1033. *Polycyclic Biphenylenes. Part II.*[1] *Dibenzo*[a,c]*biphenylene*

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Reduction of 9-phenylazophenanthrene and benzidine rearrangement of the resulting *N*-9-phenanthryl-*N'*-phenylhydrazine gives 9-amino-10-(2-aminophenyl)phenanthrene, which has been converted into the corresponding di-iodo-compound and thence into dibenzo[*a,c*]biphenylene. Other reactions leading to precursors of the biphenylene are discussed. Some reactions of dibenzo[*a,c*]biphenylene are described.

IN a previous Paper[1] the synthesis of dibenzo[*a,g*]biphenylene was described and its stability compared with that of the other two known dibenzobiphenylenes. It resembles dibenzo-[*a,i*]biphenylene[2] closely, both compounds being unstable and more deeply coloured than the linear dibenzo[*b,h*]biphenylene.[3] The colour and instability of dibenzo[*a,i*]biphenylene have been ascribed to the cyclobutadienoid character of its four-membered ring.

The present Paper describes the synthesis of dibenzo[*a,c*]biphenylene (II). In this compound the 8b,12b-bond corresponds to a phenanthrene 9,10-bond, and thus the four-membered ring might be expected to possess considerable cyclobutadienoid character. In fact, the hydrocarbon is orange-red but is much more stable than dibenzo[*a,g*]- and -[*a,i*]biphenylene. It appears that the double-bond character of bond 8b,12b is offset by bond fixation in the benzene ring, so that structure (II) represents the main contributor to

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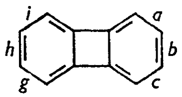
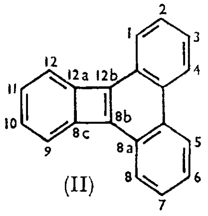
[1] The Paper by J. W. Barton, *J.*, 1964, 5161, is regarded as Part I.
[2] M. P. Cava and J. F. Stucker, *J. Amer. Chem. Soc.*, 1955, **77**, 6022.
[3] R. F. Curtis and G. Viswanath, *Chem. and Ind.*, 1954, 1174; *J.*, 1959, 1670.

the resonance hybrid. Attempts by other workers to isolate the related tetrabenzo-[*a,c,g,i*]biphenylene [4] and the derivative (III) [5] have so far proved unsuccessful.

Several routes to the required intermediates of type (IV; R = R′ = halogen) were examined. The first, utilising the known dinitro-compound (IV; R = R′ = NO_2),[6] was abandoned owing to the inaccessibility of 9-bromo-10-nitrophenanthrene used as starting material. Another route started from 9-phenylazophenanthrene, obtained in good yield by the reaction of the zinc chloride double salt of benzenediazonium chloride with 9-phenanthrylmagnesium bromide. Reduction of 9-phenylazophenanthrene followed by low-temperature rearrangement of the resulting hydrazo-compound gave 9-amino-10-(2-aminophenyl)phenanthrene (IV; R = R′ = NH_2) together with some dibenzo-[*a,c*]carbazole. The diamine was converted into the di-iodo-compound (IV; R = R′ = I) by a Sandmeyer reaction.



(I)



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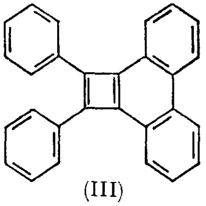

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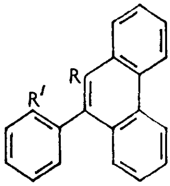

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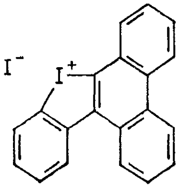
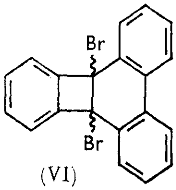


(V)



(VI)

