374. *Reduction Products of the Cyclopentadiene–Benzoquinone Adduct.*

By R. C. Cookson and R. R. Hill.

Hydrogenation of the *endo*-cyclopentadiene–benzoquinone adduct yields the *endo*-tetrahydro-derivative, isomerised by alkali to the *exo*-derivative. The high-melting substance obtained as a by-product on hydrogenation under certain conditions and previously assumed to be another isomer is in fact dimeric.

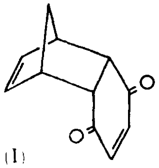
One of the first Diels–Alder reactions to be observed was that between cyclopentadiene and *p*-benzoquinone,[1] and the structure of the adduct was later established by Diels and his collaborators [2] during their classical researches. The accepted *endo-cis*-stereochemistry (I) [3] is confirmed by the conversion of the adduct into a saturated photo-isomer (II).[4] The stereochemistry of the adduct's hydrogenated derivatives, however, has never been established, and is indeed the subject of some confusion.

Albrecht [1] reduced the adduct with zinc and acetic acid to a dihydro-derivative (III), m. p. 35°, that Diels and Alder [5] hydrogenated further over palladium in ethanol to a tetrahydro-derivative (IV), m. p. 56°. By similar hydrogenation of the adduct (I) itself Diels *et al.*[2] obtained another dihydro-derivative, m. p. 190°, which we have shown to be the diol (V). Hydrogenation of the adduct in chloroform over platinum oxide was reported by Bergel and Widman [6] to yield a second tetrahydro-derivative (IV?), m. p. 246°.

Recently Wiley, Batchelder, and McRowe [7] reduced the adduct with lithium aluminium

[1] Albrecht, *Annalen*, 1906, **348**, 34.
[2] Diels, Blom, and Koll, *Annalen*, 1925, **443**, 247.
[3] Alder and Stein, *Annalen*, 1953, **501**, 247.
[4] Cookson, Crundwell, and Hudec, *Chem. and Ind.*, 1958, 1002.
[5] Diels and Alder, *Annalen*, 1928, **460**, 108.
[6] Bergel and Widman, *Annalen*, 1928, **467**, 89.
[7] Wiley, Batchelder, and McRowe, Abs. Papers 138th A.C.S. Meeting, New York, Sept. 1960, 44P. We also acknowledge private correspondence with Dr. Wiley at the beginning of 1961.

hydride to a dihydro-oxo-alcohol, which they oxidised with chromic oxide to an isomer of Albrecht's compound (III). Hydrogenation of the isomer gave the tetrahydro-compound (IV?), m. p. 246°. On this basis they assigned the original *endo*-configuration (VI) to the substance, m. p. 246°, and assumed that isomerisation to the *exo*-configuration had taken place during the zinc–acetic acid reduction, making the compound, m. p. 56°, the *exo*-isomer (VII).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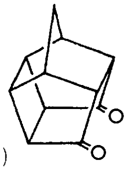
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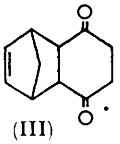
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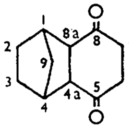

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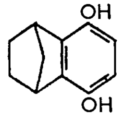
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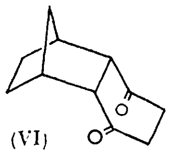
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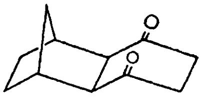
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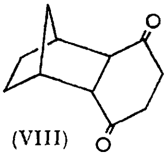
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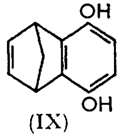
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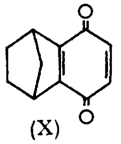

(X)

