Cyclooctatetraenoquinones. I. The synthesis and structure of dibenzo[*a*,*e*]cyclooctene-5,6-dione

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Dibenzo[*a*,*e*]cyclooctene-5,6-dione (**18**), a derivative of 1,2-cyclooctatetraenoquinone (**4**), has been synthesized by selenium dioxide oxidation of dibenzo[*a*,*e*]cycloocten-5(6*H*)-one (**26**), itself obtained from the reaction of 5,11-dibromo-5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene (**20**) with dimethyl sulfoxide and collidine. Infrared and proton magnetic resonance spectroscopic studies have shown that the 8-membered ring of **18** is not aromatic.

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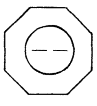
Introduction

Hückel's rule relating aromaticity to monocyclic $4n + 2$ (n integral) π-electron systems (1) and its empirical extension to polycyclic systems have stimulated studies of the synthesis and properties of a wide variety of cyclic π-electron systems (2). Prominent among these investigations are those of Katz and coworkers (3) on the dianion formed by reduction of cyclooctatetraene. It has been concluded (3, 4) that this dianion is a planar, aromatic species, **1**. This circumstance has been attributed in large part to the stabilization conferred by the 10 π-electron system ($4n + 2$), which more than offsets the angle-strain engendered by the assumption of the planar configuration. In contrast, cyclooctatetraene itself is non-planar and non-aromatic (**2**), since any stabilization conferred by the 8 π-electron system ($4n$) is small and insufficient to compensate for the angle-strain introduced in the planar configuration; indeed, the planar $4n$ π-electron system may be antiaromatic and actually destabilize this configuration (5).

Another $4n + 2$ π-electron system related to cyclooctatetraene is the dication that is formally derivable from it by removal of 2 π-electrons.



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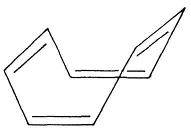

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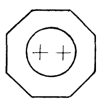

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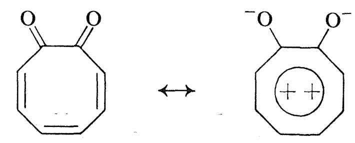
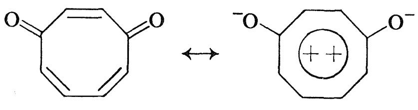
This has not been observed directly (6), although the suggestion has been made that it may be an intermediate in the anodic oxidation of cyclooctatetraene (7). It is thus not known whether the dication exists as the planar aromatic species **3**, analogous to **1**, or adopts a non-planar, non-aromatic configuration.

A closely related problem concerns the possibility of the aromaticity of 1,2-cyclooctatetraenoquinone (**4**) and its 1,4 isomer (**5**). These will be aromatic if they exist as approximately planar species to which the canonical forms symbolized by **4*a*** and **5*a***, which embody the cyclooctatetraene dication, make appreciable contributions. Additional factors that intrude in these cases are the charge separation in the canonical forms represented by **4*a*** and **5*a*** and the Coulombic interaction between the negative charges on the oxygen atoms[1] in these forms. Both of these factors will tend to increase the energy of these structures and reduce their effectiveness in conferring aromaticity on the cyclooctatetraenoquinones. The related cyclobutadienoquinones (**6**) have been studied extensively by



4 **4*a***



5 **5*a***

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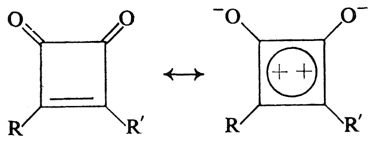
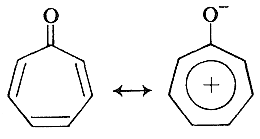
[1] The Coulombic interaction between the two positive charges on the ring atoms is common to these structures and **3**.

