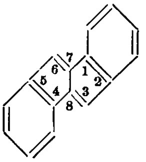
422. *Fused Carbon Rings. Part XXI.* Dibenzopentalene.*†

By C. T. Blood and R. P. Linstead.

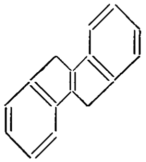
Catalytic dehydrogenation of 3 : 6 : 7 : 8-tetrahydro-1 : 2-4 : 5-dibenzopentalene (III) yielded 3 : 6-dihydrodibenzopentalene (II) and could not be taken further. Hydrogen reacted with dichlorodibenzopentalene (V; R = Cl) over metallic catalysts to give tetrahydro- or dihydro-dibenzopentalene according to the conditions. The dibromide of the dihydro-compound reacted with silver acetate to yield dibenzopentalene † (I). The structure of this was established by catalytic hydrogenation to its tetrahydride, reduction with sodium amalgam to its dihydride, and by oxidation to benzil-2 : 2′-dicarboxylic acid.

Dibenzopentalene behaves as a conjugated diene, the pentalene system showing no aromatic stability. Light-absorption data are given. The results and those of Part XX are discussed in the light of theoretical predictions.

This paper describes the synthesis and properties of 1 : 2-4 : 5-dibenzopentalene (I).† Compounds derived from this parent substance have been extensively investigated by Brand and his collaborators (*Ber.*, 1912, **45**, 3071; 1920, **53**, 807; 1922, **55**, 601; 1936, **69**, 2504; 1948, **81**, 382; *J. pr. Chem.*, 1925, **109**, 353; **110**, 1). For the present purpose, their most important findings were that the long-known diketone (IV) (Roser, *Annalen*, 1888, **247**, 153) could be converted into a 3 : 6-diphenyl- and a 3 : 6-dichloro-dibenzopentalene (V; R = Ph and Cl). The latter on reduction with zinc gave 3 : 6-dihydrodibenzopentalene (II). Brand's structure for the dihydro-compound (II) has since been confirmed by Wawzonek (*J. Amer. Chem. Soc.*, 1940, **62**, 745). The dihydro-compound could be catalytically hydrogenated to tetrahydrodibenzopentalene (III), and its 3- and 6-methylene groups were reactive. Brand's attempts to prepare dibenzopentalene itself were unsuccessful.



(I)



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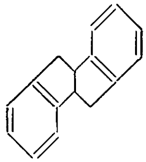

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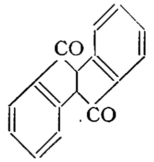

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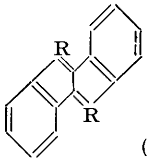

(V)

Our examination of the compounds of this group started with a study of the catalytic dehydrogenation of the tetrahydride (III). This was remarkably stable, but over palladised charcoal at 450° lost one mol. of hydrogen to yield 3 : 6-dihydrodibenzopentalene (II), identical with material prepared by Brand's method. Contact with palladium at a higher

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* Part XX, preceding paper.

† *Note on nomenclature.* The tetracyclic compounds described in this paper are named as derivatives of pentalene to bring out the central structural feature and to simplify discussion. The preface 1 : 2-4 : 5- is omitted in the remainder of the introduction. Other naming systems are given below :

Present name	Alternatives : (*a*) historical, (*b*) British modification of Richter's system, (*c*) Ring Index.
(I) Dibenzopentalene.	(*a*) Diphensuccindadien (Brand); (*b*) 1 : 1′-didehydroindeno-(3′ : 2′-2 : 3)indene; (*c*) indeno[2 : 1-*a*]indene.
(II) 3 : 6-Dihydrodibenzopentalene.	(*a*) Diphensuccinden (Brand); (*b*) indeno(3′ : 2′-2 : 3)indene; (*c*) 5 : 10-dihydroindeno[2 : 1-*a*]indene.
(III) 3 : 6 : 7 : 8-Tetrahydrodibenzopentalene.	(*a*) Diphensuccindan (Roser); (*b*) indano(2′ : 1′-1 : 2)indane; (*c*) 4*b* : 5 : 9*b* : 10-tetrahydroindeno[2 : 1-*a*]indene.

temperature led to gross decomposition. Dehydrogenation of the tetrahydride by sulphur was unsatisfactory.

