Independent Synthesis of II, $R = CH_3$, $R' = H$.—4-Methyltetralone[23] was converted to the corresponding hydroxymethylene derivative XII which was alkylated with ethyl bromoacetate as previously described[4] for 4,4-dimethyltetralone to afford methyl 4-methyl-1-tetralone-2-acetate (II, $R = CH_3$, $R' = H$) as a colorless oil, b.p. 129–135° (0.5–0.6 mm.), $n^{20}D$ 1.5576.

The 2,4-dinitrophenylhydrazone crystallized from ethanol-ethyl acetate as a red powder, m.p. 175–178° dec. The ultraviolet (λ_{max} 380 mμ, log ϵ 4.43) and infrared absorption spectra were superimposable on those from the ester separated by chromatography from the reaction between allylsuccinic anhydride and benzene.

ITHACA, NEW YORK

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[23] Prepared from benzene and γ-valerolactone by the procedure described for 1-tetralone; C. E. Olson and A. R. Bader, *Org. Syntheses*, **35**, 96 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

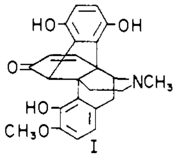
The Synthesis and Rearrangement of Some Benzonorbornenes[1a,1b]

BY J. MEINWALD AND G. A. WILEY[2]

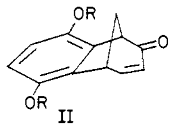
RECEIVED FEBRUARY 4, 1958

Techniques for the transformation of cyclopentadiene-quinone (VII) into 3',6'-diacetoxybenzonorbornadiene (VIIIa), 3',6'-dihydroxybenzonorbornadiene (VIIIb) and 3',6'-dimethoxybenzonorbornadiene (VIIIc) are presented, and a variety of reactions of these compounds are described. *exo*-3',6'-Diacetoxybenzonorbornadiene epoxide (XIa) was found to give rearranged derivatives of the corresponding 2,7-diol under either acidic or basic conditions. The base-induced rearrangement was unusually rapid, and the formation of an intermediary nortricyclyl dienone is suggested. Potassium permanganate oxidation of VIIIa yielded *cis-exo*-3',6'-diacetoxybenzonorbornen-2,3-diol (XIVa), but lead tetraacetate oxidation of VIIIa in wet acetic acid gave rise to the rearranged 2,7-diol derivative XIIIa. *exo*-3',6'-Dimethoxybenzonorbornadiene epoxide (XIc) gave the expected rearranged 2,7-acetoxy alcohol XIIc on acetolysis. Nucleophilic opening of the epoxide ring of XIa using sodium methoxide was slow, and gave rise to a product which is assigned the unrearranged structure XXI. Sodium permanganate and lead tetraacetate oxidations of VIIIc proceeded in strict analogy to the oxidations of VIIIa described above. A group of other transformation products of the above-mentioned compounds were prepared and characterized, of which the most interesting is probably *exo*-3',6'-dimethoxybenzonorbornen-2-ol (XX), produced by lithium aluminum hydride reduction of XIc.

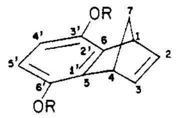
Recent studies of the chemistry of flavothebaone have led to the assignment of structure I to this compound.[3] Although this structure is in accord with all of the chemical and most of the physical data, it fails to provide a facile rationalization of the long wave length ultraviolet absorption maximum (λ_{max} 346, log ϵ 3.56) characteristic of flavothebaone. It has been suggested that the enone chromophore interacts with the non-conjugated hydroquinone system, and that this interaction is responsible for the "abnormal" spectrum.[3b] In attempting to test this hypothesis, a synthesis of the model compound II has been undertaken.[4] Although the synthesis has not been brought to completion at this time, a number of 3',6'-disubstituted benzo-(1',2',5,6)-norbornene (III) derivatives have been prepared as possibly useful intermediates. At this moment the continuation of the synthesis from these compounds does not appear attractive. However, the chemistry of these compounds is of sufficient intrinsic interest to warrant independent treatment, and it is the purpose of the present paper to set forth some of the results of these studies.