After the adduct had absorbed one mol. of hydrogen over palladium–charcoal in ethyl acetate we isolated a mixture of unchanged and dihydro-adduct (XIII) (30%), the dihydro-diol (V) (45%), the diol (IX) * (a trace), and the tetrahydro-derivative, m. p. 56° (10%). Oxidation of the diol (V) (obtained in better yield by enol-acetylation of the adduct, hydrogenation, and hydrolysis) with silver oxide gave the quinone (X), m. p. 40°, agreeing with an earlier description.[8] Hydrogenation of the adduct under Bergel and Widman's conditions [6] afforded the tetrahydro-derivative (IV?), m. p. 247° (250—253° when pure), in 20% yield, although the major product (60%) was again the tetrahydro-derivative of m. p. 56°. Dilute alkali transformed the compound of m. p. 56° into a new isomer, m. p. 68°, in 70% yield.†

If these three substances, m. p.s 56°, 68°, and 247°, really were isomers, one of them must have had the very strained *trans*-configuration (VIII). The very high m. p. of Bergel and Widman's compound, however, immediately aroused our suspicions, which were confirmed by a report [9] of its oxidation to a quinone, m. p. 125°, obviously different from the authentic quinone (X), which melts at 40°. The structure of the latter is certain, because of its spectroscopic properties, and its conversion [10] by addition of cyclopentadiene into derivatives of the benzoquinone–biscyclopentadiene adduct of known structure. Determination of the molecular weight of the isomer of m. p. 246° then revealed that it was dimeric (*M*, *ca.* 360), so that its existence has no direct bearing on the stereochemical problem, and there is no reason to doubt that the two other isomers are the *endo*- and *exo*-forms of (IV).

Presumably the substance of m. p. 246° has some such structure as (XI) ($C_{22}H_{26}O_4$). We have made one of the isomers of structure (XII) ($C_{22}H_{24}O_4$) by photodimerisation of (XIII), which in solution is very sensitive to light, but it is different from the anomalous substance, m. p. 246°.

Since the isomer of m. p. 56° is always formed on hydrogenation in greatest yield, and is converted into the isomer of m. p. 68° by base, it must have the *endo*-configuration (VI), while the more stable isomer (m. p. 68°) must be *exo* (VII). The *exo*-isomer can adopt the

* The authentic samples of (IX) and dehydro-(X) used for comparison were made by the method of Meinwald and Wiley (*J. Amer. Chem. Soc.*, 1958, **80**, 3667) in connection with other work.[10]

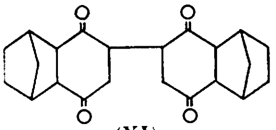
† We have since learnt that this isomer has also been isolated by Dr. M. C. Whiting and Dr. C. Swithenbank (Swithenbank, D.Phil. Thesis, Oxford, **1961**).

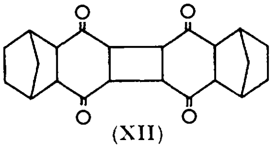
[8] Posternak and Castro, *Helv. Chim. Acta*, 1948, **31**, 536.

[9] Dauben, Boswell, and Templeton, *J. Org. Chem.*, 1960, **25**, 1853.

[10] Cookson, Hill, and Hudec, *J.*, in the press; Hill, Ph.D. Thesis, Southampton, 1961.

half-chair conformation of the cyclohexanedione ring (with some angle strain) as well as the two strain-free boat conformations (VII and XV), whereas the *endo*-isomer has open to it only the half-chair and one boat conformation (VI), the energy of the other boat (XIV) being prohibitively high because of repulsion between opposite pairs of hydrogen atoms on the concave face of the molecule (7α,2α and 6α,3α in formula IV, where the 9-bridge is given the configuration β). The proton magnetic resonance spectra of the two isomers, although similar, have conspicuous differences. Each consists of a group of bands at high field (*ca.* 1·4 δ[*]) from the three methylene groups of the bicyclo[2,2,1]heptane and another group of bands at lower field (2·1—3·1 δ) from the remaining eight protons. Probably, because the 2- and 3-protons (see numbering in formula IV) are shielded by the carbonyl groups, in the *endo*-isomer (VI) the signal from the six 2-, 3-, and 9-protons almost coalesces into a single rather sharp band at 1·36 δ. In the *exo*-isomer (VII), however, it is the 9-methylene group that is shielded by the carbonyl groups, appearing as a multiplet centred on 1·10 δ, while the other four protons appear as multiplets centred on 1·42 and 1·57 δ. The most conspicuous feature of the low-field part of the spectra is the fourteen lines of the A_2B_2 system due to the 6- and the 7-methylene group. It is particularly clear in the *endo*-isomer, where the ten lines at highest field are quite free from any overlapping absorption. In the *endo*-isomer the system extends from 2·06 to 3·02 δ, symmetrical about 2·54, whereas in the *exo*-isomer it is centred on 2·60. The two pairs of tertiary hydrogen atoms give doublets at 2·75 and 2·84 δ in the *endo*-isomer and at 2·62 and 2·82 in the *exo*-isomer. The great similarity in the low-field parts of the spectra eliminates the very remote possibility that either isomer might have had the highly strained unsymmetrical *trans*-structure (VIII).


