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CONDENSED CYCLOBUTANE AROMATIC COMPOUNDS—XXIII

SOME TRANSFORMATION PRODUCTS OF 1,2,5,6-DIBENZOCYCLO-OCTATETRAENE

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Abstract—The reaction of bromine with 1,2,5,6-dibenzocyclo-octatetraene involves normal halogen addition to the olefinic linkages, rather than transannular addition as previously assumed. Both a very unreactive tetrabromide and a highly reactive dibromide can be obtained. Solvolysis of the dibromide gives derivatives of 1,2,5,6-dibenzocycloheptatriene. The structures of several transformation products of this dibromide which appear in the literature are revised. The usual geometry of the tetrabromide of dibenzocyclo-octatetraene is correlated with the observed NMR spectrum.

It was reported recently[2] that 1,2,5,6-dibenzocyclo-octatetraene (I) reacts with only one equivalent of bromine to give, by transannular addition, the reduced benzobiphenylene derivative II, m.p. 157°. Reaction of dibromide II with potassium acetate in acetic acid gave an apparently normal diacetate III, m.p. 192°. Basic hydrolysis of III, however, produced not the expected diol but rather a hydrocarbon, m.p. 133°, assigned structure IV. In view of our interest in benzocyclobutene chemistry we have reinvestigated this sequence of reactions in the hope of explaining the unusual conversion of acetate III to the hydrocarbon IV. As outlined below, compelling evidence has been uncovered which requires the revision of all of the structures of the compounds in this series.

Addition of bromine to 1,2,5,6-*dibenzocyclo-octatetraene.* In the cold, only one equivalent of bromine was found to add to hydrocarbon I, giving the previously described dibromide, m.p. 162–165°. Examination of the nuclear magnetic resonance (NMR) spectrum of this compound indicated that it could not be the transannular addition product II, but that it was indeed the normal dibromide V. In agreement with structure V, the spectrum showed a complex envelope of aromatic and conjugated olefinic protons at 2·3–3·2τ, and a band assigned to the benzylic protons attached to carbon bearing bromine at 4·17τ. No protons appeared at higher fields. Structure II, in contrast, would contain a pair of benzylic protons in the alicyclic portion of a benzocyclobutene system. Protons of this type in the model linear benzocyclobutadiene dimer[2] (VI) were found to absorb at 6·25τ.

Elimination of both bromine atoms of V took place upon attempted reduction with lithium aluminium hydride, giving the starting dibenzocyclo-octatetraene (I) in high yield.

Although dibromide V reacted very slowly with bromine at room temperature, addition of bromine took place readily in hot carbon tetrachloride under irradiation conditions. The resulting tetrabromide (VII), m.p. 195–197°, was remarkably resistant

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[1] Alfred P. Sloan Fellow

[2] M. Avram, D. Dinu, G. Mateescu and C. D. Nenitzescu, *Chem. Ber.* 93, 1789 (1960).

to solvolysis and was recovered in 71% yield after being heated on the steam bath for ten hours with potassium acetate in acetic acid. Compound VII was unchanged also after being refluxed overnight with ethanolic iodide, although treatment with activated zinc in ethanol regenerated the parent hydrocarbon I.