The possibility of obtaining intermediates by substitution in 9-phenylphenanthrene and some of its phenyl derivatives was also examined, these compounds being readily available by the synthesis of Bradsher and Schneider.[7] Koelsch [8] reported that 9-phenylphenanthrene brominates in position 10, but no proof of structure was given for the compound obtained. Repetition of this work showed that the band at 890 cm.$^{-1}$ in the infrared spectrum of 9-phenylphenanthrene, due to the single aromatic hydrogen at position 10, disappeared on bromination, thus providing strong evidence for Koelsch's structure. When the analogous bromination of 9-(2-bromophenyl)phenanthrene (IV; R = H, R′ = Br) was attempted, no 9-bromo-10-(2-bromophenyl)phenanthrene (IV; R = R′ = Br) could be isolated. A compound, m. p. 112—114°, was obtained, the elemental analysis of which corresponded not to a dibromo-compound, but to a 2 : 1 molecular complex of a dibromo-compound with starting material, the infrared spectrum of the product still showing absorption at 890 cm.$^{-1}$. Complex formation of bromo-compounds in the phenanthrene series had been observed previously,[9] but as the product could not be obtained from a mixture of 9-bromo-10-(2-bromophenyl)phenanthrene with 9-(2-bromophenyl)-phenanthrene it was not further investigated.

Attempts were also made to prepare the cyclic iodonium salt (V) by oxidation and cyclisation of a monoiodo-compound.[10] 9-Phenylphenanthrene could not be iodinated

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[4] M. A. Ali, J. G. Carey, D. Cohen, A. J. Jones, I. T. Millar, and K. V. Wilson, *J.*, 1964, 387.

[5] M. P. Cava and D. Mangold, *Tetrahedron Letters*, 1964, **26**, 1751.

[6] J. F. Corbett, P. F. Holt, and A. N. Hughes, *J.*, 1960, 3643.

[7] C. K. Bradsher and A. K. Schneider, *J. Amer. Chem. Soc.*, 1938, **60**, 2960.

[8] C. F. Koelsch, *J. Amer. Chem. Soc.*, 1934, **56**, 480.

[9] L. F. Fieser, R. P. Jacobsen, and C. C. Price, *J. Amer. Chem. Soc.*, 1936, **58**, 2164.

[10] J. Collette, D. McGreer, R. Crawford, F. Chubb, and R. B. Sandin, *J. Amer. Chem. Soc.*, 1956, **78**, 3819.

to give 9-iodo-10-phenylphenanthrene (IV; R = I, R′ = H); however, 9-(2-iodophenyl)-phenanthrene (IV; R = H, R′ = I) gave a low yield of (V) on oxidation and cyclisation. This salt was converted into the di-iodo-compound (IV; R = R′ = I) on heating, but the overall yield by this route was much inferior to that from 9-phenylazophenanthrene.

Pyrolysis of the di-iodo-compound (IV; R = R′ = I) with cuprous oxide under reduced pressure gave dibenzo[*a,c*]biphenylene (II), isolated as its complex with 2,4,7-trinitrofluorenone. Chromatographic cleavage of the complex gave an almost quantitative recovery of the hydrocarbon which formed orange-red needles, m. p. 183—184°, quite soluble in most organic solvents. The solid is sublimable in a vacuum without significant decomposition and can be stored for long periods in the dark, but, as in the case of benzo-[*a*]biphenylene, dilute ethanolic solutions are slowly decolourised on exposure to light.[2]

The ultraviolet spectrum of the hydrocarbon exhibits ten maxima and shows a general similarity to spectra of the other angularly annelated dibenzobiphenylenes. The proton magnetic resonance spectrum at 60 Mc. shows three multiplets centred at 390, 450, and 505 c./sec. from tetramethylsilane, due to protons at positions 9—12 (4 protons), 1—3 and 6—8 (6 protons), and 4 and 5 (2 protons), respectively, and has the expected similarity to that of 1,2-benzobiphenylene which shows two multiplets at 388 c./sec. (4 protons) and 435 c./sec. (6 protons), the grouping in the latter being the reverse of that recently predicted.[11]

Dibenzo[*a,c*]biphenylene undergoes the reductive ring-opening normal for biphenylene derivatives. Thus, when it was warmed with Raney nickel in ethanolic solution, 9-phenylphenanthrene was produced in high yield. Treatment of the hydrocarbon with pyridinium perbromide in acetic acid resulted in addition rather than substitution, giving rise to a dibromide without rupture of the four-membered ring. This compound is assigned structure (VI) on the basis of its ultraviolet spectrum and the fact that it is readily reconvertible into the hydrocarbon (II) by treatment with sodium iodide in *NN*-dimethylformamide. This ease of debromination suggests a *trans* disposition of bromine atoms in the dibromide (VI).

Dibenzo[*a,c*]biphenylene shows no marked tendency to act as a diene. When solutions of the hydrocarbon and tetracyanoethylene in tetrahydrofuran were mixed there was a deepening in colour, but no adduct was isolated.