(XI)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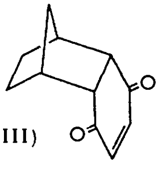
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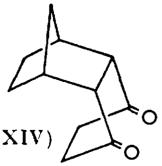
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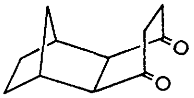
(XV)

Experimental

Infrared spectra of Nujol mulls were measured on a Unicam S.P. 100 spectrophotometer, ultraviolet spectra of ethanol solutions on a Unicam S.P. 700, and nuclear magnetic resonance spectra on a Varian A-60 machine at 60 Mc./sec. for solutions in carbon tetrachloride with tetramethylsilane as internal reference. Melting points are uncorrected. The adduct of cyclopentadiene and *p*-benzoquinone was prepared by Albrecht's method.[1]

Part Hydrogenation of 1α,4α,4aβ,8aβ-*Tetrahydro*-1,4-*methanonaphthalene*-5,8-*dione* (I) *and Oxidation of* 1,2,3,4-*Tetrahydro*-1,4-*methanonaphthalene*-5,8-*diol*.—The quinone (I) (5 g.) in ethyl acetate (300 ml.) was hydrogenated over 5% palladium–charcoal catalyst (0·2 g.). The reaction was stopped after 45 min., 670 ml. of hydrogen having then been taken up. After filtration, the solvent was removed and the resulting gum taken up in a 1 : 1 mixture of benzene–petroleum (b. p. 60—80°). This solution was chromatographed on silica, which crudely separated the products into two groups, (i) a mixture of the quinone (I) and its dihydro-derivative, 1α,2,3,4α,4aβ,8aβ-hexahydro-1,4-methanonaphthalene-5,8-dione (XIII) (1·5 g.), and (ii) a

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[*] Frequencies are given in parts per million at 60 Mc./sec. from tetramethylsilane as internal reference in carbon tetrachloride, rather than in τ values, since they refer to positions of lines, τ values in general not having been calculated.

mixture of 1,4-dihydro-1,4-methanonaphthalene-5,8-diol (IX),* its 2,3-dihydro-derivative (V) and 1α,2,3,4α,4aβ,6,7,8aβ-octahydro-1,4-methanonaphthalene-5,8-dione (VI) (3·5 g.).

Group (i): Further chromatography on silica, and many recrystallisations from light petroleum afforded fairly pure (XIII) (50 mg.), m. p. 70°, mixed m. p. with the adduct (I) 60—65°, $\nu_{max.}$ 1670, 1605, 1286, 888 cm.$^{-1}$ (Found: C, 74·9; H, 6·9. $C_{11}H_{12}O_2$ requires C, 75·0; H, 6·9%.)

During the above recrystallisations, a white solid was isolated, which, from subsequent photochemical experiments (see below), appears to be a photodimer of (XIII).