3 : 6-Dichlorodibenzopentalene (V; R = Cl) reacted rapidly with hydrogen over Adams's platinum or palladium black. Four mols. of hydrogen were taken up, corresponding to hydrogenolysis of the halogen atoms and reduction of the two double bonds, the tetrahydride (III) being isolated in good yield. There was no inflexion in the plot of hydrogen uptake against time, over these catalysts, but over Raney nickel hydrogenation of dichlorodibenzopentalene slowed somewhat after about 2·5 mols. had been absorbed. The product of hydrogenations interrupted at this point was a mixture of starting material and 3 : 6-dihydrodibenzopentalene (II). The slowing of the reaction over Raney nickel seems to be due to the hydrogen chloride eliminated, because in the presence of ammonia there is no inflexion and 4 mols. of hydrogen are steadily taken up.

Brand observed that 3 : 6-dihydrodibenzopentalene (II) added bromine but that the product readily lost hydrogen bromide with polymerisation. This can largely be avoided by rapid fixation of any hydrogen bromide formed. When the bromine adduct of (II) (3 : 6-dihydrodibenzpentalene 7 : 8-dibromide) was heated in benzene solution with silver acetate a hydrocarbon $C_{16}H_{10}$ was formed in nearly 60% yield. This has been identified as 1 : 2-4 : 5-dibenzopentalene (I). It was accompanied by a small amount of 3 : 6-dihydrodibenzopentalene, which could be separated chromatographically on alumina. Ultra-violet fluorescence was used as a control method, dibenzopentalene having a deep plum-coloured fluorescence in ultra-violet light, very different from the brilliant violet fluorescence of its dihydride.

Dibenzopentalene crystallises in leaflets with a bronze lustre. It gives orange solutions and has a normal molecular weight in benzene solution. Further properties are given on p. 2267.

The structure has been proved as follows :

(i) Catalytic hydrogenation over palladised charcoal went readily at ordinary temperature and pressure, two mols. of hydrogen being taken up without inflexion. If the reaction mixture was shaken in contact with the catalyst and hydrogen for 2 days after absorption was complete the product was tetrahydrodibenzopentalene (III), m. p. 101°, identical in all respects with that obtained in other ways, *e.g.*, by Clemmensen reduction of Roser's diketone (IV) or by catalytic hydrogenation of dihydrodibenzopentalene (II). If, however, the final shaking with catalyst was omitted and the product was isolated as soon as hydrogen uptake had ceased, the tetrahydride was not homogeneous. Possibly the initial hydrogenation does not yield a stereochemically homogeneous product, but the period of shaking with catalyst permits of inversion so that a final stable product is formed.

There is no evidence as to what effect, if any, the fused benzene rings will have on the relative stabilities of the *cis*- and the *trans*-[3 : 3 : 0]-*bicyclo*octane system. It will be assumed that the normal factors operate (see Linstead, *Ann. Reports*, 1935, **32**, 311, for a summary). *cis*-Configurations, are therefore, provisionally assigned to the stable 3 : 6 : 7 : 8-tetrahydrodibenzopentalenes derivatives described in this paper, including the hydrocarbon (III) of m. p. 101°, and Roser's diketone.

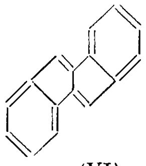
(ii) Reduction of dibenzopentalene with sodium amalgam in alcohol gave 3 : 6-dihydrodibenzopentalene (II) in almost quantitative yield.

(iii) Dibenzopentalene was very rapidly ozonised in ethyl acetate solution at —20°. The ozonide was decomposed with acetic acid and the product oxidised with alkaline permanganate. This gave a 75% yield of benzil-2 : 2′-dicarboxylic acid.

These results establish the structure of dibenzopentalene : moreover, the nature of the ozonisation product shows that main contributing canonical forms are benzenoid (such as I and VI) and not *o*-quinonoid (VII).