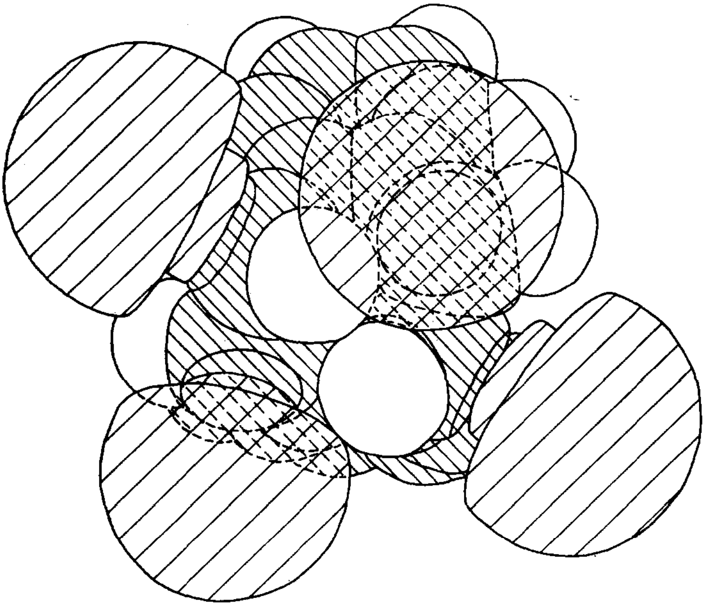

FIG. 1

The NMR spectrum of tetrabromide VII revealed, in addition to aromatic protons in the 2·20–3·38τ region, only a quartet at 4·719 and 3·710τ. This quartet represents two identical pairs of adjacent tertiary hydrogens, one pair on each side of the ring. Within each pair the chemical shift between the hydrogens is 1·009, and the coupling constant is 9·7 cps. According to the calculations of Karplus[3] and Conroy[4] this coupling constant corresponds to a dihedral angle between the adjacent tertiary hydrogens of 175°. The S.A.S.M. molecular model with this geometrical requirement (Fig. 1) shows the molecule to be in the twisted boat conformation. Since only two benzylic hydrogens are seen in the spectrum, there must be a point of symmetry in the center of the eight-membered ring. Two of the tertiary hydrogens point towards the center of the ring, and the other two are pointing away from the ring.

Furthermore, the aromatic proton multiplet at 2·20–3·38τ is more typical of an ABCD rather than a true A_2B_2 spectrum, reinforcing the conclusion that the benzene rings are twisted away from one another.

Transformation products of the dibromide of 1,2,5,6-*dibenzocyclo-octatetraene*. The reaction of dibromide V with potassium acetate in hot acetic acid was carried out as previously reported,[2] except that the reaction time was shortened from twelve hours to two hours.[5] Chromatography of the resulting gum on acid alumina afforded two

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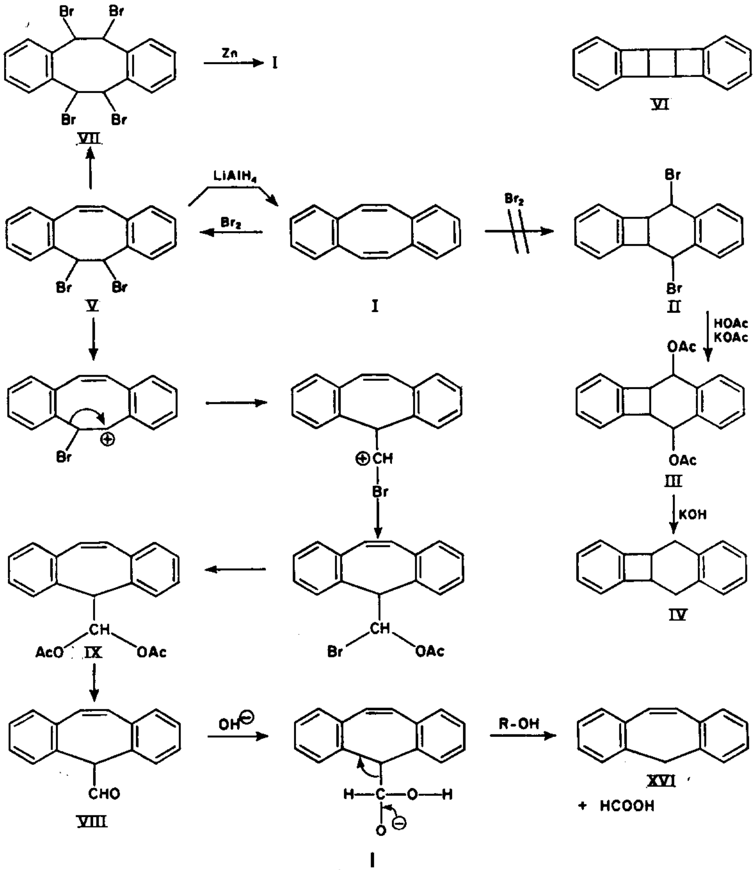
[3] M. Karplus, *J. Chem. Phys.* **30**, 11 (1959).