I

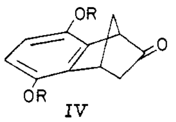


II

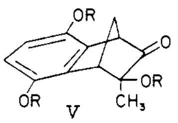


III

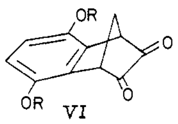
The desired key intermediates for the synthesis were compounds such as IV, V or VI, from which it is easy to imagine routes to II.



IV



V



VI

The starting material for these studies was the well known 1:1 cyclopentadiene-quinone adduct VII.[5] Early attempts to enolize VII to give derivatives of the hydroquinone VIII had been unsuccessful, presumably because of the reversibility of the initial diene addition.[5] Treatment of VII with acetic anhydride and pyridine has now been found to give the expected diacetate VIIIa in ex-

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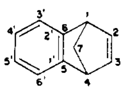
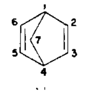
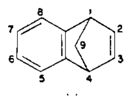
[1] (a) The ring system designated as "benzonorbornadiene" in this paper is shown below as i. The choice of this name was motivated by the authors' desire to relate this system to the parent compound norbornadiene ii, as well as to retain as simple a set of names as possible. The Ring Index would designate this system as 1,4-dihydro-1,4-methanonaphthalene, numbered as shown in iii. The authors are indebted to Mr. Leonard T. Capell for calling attention to this scheme of nomenclature. (b) See J. Meinwald, H. Nozaki and G. A. Wiley, THIS JOURNAL, **79**, 5579 (1957), for a preliminary Communication of some of the results described in this paper.



i



ii



iii

[2] Opportunity Fellow, John Hay Whitney Foundation, 1955–1956; Allied Chemical and Dye Corp. Fellow, 1956–1957.

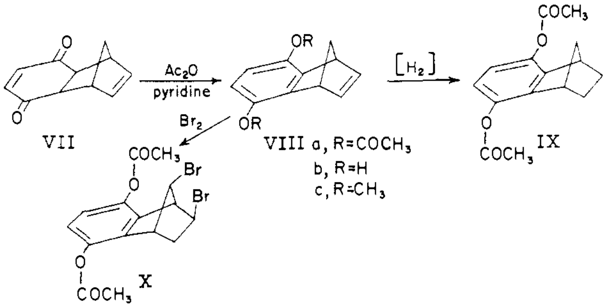
[3] (a) J. Meinwald and G. Wiley, *Chemistry & Industry*, 957 (1956); (b) J. Meinwald and G. Wiley, THIS JOURNAL, **79**, 2569 (1957); (c) K. W. Bentley, J. Dominguez and J. P. Ringe, *Chemistry & Industry*, 1353 (1956); (d) K. W. Bentley, J. Dominguez and J. P. Ringe, *J. Org. Chem.*, **22**, 418 (1957).

[4] A preliminary attempt to prepare the less exact model (iv) *via* a Diels–Alder reaction between tropone and benzoquinone was unsuccessful.

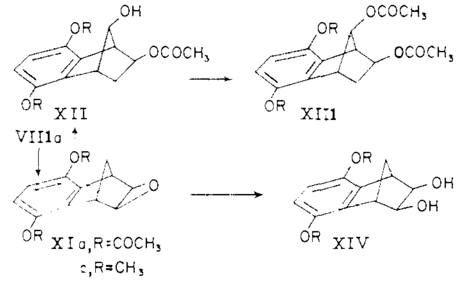
iv

[5] W. Albrecht, *Ann.*, **348**, 34 (1906); O. Diels and K. Alder, *Ber.*, **62**, 2337 (1929).

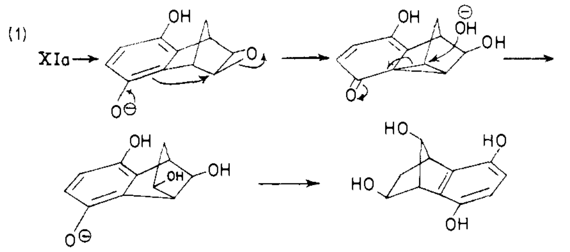
cellent yield.[6] In accord with expectation, VIIIa adds one mole of hydrogen to give IX, and one mole of bromine to give a crystalline dibromide which is probably the rearranged 2,7-dibromo compound X.