Other features of the general chemistry of dibenzopentalene are : it is not soluble in orthophosphoric acid, unlike azulenes; no observable complex formation occurs with picric acid or with 3 : 4 : 7-trinitrofluorenone; it is easily polymerised, for example, on attempted crystallisation from chloroform containing traces of hydrogen chloride; it readily reacts with bromine to give a golden-yellow crystalline addition compound, $C_{16}H_{10}Br_2$. The position of the bromine in this is not known.

Dibenzopentalene resembles *cis-cis*-1 : 4-diphenylbutadiene (VIII) in formal structure. There is, however, an important difference in light absorption in the ultra-violet region : diphenylbutadiene has one band at $\lambda_{max.}$ 299 mμ, with ε 30,000, whereas dibenzopentalene has a more intense doublet in this region ($\lambda_{max.}$ 273, 281 mμ ; ε 61,000, 69,000) and a second complex band system of longer wave-length rising to $\lambda_{max.}$ 415 mμ, ε 15,000. The 273 and the 281 band are assigned to the diaryldiene system in dibenzopentalene, and the long-wave band indicates the presence of a new chromophore.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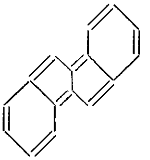
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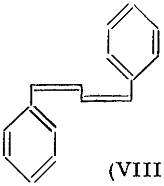
(VIII)

It has been pointed out to us by Dr. E. A. Braude that the longer-wave absorption of dibenzopentalene is intermediate in wave-length between those of anthracene and of tetracene, in keeping with the number of formal double bonds :

Compound	Number of double bonds	$\lambda_{max.}$
Anthracene	7	380
Dibenzopentalene	8	415
Tetracene	9	480

Long-wave absorption was also shown by 3 : 6-dichlorodibenzopentalene, the spectrum of which had the following peaks :

$\lambda_{max.}$, mμ	227	271	280	395	420
ε	17,000	44,000	41,000	16,000	19,000

The light absorption of Roser's diketone was also examined. This corresponded with the diketo-structure (IV) and even in the presence of alcoholic sodium ethoxide there was no spectroscopic evidence of the formation of a dienol (V ; R = OH) which would be a dibenzopentalenediol.

Discussion.—The experimental evidence presented in this and the preceding paper can be summarised as follows : (1) Pentalenes, whether fused to benzene rings or not, are not formed from their hydrides by simple catalytic dehydrogenation procedures which lead to the formation of naphthalenes and azulenes. (2) Several conventional chemical dehydrogenation procedures are also unsuccessful, possibly because the pentalene system is not stable under the experimental conditions. (3) No evidence has been obtained for the formation of hydroxypentalene systems by the enolisation of isomeric ketones of appropriate structure. (4) Dibenzopentalene is a highly reactive compound. It is very easily hydrogenated, and ozonised. Chemical reduction leads to 1 : 4-addition of hydrogen. It polymerises readily.

The general chemistry of dibenzopentalene is clearly that of a conjugated diene. There is, as yet, no chemical evidence either from formation or reaction that the pentalene system has any special stability, certainly nothing which can be dignified by the term " aromatic." Nevertheless, the long-wave absorption, at about 400—420 mμ, of dibenzopentalene and its dichloro-derivative shows a significant difference from that of linear dienes with the same number of π-electrons and indicates some degree of resonance interaction in the excited state of the molecule.

These results from the simple pentalene and dibenzopentalene systems should be compared with those from the monobenzopentalene field. A number of recent attempts to prepare 1 : 2-benzopentalene (*cyclo*pentindene) by Baker and Jones (*J.*, 1951, 787) and by Groves and Swan (*J.*, 1951, 867) have been fruitless. Moreover, Dahn's experiments (*Helv. Chim. Acta*, 1951, **34**, 1087) failed to yield a benzopentalene under very mild conditions. Dahn concluded that this gave a strong indication that the pentalene system had little aromatic character.

Theoretical calculations of the pentalene structure have led to expectations of a different kind. Craig and Maccoll (*J.*, 1949, 964) calculated that pentalene should possess a considerable resonance energy, about the same per π-electron as azulene and a little less than benzene. R. D. Brown (*Trans. Faraday Soc.*, 1949, **45**, 296; 1950, **46**, 146) obtained results differing from those of Craig and Maccoll but also concluded that pentalene, once formed, would be a reasonably stable substance, although still reactive chemically. The resonance energy was calculated to be 37 kcals. Theoretical considerations also led to deductions that pentalene would resemble azulene in being a deeply coloured hydrocarbon.