[4] H. Conroy, *Advances in Organic Chemistry* Vol. 2, p. 265. Interscience (1960).

[5] The reaction probably is complete almost as quickly as the dibromide dissolves, as evidenced by the immediate precipitation of potassium bromide.

crystalline products in moderate yield. The first compound (VIII), $C_{16}H_{12}O$, formed colorless needles, m.p. 113–114°; the second compound (IX), $C_{20}H_{18}O_4$, m.p. 204–206° formed colorless plates and was apparently identical to the previously reported diacetate, m.p. 192°. The properties of this diacetate indicated that it no longer contained the structural feature of an eight-membered ring, but must be formulated as 7-(diacetoxymethyl)-1,2,5,6-dibenzocycloheptatriene (IX). Diacetate IX was reduced by lithium aluminium hydride to a monoalcohol (X), m.p. 74–77°, as expected for a compound having both acetate groups attached to a single carbon atom. Mild hydrolysis of IX with potassium bicarbonate in methanol gave the parent aldehyde VIII, m.p. 114–116°, which was identical with the first previously mentioned acetolysis product of dibromide V. The spectral properties of VIII were in complete accord with its formulation as 1,2,5,6-dibenzocycloheptadiene-7-carboxaldehyde. The carbonyl absorbtion of VIII in the IR (5·85 μ) indicated that an unconjugated carbonyl group was present; the UV spectrum of VIII revealed a stilbene type chromophore at 288 mμ.[6] The NMR spectrum of VIII showed a dibenzylic proton at 5·45τ, two conjugated vinyl protons at 3·23τ, eight aromatic protons centered at 2·70τ, and an aldehydic proton at 0·56τ.



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[6] The known hydrocarbon XVI (λ_{max} 286 mμ) was taken as the closest model substance not showing free rotation of the aromatic rings.

Solvolysis of dibromide V in methanol gave the dimethyl acetal (XI) of aldehyde VIII, m.p. 116–117°; solvolysis in ethanol gave the corresponding diethyl acetal XII, m.p. 84–86°. Both acetals gave the identical yellow 2,4-dinitrophenylhydrazone XIII, m.p. 230–233°, which was obtained also from the aldehyde VIII.

The facile ring contraction of a derivative of 1,2,5,6-dibenzocyclo-octatriene has been encountered previously. The dehydrobromination of 7-bromo-1,2,5,6-dibenzocyclooctatriene (XIV) with picoline gives 1-methylene-2,3,6,7-dibenzocycloheptadiene (XV).[7] It was suggested that this rearrangement may proceed by an α-elimination mechanism, or that rearrangement may occur following primary ionization of bromide XIV to a carbonium ion. The ease of rearrangement of dibromide V under essentially solvolytic conditions implies that the carbonium ion path is that actually followed in the conversion of V to IX, XI and XII; it is likely that the dehydrobromination of XIV proceeds also by way of a similar ionic intermediate.

There remains to be explained the alkaline hydrolysis of diacetate IX to the hydrocarbon, $C_{16}H_{14}$, originally believed to be compound IV.[2] It was found that when the diacetate IX was refluxed with alcoholic potassium hydroxide, there was produced the reported hydrocarbon, m.p. 133°. The UV maximum of this compound (286 mμ) indicated the presence of a conjugated aromatic system, and examination of its NMR spectrum revealed peaks at $3{\cdot}09\tau$ (two conjugated vinyl protons) and at $6{\cdot}35\tau$ (two dibenzylic protons), in addition to the low field aromatic band (eight protons). Since elemental analysis of our sample was in better agreement with the composition $C_{15}H_{12}$ than with $C_{16}H_{14}$, it was concluded that the hydrocarbon was the known 1,2,5,6-dibenzocycloheptatriene (XVI). This expectation was confirmed by direct comparison with an authentic sample of XVI.[8,9,10]