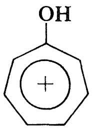
Roberts and coworkers (8); their properties and unusual stability are in accord with substantial contributions from canonical forms symbolized by **6***a* (**8***a*). However, the assumption of the planar configuration implied by **6***a* requires no increased angle strain relative to nonplanar configurations, and these compounds are not precisely analogous to the cyclooctatetraenoquinones.[2] A more closely analogous case is that of tropone (**7**), where recent results suggest that there is only a minor contribution from structures symbolized by **7***a* (9, 10). Nevertheless, it is probable that protonated tropone, i.e., the hydroxytropylium ion **8**, the formation of whose aromatic system does not require charge separation, has appreciable aromatic character (11),[3] and this suggests that although the cyclooctatetraenoquinones themselves may not be aromatic in character, protonated species derived from them, such as **9** and **10**, may be so. An alternative, but nonetheless interesting, possibility for the nature of the monoprotonated cyclooctatetraenoquinones is exemplified by the ion **11**, the analog of the homotropylium ion formed on protonation of 2,4,6-cyclooctatrienone (12).



6 **6***a*



7 **7***a*



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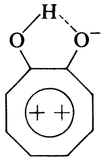

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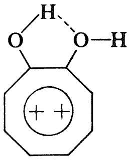

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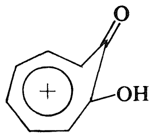

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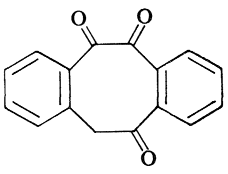

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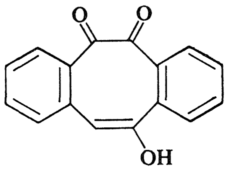

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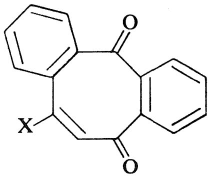
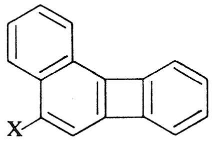
The first reference in the chemical literature to a potential cyclooctatetraenoquinone derivative appeared in 1940 when the preparation of a compound provisionally assigned structure **12** was reported (13). This would be converted by enolization to the hydroxydibenzo-1,2-cyclooctatetraenoquinone **13**. However, this compound has subsequently been shown to possess a different structure (14). Apparently, the first report of the preparation of cyclooctatetraenoquinone derivatives appeared in 1962 when Cava and Ratts (15) described the formation of the halodibenzo-1,4-cyclooctatetraenoquinones **14** and **15** on oxidation of the biphenylene derivatives **16** and **17**, respectively. The possible aromatic nature of the 8-membered ring was not alluded to. The first report of deliberate attempts to synthesize cyclooctatetraenoquinone derivatives seems to be that of McIntyre *et al.* (16); no such derivatives were obtained, however.

In the present work we have synthesized the 1,2-cyclooctatetraenoquinone derivative **18**, i.e., dibenzo[*a,e*]cyclooctene-5,6-dione,[4] and have examined its properties with especial reference to the possible aromaticity of the 8-membered ring.



14 X = Br
15 X = Cl



16 X = Br
17 X = Cl

During the course of this work, Bendall and Neumer (17) have also reported the preparation of this compound, but by a different route.

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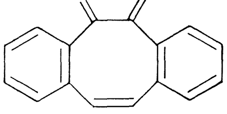
[2] Another differentiating factor is the cross-ring interaction in the case of the cyclobutadienoquinones (8*a*).

[3] The very recent results of Bertelli and coworkers (10*b*), however, suggest that the aromaticity of **8** is less pronounced than has previously been considered.

[4] Dibenzo[*a,e*]cyclooctene is the *Chemical Abstracts* and *Ring Index* name for the hydrocarbon **19**.



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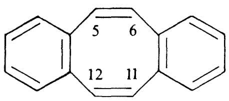

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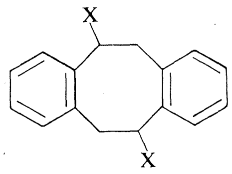
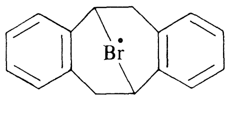
Synthesis of Dibenzo[a,e]cyclooctene-5,6-dione (18)

5,11-Dibromo-5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene (**20**) was prepared in 75% yield by bromination of the corresponding hydrocarbon (**21**) by the method of Cope and Fenton (18). The bromination is carried out with *N*-bromosuccinimide and is of interest since the 5,11-dibromo compound is formed with high selectivity. This may be due to the preferential formation of the bridged intermediate **22** in the course of the introduction of the second bromine atom (19).[5]