No final verdict is yet possible on the stability and aromatic character of the pentalene system. It is apparent that our new evidence agrees with and supplements earlier experimental results but does not fall into line with the theoretical predictions, although there is no flat contradiction. It appears that an additional factor, perhaps one of strain, has not sufficiently been allowed for in the quantum-mechanical calculations on pentalenes. It will be recalled that theoretical calculations supported an erroneous identification of Lothrop's diphenylene with benzopentalene (Coulson, *Nature*, 1942, **150**, 577). The diphenylene structure is now, however, conclusively established (Waser *et al.*, *J. Amer. Chem. Soc.*, 1943, **65**, 1451; 1944, **66**, 2035; Baker, *J.*, 1945, 266).

In the present state of knowledge it is misleading to refer to the still unknown pentalene as a non-benzenoid aromatic hydrocarbon.*

EXPERIMENTAL

3 : 6 : 7 : 8-*Tetrahydro*-3 : 6-*diketodibenzopentalene* (IV). This was prepared by cyclisation of αβ-diphenylsuccinic acid (Roser, *Annalen*, 1888, **247**, 153). Light absorption in ethanol: $\lambda_{max.}$ 2450 and 2920 Å; ε 21,000 and 3,500, respectively; light absorption in ethanol containing 1% of sodium ethoxide : $\lambda_{max.}$ 2480 Å; ε 23,000.

3 : 6 : 7 : 8-*Tetrahydrodibenzopentalene* (III).—The diketone (4·5 g.) was reduced by the Clemmensen method with zinc amalgam (60 g.) and hydrochloric acid (100 ml. of *d* 1·18, plus 50 ml. of water). The hydrocarbon, isolated in nearly pure condition by steam-distillation, had m. p. 100°. Recrystallised from ethanol, it formed white needles, m. p. 101°. Roser (*loc. cit.*) quotes m. p. 101°.

Vapour-phase Dehydrogenation of the Tetrahydride.—The apparatus was as described in the preceding paper (p. 2255). The product was collected in a 100-ml. bulb filled with glass-wool to trap smoke. The reaction tube was surrounded by a tubular electric furnace by which the catalyst could be heated to 425—450°.

The tetrahydride (1·9 g.) was volatilized in a nitrogen stream at 1 atm. pressure by means of external heating to 150°. The orange-brown product which collected in the bulb was steam-distilled to remove starting material (1·0 g.), and the residue was chromatographed in benzene on alumina. The principal substance present was 3 : 6-dihydrodibenzopentalene (II). In benzene solution it showed a strong violet fluorescence under ultra-violet light. It was sublimed at 140°/10 mm., and then crystallised from benzene and ethanol, being obtained in orange plates, m. p. 204—205° (0·6 g.) (Found : C, 94·0; H, 6·0. Calc. for $C_{16}H_{12}$: C, 94·1; H, 5·9%). It was identical with the dihydride prepared by Brand and Muller's method (*Ber.*, 1922, **55**, 601) (m. p. and mixed m. p. 204—205°). It gave a violet-black condensation product with *p*-nitrosodimethylaniline, m. p. 277°; Brand, Gabel, and Ott (*Ber.*, 1936, **69**, 2504) give m. p. 277°.

The ultra-violet light absorptions of 3 : 6-dihydrodibenzopentalene showed no unexpected features : $\lambda_{max.}$ 2370, 3080, 3150, and 3280 Å; ε 6000, 11,000, 13,000, and 8000.

Hydrogenation of the dihydride in ethanol in the presence of 20% palladium-charcoal catalyst resulted in the uptake of 1·1 mols. of hydrogen during 40 minutes. The product was identified as the tetrahydride by m. p. and mixed m. p. (101°) with an authentic specimen prepared as above.