The conversion of diacetate IX to hydrocarbon XVI involves, as its first step, the hydrolysis of IX to aldehyde VIII. Not only is it known (see above) that IX is hydrolyzed to VIII under very mildly basic conditions, but it could be shown that VIII is converted to XVI by boiling with alcoholic potassium hydroxide. The latter transformation may be formulated as a base-catalysed deformylation reaction, as illustrated above.

If the anion of aldehyde VIII is attacked by molecular oxygen, a hydroperoxide (XVII) may be formed. Base-catalyzed decomposition of XVII would give 2,3,6,7-dibenzocycloheptatrienone (XVIII). Ketone XVIII was indeed formed in small amount as a companion product of XVI in the alkaline cleavage reaction of aldehyde VIII.

When the crude acetolysis product of dibromide V was refluxed with alcoholic alkali, there was obtained not only products XVI and XVIII, but also a small amount (*ca.* 10%) of a crystalline diol, m.p. 197–198°. This product was assigned the unrearranged structure XIX. In accord with this formulation, diol XIX was cleaved by periodic acid to a dialdehyde (XX), m.p. 89–91°, the NMR spectrum of which showed only aromatic protons centered at $2{\cdot}66\tau$ and aldehydic protons at $-0{\cdot}15\tau$. Diol XIX is the hydrolysis product of the normal diacetate XXI which, although not isolated, must be present as a minor reaction product in the crude acetolysis mixture derived from dibromide V. It is worthy of notice that the methanolysis of V, which was

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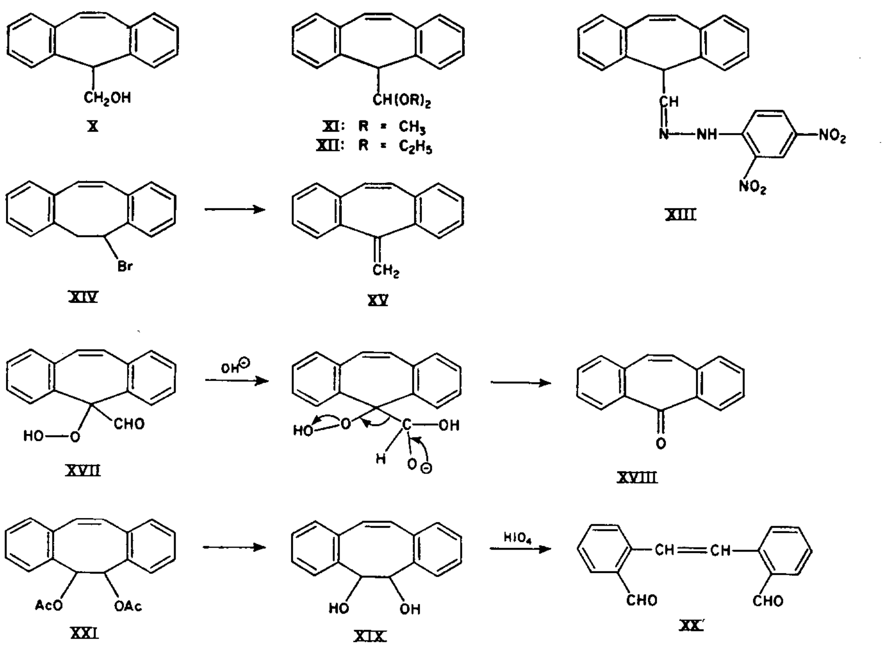
[7] A. C. Cope and R. D. Smith, *J. Amer. Chem. Soc.* **77**, 4596 (1955).

[8] T. W. Campbell, R. Ginsing, H. Schmid, *Helv. Chim. Acta* **36**, 1499 (1953).

[9] W. Treibs, H. J. Klinkhammer, *Chem. Ber.* **84**, 671 (1951).