20 X = Br
21 X = H
25 X = OH



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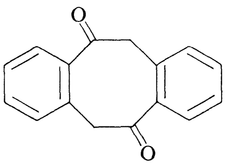
Treatment of the dibromo compound **20** with dimethyl sulfoxide and collidine (20) gave three products. The major product, obtained in ca. 40% yield, was dibenzo[*a*,*e*]cyclooctene-5,11-(6*H*,12*H*)-dione[6] (**23**), which has previously been prepared by a 6-step sequence from diphenylsuccinonitrile in an overall yield of 4% (13, 18). Another product was the hemiketal **24** (ca. 10%), which has previously been obtained by conversion of **20** to the diol **25** and oxidation of this with chromic acid, and also by Meerwein–Pondorff reduction of the dione **23** (18). The third product formed on treatment of **20** with dimethyl sulfoxide and collidine was dibenzo[*a*,*e*]cycloocten-5(6*H*)-one (**26**) (ca. 20%).

The ketone **26** has previously been prepared by oxidation of the corresponding alcohol, which was obtained from the dihydroanthracene derivative **27** (21). Since compound **26** was of crucial importance in the present investigation, it was necessary to confirm the structural assignment. Its structure was established by its spectra [λ_{max} (CCl_4) 5.98 μ; δ ($CDCl_3$) 4.02 (s, 2H), 6.88 (s, 2H),[7] 7.0–7.5 (m, 7H), and 8.25 (br d, 1H)] and the following reactions. Hydrogenation at atmospheric pressure over palladium–carbon gave 11,12-dihydrodibenzo[*a*,*e*]cycloocten-5-(6*H*)-one (**28**) (22, 23), identified by its spectra [λ_{max} (CCl_4) 5.97 μ; δ ($CDCl_3$) 3.20 (s, 4H), 4.05 (s, 2H), 6.75–7.20 (m, 7H), and 7.20–7.38 (m, 1H)] and its m.p. and that of its 2,4-dinitrophenylhydrazone (23). Wolff–Kishner reduction of **28** gave 5,6,11,12-tetrahydrodibenzo[*a*,*e*]cyclooctene (**21**), which was identified by comparison with an authentic sample (18). Wolff–Kishner reduction of **26** itself gave 5,6-dihydrodibenzo[*a*,*e*]cyclooctene (**29**) (22), identified by its proton magnetic resonance (p.m.r.) spectrum [δ ($CDCl_3$) 3.13 (s, 4H), 6.70 (s, 2H), and 7.05 (s, 8H)] and its m.p.



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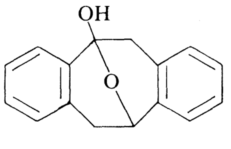

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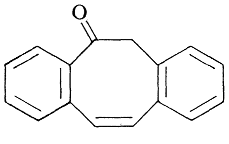

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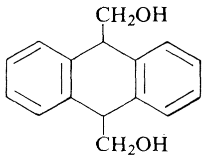

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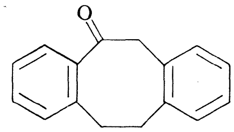
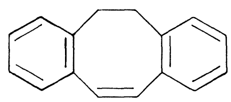
Oxidation of **26** with selenium dioxide in dioxane gave dibenzo[*a*,*e*]cyclooctene-5,6-dione



28



29

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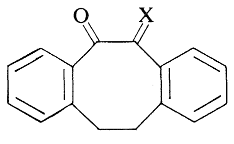
[5] This view implies that **20** is the *trans* stereoisomer; its stereochemistry has not been established, however.

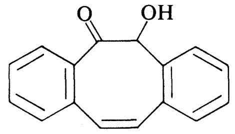
[6] This name, the *Chemical Abstracts* term for **23**, is used with some reluctance, since it fails to indicate clearly that **23** and **18** are in different oxidation states; cf. footnote 4.

[7] That this single signal is a result of the accidental superimposition of the two vinyl proton signals was shown by examination of the corresponding ^{13}C satellites (*vide infra*).

