene (V) when oxidised with chromium trioxide. An attempt was made to reduce the diketone

[1] Finkelstein, *Ber.*, 1910, **43**, 1530; *Chem. Ber.*, 1959, **92**, xxxvii.
[2] Cava and Napier, *J. Amer. Chem. Soc.*, 1956, **78**, 500; 1958, **80**, 2255.
[3] Cava and Napier, *J. Amer. Chem. Soc.*, 1957, **79**, 1701.
[4] Nenitzescu, Avram, and Dinu, *Chem. Ber.*, 1957, **90**, 2541.
[5] Cava and Mitchell, *J. Amer. Chem. Soc.*, 1959, **81**, 5409.
[6] Jensen and Coleman, *J. Amer. Chem. Soc.*, 1958, **80**, 6149.
[7] Baker, McOmie, and Preston, *Chem. and Ind.*, 1960, 1305; Part II, following paper.
[8] Adams and Gold, *J. Amer. Chem. Soc.*, 1940, **62**, 56, and earlier references given there.
[9] Willemart, *Bull. Soc. chim. France*, 1942, **9**, 83.

(V) to *o*-dibenzylbenzene (IX) by the modification of the Wolff–Kishner reduction introduced by Barton, Ives, and Thomas,[10] but the product was, not unexpectedly, 1,4-diphenylphthalazine.[11]

Clemmensen reduction of *o*-dibenzoylbenzene to *o*-dibenzylbenzene was unsuccessful, the diketone being unchanged even when we used the modification introduced by Martin,[12] which is particularly successful with sterically hindered ketones. Direct catalytic reduction of *o*-dibenzoylbenzene also proved difficult, and even under somewhat severe conditions the yield of *o*-dibenzylbenzene was only 23%. The most satisfactory procedure was found to be reduction with sodium in boiling isopentan-1-ol which gave *o*-dibenzylbenzene in 60% yield; the substance was apparently identical with that prepared in traces in a quite different manner by Huston and Friedmann.[13]

Reduction of *o*-dibenzoylbenzene with lithium aluminium hydride gave one of the two stereoisomeric forms (*meso* or racemic) of αα'-dihydroxy-*o*-dibenzylbenzene (IV), m. p. 127—128°, which is here designated as the α-form. A further route to the same diol started from 3-phenylphthalide (III), which when treated with phenylmagnesium bromide and then with aqueous ammonium chloride gave a good yield of 1-hydroxy-1,3-diphenylphthalan (II); the previously [11] described preparation of the phthalan (II) involved decomposition of the intermediate magnesium derivative with dilute mineral acid, causing dehydration to give 1,3-diphenylisobenzofuran (VI) as the major product. Reduction of the hydroxydiphenylphthalan (II) with sodium amalgam gave the α-diol (IV).



When attempting to replace the hydroxyl groups of the diol (IV) by bromine, it was found that the diol shows a remarkable tendency to undergo cyclodehydration to 9-phenylanthracene (VII), for example when treated with phosphorus tribromide and then with water (this paper); a similar dehydration occurs with sulphuric acid.[11] Again, 1,3-diphenylphthalan (VIII), prepared either by dehydration of the diol (IV) with hydrochloric acid or by reduction of 1,3-diphenylisobenzofuran (VI) with sodium amalgam,[11] also yields

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[10] Barton, Ives, and Thomas, *J.*, 1955, 2056.

[11] Guyot and Catel, *Bull. Soc. chim. France*, 1906, **35**, 1124, 1135.

[12] Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1438.

[13] Huston and Friedmann, *J. Amer. Chem. Soc.*, 1916, **38**, 2527.

9-phenylanthracene when boiled with hydrobromic acid (this paper), rather than giving αα′-dibromo-*o*-dibenzylbenzene (XI).