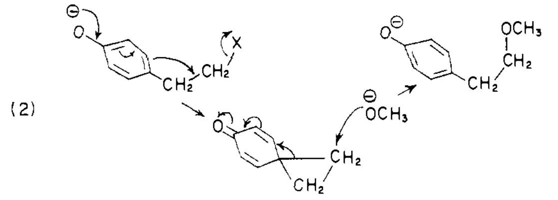
In attempting to prepare the desired intermediates, a series of oxidative experiments was carried out on VIIIa. Treatment with trifluoroperacetic or peracetic acid gave rise to the expected *exo*-epoxide XIa. Acid-catalyzed acetolysis of XIa gave a hydroxy acetate, which, in analogy to the product formed from norbornene epoxide under similar conditions,[7] is probably (XIIa) *exo-anti*-3′,6′-diacetoxybenzo-2-acetoxynorborne-7-ol. Acetylation of this product gave the completely acetylated derivative, XIIIa. These results are unexceptional; very facile rearrangement of XIa to XIIa would be expected to accompany carbonium ion formation in view of the known tendency of norbornyl systems to rearrange, coupled with the excellence of the hydroquinone ring in the role of migrating and participating group. What is much more striking is the behavior of the epoxide XIa on treatment with base. Norbornene epoxide is exceedingly resistant to nucleophilic attack,[8] and the general inertness of *exo*-norbornyl systems to such displacement reactions is well known. In the hope of simply hydrolyzing the two acetoxyl groups of XIa using aqueous base, it was found that a rearranged phenolic product was formed rapidly. This product, which could not be crystallized, *lacked the strong 11.7 μ (epoxide) band of XIa*. Upon reacetylation with acetic anhydride in pyridine it gave rise to XIIIa rather than XIa. This remarkable *base-initiated rearrangement of the norbornyl system* is without precedent, and suggests a special role for the fused hydroquinone ring. The reaction sequence shown in equation 1 would provide a ready rationalization for these observations, and finds analogy in the case of Ar_1-3 participation (equation 2) recently uncovered by Winstein and Baird.[9]



(1)

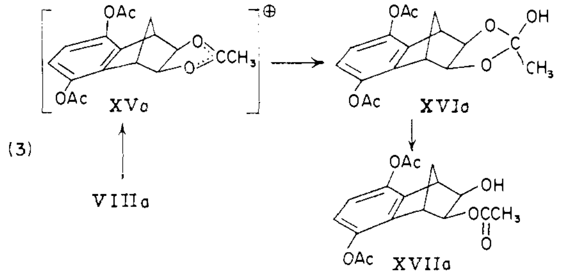


(2)



Potassium permanganate oxidation of VIIIa was difficult to control, but under some conditions gave rise to *cis-exo*-3′,6′-diacetoxybenzonorbornen-2,3-diol (XIVa) isolated as its acetate in small yield. All attempts to obtain the corresponding acyloin or diacid in one step were unrewarding. The oxidation of VIIIa by lead tetraacetate in wet acetic acid was investigated in the hope that it would proceed *via* addition of $CH_3CO_2^{\oplus}$[10] to give the bridged ion XVa and ultimately the *cis*-diol monoacetate XVIIa (see equation 3). Contrary to expectation, the product was found to be chiefly the rearranged tetraacetate XIIIa. This finding could be reconciled with the view that lead tetraacetate acts as a source of $CH_3CO_2^{\oplus}$, but would imply either that the participation of the aromatic ring competes favorably with ring closure to give XVa, or that XVa itself rearranges faster than it reacts with water to give XVIIa.

(3)



An alternate explanation of the course of the lead tetraacetate is provided by the recent work of Criegee, *et al.*, who have postulated stepwise addition of the fragments $Pb(OAc)_3^{\oplus}$ and $OAc^{\ominus}$, followed by loss of $Pb(OAc)_3^{\ominus}$ and recombination of the resultant (possibly rearranged) carbonium ion with acetate ion.[11] In the case of the olefin VIIIa,

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(6) An acid-catalyzed acetylation of VII, which proceeds in somewhat lower yields, has been reported since the completion of this work by W. R. Vaughan and M. Yoshimine, *J. Org. Chem.*, **22**, 7 (1957).