Group (ii): A small sample of this material was recrystallised from benzene, giving a few mg. of pure quinol (V), recognised by comparison with an authentic sample.[10]

The main bulk of this group was dissolved in benzene and treated with silver oxide (2 g.) and anhydrous magnesium sulphate (3 g.). The mixture was shaken for 1 hr., filtered, and concentrated to about 30 ml., and an equal volume of petroleum (b. p. 60—80°) added. This solution was chromatographed on silica, whereby the quinones 1,2,3,4-tetrahydro-1,4-methanonaphthalene-5,8-dione (X) and its 2,3-dehydro-derivative * were separated from the diketone (VI), m. p. 57° (250 mg.). The quinones were rechromatographed on silica giving (X) (600 mg.) and 2,3-dehydro- (X) * (20 mg.). *Quinone* (X), m. p. 40°, exhibited $\nu_{max.}$ 1651, 1580, 1326, 841 cm.$^{-1}$ and $\lambda_{max.}$ 256 mμ (15,500), λ_{sh} 263 mμ (13,700), $\lambda_{max.}$ 360 (700) and λ_{sh} 445 mμ (52) (Found: C, 76·2; H, 5·75%. $C_{11}H_{10}O_2$ requires C, 75·8; H, 5·8%.)

Hydrogenation of the Adduct (I) *under Bergel and Widman's Conditions.*—The adduct (I) (3·2 g.) in chloroform (50 ml.) was hydrogenated for 2½ hr. over Adams catalyst (0·13 g.), by which time the theoretical amount of hydrogen (2 moles) had been absorbed. A little more chloroform was added and the solution filtered through kieselghur. The solvent was removed from the filtrate to give an oil, and a benzene solution of this was chromatographed on silica. Three products came off the column in the order (i) diketone (VI), m. p. 57° (1·6 g.); (ii) a dimeric *product*, m. p. 250—253° (0·5 g.), $\nu_{max.}$ 1701, 1301, 1281, 838 cm.$^{-1}$ (Found: C, 74·6; H, 7·3%; *M*, 361, 373. $C_{22}H_{26}O_4$ requires C, 74·55; H, 7·4%; *M*, 354); (iii) a keto-alcohol, m. p. 179°, which was not investigated (0·15 g.).

Base-catalysed Isomerisation of Diketone (*VI*); 1α,2,3,4α,4*a*α,6,7,8*a*α-*Octahydro*-1,4-*methanonaphthalene*-5,8-*dione* (VII).—To the adduct (I) (280 mg.) in ethanol (20 ml.) was added, slowly with stirring, ethanol (5 ml.) containing potassium hydroxide (100 mg.). The operation was performed under nitrogen. A dark red colour developed which gradually changed to pale yellow during 20 minutes' refluxing under nitrogen. After being cooled and neutralised with dilute hydrochloric acid, the solution was diluted with water and extracted with ether. The extract was dried ($MgSO_4$) and filtered, and the solvent removed. The resulting gum was dissolved in 1 : 1 benzene–petroleum (b. p. 60—80°) and chromatographed on silica, whereby was isolated (VII) (200 mg.), m. p. 68°, [mixed m. p. with (VI), 35—45°] $\nu_{max.}$ (in chloroform) 1715, 1192, 1165, 1125 cm.$^{-1}$, (Found: C, 74·3; H, 8·0%. $C_{11}H_{14}O_2$ requires C, 74·1; H, 7·9%).

Photodimerisation of the Enedione (XIII).—The enedione (XIII) (50 mg.) was irradiated by an 80 w medium-pressure mercury lamp situated 4 in. above the sample for 6 hr. with frequent turning over of the crystals. A Pyrex glass filter was used. The white *product*, which was very insoluble in most organic solvents, was recrystallised from acetonitrile (80% yield); it had m. p. 250° (decomp.), $\nu_{max.}$ 1700, 1202 cm.$^{-1}$ [Found: C, 75·0; H, 6·5%. $(C_{11}H_{12}O_2)_2$ requires C, 75·0; H, 6·9%].

We are indebted to Dr. A. Melera for measurement of the nuclear magnetic resonance spectra.

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* See footnote on p. 2024.