melted at 183–184°, and a nitrous acid solution of XIII did not react with alkaline β-naphthol solution; thus, an amine function other than primary aromatic was indicated.[17] None of the desired 5,6-dihydro-3H-2,3-bis(2-pyridyl)pyrrolo[1,2,3-*de*]quinoxaline was isolated.

4,4'-Diethylbenzoin (XVI).—A mixture of 55.0 g. (0.244 mole) of *p*-ethylbenzaldehyde,[18] 7.8 g. (0.12 mole) of potassium cyanide, 75 g. of ethanol, and 75 g. of water was refluxed. A small amount of ethanol was subsequently added to effect the complete solution of all of the reactants. After 2 hr. at reflux temperature, the solution was cooled. Two volumes of water was added and the oily layer which separated was extracted with ether. The ethereal solution was shaken with aqueous sodium bisulfite solution, dried over magnesium sulfate, filtered, and evaporated *in vacuo*. Of the 17.7 g. of oily residue which remained, 11.7 g. was distilled *in vacuo*. The product obtained boiled at 180–185° (0.2–0.5 mm.), n^{21}_{D} 1.5725, and weighed 9.6 g. (26% based upon an extrapolation back to the original 17.7 g.).

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.41; H, 7.34.

A strong carbonyl band appeared at 5.98 μ in the infrared spectrum of the product.

Pyrrolo- and Pyrido[1,2,3-*de*]quinoxalines (Tables II and III). General Procedures Are Illustrated by Methods A and B. Method A.—Equimolar amounts of the diamine[19] and the appropriate benzoin were mixed and heated to 150–190° for 0.5 hr. during which time effervescence occurred. The melt was cooled and taken up in warm ethanol. With continued standing, the product crystallized from the ethanolic solution. Recrystallizations were performed as necessary.

Method B.—Equimolar quantities of the diamine and the appropriate benzoin were dissolved in a weight of toluene of about ten times that of the diamine. A trace of *p*-toluenesulfonic acid was added and the solution was refluxed. The water which evolved was collected in a Dean–Stark trap by azeotropic distillation. After the theoretical amount of water had collected or after water ceased to evolve, the reaction mixture was cooled, filtered, and diluted with 3 vol. of petroleum ether (b.p. 75–90°). The material which separated was recrystallized from ethanol as required.

Method C. 5,6-Dihydro-2-hydroxy-3H-pyrrolo[1,2,3-*de*]quinoxaline-3-one (XII).[5a]—A solution of 5.0 g. (0.037 mole) of 7-aminoindoline (I) and 5.5 g. (0.037 mole) of diethyl oxalate (U. S. I.[20]) in 100 ml. of toluene was refluxed for 1 hr. during which time a solid separated. The reaction mixture was cooled and filtered, and the solid was recrystallized once from dimethylformamide–ether and twice from ethanol. The product weighed 1.3 g. (19%, Table II): $\lambda_{max}^{CH_3OH}$ 235 mμ (log ε 3.98), 242 (3.92), 262 (3.71), 272 (3.71), 314 (3.99), 322 (3.95), and 340 (sh, 3.59).

Method D. 2,3-Diphenyl-3H-pyrrolo[1,2,3-*de*]quinoxaline (XIV).—A solution of 5.0 g. (0.037 mole) of 7-aminoindoline (I), 7.8 g. (0.037 mole) of benzil (Matheson Coleman and Bell), and a trace of *p*-toluenesulfonic acid in 150 ml. of toluene was treated according to method B. The gummy residue which remained after treatment of the cooled reaction mixture with petroleum ether (b.p. 75–90°) was extracted with ether. The ether-insoluble residue was recrystallized three times from ethanol and dried. The product weighed 1.0 g. (9%) and melted at 151.5–153.0°. A mixture melting point with VIII was depressed considerably (Table II).

The structure of this product was further confirmed by ultraviolet, visible, infrared, and n.m.r. spectroscopy as described in the text.

Method E. 6,7-Dihydro-2-hydroxy-3H,5H-pyrido[1,2,3-*de*]quinoxaline-3-one (XIX).[5a]—A solution of 5.0 g. (0.034 mole) of 8-amino-1,2,3,4-tetrahydroquinoline[1] in 50 ml. of benzene was stirred and treated dropwise with a solution of 4.6 g. (0.034 mole) of ethyl oxalyl chloride (Eastman) in 25 ml. of benzene. The slurry which formed was stirred for 1 hr. and filtered. The solid was washed with benzene and dried. It was slurried with aqueous sodium bicarbonate solution, and then made more alkaline with 10% aqueous sodium hydroxide solution The solid residue was filtered, washed with water, and recrystallized twice from ethanol. The product weighed 1.1 g. (16%, Table III): $\lambda_{max}^{CH_3OH}$ 236 mμ (log ε 3.98), 242 (3.93), 261 (3.73), 270 (3.69), 312 (3.97), 325 (3.91), and 340 (sh 3.55).

Acknowledgment.—The author wishes to express his thanks to Mrs. Janice Hall, who measured the ultraviolet, visible, and infrared spectra, to Mr. Martin Gordon and Mr. Raymond Snider, who performed the microanalyses, to Mr. Mark Rycheck of The University of Cincinnati who measured the n.m.r. spectra, and to Dr. Fred Kaplan of The University of Cincinnati for his comments regarding the interpretation of the n.m.r. spectra. The author also appreciates the advice offered by his colleagues, Dr. Albert A. Carr, Dr. Robert W. Fleming, Dr. Frederick J. McCarty, and Dr. Edward McC. Roberts, relative to the preparation of this manuscript.

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[18] M. H. Klouwen and H. Boelens, *Rec. trav. chim.*, **79**, 1022 (1960).

[19] 7-Aminoindoline (I) or 8-amino-1,2,3,4-tetrahydroquinoline (ref. 1).

[20] U. S. Industrial Chemicals Co.

The Configurations of the 2,3-Epoxides of Some Diels–Alder Adducts of 1,4-Benzoquinones

D. F. O'BRIEN AND J. W. GATES, JR.

Research Laboratories, Eastman Kodak Company, Rochester, New York 14650

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Alkaline epoxidation of the Diels–Alder adducts from cyclic dienes and *p*-benzoquinones yields the appropriate 2,3-epoxides. The epoxides may differ stereochemically from the Diels–Alder adducts. They react with various mercaptans to give 2-thioether enediones. The configurations of these compounds were established to be *endo* by the use of n.m.r. spectroscopy. The epoxide ring was assigned the *exo* configuration. It was found that peracetic acid converts the 2,3-epoxides to 2,3,6,7-diepoxides. Permanganate oxidation of 5,8-methano-4a,5,6,7,8,8a-hexahydro-1,4-naphthoquinone 2,3-epoxide gave cyclopentane-1,3-dicarboxylic acid. Representative enediones were photochemically isomerized to their corresponding cage diketones.

The reaction of equimolar quantities of cyclopentadiene and *p*-benzoquinone at room temperature in numerous solvents gives a homogeneous product in high yield.[1–3] The product was identified as 5,8-methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (1),[1,2] and assigned the *cis-endo* configuration.[3] This designation was based on the postulated lower enthalpy of activation for *endo* addition. The assignment preceded the formulation of the Alder rule of "maximum accumulation of unsaturation."[4] Attempts to prepare the isomeric *exo* material by chemical means

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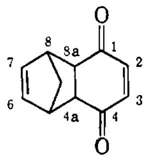
[1] W. Albrecht, *Ann.*, **348**, 31 (1906).

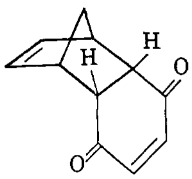
[2] O. Diels and K. Alder, *ibid.*, **460**, 98 (1928).