(**18**) in 24% yield. The structure of this product was established by its spectra [λ_{max} (CCl_4) 5.83 and 6.00 μ; δ ($CDCl_3$) 6.83 (s, 2H), and 7.0–7.7 (m, 8H)], which will be discussed in detail subsequently, and its conversion on hydrogenation over palladium–carbon to 11,12-dihydrodibenzo[*a*,*e*]cyclooctene-5,6-dione (**31**), identified by direct comparison with an authentic sample prepared from **28** via the α-oximino derivative **30** (23). The melting point of **18** was undepressed on admixture with a sample of the product obtained by Bendall and Neumer (17) by oxidation of **32**, itself prepared by a benzoin condensation.[8] The infrared (i.r.) spectra of the two samples were identical.



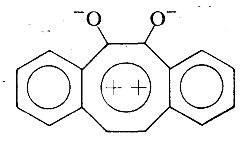
30 X = NOH
31 X = O



32

Properties of Dibenzo[a,e]cyclooctene-5,6-dione (18)

The i.r. spectrum of **18** shows two strong bands in the carbonyl-stretching region [λ_{max} (CCl_4) 5.83 and 6.00 μ]. In analogy with the spectra of many other α-diketones (24), these can be attributed to the antisymmetrical and symmetrical coupled stretching vibrations of the two carbonyl groups. Models suggest that the dihedral angle between the carbonyl groups is in the range 0–40°. This is consistent with the occurrence of strong coupling between the stretching vibrations of these groups; were the dihedral angle close to 90°, little or no coupling would be expected (25). The case of **18** may be contrasted with that of its dihydro derivative **31**, whose i.r. spectrum shows a strong carbonyl-stretching band at 5.97 μ (CCl_4) with a shoulder at 5.88 μ. It has previously been concluded on the basis of ultraviolet (u.v.) spectroscopic measurements that **31** exists in a crown-type conformation in which the intercarbonyl angle approaches 90° (23). Such a conformation would account for the weakness of the vibrational coupling. Davison (24*b*) has suggested that the mean of the 2 frequencies may be taken as the unperturbed frequency of the individual carbonyl groups. We consider that this is an acceptable approximation in a case such as **18** where the two bands are of comparable intensity, but is of dubious applicability in a case such as **31** where one band is very much stronger than the other. The estimate thus obtained for the approximate unperturbed position of the carbonyl-stretching band in **18** is 5.91 μ. For **31** the unperturbed position is taken as lying in the range between the mean frequency and that of the strong band, i.e., 5.92–5.97 μ. Comparison of these positions with each other and with the positions of the single carbonyl-stretching bands in the i.r. spectra of compounds **23** (5.95 μ), **26** (5.98 μ), and **28** (5.97 μ) shows that the position in the case of **18** is at shorter wavelength than in the other cases. Now, were the 8-membered ring of **18** aromatic in character, this would require, as discussed earlier, substantial contributions from canonical forms symbolized by **33**. If such contributions were important, it would be expected that the unperturbed carbonyl-stretching band of **18** would lie at an appreciably *longer* wavelength than the bands of **23**, **26**, **28**, and **31**. This would result from both the increased single bond character of the carbonyl bonds in **33** (26), and from the increased C—C—C angle at the carbonyl group (27). The fact that the band of **18** lies at *shorter* wavelength than the bands of the other compounds strongly contraindicates the aromaticity of the 8-membered ring.[9]



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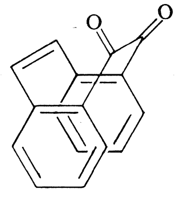

34

Additional evidence for this lack of aromaticity comes from p.m.r. studies. The two protons on the 8-membered ring of **18** give rise to a singlet at δ 6.83. The signals due to the corresponding protons in the enone **26** and the hydrocarbon **29** appear at δ 6.88 and 6.70 μ, respectively. Had the

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[8] We thank Dr. J. F. Neumer, E. I. du Pont de Nemours and Co., for generously providing us with a sample of his product.

[9] The shift to shorter wavelength may be attributed to dipole–dipole interaction between the carbonyl groups, exacerbated by a relatively small dihedral angle between them.