EXPERIMENTAL

9-*Phenylazophenanthrene*.—Addition of zinc chloride (26 g.) in 2N-hydrochloric acid (12 ml.) to a solution of benzenediazonium chloride [from aniline (28 g.) in concentrated hydrochloric acid (90 ml.) and water (38 ml.), diazotised at 0—5° with sodium nitrite (20·5 g.) in water (25 ml.)] gave a precipitate of the double salt which was collected and washed with dry acetone and dry ether. The salt was stirred rapidly in ether (300 ml.) while a solution of 9-phenanthrylmagnesium bromide [from 9-bromophenanthrene (64·5 g.) and magnesium (6·5 g.) in ether (150 ml.) and benzene (150 ml.)] was added in portions. After 30 min., 2N-hydrochloric acid was added and the product extracted with benzene. Evaporation of the extracts and chromatography of the residue on alumina in benzene–hexane (1 : 1) gave 9-*phenylazophenanthrene* (31 g., 44%) as red needles, m. p. 160—161·5°, from the same solvent mixture (Found: C, 85·15; H, 5·1; N, 9·9. $C_{20}H_{14}N_2$ requires C, 85·1; H, 5·0; N, 9·9%).

9-*Amino*-10-(2-*aminophenyl*)*phenanthrene*. Zinc dust (30 g.) and ammonia (100 ml.; *d* 0·880) were added to a refluxing solution of 9-phenylazophenanthrene (20 g.) in acetone (1 l.). After 10 min. the addition was repeated and the refluxing continued for a further 30 min., the solution was filtered, and the zinc residues were extracted with hot acetone. The solution was kept below 0° while concentrated hydrochloric acid (100 ml.) was added dropwise, after which it was allowed to come to room temperature during 3 hr., then diluted with water (3 l.). After 1 hr. the solution was filtered and neutralised with ammonia, precipitating 9-*amino*-10-(2-*aminophenyl*)*phenanthrene* (13·5 g., 67%), m. p. 180—190°. Crystallisation from benzene–hexane gave colourless leaflets, m. p. 202—203° (Found: C, 84·3; H, 5·9; N, 9·6. $C_{20}H_{16}N_2$

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[11] R. H. Martin, J. P. Van Trappen, N. Defay, and J. F. W. McOmie, *Tetrahedron*, 1964, **20**, 2373.

requires C, 84·5; H, 5·6; N, 9·9%). The tarry, acid-insoluble material was crystallised from benzene–hexane (charcoal), giving dibenzo[*a,c*]carbazole (0·6 g., 3%), m. p. 193—194° (lit.,[12] 188—189°).

9-*Iodo*-10-(2-*iodophenyl*)*phenanthrene*. A suspension of 9-amino-10-(2-aminophenyl)phenanthrene (10 g.) in concentrated hydrochloric acid (37·5 ml.) and water (70 ml.) was stirred rapidly and treated at 0—5° with sodium nitrite (5 g.) in water (20 ml.). The stirring was continued for a further 15 min., then the solution was filtered and added to an ice-cold solution of potassium iodide (40 g.) in water (225 ml.) and sulphuric acid (25 ml.). The mixture was allowed to come slowly to room temperature and finally warmed on a water-bath. On cooling, sodium pyrosulphite was added, and the solid was filtered off and extracted with benzene. Filtration of the extract through alumina, and evaporation, gave a red-brown residue which was sublimed at 180° (bath)/1 mm. and crystallised from acetone–methanol, giving 9-*iodo*-10-(2-*iodophenylphenanthrene*) as cream-coloured needles (4·8 g., 27%), m. p. 170·5—171·5° (Found: C, 47·2; H, 1·9. $C_{20}H_{12}I_2$ requires C, 47·4; H, 2·4%).

9-*Bromo*-10-(2-*bromophenyl*)*phenanthrene*.—The diamine (1 g.) was diazotised in hydrobromic acid as described in the preparation of the above di-iodo-compound, and the resulting solution treated with excess of a concentrated solution of potassium mercuribromide. The green double salt was collected, washed with water and ether, and dried (2·55 g.). It was mixed with twice its weight of powdered potassium bromide and decomposed by gradual heating. The product was extracted with portions of an ether–water mixture, the organic extracts were evaporated, and the residue was chromatographed on alumina in benzene, giving a pale brown oil. Short-path distillation at 180—200°/15 mm., and crystallisation from acetone–methanol, gave 9-*bromo*-10-(2-*bromophenyl*)*phenanthrene* as colourless prisms (0·4 g., 27%), m. p. 136—138° (Found: C, 58·4; H, 3·0; Br, 38·8. $C_{20}H_{12}Br_2$ requires C, 58·3; H, 2·9; Br, 38·8%).