(7) H. M. Walborsky and D. F. Loncrini, This Journal, **76**, 5396 (1954); H. Kwart and W. G. Vosburgh, *ibid.*, **76**, 5400 (1954).

(8) Unpublished results with N. J. Hudak.

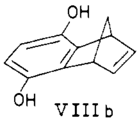
(9) S. Winstein and R. Baird, This Journal, **79**, 756 (1957).

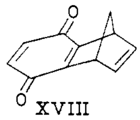
(10) W. A. Mosher and C. L. Kehr, *ibid.*, **75**, 3172 (1953); F. V. Brutcher and F. J. Vara, *ibid.*, **78**, 5695 (1956).

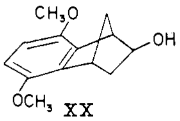
(11) R. Criegee, P. Dimroth, K. Noll, R. Simon and C. Weis, *Chem. Ber.*, **90**, 1070 (1957).

the product to be expected if the Criegee mechanism were operative would be the observed tetraacetate XIIIa.

Some of the difficulties encountered in the synthetic efforts were attributable to the hydrolytic lability of the phenolic acetate groups in VIIIa. It was decided therefore to protect the hydroquinone ring as an ether rather than as an ester. Various attempts at direct enolization and benzylation or methylation of cyclopentadienequinone (VII) were unsuccessful. However, a satisfactory indirect path to the desired 3′,6′-dimethoxybenzonorbornadiene (VIIIc) was found. Lithium aluminum hydride reduction of VIIIa gave the free hydroquinone (VIIIb), which could be methylated using dimethyl sulfate and base to give VIIIc in excellent over-all yield; VIIIb, characterized for the first time, was oxidized readily by silver oxide to the quinone XVIII, which had been prepared previously only with great difficulty.[5,6] Of the various transformations carried out on VIIIc, only those which parallel the reactions of the corresponding diacetate as described above will be presented.


VIII b


XVIII


XX

Epoxidation of VIIIc proceeded only in the presence of peracetic acid, and gave rise to mixtures of the desired epoxide XIc and the rearranged glycol monoacetate XIIc which were difficult to separate. Although this reaction was not completely satisfactory, no improvement could be developed since perbenzoic and monoperphthalic acids failed completely to react with VIIIc, while trifluoroperacetic acid invariably gave only the 2,7-diol XIX. Lithium aluminum hydride reduction of the epoxide, which is undoubtedly the *exo*-isomer from its mode of formation, yielded the corresponding *exo*-alcohol XX.[12] Acetolysis of the epoxide in the presence of *o*-toluenesulfonic acid gave the previously mentioned rearranged glycol monoacetate XIIc, as expected. The related 2,7-diol XIX and 2,7-diacetate XIIIc were prepared easily from this product.

In sharp contrast to the case of the diacetate epoxide XIa, XIc was attacked only slowly by sodium hydroxide solution, giving rise to a ketonic material of unknown structure.[13] Sodium methoxide in methanol slowly converted the epoxide into what is regarded as the normal *trans*-glycol monomethyl ether XXI.

Sodium permanganate oxidation of VIIIc gave the *cis*-*exo*-diol XIVc under carefully controlled conditions. This diol reduced periodic acid readily, in contrast to the isomeric 2,7-diol XIX mentioned above. These experiments lend support to the structural assignments. In complete analogy to the results obtained with VIIIa, VIIIc was converted into the 2,7-diacetate XIIIc by treatment with lead tetraacetate in wet acetic acid.

Further work directed toward the synthesis of II is now in progress, and should be the subject of a subsequent communication.

Experimental[14]

Cyclopentadiene-quinone (VII).—The addition of cyclopentadiene (92 g.) to *p*-benzoquinone (150 g.) as described by Albrecht[5] gave a 70% yield (169 g.) of adduct as yellow-green plates, m.p. 77–78° (lit.[5] 77–78°).