[3] A. Wasserman, *J. Chem. Soc.*, 1511 (1935). see also A. Wasserman, *ibid.*, 828 (1935); 432 (1936); 612 (1942); *Trans. Faraday Soc.*, **34**, 128 (1938); **35**, 841 (1939). R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **66**, 645 (1944).

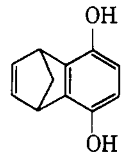
[4] K. Alder and G. Stein, *Angew. Chem.*, **50**, 514 (1937).



1



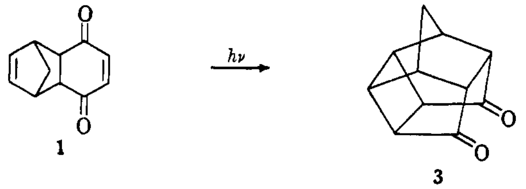
1a



2

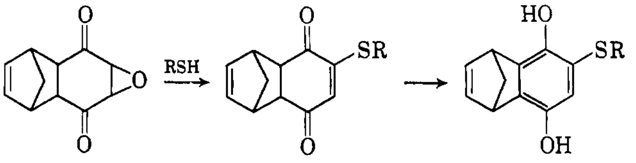
produced the hydroquinone (2).[5,6] The *cis–exo* isomer is unknown. Because only one of the two possible *cis* isomers is known, confirmation of the assigned configuration by comparison of the physical properties of the isomers is not possible. Recently, exceptions to the Alder rule have been reported,[7] and in some cases the *exo* isomer has been shown to be favored under kinetically controlled conditions.[8] The desirability of establishing the configuration independent of the Alder rule is evident.

The observed photolysis of 1 in a Pyrex vessel with a mercury-vapor arc to give the saturated diketone 3 appears to satisfy this need.[9] However, the possibility that 1 is the *cis-exo* isomer which isomerized photochemically to the *endo* isomer or an *endo*-like intermediate, followed by ring closure, cannot be ruled out.[10]



1 3

α,β-Unsaturated ketones may be epoxidized in the presence of isolated double bonds by alkaline hydrogen peroxide.[11] Application of this procedure to 1 gives excellent yields of the 2,3-epoxide 4.[12] The configuration of this compound has hitherto not been established.



4 5 6

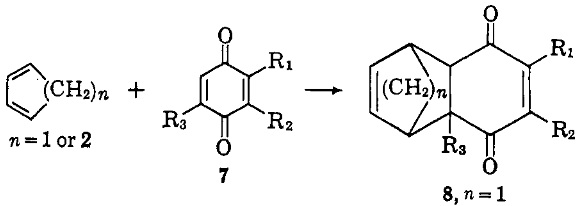
Recent work in these laboratories indicates that the epoxide 4 reacts readily with mercaptans to give the 2-thioether enedione 5. When vigorous conditions are employed, the product is the isomeric 2-thioether hydroquinone 6.[13]

Our interest in the mechanism of the epoxide ring opening spurred us to determine the configurations of the 2,3-epoxide and the resultant 2-thioether enedione 5. The data presented here confirm the original assignment for 1.

Results and Discussion

We hoped that examination of n.m.r. spectra of appropriate Diels–Alder adducts, their 2,3-epoxides, and 2-thioether enediones would serve to establish their configurations.

Diels–Alder adducts (8 and 9) studied were derived from cyclopentadiene and 1,3-cyclohexadiene. *p*-Benzoquinone (7a), 2-methyl-*p*-benzoquinone (7b), 2-*t*-butyl-*p*-benzoquinone (7c), 2,5-dimethyl-*p*-benzoquinone (7d), and 2,6-dimethyl-*p*-benzoquinone (7e) were the dienophiles.



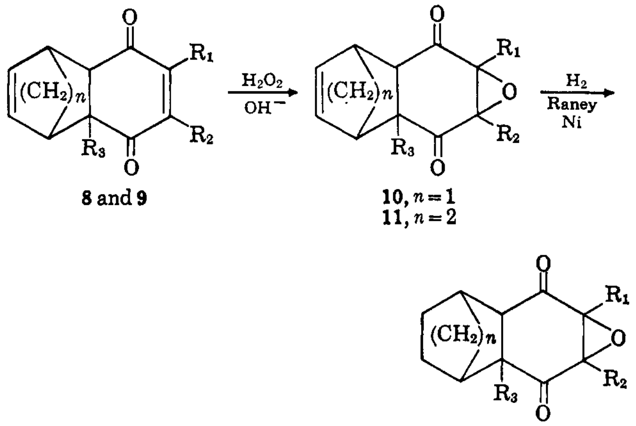
$n = 1$ or 2

7

8, $n = 1$
9, $n = 2$

a, $R_1 = R_2 = R_3 = H$
b, $R_1 = CH_3;\ R_2 = R_3 = H$
c, $R_1 = C(CH_3)_3;\ R_2 = R_3 = H$
d, $R_1 = R_3 = CH_3;\ R_2 = H$
e, $R_2 = R_3 = CH_3;\ R_1 = H$

The 2,3-epoxides (10 and 11) were prepared by the method of Alder.[12] In some cases the isolated double bond was hydrogenated over Raney nickel catalyst to give the saturated 2,3-epoxides (12 and 13).[13]



8 and 9

10, $n = 1$
11, $n = 2$

12, $n = 1$
13, $n = 2$

The 2-thioether enediones (14 and 15) and hydroquinones (16 and 17) were prepared by the methods first mentioned.[13] The mercaptan was 1-phenyl-5-mercaptotetrazole (HPMT).

The peak positions in the n.m.r. spectra of the compounds examined are given in Tables I and II. The compounds are divided into those derived from cyclopentadiene (Table I) and those from 1,3-cyclohexadiene (Table II). They are arranged for each *p*-benzoquinone in the following order: enedione, 2,3-epoxide, saturated 2,3-epoxide, 2-thioether enedione, and hydroquinone.

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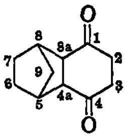
TABLE I

PEAK POSITIONS FOR DIELS–ALDER ADDUCTS OF CYCLOPENTADIENE AND *p*-BENZOQUINONES[a]

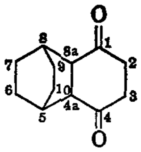


Compd.	2,3-Olefinic	6,7-Olefinic	2,3-Epoxy	4a,8a[b]	5,8	6,7-Saturated	9	Other
8a	3.55	3.88	...	6.77	6.45	...	8.48	
10a	...	3.98	6.50	6.55	6.68	...	8.59	
12a	...	...	6.32	6.86	7.31	8.64	8.64	
14a	3.31	4.01	...	6.71	6.47	...	8.50	Phenyl, 2.45
16a[c]	3.50	3.21	...	...	5.85	...	7.97	Phenyl, 2.33 OH, 1.16 1.11
8b	3.52	4.00	...	6.78	6.48	...	8.50	2-CH$_3$, 8.08
10b	...	3.96	6.62	6.55	6.68	...	8.59	2-CH$_3$, 8.53
12b	...	...	6.63	6.92	7.36	8.65	8.65	2-CH$_3$, 8.48
8d	3.55	3.93	...	7.18 (3.6)	6.95 6.60	...	8.35	2-CH$_3$, 8.05 4a-CH$_3$, 8.52
10d	...	3.96	6.63	7.10 (3.5)	7.10 6.72	...	8.47	2-CH$_3$, 8.52 4a-CH$_3$, 8.37
12d	...	...	6.53	7.33	7.62 7.31	8.68	8.68	2-CH$_3$, 8.48 4a-CH$_3$, 8.57
14d	...	3.91	...	7.06 (3.6)	6.98 6.55	...	8.36	Phenyl, 2.36 2-CH$_3$, 7.78 4a-CH$_3$, 8.46
8e	3.50	3.97	...	7.16 (3.6)	6.90 6.58	...	8.37	3-CH$_3$, 8.04 4a-CH$_3$, 8.52
10e	...	3.97	6.61	7.12 (3.3)	7.05 6.71	...	8.47	3-CH$_3$, 8.52 4a-CH$_3$, 8.37
8c	3.54	3.96	...	6.80	6.50	...	8.49	2-*t*-Bu, 8.78
10c	...	3.93	6.52	6.55	6.76	...	8.60	2-*t*-Bu, 8.94
20	...	...	6.38	6.67	7.07	6.89[d]	8.51[e] 9.31	2-*t*-Bu, 8.91