9-(2-*Bromophenyl*)*phenanthrene*.—2-Bromoacetophenone was prepared by the reaction of 2-bromobenzoyl chloride with ethyl ethoxymagnesiomalonate [13] (94·5%; b. p. 122—124°/18 mm.). Bromination in ether solution gave ω,2-dibromoacetophenone [14] (95%; b. p. 112—132°/0·7 mm.), which reacted with phenol in sodium hydroxide solution, by the method of Mohlau,[15] giving 2-bromo-ω-phenoxyacetophenone (31%; b. p. 155—175°/0·65 mm.). This ketone reacted with biphenyl-2-ylmagnesium iodide,[7] and the resulting crude carbinol was refluxed with hydrobromic–acetic acid mixture, giving 9-(2-*bromophenyl*)*phenanthrene* (42·5%) as colourless needles, m. p. 126—127° (from ethanol) (Found: C, 72·05; H, 3·9; Br, 24·2. $C_{20}H_{13}Br$ requires C, 72·1; H, 3·9; Br, 24·0%).

Bromination of 9-(2-*Bromophenyl*)*phenanthrene*.—Treatment of 9-(2-bromophenyl)phenanthrene (3·3 g.) with bromine (1·6 g.) and a small crystal of iodine in dry carbon tetrachloride (10 ml.) led to a slow evolution of hydrogen bromide. The mixture was heated on a water-bath for 1 hr., and poured into sodium hydrogen sulphite solution. The product, collected by extraction with carbon tetrachloride, was a pale yellow oil. Chromatography over alumina or silica gave no crystalline material, but an acetone–methanol solution eventually deposited a solid (1·5 g.) which, after several recrystallisations, gave colourless *needles*, m. p. 112—114° (Found: C, 62·4, 62·2; H, 3·0, 3·4; Br, 34·7, 34·5. $2C_{20}H_{12}Br_2,C_{20}H_{13}Br$ requires C, 62·2; H, 3·2; Br, 34·6%).

9-(2-*Iodophenyl*)*phenanthrene*. By a sequence analogous to that used for the corresponding bromophenylphenanthrene the following intermediates were obtained: 2-iodoacetophenone (89%; b. p. 146—148°/18 mm.), cf. Bruce; [16] ω-bromo-2-iodoacetophenone (92%; b. p. 130—160°/0·7 mm.); 2-iodo-ω-phenoxyacetophenone (50%; b. p. 175—185°/0·65 mm.). Reaction of the phenoxy-ketone with biphenyl-2-ylmagnesium iodide, and subsequent treatment with hydrobromic–acetic acid mixture, gave 9-(2-*iodophenyl*)*phenanthrene* (38%) as very pale yellow needles, m. p. 116—118° (from ethanol) (Found: C, 63·2; H, 3·65; I, 33·4. $C_{20}H_{13}I$ requires C, 63·2; H, 3·4; I, 33·4%).

Oxidation and Cyclisation of 9-(2-*Iodophenyl*)*phenanthrene*.[10]—The iodo-compound (1 g.) in acetic anhydride (2 ml.) was treated with a solution of peracetic acid [from 30% hydrogen

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[12] F. R. Japp and A. Findlay, *J.*, 1897, **71**, 1115.
[13] H. G. Walker and C. R. Hauser, *J. Amer. Chem. Soc.*, 1946, **68**, 1386.
[14] R. E. Lutz, *J. Org. Chem.*, 1947, **12**, 666.
[15] R. Mohlau, *Ber.*, 1882, **15**, 2497.
[16] J. M. Bruce, *J.*, 1962, 1514.