Several attempts to effect a pinacol reduction of 1,2-dibenzoylbenzene (V) to 1,2-dihydroxy-1,2-diphenylbenzocyclobutene were unsuccessful. Reduction with aluminium amalgam in benzene–ethanol or in aqueous ethanol (cf. ref.14) gave 1,3-diphenylisobenzofuran (VI), and the same product was obtained by reduction with sodium amalgam, with sodium in ether,[15] or with magnesium–magnesium iodide.[16] Reduction of *o*-dibenzoylbenzene with sodium amalgam in ethanol yielded the second stereoisomeric, β-form of αα′-dihydroxy-*o*-dibenzylbenzene (IV), m. p. 105—106°, which with acetic anhydride yielded the same diacetyl derivative as had been similarly prepared from the α-form of the diol; a geometrical rearrangement must be involved in one of these acetylations. A similar reduction in propanol–acetic acid gave the α-form of the diol (IV). Attempted pinacol reduction with zinc dust and alkali [17] again yielded the β-form of the diol (IV) and, curiously, a small quantity of anthraquinone. Treatment of *o*-dibenzoylbenzene with zinc dust in acetic acid was found by Boyd and Ladhams [18] and by Adams and Gold [8] to give 1,3-diphenylisobenzofuran (VI), whereas in boiling acetic acid (under which conditions pinacols are known to have been produced [19]) reduction proceeds further to give 9,9′,10,10′-tetrahydro-10,10′-diphenyl-9,9′-bianthryl.

In view of the failures to effect either a pinacol reduction of *o*-dibenzoylbenzene or conversion of the diol (IV) into a related dihalogen compound, the required αα′-dibromo-*o*-dibenzylbenzene (XI) was prepared by treatment of *o*-dibenzylbenzene (IX) with two equivalents of *N*-bromosuccinimide in carbon tetrachloride. When one equivalent of *N*-bromosuccinimide was used the monobromo-derivative of *o*-dibenzylbenzene was obtained. When *o*-dibenzylbenzene in carbon tetrachloride was boiled with an excess of brominating agent the product was 1,2,3,4,9-pentabromo-1,2,3,4-tetrahydro-10-phenylanthracene (XII), a compound which was also obtained by the addition of bromine to 9-bromo-10-phenylanthracene (X).

The dibromo-compound (XI) resembles other compounds in this series in its ready conversion into 9-phenylanthracenes on attempted cyclisation to a benzocyclobutene derivative. (*a*) When treated with sodium in ether under high-dilution conditions [20] it yielded 9-phenylanthracene (VII) and 10,10′-diphenyl-9,9′-bianthryl.[21] (*b*) With zinc dust and ethanol the product was the known adduct of 9-phenylanthracene and 9,10-dihydro-9-phenylanthracene.[22] (*c*) With potassium t-butoxide it yielded 9-bromo-10-phenylanthracene (X). (*d*) With sodium iodide in ethanol or acetone at temperatures from −80° to reflux temperature the products were 9-phenylanthracene, 9-bromo-10-phenylanthracene, and 9,9′,10,10′-tetrahydro-10,10′-diphenyl-9,9′-bianthryl.[23] Similarly, the reaction of α-bromo-*o*-dibenzylbenzene with ethanolic potassium hydroxide or t-butanolic potassium t-butoxide gave 9-phenylanthracene and the corresponding dihydro-compound as the only isolable products when the reaction was carried out at temperatures from 0° to reflux.

After the completion of this work, Jensen and Coleman [6] reported that they had prepared 1,2-diphenylbenzocyclobutene (I) by the action of sodium iodide on αα′-dibromo-*o*-dibenzylbenzene (XI) and by the action of bases on α-bromo-*o*-dibenzylbenzene, but no experimental details were given of these reactions or of the preparation of the bromo-compounds. In a subsequent communication [24] Jensen described the preparation of *o*-dibenzylbenzene (IX)