8-membered ring of **18** been aromatic in character, it would have been expected to support a diamagnetic ring current that would lead to a significant deshielding of the protons attached to this ring (28). The fact that the signals that arise from these protons are closely similar in position to the vinylic proton signals of **26** and **29** again shows that the 8-membered ring of **18** is not aromatic. This is confirmed by the magnitude of the coupling constant between the protons on the 8-membered ring of **18**. This could not be measured directly because these protons have identical chemical shifts, but was obtained from observation of the upfield ^{13}C satellite signals, which gave $J_{H,H} = 12.8$ and $J_{H,^{13}C} = 160$ Hz. For comparison, the coupling constant between the corresponding protons in the enone **26** was measured. Resort again was had to the ^{13}C satellite signals because of the accidental identity of the chemical shifts of these protons in **26**. Observations of the upfield satellite signals gave $J_{H,H} = 12.6$ Hz; interestingly the two protons had different values of $J_{H,^{13}C}$, viz., 155 and 160 Hz.[10] The essential identity of $J_{H,H}$ for **18** and **26** demonstrates that in the former, like the latter, the protons on the 8-membered ring are olefinic rather than aromatic. Had those of **18** been aromatic in character, their coupling constant would have been significantly smaller than that observed (29), which falls within the range expected for *cis*-olefinic protons on medium-sized rings (30).

All of the evidence obtained thus shows that the 8-membered ring of **18** is not aromatic, and can be interpreted in terms of the nonplanar conformation **34** for this compound.[11]

Compound **18** is insoluble in concentrated hydrochloric acid and cannot be extracted from carbon tetrachloride with 50% sulfuric acid. The p.m.r. spectrum of **18** in trifluoroacetic acid is essentially identical with that in deuteriochloroform. Thus there is no indication of any special stability of the mono- or diprotonated forms of **18** attributable to structures of type **9**, **10**, or **11**.[12] The p.m.r. spectrum of the enone **26** in trifluoroacetic acid was also essentially identical to its spectrum in deuteriochloroform. This colorless compound gave a bright yellow solution in trifluoroacetic acid from which it could be recovered unchanged, perhaps indicating the formation of a small amount of protonated species, but the p.m.r. spectrum showed no sign of the dibenzo derivative of the homotropylium ion (33).

That the 8-membered rings of **18** and its protonated derivatives are nonaromatic does not rule out the possibility that the monocyclic compounds **4** and **5** or their protonated derivatives are aromatic. The fusion of the two benzene rings to the 8-membered ring in **18** could damp the aromaticity of this ring because of their tendency to appropriate π-electrons for their individual aromatic systems (34). Whether this is the origin of the failure to observe an aromatic 8-membered ring in the present work will not be known until the more challenging synthetic problem of preparing analogous compounds in the monocyclic series has been solved.

Experimental

Melting points were determined in capillary tubes with a Thomas-Hoover "Uni-Melt" apparatus and are uncorrected.

Infrared spectra were recorded in carbon tetrachloride solutions, unless otherwise stated, and were calibrated with the 3.51, 6.24, and 9.72 μ bands of polystyrene film. Proton magnetic resonance spectra were recorded in deuteriochloroform solutions, unless otherwise stated. The band positions are reported in parts per million downfield from tetramethylsilane as internal reference (δ scale).

Analytical thin-layer chromatography (t.l.c.) was carried out with thin layers of silica gel (Merck) on microscope slides. Preparative t.l.c. was carried out with 1.0 mm thick layers of silica gel (Merck) on 20 × 20 cm square glass plates. Analytical chromatograms were made visible with iodine vapor, and preparative chromatograms by the quenching of an u.v. phosphor added to the silica gel.

Solutions in organic solvents were dried over anhydrous magnesium sulfate and stripped of solvent with a rotary evaporator in conjunction with a water aspirator.

5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene (21)

Compound **21** was prepared from α,α′-dibromo-*o*-xylene according to the method of Cope and Fenton (18). The isolation of the compound was greatly facilitated by the use of a combined steam-distillation–extraction unit.[13] After 4 days, the chloroform solution was dried and evaporated, giving **21** as a colorless solid, m.p. 103–108°,

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[10] We thank Professor W. F. Reynolds, University of Toronto, for a helpful discussion of these spectra.

[11] Dr. J. F. Neumer has kindly informed us that he and Dr. V. I. Bendall have reached the same conclusion regarding the non-planar (non-aromatic) character of **18** (31).