[a] Peak positions are expressed in parts per million relative to an internal tetramethylsilane standard, which is given an arbitrary position of 10 (τ scale). The positions indicate the center of the multiplets. The spectra were obtained from 10% solutions in deuteriochloroform unless otherwise noted. [b] The coupling constants listed in parentheses are $J_{8a,8}$ in c.p.s. [c] Methyl sulfoxide. [d] The α-protons on the 6,7-epoxide. [e] The resonance due to the 9-protons is an AX system each line of which is further split into a multiplet. The coupling constant between the 9-protons is 10.5 c.p.s., and the δ_{AB} is 47.8 c.p.s.

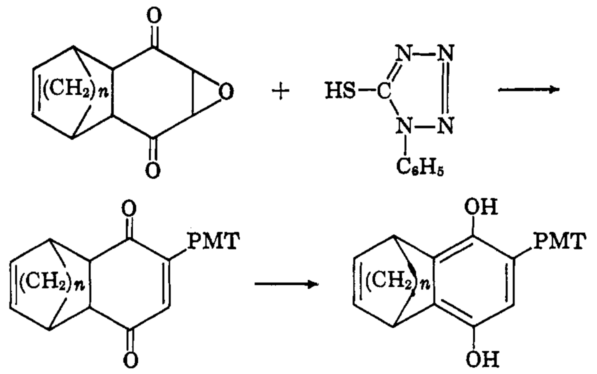
TABLE II

PEAK POSITIONS FOR DIELS–ALDER ADDUCTS OF 1,3-CYCLOHEXADIENE AND *p*-BENZOQUINONES[a]



Compd.	2,3-Olefinic	6,7-Olefinic	2,3-Epoxy	4a,8a[b]	5,8	6,7-Saturated	9,10	Other
9a	3.37	3.78	...	6.99	6.78	...	8.43	
11a	...	3.83	6.40	6.72	6.83	...	8.53	
13a	...	...	6.28	6.84	7.85	8.39 8.59	8.39 8.59	
15a	3.18	3.79	...	6.91 (2.3)	6.82	...	8.45	Phenyl, 2.44
17a[c]	3.45	3.53	...	...	5.52	...	8.65	Phenyl, 2.35 OH, 1.36, 1.07
9b	3.44	3.78	...	7.01	6.78	...	8.45	2-CH$_3$, 8.04
11b	...	3.83	6.45	6.74	6.86	...	8.55	2-CH$_3$, 8.52
13b	...	...	6.42	6.81	7.61	8.53	8.53	2-CH$_3$, 8.33
9d	3.47	3.80	...	7.48 (2.1)	6.99	...	8.47	2-CH$_3$, 8.06 4a-CH$_3$, 8.66
11d	...	3.82	6.54	7.33 (2.7)	6.83 7.15	...	8.62	2-CH$_3$, 8.53 4a-CH$_3$, 8.45

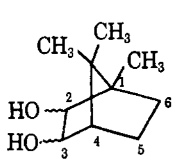
[a] Peak positions are expressed in parts per million relative to an internal tetramethylsilane standard, which is given an arbitrary position of 10 (τ scale). The positions indicate the center of the multiplets. The spectra were obtained from 10% solutions in deuteriochloroform unless otherwise noted. [b] The coupling constants listed in parentheses are $J_{8a,8}$ in c.p.s. [c] Methyl sulfoxide.

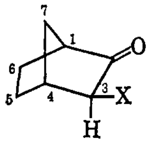


14, n = 1
15, n = 2

16, n = 1
17, n = 2

Anet studied the spectra of the four diastereomeric camphane-2,3-diols.[14] The magnitude of the coupling constant between the 3- and 4-protons depends on whether the 3-proton is *exo* ($J \sim 4$ c.p.s.) or *endo* ($J \cong 0$ c.p.s.). Similar observations have been made from the spectra of α-chlorocamphor,[15] 3,8-cyclocamphor,[16] and other norbornene systems.[17] Anet noted

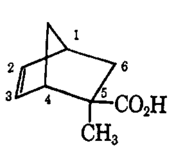




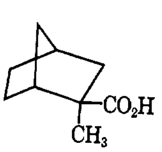
long-range coupling between the *exo* 2- and *exo* 6-protons ($J \cong 1$ c.p.s.).[14] Meinwald and Meinwald[18] have reported larger 1,3 spin–spin interactions in the *exo*-3-substituted norcamphors and dihydronorcamphors. They concluded that these α-halo ketones exhibit coupling between the *endo* 3- and *anti* 7-protons ($J \cong 3$–4 c.p.s.).

Presumably we should be able to identify the configuration of our compounds by the appearance of the resonance due to the 4a,8a-protons. However, if the long-range coupling between the *anti* 9-proton and the 4a,8a-protons is as large as that reported by the Meinwalds, the results would be equivocal.

Fraser reports the spectra of some 5-methylbicyclo[2.2.1]hept-2-ene-5-carboxylic acids and 5-methylbicyclo[2.2.1]heptane-5-carboxylic acids.[19] The coupling constant between the *exo* 6- and *exo* 1-protons



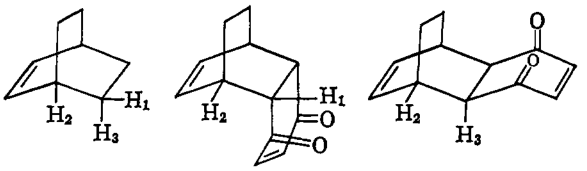
18



19

in olefin **18** was 3.8 c.p.s. Coupling between the *exo* 6- and *exo* 2-protons was not observed in **18**, but was in **19**. The *endo* 6-proton is weakly coupled ($J \cong 1$ c.p.s.) with the *anti* 7-proton and bridgehead protons.

The compounds examined in our work are closely related to those of Fraser. Their resemblance to the α-halo ketones of Meinwald is limited. We would expect long-range interactions between the methano bridge and *endo* 4a,8a-protons to be small. Those compounds derived from cyclopentadiene (Table I) should be readily identified as to their configuration. However, the configuration of the compounds prepared from 1,3-cyclohexadiene will not be discernible on this basis. In those compounds, the situation is analogous to that of bicyclo[2.2.2]octene. The magnitude of the coupling constant between vicinal protons is dependent in part on the size of the dihedral angle.[20] The angle H_1CCH_2 is slightly larger than angle H_2CCH_3.



The magnitude of the coupling constants would be expected to vary inversely. Inspection of Dreiding models of the *exo* and *endo* isomers indicated the angle difference to be about 5°. This is not great enough to provide a predictable experimental distinction between $J_{\mathrm{H_1H_2}}$ and $J_{\mathrm{H_2H_3}}$ and therefore between the isomers.