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[14] Newman, *J. Amer. Chem. Soc.*, 1940, **62**, 1683; Lloyd and Rowe, *J.*, 1954, 4232.
[15] Bachmann, *J. Amer. Chem. Soc.*, 1933, **55**, 1179.
[16] Gomberg and Bachmann, *J. Amer. Chem. Soc.*, 1927, **49**, 236.
[17] Baker and McGowan, *J.*, 1937, 559.
[18] Boyd and Ladhams, *J.*, 1928, 2089.
[19] Pauson, *J. Amer. Chem. Soc.*, 1954, **76**, 2187.
[20] Cope and Fenton, *J. Amer. Chem. Soc.*, 1951, **73**, 1668.
[21] Barnett and Cook, *J.*, 1923, **123**, 2639.
[22] Haack, *Ber.*, 1929, **62**, 1771.
[23] Schlenk and Bergmann, *Annalen*, 1928, **464**, 40.
[24] Jensen, *J. Org. Chem.*, 1960, **25**, 269.

by catalytic reduction of *o*-dibenzoylbenzene, itself made in 32% yield by the action of phenylmagnesium bromide on phthaloyl chloride at −55°. More recently, Cava, Mitchell, and Deana[25] tried to prepare compound (I) by pyrolysis of 1,3-diphenyl-2-thiaindane 2,2-dioxide, but they obtained only 9-phenylanthracene. Likewise, dehydrogenation and decarboxylation of 7,8-diphenylbicyclo[4,2,0]oct-6-ene-3,4-dicarboxylic acid gave, not the benzocyclobutene (I), but a mixture of 9-phenylanthracene and *o*-dibenzylbenzene.[26] A synthesis of the benzocyclobutene (I) has, however, been achieved[7] from 1,3-dihydro-1,3-diphenylisoindole and is fully described in the following paper.

EXPERIMENTAL

o-*Dibenzoylbenzene* (V).—9,10-Dihydro-9,10-dihydroxy-9,10-diphenylanthracene[9] (10·9 g.) in glacial acetic acid (75 ml.) was oxidised by addition during ½ hr. of a solution of chromium trioxide (30 g.) in acetic acid (150 ml.) and water (50 ml.) at 70° with constant stirring. After being heated for a further 2 hr. on the steam-bath, the cooled mixture was poured into water, and the product was collected, washed with water and with dilute alkali, and crystallised from ethanol, giving *o*-dibenzoylbenzene as colourless rhombs, m. p. 145—146° (6·8 g., 79%) (lit.,[11] m. p. 146°). The *mono*-2,4-*dinitrophenylhydrazone*, prepared in ethanol–hydrochloric acid solution, separated from ethanol in rhombic prisms, m. p. 199—200° (Found: C, 66·8; H, 3·9; N, 12·3. $C_{26}H_{18}N_4O_5$ requires C, 66·9; H, 3·8; N, 12·0%).

o-*Dibenzylbenzene* (IX).—(*a*) *o*-Dibenzoylbenzene (2·0 g.) in ethanol (120 ml.) was shaken at 70° for 12 hr. in hydrogen at 23 atm. pressure in presence of 10% palladium–charcoal. The filtered solution was evaporated, and the residue extracted with ether (the diketone is sparingly soluble), giving *o*-dibenzylbenzene which separated from ethanol in thin prisms, m. p. 77—78° (0·43 g.) (Found: C, 93·0; H, 7·1. Calc. for $C_{20}H_{18}$: C, 93·0; H, 7·0%). Huston and Friedemann[13] give m. p. 78°.

(*b*) *o*-Dibenzoylbenzene (2·0 g.) dissolved in isopentan-1-ol (200 ml.; redistilled) was added at the b. p. to small pieces of sodium (20 g.) with vigorous stirring. When the reaction had subsided a further volume of isopentanol was added; when all sodium had reacted, the solvent was removed in steam, and the residual oil which solidified was crystallised twice from ethanol, giving *o*-dibenzylbenzene, m. p. 77—78° (1·1 g.).