[12] Cf. the low basicity of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (2,3,6,7-dibenzotropone) (32).

[13] Designed and constructed by Dr. A. C. Mackay.

which was consistently obtained in a yield of 33–40%. A sample recrystallized from 95% ethanol had m.p. 107.5–108.5° [lit. (18) m.p. 108.5–109°]; δ 3.03 (s, 8H) and 6.96 (s, 8H).

5,11-Dibromo-5,6,11,12-tetrahydrodibenzo[a,e]cyclooctene (20)

Compound **20** was prepared by treating **21** (recrystallized once from 95% ethanol) with *N*-bromosuccinimide as described by Cope and Fenton (18). The crude product, which was consistently obtained in ca. 75% yield, had m.p. 184–188° and was used without further purification. A sample recrystallized from 95% ethanol had m.p. 185–186° [lit. (18) m.p. 188.1–189°]; δ 3.62 (A part of ABX system, $J_{AB} \sim 14$, $J_{AX} \sim 8$ Hz, 2H), 4.32 (B part of ABX system, $J_{AB} \sim 14$, $J_{BX} \sim 11$ Hz, 2H), 5.35 (X part of ABX system $J_{AX} = 8$, $J_{BX} = 11$ Hz, 2H), and 6.9–7.2 (m, 8H).

The dibromo compound **20** was also formed when the hydrocarbon **21** was treated with bromine in carbon tetrachloride.

*Treatment of Compound **20** with Dimethyl Sulfoxide and Collidine. Formation of Dibenzo[a,e]cyclooctene-5,11(6H,12H)-dione (23), Dibenzo[a,e]cycloocten-5(6H)-one (26), and the Hemiketal 24*

In a 500 ml round-bottomed flask equipped with a condenser fitted with a drying tube were placed collidine (22 ml, 0.17 mole) and a solution of **20** (20.0 g, 0.055 mole) in dimethyl sulfoxide [Fisher Certified from a freshly opened bottle or from a previously opened bottle to which molecular sieves (Linde type 4A) had been added after opening; 300 ml]. The mixture was magnetically stirred and heated at 130° for 1.3 h. The solution was then allowed to cool to ca. 25° and poured into 1.5 l of cold water. The resulting suspension was filtered to give an off-white solid that was dried in a vacuum desiccator over phosphorus pentoxide, when it weighed 10.5 g. On t.l.c. it showed only 3 spots, corresponding to the starting material (**20**), the dione **23**, and the enone **26**. A 9.49 g portion of this mixture was chromatographed on a column of silica gel (470 g, 58 × 4 cm); fractions were combined on the basis of t.l.c. (with dichloromethane as developer) and i.r. spectra. Elution with benzene gave starting material (0.90 g), followed by the enone **26** (2.55 g). Elution with dichloromethane and with dichloromethane containing 0.5% of methanol gave the dione **23** (5.72 g).

The enone **26** was recrystallized from dichloromethane–hexane to give colorless needles (1.65 g, 15%), m.p. 114–115° [lit. (21) m.p. 114–116°]; λ_{max} 5.98 μ; δ 4.02 (s, 2H), 6.88 (s, 2H), 7.0–7.5 (m, 7H), and 8.25 (d, each component broad, *J* = ca. 8 Hz, 1H); δ (CF_3CO_2H) 3.98 (s, 2H), 7.02 (s, 2H), 7.1–7.6 (m, 7H), and 8.20 (d, 1H); a p.m.r. spectrum recorded at 100 MHz with high spectrum amplitude on a concentrated solution (160 mg in 0.3 ml of $CDCl_3$) showed the upfield ^{13}C satellites of the δ 6.88 signal as a pair of overlapping doublets; $J_{H,H'} = J_{H',H} = 12.6$, $J_{H,^{13}C} = 155$, $J_{H',^{13}C} = 160$ Hz.

Anal. Calcd. for $C_{16}H_{12}O$ (mol. wt. 220): C, 87.24; H, 5.45. Found (*m/e* 220): C, 87.24; H, 5.53.