Fraser reports that the chemical shift of the 5-methyl and 6-protons is affected systematically by removal of the double bond going from acid **18** to **19**.[19] For the *endo* 5-methyl and *endo* 6-proton, the resonances are shifted paramagnetically 0.12 and 0.05 p.p.m., respectively. In compounds with an *exo* 5-methyl and *exo* 6-proton, the resonances appear further upfield 0.22 and 0.14 p.p.m., respectively. This was ascribed to the magnetic anisotropy of the double bond. Similar results in the bicyclo[2.2.2]octane series were mentioned.[19]

Wong and Lee examined the spectra of some *endo*- and *exo*-dehydronorbornyl and -norbornyl derivatives (alcohol, acetate, and brosylate).[21] Hydrogenation resulted in a paramagnetic shift of both *exo* and *endo* protons. In the brosylate, $\Delta\tau$ was 0.31 and 0.04, respectively.

It may be possible to assign the configuration of the adducts of 1,3-cyclohexadiene by the magnitude and direction of the shift of the 4a,8a-proton resonance on going from an unsaturated to a saturated epoxide.

The striking similarity between the spectra of the enediones and of the corresponding 2-thioether enediones is noted immediately, *e.g.*, **8a** and **14a**, and **9a** and **15a**. This is true of peak positions and multiplet appearance. Indeed the spectra are virtually superimposable except for the position of the olefinic protons. This indicates that they have the same configuration. Furthermore, the configuration of the 2,3-epoxides (**10** and **11**) and 2-thioether enediones (**14** and **15**) must be the same. Therefore, all three (enedione, epoxide, and thioether enedione) have the same stereochemistry.

The peaks due to the 4a,8a-protons appear as multiplets in those compounds having a methano bridge.

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(14) F. A. L. Anet, *Can. J. Chem.*, **39**, 789 (1961).

(15) W. D. Kumler, J. N. Shoolery, and F. V. Butcher, Jr., *J. Am. Chem. Soc.*, **80**, 2533 (1958).

(16) E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *ibid.*, **81**, 6305 (1959).

(17) P. Laszlo and P. v. R. Schleyer, *ibid.*, **86**, 1171 (1964), and references cited therein.

(18) J. Meinwald and Y. C. Meinwald, *ibid.*, **85**, 2514 (1963).

(19) R. F. Fraser, *Can. J. Chem.*, **40**, 78 (1962).

(20) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959). Other factors such as bond length and electronegativity of substituents must not be ignored: M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

(21) E. W. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964).

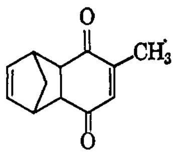
This indicates a measurable coupling constant between the 8a- and 8-protons. Because of the large number of protons interacting, it is not possible to determine $J_{8a,8}$ by first-order analysis. However, in those compounds (**8d, 10d, 12d, 14d, 8e,** and **10e**) having a 4a-methyl group, the spin system is simplified. The 8a-proton appears as a doublet in all these compounds, with a line separation of 3.3 to 3.6 c.p.s. (Table I). This is the magnitude of effect we would expect for compounds having *endo* configuration. Comparison of the 4a,8a-proton peak positions for unsaturated and saturated epoxides reveals that, upon hydrogenation, the resonance has moved upfield (Table III). From these results we conclude that all the methano bridge compounds have *endo* configuration.

TABLE III

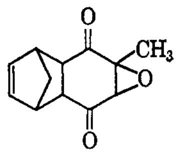
CHANGE IN PEAK POSITION ($\Delta\tau$) ON HYDROGENATION

Compd.	4a,8a-H	4a-CH
10a → **12a**	0.31	
10b → **12b**	0.37	
10d → **12d**	0.23	0.20
11a → **13a**	0.12	
11b → **13b**	0.07	

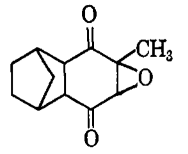
The assignment of the methyl resonances in the adducts from dimethyl-*p*-benzoquinone follows from peak positions in **8b** and **10b**. The methyl group appears as a doublet at 8.08 in **8b**. In **10b** the singlet due to the methyl is at 8.53. In the corresponding saturated epoxide **12b** it is at 8.48. One methyl group appears as a doublet at 8.05, the 2-methyl in the 2,4a-dimethyl analog of **8b**. The 4a-methyl comes at 8.52. The 2,4a-dimethyl epoxide **10d** has methyl resonances at 8.37 and 8.52. On the basis of the spectra of **10b** the peak at 8.52 was assigned to the 2-methyl, leaving the 4a-methyl at 8.37. The saturated 2,4a-dimethyl epoxide **12d** displays singlets at 8.48 and 8.57. The peak at 8.48 was assigned to the 2-methyl group. The 4a-methyl protons are those at 8.57. As in the case of the 4a,8a-protons, the reduction of the double bond causes a diamagnetic shift of the methyl resonance, 8.37 to 8.57.



8b



10b

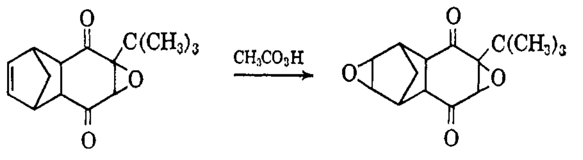


12b

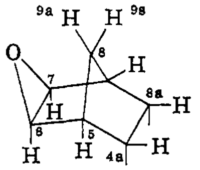
Those compounds derived from 1,3-cyclohexadiene are assumed to have the *endo* configuration also. As noted earlier, the spectra of the enedione **9a** and 2-thioether enedione **15a** are so similar that they must have the same stereochemistry. The epoxide **11a** has the same configuration as **15a**. The reduction of **11a** to the saturated epoxide **13a** results in an upfield shift of the 4a,8a-protons from 6.72 to 6.84. The magnitude of this change is too small to definitely assign the configuration of the compounds. Probably the ethano bridge compounds have the same stereochemistry (*endo*) as their analogs derived from cyclopentadiene.

Comparison of the spectra of 2,3-epoxides (**10a, b,** and **d,** and **11a** and **b**) and saturated 2,3-epoxides (**12a, b,** and **d,** and **13a** and **b**) reveals a broadening of the peaks due to 4a,8a-protons on going to the saturated compound. This may be due to long-range coupling between the 4a,8a- and *exo* 6,7-protons.

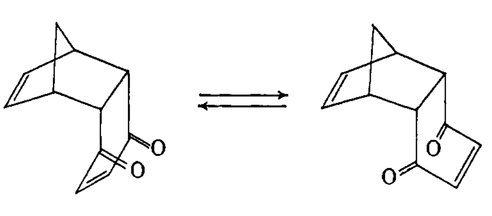
The reaction of epoxide **10c** and peracetic acid gave the diepoxide **20**. A similar diepoxide was prepared from cyclopentadienequinone epoxide (**10a**) but was too insoluble for n.m.r. analysis. The 6,7-protons appear as a broadened singlet at 6.89, indicating they are *endo*. The peak has a half-height width of 1.5 c.p.s. Both $J_{5,6}$ and $J_{6,9s}$ may contribute to the broadening. The bridge protons appear as two pairs of multiplets. The difference in chemical shift is about 48 c.p.s. with a coupling constant of 10.5 c.p.s. between the geminal protons. The large difference in chemical shift is due to the proximity of the *exo*-epoxide oxygen to one of the methylene protons. Similar observations have been reported by Tori, *et al.*[22] The *anti* proton (9a) was assigned the peaks at 8.51, whereas the *syn* proton (9s) was at 9.31. The small, long-range coupling between the 9s- and 6,7-protons is consistent with the previous assignment of the splitting of the 4a,8a-proton resonance to $J_{4a,5}$ rather than $J_{4a,9a}$.



10c **20**



The configuration at the 4a,8a-positions in the compounds studied is *endo*. Examination of molecular models indicates that there is little or no constraint to the motion of the enedione system just formulated.



However, the compound may not be best represented by an equilibrium between two conformers. It may have a planar enedione ring (**1a**), which is stabilized by π overlap. An attempt to slow down the possible equilibration was unsuccessful. The n.m.r. spectrum of the enedione in deuteriochloroform at −60° was not significantly different from that at room temperature.