*αα′-Dihydroxy-*o*-dibenzylbenzene* (IV) (*α-Form*).—(a) *By reduction of* o-*dibenzoylbenzene.* *o*-Dibenzoylbenzene (2·8 g.) was added by extraction from a Soxhlet thimble, to a refluxing solution of lithium aluminium hydride (2·2 g.) in anhydrous ether (200 ml.), and after treatment with dilute sulphuric acid the ethereal layer yielded a yellow oil (2·7 g.). This product was adsorbed on a column of alumina and eluted with benzene; of the two bands detected in ultraviolet light the upper yielded a solid which was crystallised twice from 50% methanol–water, giving αα′-dihydroxy-*o*-dibenzylbenzene (IV) as rhombs, m. p. 127—128° (α-form) (1·3 g., 45%). The m. p. was undepressed on admixture with a specimen of the diol prepared as described by Guyot and Catel.[11] The *diacetyl derivative* of (IV), prepared by reaction with acetic anhydride at 100° and crystallised from ethanol, had m. p. 107—108° (Found: C, 76·9; H, 6·1. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%).

(b) *By reduction of* 1-*hydroxy*-1,3-*diphenylphthalan.* A solution of the phthalan[11] (11·5 g.) in methanol (130 ml.) was boiled for 6 hr. with 2% sodium amalgam (100 g.), and the residue left on evaporation of the solvent was crystallised from methanol–water (1 : 1). The dihydroxy-compound separated in rhombs (8·5 g.), m. p. 127—128°.

9-*Phenylanthracene* (VII).—(a) *From* 1,3-*diphenylphthalan.* 1,3-Diphenylphthalan[11] (5·4 g.) was boiled under reflux for 5 hr. with 48% aqueous hydrogen bromide (10 ml.). Neutralisation with sodium carbonate and extraction with ether gave 9-phenylanthracene which separated from ethanol as pale green leaflets, m. p. 153—154° (2·5 g.; 48%) (lit.,[27] m. p. 152—153°).

(b) *From αα′-dihydroxy-*o*-dibenzylbenzene.* The diol (IV) (1·0 g.; m. p. 127—128°) in benzene (75 ml.) containing a few drops of pyridine was treated dropwise at 70° with phosphorus tribromide (1·6 ml.) and then kept at 55° for 2 hr. After treatment with aqueous alkali the benzene solution yielded 9-phenylanthracene, m. p. 153—154° (0·49 g., 57%) after crystallisation from ethanol.

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[25] Cava, Mitchell, and Deana, *J. Org. Chem.*, 1960, **25**, 1481.

[26] Blomquist and Meinwald, *J. Amer. Chem. Soc.*, 1960, **82**, 3619.

[27] Baeyer and Schillinger, *Annalen*, 1880, **202**, 61.

Reduction of o-*Dibenzoylbenzene* (V). *Formation of* 1,3-*Diphenylisobenzofuran* (VI).—(a) *With aluminium amalgam.* Aluminium foil (12 g.; previously etched with 10% aqueous sodium hydroxide, washed, and dried) and mercuric chloride (0·5 g.) were added to *o*-dibenzoylbenzene (8·6 g.) in benzene (200 ml.) and absolute ethanol (300 ml.). Reaction was initiated by warming and, when it had subsided, the mixture was heated on the water-bath for 6 hr. and poured into dilute hydrochloric acid. The benzene layer yielded a solid which was crystallised from light petroleum (b. p. 60—80°) giving 1,3-diphenylisobenzofuran as thin yellow plates, m. p. 124—125° (lit.,[11] m. p. 125°) (5·5 g., 68%) (Found: C, 89·2; H, 5·3. Calc. for $C_{20}H_{14}O$: C, 88·9; H, 5·2%).

(b) *With sodium amalgam in ether.* *o*-Dibenzoylbenzene (5·7 g.) in anhydrous ether (200 ml.) was shaken for 100 hr. with 2% sodium amalgam (50 g.) under nitrogen, and the mixture added to 10% acetic acid (400 ml.), also under nitrogen. The ethereal layer yielded a colourless powder which slowly became yellow, and after crystallisation from light petroleum gave 1,3-diphenylisobenzofuran, m. p. 124—125° (3·0 g., 56%). A similar experiment with an excess of sodium wire in place of the sodium amalgam gave 1,3-diphenylisobenzofuran in 42% yield.