[10] V. Mijchajlyszyn, M. Protiva, *Coll. Czech. Chem. Comm.* **24**, 3955 (1959).



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conducted in the absence of good nucleophilic species, gave only the rearranged acetal XI in almost quantitative yield.

EXPERIMENTAL*

7,8-*Dibromo*-1,2,5,6-*dibenzocyclo-octatriene* (V)

A solution of 1,2,5,6-dibenzocyclo-octatetraene (I, 2·00 g) in methylene chloride (20 ml) was cooled to 0°, and bromine (2·0 g) was added slowly. After 20 min the solvent was evaporated under red press at room temp. The remaining crystalline mass (3·80 g) was crystallized from cyclohexane–carbon tetrachloride to give colorless crystals of V (2·78 g, 78%), m.p. 160–163°. Recrystallization of a sample raised the m.p. to 162–163° (reported,[2] 157°).

Reaction of dibromide V *with lithium aluminum hydride*

A solution of dibromide V (0·511 g) in benzene (5 ml) was added dropwise to a suspension of lithium aluminum hydride (0·140 g) in dry ether (10 ml). Gas was evolved during the addition, and the mixture became warm. After standing at room temp overnight, excess hydride was decomposed by the addition of a few drops of saturated aqueous sodium sulfate. Evaporation of the organic phase gave crude octatetraene I (0·295 g, 100%), m.p. ~103°. Recrystallization from ethanol gave pure hydrocarbon I (0·184 g, 65%), m.p. 106–108°, identified by IR comparison with authentic material.

3,4,7,8-*Tetrabromo*-1,2,5,6-*dibenzocyclo-octadiene* (VII)

To a solution of dibromide V (0·364 g) in boiling carbon tetrachloride (20 ml) was added 1 ml of a 1M solution of bromine in carbon tetrachloride. The solution, which was irradiated with a sun lamp, decolorized rapidly. Evaporation of the solvent, followed by recrystallization of the residue from cyclohexane, gave tetrabromide VII (0·415 g, 76%), m.p. 192–197°. The analytical sample, m.p. 195–197°, was further crystallized from benzene–petroleum ether. Found: C, 36·62; H, 2·40; Br, 61·53; Calc. for $C_{16}H_{12}Br_4$: C, 36·68; H, 2·36; Br, 61·02%).

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* Analyses were carried out by Schwarzkopf Laboratories, Woodside, N.Y. and by Midwest Microlab, Indianapolis, Ind. M.ps. are uncorrected.

Reactions of tetrabromide VII

A. *With zinc.* A solution of tetrabromide VII (0·400 g) in tetrahydrofuran (15 ml) was stirred with zinc dust (0·200 g, activated by ammonium chloride) for 6 hr at room temp. The solution was filtered, the filtrate evaporated, the sticky yellow residue was extracted with benzene. Chromatography of the extract over neutral alumina afforded white crystals of hydrocarbon I (0·066 g, 41 %), m.p. 105–108°. A sample (m.p. 107–110°) further purified by chromatography and recrystallization was positively identified as 1,2,5,6-dibenzocyclo-octatetraene by mixed m.p. behavior and IR comparison with authentic material.

B. *With sodium iodide.* A solution of tetrabromide VII (0·170 g) and sodium iodide (0·400 g) in ethanol (20 ml) was refluxed overnight on the steam bath. The pale yellow solution was diluted slowly with water and the white solid which separated was removed by filtration. The dried precipitate, m.p. 197–198°, was identified as starting material (0·155 g, 91 %) since it did not depress the m.p. of a sample of authentic VII.

C. *With potassium acetate in acetic acid.* A solution of tetrabromide VII (0·105 g) and potassium acetate (0·220 g) in acetic acid (5 ml) was heated for 10 hr on the steam bath. Dilution of the hot solution with water caused the precipitation of starting material (0·075 g, 71 %), m.p. 195–197°, identified by mixed m.p. behavior with authentic VII.