The dione **23** was recrystallized from dichloromethane–hexane to give colorless needles (4.12 g, 35%), m.p. 203–204° [lit. (13) m.p. 203.5–204.5°]; λ_{max} 5.95 μ; δ 4.42 (s, 4H), 7.06–7.46 (m, 6H), and 7.61–7.85 (m, 2H).

Mol. Wt. Calcd. for $C_{16}H_{12}O_2$: 236. Found: *m/e* 236.

The original aqueous filtrate was extracted twice with chloroform, and the chloroform solution was washed once with dilute hydrochloric acid, twice with water, and once with aqueous sodium bicarbonate. The chloroform solution was then dried and stripped of solvent to give a sticky solid (1.29 g). This was recrystallized from dichloromethane–hexane to give the hemiacetal **24** as colorless prisms (0.53 g, 4.5%), m.p. 171–174°. This material was recrystallized from 95% ethanol to give colorless prisms, m.p. 177.5–178.5°; λ_{max} 3.03 (wm), 9.19, and 9.28 μ; δ 2.3–3.6 (m, 4H), 4.33 (s, 1H, absent after treatment with D_2O), 5.38 (d, *J* = 5 Hz, each component broad, 1H), 6.7–7.35 (m, 7H), and 7.35–7.65 (m, 1H). A mixture with authentic **24**, m.p. 178.5–180°, prepared by Meerwein–Ponndorf reduction of the dione **23** (18), had m.p. 177.5–179°; the i.r. spectra and t.l.c. behavior of the two samples were identical.

*Hydrogenation of **26**. Formation of 11,12-Dihydrodibenzo[a,e]cycloocten-5(6H)-one (28)*

The enone **26** (45 mg) in ethyl acetate (8 ml) was stirred with 10% palladium-on-charcoal (5 mg) at 15° under hydrogen at atmospheric pressure. During 45 min 1.05 molar equivalents of hydrogen were absorbed, after which the rate of uptake of hydrogen became very slow. The mixture was filtered, and the filtrate was evaporated to give the ketone **28** (44 mg, 97%) as colorless needles, m.p. 83–88°. This material was recrystallized from aqueous methanol to give colorless needles, m.p. 93.5–94° [lit. m.p. 95.2–96.5° (22), 93–94° (23)]; λ_{max} 5.97 μ; δ 3.20 (s, 4H), 4.05 (s, 2H), 6.75–7.20 (m with spike at δ 6.87, 7H), and 7.20–7.38 (m, 1H).

Mol. Wt. Calcd. for $C_{16}H_{14}O$: 222. Found: *m/e* 222.

The hydrogenation product gave a 2,4-dinitrophenylhydrazone, m.p. 194–197° [lit. (13) m.p. 196–197°].

*Wolff–Kishner Reduction of **28**. Formation of 5,6,11,12-Tetrahydrodibenzo[a,e]cyclooctene (21)*

In a 5 ml round-bottomed flask equipped with a condenser were placed the ketone **28** (20 mg, 0.089 mmole), potassium hydroxide (100 mg, ca. 2 mmoles), 85% hydrazine (0.2 ml, 3 mmoles), and diethylene glycol (1 ml). The mixture was heated at reflux for 2 h, the condenser was removed, and the temperature was allowed to rise to 200°; the condenser was then replaced, and the mixture was heated at reflux for a further 3 h. It was poured into dilute hydrochloric acid, and the organic products were extracted 3 times with dichloromethane. The extracts were washed twice with water, and the organic layer was dried and evaporated to give a colorless solid, which was recrystallized from 95% ethanol to give **21** as colorless prisms, m.p. 108–108.5°. A mixture with authentic **21** (*vide supra*) had m.p. 108–109°; the i.r. spectra of the two samples were identical.

*Wolff–Kishner Reduction of **26**. Formation of 5,6-Dihydrodibenzo[a,e]cyclooctene (29)*

This reduction of **26** (49 mg, 0.223 mmole) was carried out as described for **28**. The crude product was a colorless oil, which was sublimed at 90° (10^{-2} mm) to give **29** as a colorless solid, m.p. 47–50°, which on recrystallization from 95% ethanol gave colorless prisms, m.p. 53.5–54.5° [lit. (22) m.p. 53.6–54.6°]; δ 3.13 (s, 4H), 6.70 (s, 2H), and 7.05 (s, 8H).