(c) *With magnesium and magnesium iodide.* A solution of *o*-dibenzoylbenzene (3·0 g.) in benzene (50 ml.) was added slowly to a solution of magnesium and magnesium iodide in benzene–ether made according to Gomberg and Bachmann's directions [16] from magnesium (2 g.). After being boiled for 3 hr. the filtered benzene solution was washed with dilute hydrochloric acid, dried, and evaporated, and the residue was crystallised from light petroleum (b. p. 60—80°), purified by passage in benzene over alumina, and finally recrystallised from light petroleum, giving 1,3-diphenylisobenzofuran, m. p. 124—125° (1·8 g., 63%).

Reduction of o-*Dibenzoylbenzene with Sodium Amalgam.*—(a) *In ethanol. Formation of* αα′-*dihydroxy*-o-*dibenzylbenzene, m. p.* 105—106° (β-*form*). 2% Sodium amalgam (300 g.) was added during ½ hr. to a solution of *o*-dibenzoylbenzene (4·6 g.) in 95% ethanol (100 ml.). When the strongly exothermic reaction had ended the alcoholic solution was poured into water and extracted with ether from which an oil was obtained. Treatment with boiling aqueous ethanol yielded the β-*isomer* of αα′-dihydroxy-*o*-dibenzylbenzene as thin, colourless prisms, m. p. 105—106° (1·8 g., 39%) (Found: C, 83·2; H, 6·1. $C_{20}H_{18}O_2$ requires C, 82·8; H, 6·2%). The diacetyl derivative, prepared by heating it with acetic anhydride at 100° and crystallised from ethanol, had m. p. 107—108°, undepressed on admixture with the diacetyl derivative of the α-diol.

(b) *In propanol–acetic acid. Formation of* αα′-*dihydroxy*-o-*dibenzylbenzene, m. p.* 127—128°. The above reaction when repeated with *o*-dibenzoylbenzene (2·9 g.) in propanol (75 ml.) and acetic acid (75 ml.) and 2% sodium amalgam (200 g.) gave αα′-dihydroxy-*o*-dibenzylbenzene, m. p. 127—128° (1·2 g., 42%).

Reduction of o-*Dibenzoylbenzene with Zinc Dust.*—(a) *In alkali.* A mixture of *o*-dibenzoylbenzene (2·9 g.) in ethanol (50 ml.), zinc dust (20 g.) and 10% aqueous potassium hydroxide (20 ml.) was heated on the water-bath for 8 hr., filtered, concentrated to ½ volume, added to water, and extracted with ether. The product was crystallised from ethanol, giving pale yellow needles, m. p. 283—284° (0·3 g.) (Found: C, 80·6; H, 3·9. Calc. for $C_{14}H_8O_2$: C, 80·7; H, 3·9%). A mixed m. p. with anthraquinone showed no depression. The mother-liquors gave a product which crystallised from aqueous ethanol in prisms, m. p. 105—106° (1·6 g., 56%), undepressed on admixture with the previously prepared αα′-dihydroxy-*o*-dibenzylbenzene of the same m. p. The diacetyl derivative had m. p. 107—108°.

(b) *In acetic acid.* Zinc dust (60 g.) was added in portions during 15 min. to *o*-dibenzoylbenzene (11·5 g.) in boiling acetic acid (250 ml.). After being boiled for 3 hr. the hot solution was filtered and then poured into water (1 l.). Next day the solid was collected and recrystallised from ethanol, giving 9,9′,10,10′-tetrahydro-10,10′-diphenyl-9,9′-bianthryl (8·4 g.) as yellow prisms, m. p. 254—255·5° (lit.,[23] m. p. 260°). This compound is identical (mixed m. p., ultraviolet and infrared spectra) with that obtained by the action of sodium iodide on αα′-dibromo-*o*-dibenzylbenzene.