The epoxidation with basic hydrogen peroxide proceeded readily to give a high yield of one compound. This was true with R being H, CH_3, *i*-Pr, or *t*-Bu. When R = H, a reaction time of 0.5 hr. at 0–5° re-

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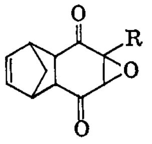
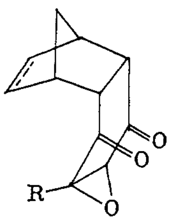
[22] K. Tori, K. Kitahonki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Letters*, 559 (1964).

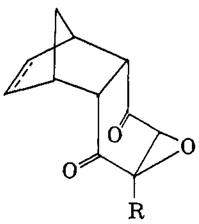


sulted in a 90% yield of product.[13] When R = *t*-Bu, after 30 min., the reaction product was about 50% epoxide and 50% starting material.

The active intermediate in this reaction is the hydrogen peroxide anion, OOH^-.[23,24] It could be argued that a frontside attack would be favored sterically. Another means of epoxidizing α,β-unsaturated ketones is with *t*-butyl hydroperoxide and Triton-B.[25] The suggested intermediate in this case is the *t*-butyl hydroperoxide anion. Reaction of cyclopentadienequinones **10a** and **10b** with *t*-butyl hydroperoxide gave the epoxides **12a** and **12b**, respectively. These materials were identical with those prepared with hydrogen peroxide. The *t*-butyl hydroperoxide anion should attack preferentially from the front to give *exo*-epoxide.



A



B

The *exo*-epoxide may exist as one of two conformers (A or B) or as a mixture of both. The n.m.r. spectra of **10a** (R = H), **10b** (R = CH_3), and **10c** (R = *t*-Bu) are very similar, indicating that the size of R does not affect the distribution of conformers. The spectra of **12a** (R = H) and **12b** (R = CH_3) are also similar. Catlin models show steric crowding in conformer A for R = CH_3 and *t*-Bu, whether the double bond is present or not. The n.m.r. spectrum of **10a** in deuteriochloroform at −60° was little altered from that at room temperature. The spectra in dichlorobenzene at 35 and 135° were not significantly different. These data favor conformer B as the major or only species.

Attempts to isomerize the 2,3-epoxide (**10a**) were unsuccessful. Heating at 170° (m.p. 120°) for 3 hr. resulted in some tarring. However, 72% starting material was recovered. No isomeric product was found. These conditions are similar to those used to convert *endo-cis*-norbornene-2,3-dicarboxylic acid to the *exo* isomer.[26,27]

The 2,3-epoxide (**10a**) was treated with sodium carbonate in D_2O–dioxane under nitrogen at 25°. After 35 min., the epoxide was recovered. The n.m.r. indicated a decrease in the intensity of the peak at 6.55 (4a,8a-H). No isomers were evident. The mass spectrum of **10a** showed *m/e* peaks corresponding to $C_5H_6^+$ (66) and $C_6H_4O_3^+$ (124). These are probably due to cyclopentadiene and *p*-benzoquinone epoxide, respectively.[12] The spectrum of the deuterated material showed increases in intensity at *m/e* 125 and 126. From the relative intensities at *m/e* 124, 125, and 126 it was estimated that 60% of the sample was undeuterated, 30% monodeuterated, and 10% dideuterated. The reaction was repeated for 20 hr. The mass spectrum indicated the product was 95% deuterated in the 4a,8a-positions. The n.m.r. spectra showed no evidence of isomeric products.

A similar experiment with epoxide **11a** yielded material which was 98% undeuterated, 1.5% monodeuterated, and 0.5% dideuterated. A competition experiment between **10a** and **11a** was performed in D_2O–dioxane with potassium carbonate at 43–45°. Analysis by mass spectra indicated the distribution of the deuterium shown in Table IV.

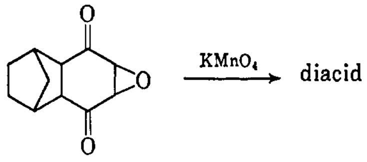
TABLE IV
DEUTERIUM DISTRIBUTION IN THE UNSUBSTITUTED 2,3-EPOXIDES

Compd.	H_2	HD	D_2
10a	71	25	4
11a	88	12	0.3

The saturated epoxide **12a** in D_2O–dioxane with sodium carbonate for 4 hr. at 25° gave a product with deuterium exclusively at the 4a,8a-positions. The material was 40% monodeuterated and 8% dideuterated. It had the same configuration as the starting epoxide. No peaks attributable to isomers were apparent in the n.m.r. spectrum.

The incorporation of deuterium into the 4a,8a-positions under alkaline conditions reveals that enolization occurs readily in these epoxides. The product retains the *endo* configuration, although this is the less stable isomer. The double bond has no effect on the steric course. Protonation to give retention of configuration is favored by the steric demands of the system.

Oxidation of the epoxide appeared to offer an alternative route to establishing the configuration of the compounds. Acidic or neutral potassium permanganate oxidized the saturated 2,3-epoxide **12a** to a diacid. The acid was converted to its dimethyl ester. Comparison of the diester with authentic samples of dimethyl *exo*- and *endo-cis*-norbornene-2,3-dicarboxylate[28]



12a

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[23] C. A. Bunton and G. J. Minkoff, *J. Chem. Soc.*, 665 (1949).

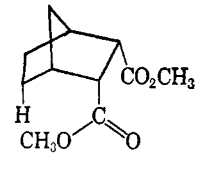
[24] H. E. Zimmerman, L. Singer, and B. S. Thyagarajan, *J. Am. Chem. Soc.*, **81**, 108 (1959).

[25] N. C. Yang and R. A. Finnegan, *ibid.*, **80**, 5845 (1958).

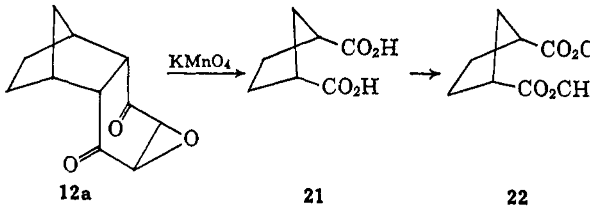
[26] D. Craig, *ibid.*, **73**, 4889 (1951).

[27] Recently, M. J. Youngquist, of these research laboratories, has found that compounds **10a**, **10b**, and the analogous 2-phenyl derivative may be thermally isomerized at approximately 220° to their *exo* isomers. The n.m.r. spectra of these compounds show $J_{4a,9a} \sim 2$ c.p.s., $J_{4,5} < 1$ c.p.s.

[28] The mass spectra of the dimethyl *exo*- and *endo-cis*-norbornene-2,3-dicarboxylate differed significantly. Both compounds show peaks at *m/e* 181 (M − 31), 153, and 59. The *endo* isomer also displays strong *m/e* peaks at 180 and 152. The *m/e* 181 is due to the loss of OCH_3 and that at 153 to the loss of CO_2CH_3. In the *endo* isomer, $HOCH_3$ and HCO_2CH_3 are major fragments also. This pattern may be explained by assuming that the proton abstracted is the *endo* 5-H.



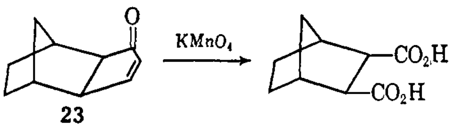
showed it to be neither. The n.m.r. spectrum had a singlet at 6.32 (area 3), multiplets at 7.17 (area 1), 7.71 (area 1), and 7.98 (area 2). The mass spectrum showed *m/e* peaks at 155 (M −31), 154, 127, 126, and 59. The dimethyl ester has a molecular weight of 186. The analytical data are correct for a formula of $C_9H_{14}O_4$. The compound has six methyl ester protons, two methine protons, and two kinds of methylene protons (2 to 4). The compound is dimethyl cyclopentane-1,3-dicarboxylate (**22**) and the oxidation product is cyclopentane-1,3-dicarboxylic acid (**21**).