Mol. Wt. Calcd. for $C_{16}H_{14}$: 206. Found: *m/e* 206.

Oxidation of 26 with Selenium Dioxide. Formation of Dibenzo[a,e]cyclooctene-5,6-dione (18)

The enone **26** (500 mg, 2.27 mmoles), selenium dioxide (B.D.H.; 295 mg, 2.33 mmoles), dioxane (Fisher Certified, freshly refluxed and distilled over sodium under nitrogen, 8.3 ml), and water (0.7 ml) were heated at reflux for 127 h. The reaction was monitored by t.l.c. with hexane–acetone (1:1) as developer. The reaction mixture was poured into about 3 times its volume of water and extracted 3 times with dichloromethane. The extracts were combined and washed 3 times with water, dried, and stripped of solvent to give a bright yellow gum (587 mg). Preparative t.l.c. with hexane–acetone (1:1) as developer gave 4 fractions. The most mobile was a colorless solid (65 mg), which was shown to be the starting material **26** by mixture m.p. and i.r. spectral comparison. The next most mobile fraction was the major component (190 mg) of the mixture: on sublimation at 90° (10^{-2} mm) it gave **18** as a bright yellow powder (130 mg, 24%), m.p. 96–101°. Recrystallization from dichloromethane–hexane followed by resublimation at 85–90° (10^{-2} mm) gave yellow microprisms, m.p. 101–102°; λ_{max} 5.83 and 6.00 μ; λ_{max} (C_6H_{12}) 245 (log ε 4.30), 318 (log ε 3.41), 385 (log ε 2.18), and 407 mμ (log ε 2.00); δ 6.83 (s, 2H) and 7.0–7.7 (m, 8H); δ (CF_3CO_2H) 6.90 (s, 2H) and 7.1–7.7 (m, 8H); a p.m.r. spectrum recorded at 100 MHz with high spectrum amplitude on a concentrated solution (135 mg in 0.3 ml of $CDCl_3$) showed the upfield ^{13}C satellite of the δ 6.83 signal as a doublet; $J_{H,H} = 12.8$ and $J_{H,^{13}C} = 160$ Hz. A mixture with a sample[8] of the product obtained by Bendall and Neumer (17, 31) had m.p. 101–102°; the i.r. spectra of the two samples were identical.

Anal. Calcd. for $C_{16}H_{10}O_2$: C, 82.04; H, 4.30. Found: C, 82.18; H, 4.04.

Compound **18** was insoluble in cold or boiling concentrated hydrochloric acid; it was rapidly destroyed by concentrated sulfuric acid. When a solution of **18** in carbon tetrachloride was shaken with 50% sulfuric acid, the yellow color of the organic solution persisted and the aqueous solution remained colorless.

Hydrogenation of 18. Formation of 11,12-Dihydrodibenzo[a,e]cyclooctene-5,6-dione (31)

Compound **18** (46 mg) in ethyl acetate (6 ml) was stirred with 10% palladium-on-charcoal (5 mg) at room temperature under hydrogen at atmospheric pressure. After 45 min 1.14 molar equivalents of hydrogen had been absorbed, the rate of uptake of hydrogen had greatly diminished, and the yellow color of the solution had been discharged. Filtration and removal of solvent gave an almost colorless oil, which slowly solidified on standing. This was subjected to preparative t.l.c. with acetone–hexane (3:7) as developer; elution of the major band with dichloromethane–chloroform (1:1) gave **31** as a colorless solid (36 mg, 78%); crystallization from methanol gave colorless plates, m.p. 131–132° [lit. (23) m.p. 131–132°]; λ_{max} 5.88 (sh, m) and 5.97 μ; δ 3.25 (s, 4H), 7.07–7.53 (m, 6H), and 7.60–7.85 (m, 2H).

Authentic **31** was prepared following the method of Leonard and coworkers (23) by treatment of the ketone **29** with isoamyl nitrite and sodium ethoxide to give the α-oximino derivative **30**, followed by reaction of this with aqueous formaldehyde. Recrystallization from aqueous ethanol gave colorless plates, m.p. 131–132°. A mixture with the hydrogenation product from **18** had m.p. 131–132°; the i.r. and p.m.r. spectra of the two samples were identical.

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