α-*Bromo*-o-*dibenzylbenzene.*—A mixture of *o*-dibenzylbenzene (1·0 g.), *N*-bromosuccinimide (0·69 g.), benzoyl peroxide (10 mg.), and carbon tetrachloride (15 ml.) was stirred at 40° for 3 hr. under illumination from a 200-w tungsten-filament lamp. More benzoyl peroxide (10 mg.) was added after the first 1·5 hr. The cooled solution was filtered and concentrated under reduced pressure. The residual yellow oil (1·33 g., 99%) consisted of essentially pure α-*bromo*-o-*dibenzylbenzene* (Found: C, 70·8; H, 5·1. $C_{20}H_{17}Br$ requires C, 71·1; H, 5·4%). It decomposed on attempted distillation.

*αα′-Dibromo-*o*-dibenzylbenzene* (XI).—The preceding experiment was repeated with 2 equivalents of *N*-bromosuccinimide (*i.e.* 1·39 g.) and gave the *dibromo-compound* as a yellow oil (1·60 g., 96%) which did not crystallise and decomposed when heated above 40° (Found: C, 57·2; H, 3·8. $C_{20}H_{16}Br_2$ requires C, 57·7; H, 3·8%).

1,2,3,4,10-*Pentabromo*-1,2,3,4-*tetrahydro*-9-*phenylanthracene* (XII).—(a) *From* o-*dibenzylbenzene and* N-*bromosuccinimide.* *o*-Dibenzylbenzene (1·0 g.) in carbon tetrachloride (20 ml.) was boiled for 5 hr. with *N*-bromosuccinimide (3·44 g., 5 equiv.) and a trace of dibenzoyl peroxide, then cooled and filtered. The filtrate, on being shaken with aqueous sodium hydrogen sulphite and then evaporated, left a residue which after several crystallisations from acetone yielded the *pentabromo-derivative* as prisms, m. p. 160—161° (0·5 g.) (Found: C, 37·4; H, 2·3; Br, 60·3. $C_{20}H_{13}Br_5$ requires C, 36·8; H, 1·9; Br, 61·2%).

(b) *From* 9-*bromo*-10-*phenylanthracene* (X). A solution of the bromo-compound (X) (0·5 g.) and bromine (0·5 g.) in carbon tetrachloride (10 ml.) was boiled for 12 hr., and after evaporation the product was crystallised from acetone, giving the pentabromo-derivative, m. p. and mixed m. p. 160—161°.

*Reaction of αα′-Dibromo-*o*-dibenzylbenzene with Sodium in Ether.*—The experiment was carried out with carefully dried materials and a high-dilution apparatus.[20] The dibromo-compound (9·0 g.) in ether (200 ml.) was added during 12 hr. to a stirred boiling mixture of ether (200 ml.) and powdered sodium (4 g.); stirring and boiling were continued for a further 8 hr. The filtered solution was distilled, and the fraction of b. p. 194—200°/1 mm., which solidified, was recrystallised from ethanol, giving 9-phenylanthracene (VII) as pale green leaflets, m. p. 153—154° (1·4 g.) (Found: C, 94·5; H, 5·5. Calc. for $C_{20}H_{14}$: C, 94·5; H, 5·5%). The residual material from the distillation was extracted with boiling toluene, and the solution deposited 10,10′-diphenyl-9,9′-bianthryl as a faintly yellow powder (2·4 g.), m. p. >300° (lit.,[21] m. p. >300°) (Found: C, 95·1; H, 5·3. Calc. for $C_{40}H_{26}$: C, 94·9; H, 5·1%).

*Reaction of αα′-Dibromo-*o*-dibenzylbenzene with Zinc and Ethanol.*—The dibromo-compound (4·2 g.) in 95% ethanol (50 ml.) was added slowly to a boiling mixture of 95% ethanol (100 ml.) and zinc dust (1·3 g.), and boiling was continued for a further 4 hr. The filtered solution was concentrated, water added, and the whole extracted with ether. The extract yielded a product which solidified (2·5 g.) and was crystallised four times from ethanol, giving almost colourless needles, m. p. 119—120° (1·9 g.) (Found: C, 94·0; H, 6·1. Calc. for $C_{40}H_{30}$: C, 94·0; H, 6·0%). This substance appears to be a 1 : 1 adduct of 9-phenylanthracene and 9,10-dihydro-9-phenylanthracene which has been described by Haack [22] as having m. p. 119—120°.