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* Since the above was written, three relevant papers have come to hand. In a further theoretical paper Craig (*J.*, 1951, 3175) now concludes that pentalene would be expected to show marked unsaturation and not typically aromatic properties. Further approaches towards monobenzopentalene (*cyclo*pent[*a*]indene) have been described by Baker, Glockling, and McOmie (*J.*, 1951, 3357). Thirdly, Professor John D. Roberts has kindly sent me an account in advance of publication of his work with W. F. Gorham. Using different and elegant methods of approach, they have obtained results very similar to those described in Part XX. In brief, tetrahydropentalenes have been obtained which resist dehydrogenation. These further results fall into line with those described in these papers, so that there is now a considerable bulk of experimental evidence pointing in the same direction, with which some of the predictions of theory are now not inconsistent. R.P.L.

Hydrogenation of 3 : 6-*Dichlorodibenzopentalene*.—Dichlorodibenzopentalene was prepared by Wawzonek's method (*J. Amer. Chem. Soc.*, 1940, **62**, 745). Ultra-violet light absorption : $\lambda_{max.}$ 2270, 2710, 2800, 3950, and 4200 Å; ε 17,000, 44,000, 41,000, 16,000, and 19,000.

Hydrogenation. (i) Over Adams's platinum catalyst. The substance (100 mg.), dissolved in ethanol (80 ml.), was hydrogenated at room temperature and atmospheric pressure over 10 mg. of catalyst. The total absorption of hydrogen, completed in 20 minutes, was 4·4 mols. (36·4 ml.). The colourless solution yielded tetrahydrodibenzopentalene (60 mg.) on evaporation, identified as before. The plot of volume of hydrogen absorbed against time was a smooth curve showing no sharp change in slope. (ii) Over palladium-black catalyst a similar result was obtained, the rate of absorption of hydrogen being somewhat slower. (iii) Over Raney nickel (30 mg.) an inflexion was noted in the rate of hydrogen uptake after 2·5 mols. had been absorbed. A separate experiment over this catalyst was accordingly stopped at an uptake of 2 mols. of hydrogen. The product, a mixture of grey flakes and red needles, on fractional crystallisation from ethanol gave (from 100 mg. of dichloro-compound) 30 mg. of 3 : 6-dihydrodibenzopentalene, yellow flakes, m. p. and mixed m. p. 204—205°, and 40 mg. of unchanged dichlorodibenzopentalene, red needles, m. p. and mixed m. p. 190—191°. A similar experiment over Raney nickel in the presence of ammonia solution (0·5 ml.; *d* 0·880) showed no inflexion and yielded the tetrahydride.

1 : 2-4 : 5-*Dibenzopentalene*.—Bromine (0·33 ml., 1 mol.) in carbon disulphide (7 ml.) was added dropwise during 1 minute to a solution of 3 : 6-dihydrodibenzopentalene (1·3 g.) in carbon disulphide (100 ml.) at 0°. A rapid stream of nitrogen was bubbled through the liquid until no more hydrogen bromide was evolved. The solvent was distilled off in a vacuum. The residue was dissolved in dry benzene (50 ml.), silver acetate (4 g.) was added, and the suspension was boiled under reflux for 2 hours. The liquid was filtered; after concentration under reduced pressure, the filtrate was chromatographed in benzene on alumina. Unchanged dihydride (0·1 g.) was obtained from the first eluate; the second and principal fraction (deep purplish-brown under ultra-violet illumination and pale orange-coloured in daylight) yielded 1 : 2-4 : 5-*dibenzopentalene* upon evaporation in a vacuum. The compound crystallised from warm (not boiling) benzene solution as glistening bronze-coloured flakes (0·7 g., 59%) [Found : C, 95·0; H, 5·2; *M* (cryoscopic in benzene), 190. $C_{16}H_{10}$ requires C, 95·0; H, 5·0%; *M*, 202]. It had no definite m. p., but softened at 275—280° and charred at higher temperatures. It was readily soluble in benzene and chloroform, moderately soluble in ethyl acetate, and slightly soluble in ethanol. Solutions of the substance precipitated an insoluble polymer upon being boiled, especially in the presence of traces of mineral acid. Ultra-violet absorption spectrum : $\lambda_{max.}$ 2730, 2810, 3600, 3700, 3810, 3940, and 4150; ε 61,000, 69,000, 4000, 6000, 6000, 12,000, and 15,000.