12a **21** **22**

Authentic *endo-cis*-norbornane-2,3-dicarboxylic acid was subjected to the acidic potassium permanganate conditions used on **12a**. The diacid recovered had an infrared spectrum similar to that of the material identified as cyclopentane-1,3-dicarboxylic acid (**21**). The dimethyl ester was prepared and its infrared spectrum was the same as that of **22**. Apparently, the epoxide **12a** could have been oxidized to the desired diacid and then to **21**.

Bartlett prepared *exo-cis*-norbornane-2,3-dicarboxylic acid by the neutral permanganate oxidation of



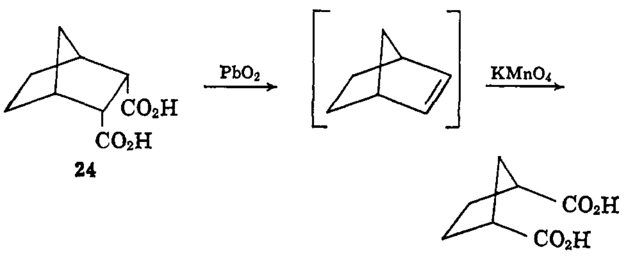
23

compound **23**.[29] The oxidation conditions used by Bartlett were permanganate in acetone at room temperature for 2 hr. The *endo-cis*-norbornane-2,3-dicarboxylic acid was oxidized under comparable conditions. After 2 hr., the unreacted permanganate was destroyed and the isolated acid was converted to its dimethyl ester. Gas chromatographic examination of the ester revealed it to be 15% dimethyl cyclopentane-1,3-dicarboxylate, 70% dimethyl *endo-cis*-norbornane-2,3-dicarboxylate, and 15% unknown.

Since the *endo-cis*-norbornane-2,3-dicarboxylic acid is somewhat stable to these conditions, the saturated epoxide **12a** was oxidized by the same procedure. Some epoxide was recovered (56%). The isolated product was cyclopentane-1,3-dicarboxylic acid, 49% yield based on unrecovered epoxide. The oxidation does not give the norbornane diacid first.

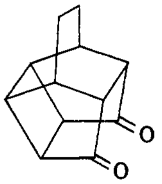
The oxidation of *endo-cis*-norbornane-2,3-dicarboxylic acid, compound **24**, was unexpected. The only similar reaction reported is the decarboxylation of **24** with lead dioxide to give unisolated norbornene.[30] The product was oxidized with permanganate to give compound **21**.

The recent interest in the photoisomerization of the adduct of 1,3-cyclohexadiene and *p*-benzoquinone,[31]

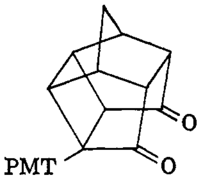


24 **21**

which is analogous to the work of Cookson,[9] prompts us to record our observations. Three enediones **8a**, **9a**, and **14a** were irradiated in solution. The properties of the photoisomer of **8a** obtained by us were consistent with the data reported for **3**.[9] The isomer of **9a** was assigned the structure **22**, and **23** was derived from **14a**. The physical and spectral



22



23

properties of **3** and **22** are similar. Both crystallized as white needles from acetone. They show saturated carbonyls in their infrared spectra, and only secondary and tertiary saturated protons in their n.m.r. spectra. The substituted "cage" compound **23** has a saturated carbonyl in the infrared spectrum. The substitution lowered its melting point to 125° compared to 238° for **3** and 248° for **22**.

Experimental

N.m.r. spectra were measured with a Varian 60-Mc. high-resolution spectrometer, Model V-4302, equipped with a field homogeneity control, or a Varian A-60 spectrometer. Peak positions are expressed in parts per million relative to an internal tetramethylsilane standard (taken as τ 10). The audio sideband method of calibration was used. The standard deviation of the determination of peak positions is 0.9 c.p.s.

All melting and boiling points are uncorrected. Infrared spectra were obtained with Baird Models AK-1 or NK-1 or Perkin-Elmer Infracord Model 137 double-beam recording spectrophotometers with sodium chloride optics. Samples were examined as KBr pressings.

Diels–Alder Adducts of Cyclopenta- and -hexadienes with *p*-Benzoquinones.—The yellow enediones were prepared from the appropriate cyclic diene and *p*-benzoquinone by the method of Albrecht,[1] and of Diels and Alder.[2]

2,3-Epoxides of Diels–Alder Adducts.—The conjugated double bond of the Diels–Alder adducts was epoxidized by the method of Alder.[12]

Reduction of the 2,3-Epoxides of Diels–Alder Adducts.—The 2,3-epoxides were hydrogenated by using Raney nickel catalyst in ethyl acetate.[13]

2-Thioether-Substituted Diels–Alder Adducts.—The reaction of 1-phenyl-5-mercaptotetrazole with the 2,3-epoxides was conducted following the method mentioned above.[13]

Diepoxide of 2-*t*-Butyl-5,8-methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone.—2-*t*-Butyl-5,8-methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 2,3-epoxide (**10c**, 2.5 g., 0.01 mole) was added to a solution of 12 ml. of glacial acetic acid, 12 ml. of acetic anhydride, and 3 ml. of 30% hydrogen peroxide. The reaction mixture was warmed for 1 hr. at 80° and poured into 200 g. of ice, and the solid was collected. The crude diepoxide (**20**) was crystallized from ethanol: m.p. 181–182°, 2.1 g. The infrared spectrum showed a band at 1705 cm.$^{-1}$.

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[29] P. D. Bartlett and A. Schneider, *J. Am. Chem. Soc.*, **68**, 6 (1946).

[30] W. v. E. Doering, M. Farber, and A. Sayigh, *ibid.*, **74**, 4370 (1952).

[31] D. Valentine, N. J. Turro, Jr., and G. S. Hammond, *ibid.*, **86**, 5203 (1964).

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 68.7; H, 6.9. Found: C, 69.0; H, 7.2.

Reaction of *t*-Butyl Hydroperoxide with Diels–Alder Adducts.—A modification of the procedure of Yang[25] was used to epoxidize 5,8-methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (**8a**) and 2-methyl-5,8-methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone (**8b**).

A solution of 4.7 g. of **8b** (0.025 mole) in 20 ml. of benzene under nitrogen was cooled to 15°. *t*-Butyl hydroperoxide (2.75 ml., 0.025 mole) was added to the stirred solution, followed by 0.36 g. of Triton-B (0.0007 mole). The reaction mixture became dark brown. It was allowed to come to room temperature overnight. Water was added, and the layers were separated. The aqueous solution was extracted with ether. The organic portions were combined and dried over anhydrous magnesium sulfate. The organic solvent was removed under reduced pressure, leaving a yellow solid which was crystallized from ethanol, giving white crystals, m.p. 136–138°, 2.0 g. Approximately 1.8 g. of the starting enedione was recovered. The yield was 60% based on unrecovered starting material. The product was identical in melting point and infrared spectrum with the epoxide **10b** prepared by Alder's method.[12]

Enedione **8a** was converted to an epoxide by the same procedure. It was identical in melting point and infrared spectrum with **10a**.

Attempted Thermal Isomerization of 5,8-Methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 2,3-Epoxide (10a).—Three grams of epoxide **10a** was heated for 3 hr. at 170°. The tarry residue was cooled and crystallized from ethanol. A white solid identical with the starting epoxide was recovered: 2.15 g., yield 72%.