peroxide (1 ml.) and acetic anhydride (4 ml.)]. The solution was irradiated for 24 hr. using a low-power ultraviolet source, with occasional slight warming to maintain solution of the compound. Water (0·5 ml.) was added, and after 1 hr. the solution was cooled to 0° and stirred during the dropwise addition of sulphuric acid (1 ml.). After a further 6 hr., water (100 ml.) was added and the resulting emulsion extracted with benzene. The benzene extract yielded starting material (0·3 g.). Treatment of the aqueous solution with sodium pyrosulphite followed by excess of potassium iodide gave 9-phenylphenanthrylyl-10,2′-iodonium iodide as a yellow powder (0·15 g.; 16%), m. p. 156—159° (decomp.). A sample of the salt was decomposed by heating gently and the product purified by short-path distillation at 190—195°/15 mm. Crystallisation of the resulting glass from acetone–methanol gave 9-iodo-10-(2-iodophenyl)-phenanthrene, m. p. 166—169°, identical with that obtained from the corresponding diamine, above.

Dibenzo[a,c]*biphenylene.*—An intimate mixture of 9-iodo-10-(2-iodophenyl)phenanthrene (0·4 g.) with dry cuprous oxide (20 g.) was pyrolysed in a cold-finger sublimation apparatus under nitrogen at 15 mm. pressure. The bath temperature was raised from 240° to 340° during 15 min. and maintained at 340° for a further 15 min. The orange sublimate was washed off the cold finger into a solution of 2,4,7-trinitrofluorenone (0·1 g.) in warm benzene (10 ml.). Methanol was added, and the *complex* of dibenzo[*a,c*]biphenylene separated as deep purple needles, m. p. 213—215° after recrystallisation (Found: C, 69·7; H, 2·85; N, 7·25. $C_{33}H_{17}N_3O_7$ requires C, 69·9; H, 3·0; N, 7·4%). The yield of complex from 10 runs was 0·72 g. (21%). Passage of a benzene solution of the complex through a short alumina column, vacuum evaporation of the eluate, and crystallisation of the residue from hexane gave *dibenzo*[a,c]*biphenylene* as orange-red, fluffy needles, m. p. 183—184° (decomp.) (Found: C, 95·35; H, 4·9. $C_{20}H_{12}$ requires C, 95·2; H, 4·8%), $\lambda_{max.}$ (EtOH) 251·5, 263, 267·5, 292·5, 304, 316, 337sh, 359, 400, 420 mμ (log ε 4·33, 4·25, 4·22, 3·57, 4·75, 4·73, 3·19, 2·97, 3·34, 3·40). Evaporation of the pyrolysate mother-liquors and chromatography of the residue on alumina in benzene solution gave starting material (0·95 g.).

Reduction of Dibenzo[a,c]*biphenylene.*—When a solution of the biphenylene (0·026 g.) in warm ethanol (5 ml.) was shaken with fresh Raney nickel (*ca.* 0·5 g.) the orange colour was slowly discharged. After 15 min. the solution was filtered, evaporated, and the residue subjected to short-path distillation at 140°/15 mm., giving a colourless solid (0·023 g.). Crystallisation from ethanol gave 9-phenylphenanthrene as leaflets, m. p. 103—104°, identical with an authentic sample.[7]

Dibromide (VI) *of Dibenzo*[a,c]*biphenylene.*—Finely-powdered pyridinium perbromide (0·07 g.) was added to a solution of the biphenylene (0·05 g.) in acetic acid at 30—40°. The orange colour of the solution was discharged and a crystalline precipitate formed. After 15 min. the solution was diluted and treated with a little sodium pyrosulphite. The *dibromide* was recrystallised from benzene–hexane, and formed straw-coloured prisms (0·076 g., 93%), m. p. 198—200° (decomp.) (Found: C, 58·5; H, 2·7. $C_{20}H_{12}Br_2$ requires C, 58·3; H, 2·9%), $\lambda_{max.}$ (EtOH) 225, 272·5 mμ (log ε 4·44, 4·19).

Reaction of the Dibromide (VI) *with Sodium Iodide.*—When the dibromide (0·023 g.) and sodium iodide (0·1 g.) in *NN*-dimethylformamide (1 ml.) were heated on a water-bath there was an immediate liberation of iodine. After 30 min., the solution was cooled, diluted with water, and treated with an excess of sodium pyrosulphite. The orange-red solid was collected and treated with 2,4,7-trinitrofluorenone in benzene–methanol solution, giving the complex of dibenzo[*a,c*]biphenylene (0·016 g., 51%), m. p. 213—215°.

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