Reaction of dibromide V *with potassium acetate in acetic acid*

A mixture of dibromide V (4·00 g), potassium acetate (4·00 g) and acetic acid (20 ml) was heated on the steam bath with occasional swirling for 2 hr. The reaction mixture was diluted with water (30 ml) and the yellow oil which separated was extracted into ether. The extract was washed successively with water, aqueous sodium bicarbonate, and water, then dried (Na_2SO_4) and evaporated. The partially crystalline residue was chromatographed in benzene over alumina (Woelm acid-washed, Grade I), the column being eluted first with benzene and then with benzene–ether mixtures and finally pure ether. Evaporation of the combined benzene–ether and ether eluates and crystallization of the residue from cyclohexane gave crude diacetate IX (0·90 g, 25 %), m.p. 193–201° (reported[2] as acetate III, m.p. 192°). After several crystallizations from methanol the compound formed small rectangular crystals, m.p. 204–206°. (Found: C, 75·10; H, 5·70; Calc. for $C_{20}H_{18}O_4$: C, 74·52; H, 5·63 %). The UV spectrum of IX in ethanol showed maxima at 227, 238 and 290 mμ. The NMR spectrum of IX in deuterochloroform showed aromatic protons (around 2·70τ), conjugated vinyl protons (3·04τ), a dibenzylic proton (doublet centered at 5·73τ), and acetoxy protons (8·30τ).

Evaporation of the benzene eluate of the acid alumina column and crystallization of the residue from methanol gave needles of aldehyde VIII (0·50 g, 21 %), m.p. 113–114°, identical by IR comparison with a sample obtained by hydrolysis of acetate IX (see below).

1,2,5,6-*Dibenzocycloheptatriene-7-carboxaldehyde* (VIII)

A solution of diacetate IX (0·083 g) in methanol (20 ml) was heated with potassium bicarbonate (0·300 g) and water (5 ml) for 1 hr on the steam bath. Water was added until the solution became cloudy, and the mixture was allowed to stand overnight, when white needles of aldehyde VIII (0·042 g, 74 %), m.p. 113–114°, separated. Recrystallization from aqueous methanol gave pure aldehyde VIII, m.p. 114–116°. Found: C, 87·29; H, 5·61; Calc. for $C_{16}H_{12}O$: C, 87·24; H, 5·49 %).

The spectral properties of VIII are given in the discussion section.

Lithium aluminum hydride reduction of diacetate IX

To a solution of aluminum hydride (0·200 g) in ether (10 ml) was added a solution of diacetate IX (0·150 g) in benzene (10 ml). After 6 hr at room temp the reaction mixture was decomposed by the addition of aqueous sodium sulfate. Extraction with benzene and evaporation of the solvent gave an oil (0·108 g) which gave oily crystals of alcohol X, m.p. 70–80° on crystallization from aqueous alcohol. Chromatography of this material in ether over neutral alumina (Woelm, Grade IV) gave pure alcohol X, m.p. 82–84°. Found: C, 86·22; H, 6·65; Calc. for $C_{16}H_{14}O$: C, 86·45; H, 6·35 %).

Dimethyl acetal (XI) *of aldehyde* VIII

A mixture of dibromide V (0·360 g), potassium bicarbonate (0·200 g) and methanol (30 ml) was refluxed for 2 hr. Addition of water gave a crystalline precipitate of acetal XI (0·264 g, 95 %), m.p.

116–117°. Recrystallization from methanol did not raise the m.p. (Found: C, 81·01; H, 6·83; Calc. for $C_{18}H_{18}O_2$: C, 81·17; H, 6·81%).

Diethyl acetal (XII) *of aldehyde* VIII

A solution of dibromide V (0·208 g) in absolute ethanol (40 ml) was refluxed for 12 hr, then diluted with water to give a gum which crystallized slowly. The crude product (0·152 g, 74%), m.p. 70–80°, was recrystallized from ethanol to give pure acetal XII, m.p. 80–83°. Found: C, 81·38; H, 7·65; Calc. for $C_{20}H_{22}O_2$: C, 81·60; H, 7·53%).