Dibenzopentalene gave neither a picrate in benzene nor a complex with 3 : 4 : 7-trinitrofluorenone in acetic acid. It is insoluble in orthophosphoric acid but dissolves in concentrated sulphuric acid giving a green solution, the colour being destroyed on dilution with ice-water.

Ozonolysis of dibenzopentalene. Ozonised oxygen was bubbled at −20° through a solution of the substance (110 mg.) in ethyl acetate (800 ml.) until the colour had been destroyed (4—5 minutes). The ozonide obtained on vacuum-evaporation of the solution was decomposed by heating it with glacial acetic acid (50 ml.) on the steam-bath for 2 hours. The acetic acid was distilled off in a vacuum, water (10 ml.) and 2N-sodium hydroxide (5 ml.) were added to the residue, the suspension was warmed, and a slight excess of 5% potassium permanganate solution was added in small portions. The solution was filtered and concentrated; benzil-2 : 2′-dicarboxylic acid (125 mg., 75%) was precipitated on addition of excess of hydrochloric acid. The product, crystallised from acetic acid, was identical with an authentic specimen prepared by Graebe and Juillard's method (*Annalen*, 1887, **242**, 221); m. p. and mixed m. p. 271°. The dimethyl ester, obtained by treatment with diazomethane, had m. p. 191°; Brand and Loehr (*J. pr. Chem.*, 1925, **109**, 353) give m. p. 191° for dimethyl benzil-2 : 2′-dicarboxylate.

Reduction of dibenzopentalene with sodium amalgam. Dibenzopentalene (100 mg.) and 2% sodium amalgam (30 g.), suspended in ethanol (30 ml.), were shaken together vigorously for 20 minutes. The colourless aqueous solution was decanted from mercury, neutralised, and evaporated. The solid product was washed with water and crystallised from ethanol, giving orange plates of dihydrodibenzopentalene (50 mg.), m. p. 204—205°, undepressed by addition of authentic material.

Hydrogenation of dibenzopentalene. Dibenzopentalene (150 mg.), dissolved in ethyl acetate (120 ml.), was hydrogenated at atmospheric pressure and temperature, 20% palladium–charcoal catalyst being used. Two mols. (39·0 ml., 2·1 mols.) of hydrogen were absorbed during 2·5 hours. The colourless solution was shaken in an atmosphere of hydrogen with the catalyst still in suspension for a further 2 days. The solvent was distilled off in a vacuum at 40°. The residue was steam-distilled, and the volatile tetrahydrodibenzopentalene was crystallised from ethanol; m. p. 101° (yield : 120 mg.). The m. p. was not depressed by admixture with authentic material.

If the mixture was worked up immediately after absorption of hydrogen had ceased, the product was a white, steam-volatile solid of m. p. 89—91°, unchanged by admixture with authentic tetrahydrodibenzopentalene.

Addition of bromine to dibenzopentalene. Bromine (1 mol.), diluted with chloroform, was added to a solution of dibenzopentalene (50 mg.) in chloroform (25 ml.). After 30 minutes, the solution was evaporated to dryness in a vacuum. The product was crystallised from benzene–ethyl acetate : yellow needles of the *dibromo*-compound (75 mg.) were obtained which had no definite m. p., but decomposed at *ca.* 240° (Found : Br, 44·2. $C_{16}H_{10}Br_2$ requires Br, 44·2%). Ultra-violet light absorption : $\lambda_{max.}$ 2560, 2640, 3050, 3140, and 3630 Å; ε 35,000, 39,000, 5000, 5000, and 5000.

A solution of the substance in ethanol gave silver bromide with ethanolic silver nitrate only very slowly, even at the b. p.

Analyses were carried out in the microanalytical laboratory (Mr. F. H. Oliver) and measurements of light absorption in the spectrographic laboratory (Mrs. A. L. Boston) of this department. We are indebted to Dr. E. A. Braude for helpful discussion of the spectroscopic data. Grateful acknowledgment is made to the Department of Scientific and Industrial Research for a maintenance grant (to C. T. B.).

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