Deuteration of 5,8-Methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 2,3-Epoxide (10a) and 5,8-Ethano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 2,3-Epoxide (11a).—A solution of 1.80 g. of 5,8-methano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 2,3-epoxide (**10a**) (0.01 mole), m.p. 118–119°, in 30 ml. of *p*-dioxane was added to a stirred solution of 1.05 g. of anhydrous sodium carbonate in 10 ml. of 99% D_2O under a nitrogen atmosphere at room temperature. The reaction mixture was stirred for 35 min., then added to 200 ml. of ice–water. The cloudy mixture was neutralized with a few drops of acetic acid. The mixture was extracted with ether immediately. The ether was dried over anhydrous magnesium sulfate and removed on the rotary film evaporator. The white residue was crystallized from ethanol: m.p. 118–119°, 1.68 g.

Comparison of the infrared spectra of the reactant and the product indicated a decrease in the intensity of the band at 2900 cm.$^{-1}$. New bands were observed at 1290, 1210, 1046, 990, 957, 780, 758, and 752 cm.$^{-1}$. The n.m.r. spectrum of the product was identical with that of the reactant, except for the decreased intensity of the peaks centered at 6.55. The mass spectrum of the reactant displayed *m/e* peaks at 66 and 124. The product had *m/e* 66, 124, 125, 126. The ratios of these *m/e* peaks indicate that the product is ~60% $C_{11}H_{10}O_3$, ~30% $C_{11}H_9DO_3$, and ~10% $C_{11}H_8D_2O_3$.

The reaction was repeated for 20 hr. The product was a white crystalline solid, m.p. 115–117°, 96% yield. The mass spectrum had peaks of *m/e* at 192, 126, 124, and 66. The peak at *m/e* 190 was too small to measure. The ratio of *m/e* 126 to 124 was 700 to 27. The n.m.r. spectrum had no band at 6.55 and the multiplet at 6.68 appeared as a quintet. No new peaks appeared in the spectrum.

A similar experiment was carried out with 0.96 g. of 5,8-ethano-4a,5,8,8a-tetrahydro-1,4-naphthoquinone 2,3-epoxide (**11a**), m.p. 138–139°. The white crystalline solid, m.p. 137.5–139°, 0.81 g., isolated differed little in its infrared spectrum from that of the reactant. The mass spectrum of the product had *m/e* peaks at 206, 205, and 204 (parent peak). The ratio of these peaks showed that the product was ~98% $C_{12}H_{12}O_3$, ~1.5% $C_{12}H_{11}DO_3$, and ~0.5% $C_{12}H_{10}D_2O_3$.

A mixture of 0.96 g. of **10a** (0.0051 mole) and 1.02 g. of **11a** (0.0050 mole) was dissolved in ether. The ether was evaporated and the residue was ground up. A sample was taken to represent the starting mixture. The remaining material, 1.50 g., was dissolved in 30 ml. of *p*-dioxane and added to a stirred solution of 1.05 g. of anhydrous sodium carbonate in 10 ml. of 99% D_2O under nitrogen at 43–45° for 45 min.

The reaction mixture was treated as before, leaving a white solid after ether evaporation; 1.46 g. The mass spectra of the reactant and product mixtures were obtained. Inspection of the *m/e* peaks at 206, 205, 204, and 124, 125, 126 allowed estimation of the relative amounts of deuteration. The mass spectrum of **11a** did not have *m/e* peaks at 124, 125, or 126. The estimated species present were $C_{12}H_{10}D_2O_3$ 0.3%, $C_{12}H_{11}DO_3$ 12%, $C_{12}H_{12}O_3$ 88%, and $C_{11}H_8D_2O_3$ 4%, $C_{11}H_9DO_3$ 25%, $C_{11}H_{10}O_3$ 71%.

Deuteration of 5,8-Methano-4a,5,6,7,8,8a-hexahydro-1,4-naphthoquinone 2,3-Epoxide (12a).—A solution of 1.90 g. of epoxide (0.01 mole), m.p. 110–111°, in 30 ml. of *p*-dioxane was added to a stirred solution of 1.05 g. of anhydrous sodium carbonate in 10 ml. of 99% D_2O under nitrogen at room temperature. The reaction mixture immediately became violet. After 4 hr., the violet solution was treated as described earlier. The product was a white crystalline solid, m.p. 106–108°, 1.69 g.

The infrared spectrum displayed bands not present in the reactant at 2150, 1275, 1120, 1065, 985, 935, and 745 cm.$^{-1}$. The n.m.r. spectrum of the product was the same as that of the reactant except for the decreased intensity of the multiplet centered at 6.86. The mass spectrum of the starting material had a parent peak at *m/e* 192. The product showed additional peaks at *m/e* 194 and 193. The ratio of these peaks showed that the product was 52% $C_{11}H_{12}O_3$, 40% $C_{11}H_{11}DO_3$, and 8% $C_{11}H_{10}D_2O_3$.

Reaction of Neutral Potassium Permanganate and 5,8-Methano-4a,5,6,7,8,8a-hexahydro-1,4-naphthoquinone 2,3-Epoxide (12a).—A solution of 8.0 g. of potassium permanganate (0.05 mole) in 200 ml. of water was treated with 2.5 g. of 5,8-methano-4a,5,6,7,8,8a-hexahydro-1,4-naphthoquinone 2,3-epoxide (**12a**, 0.013 mole). The stirred mixture slowly turned brown. After 3 hr., a spot test for unreacted permanganate was negative. An additional 2.0 g. of permanganate in 50 ml. of water was added. The mixture was stirred overnight. The manganese dioxide was then collected and washed with water. The filtrate was acidified and reduced in volume to yield a pale yellow solid, m.p. 96–105°, 1.2 g. The infrared spectrum of the products displayed a broad band from 3100 to 2600 cm.$^{-1}$ and a strong one at 1700 cm.$^{-1}$.

A sample of *endo–cis*-norbornane-2,3-dicarboxylic acid,[2,29] m.p. 164–166°, was prepared by hydrolysis of the corresponding anhydride.[32] *exo-cis*-Norbornane-2,3-dicarboxylic acid,[29] m.p. 151–152.5°, was prepared by hydrolysis of the *exo*-anhydride.[27,29] The infrared spectra of the authentic diacids differ from that of the oxidation product.

The oxidation product was dissolved in 50 ml. of methanol. To this cooled solution, 5 ml. of concentrated sulfuric acid was added slowly. The reaction mixture was refluxed for 2 hr., then cooled at room temperature. The methanol was partially removed under reduced pressure. The concentrate was treated with 10% sodium carbonate solution, then extracted with ether. The ether was dried over anhydrous magnesium sulfate and removed under reduced pressure. The remaining liquid had an ester odor. The infrared spectrum had bands at 2980 and 1750 cm.$^{-1}$. The n.m.r. spectrum had multiplets at 7.98, 7.71, and 7.17 and a singlet at 6.32. The areas were 2:1:1:3, respectively. The mass spectrum showed *m/e* peaks at 155 (M − 31), 154, 127, 126, and 59. The indicated molecular weight was 186. From these data the ester was identified as dimethyl cyclopentane-1,3-carboxylate.

Anal. Calcd. for $C_9H_{14}O_4$: C, 58.05; H, 7.58. Found: C, 58.8; H, 8.0, 7.9.

Dimethyl *endo-cis*-norbornane-2,3-dicarboxylate,[33,34] m.p. 51–54°, was prepared by esterification of the *endo-cis*-anhydride in refluxing methanol with *p*-toluenesulfonic acid. The infrared spectrum showed a carbonyl band at 1745 cm.$^{-1}$. The n.m.r. spectrum showed methylene protons as multiplets at 8.61, 8.27, and 8.15, with a total area 6. The methine protons are at 7.56 and 7.03, each of area 2, and the methyl protons at 6.35, of area 6. The mass spectrum displayed *m/e* peaks at 181 (M − 31), 180, 153, 152, and 59.