*Reaction of αα′-Dibromo-*o*-dibenzylbenzene with Potassium t-Butoxide. Formation of* 9-*Bromo*-10-*phenylanthracene* (X).—The dibromo-compound (4·2 g.) was boiled with potassium t-butoxide in t-butyl alcohol (from potassium 0·46 g., and the alcohol 20 ml.) for 4 hr., then evaporated under diminished pressure, and the residue was treated with dilute acid and extracted with ether. The extract yielded a product which was twice crystallised from ethanol, giving 9-bromo-10-phenylanthracene (1·4 g.), m. p. and mixed m. p. with an authentic specimen 154—155° (lit.,[28] m. p. 154—155°).

*Reaction of αα′-Dibromo-*o*-dibenzylbenzene with Sodium Iodide.*—A mixture of the dibromo-compound (2·0 g.), sodium iodide (1·6 g., 2·2 equiv.), and ethanol was stirred at 40° for 12 hr. The cooled solution was filtered and dilute aqueous sodium thiosulphate was added to the filtrate until all the iodine had reacted. The resulting mixture yielded to ether a yellow oil which partly solidified. Recrystallisation from ethanol gave 9,9′,10,10′-tetrahydro-10,10-diphenyl-9,9′-bianthryl (0·45 g., 35%), m. p. 257—258°. The mother-liquor was evaporated and the residue, dissolved in benzene, was chromatographed on alumina, giving 9-bromo-10-phenylanthracene (0·16 g., 10%), m. p. and mixed m. p. 154—155° (from ethanol), and 9-phenylanthracene (0·20 g., 15%), m. p. and mixed m. p. 150—151° (from ethanol).

Similar results were obtained when the reaction was carried out at −80°, −40°, 0°, 20°, or reflux temperature and when acetone was used in place of ethanol as the solvent and the reaction was carried out at −80°, 0°, 20°, and reflux temperature.

*Reaction of α-Bromo-*o*-dibenzylbenzene with Bases.*—(a) *With potassium hydroxide.* A solution of the bromo-compound (1·06 g.) in ethanol (12 ml.) containing potassium hydroxide (0·27 g., 1·5 equiv.) was stirred at room temperature for 6 hr. The solution was then filtered and the solid was washed with water, leaving 9,9′,10,10′-tetrahydro-10,10′-diphenyl-9,9′-bianthryl (14 mg.), m. p. 220—235° (identified by its infrared spectrum: it had possibly originated from

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[28] Cook, *J.*, 1926, 2168.

traces of dibromo-compound in the starting material). The ethanolic filtrate was diluted with water (50 ml.) and then extracted with ether. Distillation of the dried ethereal solution gave an oil (800 mg.; b. p. 110—120°/0·05 mm.) which partly solidified. Recrystallisation of the solid from ethanol gave the 1 : 1 adduct of 9-phenylanthracene and 9,10-dihydro-9-phenylanthracene (500 mg., 62%), m. p. and mixed m. p. 117—118°.

When the reaction was carried out at 0° or at the reflux temperature of ethanol similar results were obtained.

(b) *With potassium t-butoxide.* The bromo-compound (1·27 g.) in t-butyl alcohol (20 ml.) containing potassium t-butoxide (0·63 g., 1·5 equiv.) was stirred at 35° for 24 hr., then water (100 ml.) was added and the whole was extracted with ether. The extracts yielded a yellow oily solid which recrystallised from ethanol, giving the 1 : 1 adduct as above (550 mg., 57%), m. p. 117—118°. Chromatography on alumina of the mother-liquors in benzene gave 9,10-dihydro-9-phenylanthracene (85 mg., 9%), m. p. 85—86°, and 9-phenylanthracene (160 mg., 16·5%), m. p. 149—151°. The same products were obtained when the reaction was carried out for shorter times at these temperatures or at 80°.

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