2,4-*Dinitrophenylhydrazone* (XIII) *of aldehyde* VIII

The 2,4-dinitrophenylhydrazone XIII was obtained by warming either aldehyde VIII, acetal XI or acetal XII with an ethanol solution of 2,4-dinitrophenylhydrazine containing a little sulfuric acid. Recrystallization from ethanol gave small yellow crystals, m.p. 227–229°. Found: C, 65·49; H, 4·06; N, 13·60; Calc. for $C_{22}H_{16}N_4O_4$: C, 65·99; H, 4·03; N, 13·99%).

Reaction of diacetate IX *with potassium hydroxide*

Diacetate IX (0·118 g) was refluxed for 2 hr with 95% ethanol (5 ml) containing potassium hydroxide (0·100 g). The resulting yellow solution was diluted with water and the gum which separated was extracted with ether. Evaporation of the dried ether layer left a glass which was extracted with hot cyclohexane. Chromatography of the concentrated extract on alumina (Woelm neutral, Grade I) and elution of the column with cyclohexane (violet fluorescent band) gave hydrocarbon XVI (0·037 g), m.p. 121–127°. Recrystallization from aqueous ethanol gave white plates which were sublimed *in vacuo* to give crystals, m.p. 132·5–133·5° (reported[3] as hydrocarbon IV, m.p. 133°). Found: C, 93·90; H, 6·26; Calc. for $C_{15}H_{12}$: C, 93·74; H, 6·26; Calc. for $C_{16}H_{14}$: C, 93·16; H, 6·84%).

The identification of this compound as 1,2,5,6-*dibenzocycloheptatriene* (XVI) was made by mixed m.p. determination and IR comparison with a sample of authentic material.[9]

Elution of the alumina column with benzene gave 2,3,6,7-*dibenzocycloheptatrienone* (XVIII) (0·022 g), m.p. 89–90°, identified by mixed m.p. and IR comparison with a sample of authentic material.[9]

Reaction of aldehyde VIII *with potassium hydroxide*

Aldehyde VIII (0·090 g) was refluxed for 2 hr with 95% ethanol (5 ml) containing potassium hydroxide (0·100 g). The reaction mixture was worked up exactly as described in the experiment immediately above. There was obtained, after chromatography, hydrocarbon XVI (0·014 g, m.p. 132–133°) and the ketone XVIII (0·013 g, m.p. 89–90°).

Isolation of unrearranged diol XIX

The unresolved amorphous reaction product (1·83 g), collected from several acetolyses of dibromide V, was refluxed for 2 hr with 95% ethanol (15 ml) containing potassium hydroxide (2·0 g). The diluted reaction mixture was extracted with ether and the dried ether solution was evaporated. Exhaustive extraction of the residue with hot petroleum ether gave a solution from which hydrocarbon XVI (0·38 g) and ketone XVIII (0·008 g) were isolated by chromatography. The portion of the residue which was insoluble in pet ether crystallized from benzene to give fine white needles of XIX (0·180 g), m.p. 197–198°. Recrystallization did not raise the m.p. Found: C, 80·49; H, 5·97; Calc. for $C_{16}H_{14}O_2$: C, 80·64; H, 5·92%).

Periodic acid cleavage of diol XIX

To a suspension of diol XIX (0·048 g) in methanol (2 ml) was added a solution of metaperiodic acid (0·065 g) in 5 drops water. After 10 min the almost clear solution was diluted with water until milky, and then allowed to stand for 7 hr. The crystalline precipitate of dialdehyde XX (0·034 g), m.p. 89–91°, was recrystallized from aqueous methanol before analysis. A small sample, dissolved in alcohol, gave an orange precipitate with 2,4-dinitrophenylhydrazine. (Found: C, 81·29; H, 5·07; Calc. for $C_{16}H_{12}O_2$: C, 81·34; H, 5·12%).

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