Dimethyl *exo-cis*-norbornane-2,3-dicarboxylate[33-35] was prepared by esterification of the *exo-cis*-diacid in refluxing methanol with sulfuric acid. The n.m.r. spectrum has multiplets due to the methylene protons at 8.62 and 7.98, with a total area 6. The methine protons are at 7.41 and 7.26, and the methyl groups at 6.46. The mass spectrum has *m/e* peaks at 181 (M − 31), 153, and 59.

Gas chromatographic analysis of the three esters was per-

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formed by means of a 6-ft. silicone gum rubber column, temperature programmed from 100° at 10°/min. Dimethyl cyclopentane-1,3-dicarboxylate had a retention time of 8.5 min. Both norbornane diesters had retention times of 10.5 min.

Reaction of Acidic Potassium Permanganate and 5,8-Methano-4a,5,6,7,8,8a-hexahydro-1,4-naphthoquinone 2,3-Epoxide (12a).—A solution of 10 ml. of concentrated sulfuric acid and 100 ml. of water was cooled to room temperature and 2.5 g. of **12a**, followed by 8.0 g. of potassium permanganate, was added. The reaction mixture was stirred for 2 hr., then warmed on a steam bath for 20 min. Sodium bisulfite was added, and the resulting yellow solution was extracted with ether. The ether was dried with anhydrous magnesium sulfate, then removed on a rotary evaporator. The residual oil was esterified with 50 ml. of methanol and 5 ml. of sulfuric acid. The mixture was refluxed for 1.5 hr., the methanol was then removed, and the residue was treated with 10% sodium carbonate. After ether extraction the ether solution was dried, and the ether was removed. The resulting liquid had the same infrared spectrum as that of the ester obtained from neutral oxidation.

Reaction of Acidic Potassium Permanganate and *endo-cis*-Norbornane-2,3-dicarboxylic Acid.—A solution of 2 ml. of concentrated sulfuric acid and 20 ml. of water was cooled to room temperature and 0.25 g. of *endo-cis*-norbornane-2,3-dicarboxylic acid (0.0014 mole) was added. To this mixture was added 1.8 g. of potassium permanganate. It was stirred for 2 hr., then warmed on a steam bath. After cooling, sodium bisulfite was added, and the solution was extracted with ether. The ether was washed with water and dried with anhydrous magnesium sulfate, then removed on a rotary evaporator. The residual oil solidified; 0.15 g. The product was dissolved in a cold solution of 2 ml. of sulfuric acid and 25 ml. of methanol. The mixture was refluxed overnight and treated as described earlier. The product was a pale yellow liquid, 0.15 g. The infrared spectrum was nearly the same as that of dimethyl cyclopentane-1,3-dicarboxylate. Gas chromatographic analysis showed the liquid to be 70% dimethyl cyclopentane-1,3-dicarboxylate plus three other components.

Reaction of Neutral Potassium Permanganate and *endo-cis*-Norbornane-2,3-dicarboxylic Acid.—The procedure followed was adapted from that of Bartlett.[28] A solution of 0.40 g. of *endo-cis*-norbornane-2,3-dicarboxylic acid (0.002 mole) in 8 ml. of acetone was treated with 2.1 g. of potassium permanganate. After 2 hr., 3 ml. of water was added, and the mixture was filtered. The solution was acidified and treated with sodium bisulfite. The acetone was evaporated, and the remaining aqueous solution was extracted with ether. The ether was dried over magnesium sulfate and removed under reduced pressure, leaving a white solid, which was recrystallized from benzene: m.p. 118–121°, 0.32 g.

The diacid was converted to its dimethyl ester by the same procedure used above. The resulting liquid, 0.30 g., displayed a carbonyl band at 1745 cm.$^{-1}$ with a shoulder at 1750 cm.$^{-1}$. Gas chromatographic analysis, with a 6-ft. silicone gum rubber column, whose temperature was programmed from 100° at 10°/min., showed three peaks. Their retention times corresponded to dimethyl cyclopentane-1,3-dicarboxylate (8.5 min.) 15%, dimethyl *endo-cis*-norbornane-2,3-dicarboxylate (10.5 min.) 70% and an unknown (11.0 min.) 15%.

Reaction of Neutral Potassium Permanganate with 5,8-Methano-4a,5,6,7,8,8a-hexahydro-1,4-naphthoquinone 2,3-Epoxide (12a).—A solution of 3.80 g. of epoxide (0.02 mole) in 60 ml. of acetone was stirred and cooled in a water bath, while 16 g. of potassium permanganate was added in small portions. After 6 hr., the mixture was filtered. The filtrate was cooled in ice, acidified, and treated with aqueous sodium bisulfite. The resulting solution was extracted with ether. The ether extracts were washed with sodium bicarbonate solution and water, dried over magnesium sulfate, and removed under reduced pressure. The resulting pale yellow solid, 2.17 g., m.p. 105–107°, 56% yield, had an infrared spectrum essentially the same as that of the reactant.

The bicarbonate solution was acidified and extracted with ether. The ether was washed with water, dried with magnesium sulfate, and removed on the rotary evaporator. The resulting oil solidified: 0.62 g., a 49% yield, based on unrecovered starting material. It was recrystallized from benzene: m.p. 116–118°. The infrared spectrum was identical with that of the diacid identified as above as cyclopentane-1,3-dicarboxylic acid.

Photoisomerization of Diels–Alder Adducts of *p*-Benzoquinones.—A cooled solution (10–15°) of 5,8-ethano-4a,5,8,8a-tetrahydronaphtho-1,4-quinone (**9a**, 1.50 g., 0.008 mole) and 250 ml. of *n*-hexane in a Pyrex flask was irradiated for 1 day with a GE Type RS sunlamp. The procedure was adapted from that of Cookson[9] for 5,8-methano-4a,5,8,8a-tetrahydronaphtho-1,4-quinone (**8a**). The solvent was removed to give an off-white solid. Crystallization twice from acetone gave white needles, m.p. 248–250°, 0.62 g. The infrared spectrum had maxima at 3000, 2950, 2895, 1757, 1730, 1260, 1240, 1200, 1130, 1055, 930, 908, 848, and 755 cm.$^{-1}$. The n.m.r. spectrum ($CDCl_3$) showed multiplets at 6.93 (area 4), 7.48 (area 2), 7.90 (area 2), and 8.17 (area 4). The ultraviolet spectrum in ethanol had λ_{max} 302 mμ (ϵ 48).

Anal. Calcd. for $C_{12}H_{12}O_2$: C, 76.6; H, 6.4. Found: C, 76.8; H, 6.5.

A similar procedure was utilized for 2-(1-phenyl-5-tetrazolylthio)-5,8-methano-4a,5,8,8a-tetrahydronaphtho-1,4-quinone (**14a**). The solvent was chloroform–*n*-hexane (1:1). The product was crystallized three times from acetone to give a white solid, m.p. 125–127°, 38% yield. The infrared spectrum had bands at 3250, 3000, 2950, 2895, and 1740 cm.$^{-1}$. The material was too insoluble for n.m.r. analysis except in methyl sulfoxide which obscures the region of interest.

Anal. Calcd. for $C_{18}H_{14}N_4O_2S$: C, 61.7; H, 4.0; N, 16.0; S, 9.2. Found: C, 61.7; H, 4.0; N, 16.3; S, 9.1.

A sample of the material described by Cookson[9] was prepared from 5,8-methano-4a,5,8,8a-tetrahydronaphtho-1,4-quinone (**8a**). The n.m.r. spectrum of the white needles, m.p. 238–240°, consists of five multiplets of equal area at 6.84, 7.00, 7.13, 7.25, and 8.00. The infrared and ultraviolet spectra are consistent with the literature data.[9]

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