3′,6′-Diacetoxybenzonorbornadiene (VIIIa).—A 135-g. sample of VII was dissolved in 150 ml. of pyridine. Seventy-five ml. of acetic anhydride was added slowly with cooling to keep the temperature below 20°. This homogeneous reaction mixture was allowed to stand at room temperature for seven days. It was then poured into several times its volume of cold water with vigorous agitation. The crude, red-brown product was filtered and washed thoroughly with water. It was dissolved in ether and washed several times with aqueous sodium hydroxide, which removed much of the dark material. After drying the ether layer over sodium sulfate and evaporating the ether, an off-white crystalline solid remained in 94% yield. It could be recrystallized from ether as chunky, colorless prisms. For analytical purposes, it was crystallized from absolute ethanol to give colorless needles, m.p. 106.0–106.5° (lit.[6] 106°); infrared spectrum ($CHCl_3$): 5.72, 6.17, 6.30, 6.44 μ; ultraviolet spectrum: λ_{max}^{EtOH} 265 mμ (2.50) plateau, shoulder *ca.* 270 mμ.

Anal. Calcd. for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46; acetyl, 33.34. Found: C, 69.88; H, 5.55; acetyl, 32.50.

3′,6′-Diacetoxybenzonorbornene (IX).—A 118.3-mg. sample of VIIIa was hydrogenated in methanol–water solution using 10% Pd·$BaSO_4$ catalyst plus 3 ml. of 0.2% palladium chloride solution. In 45 minutes, 0.98 mole of hydrogen had been taken up. The catalyst was filtered off and the mixture extracted with benzene. The benzene solution was washed with 10% sodium hydroxide solution, dried over magnesium sulfate and the solvent evaporated. Recrystallization of the residue gave white needles, m.p. 121–122°.

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.04; H, 5.96.

***exo-anti*-2,7-Dibromo-3′,6′-diacetoxybenzonorbornene (X).**—A 5% solution of bromine in carbon tetrachloride was added to a 0.1-g. sample of VIIIa. About 25 drops were taken up rapidly. After distilling off the solvent and recrystallizing the residue from ethanol, hexagonal prisms, m.p. 153.0–153.5°, were obtained.

Anal. Calcd. for $C_{15}H_{14}O_4Br_2$: C, 43.49; H, 3.41; Br, 38.5. Found: C, 43.73; H, 3.33; Br, 38.0.

***exo*-3′,6′-Diacetoxybenzonorbornadiene Epoxide (XIa).**[15]—A solution of trifluoroperacetic acid[16] prepared from 9.0 ml. of perfluoroacetic anhydride, 1.7 ml. of 90% hydrogen peroxide and 12 ml. of methylene chloride was added dropwise to a mixture of 10.3 g. of VIIIa, 18 g. of sodium carbonate and 40 ml. of methylene chloride over a 40-minute period. The reaction mixture was refluxed and stirred for an additional 30 minutes, after which water was added to dissolve the solid material. The organic layer was separated, washed with saturated sodium bicarbonate solution, and dried over magnesium sulfate.

Evaporation of the solvent, followed by recrystallization from a mixture of methylene chloride and 30–60° petroleum

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[12] A study of the solvolysis rates of esters of this alcohol should be of particular interest in conjunction with the classical work of Winstein on the solvolysis of *exo*-norbornyl compounds (see, for example, S. Winstein and D. S. Trifan, THIS JOURNAL, **71**, 2953 (1949); **74**, 1154 (1952)). Further investigation of this alcohol is therefore planned.

[13] The relative stability of this epoxide to base supports the suggestion made above that the rearrangement of XIa in base involves a phenoxide ion intermediate, which could not be formed in the case of XIc. It is possible that the ketone derived from XIc was the desired ketone VI (R = CH_3). However, oxidation of the alcohol XX gave a *different* ketonic material. Because of the small amounts of epoxide XIc available, neither of these substances could be fully characterized.

[14] All melting points were taken on a calibrated Fisher–Johns hot-stage. Ultraviolet spectra were recorded using a Beckman ultraviolet spectrophotometer, model DK. Infrared spectra were recorded using a Perkin–Elmer double beam model 21 instrument.

[15] The authors are grateful to Dr. Hitosi Nozaki for carrying out this experiment.

[16] W. D. Emmons and A. S. Pagano, THIS JOURNAL, **77**, 89 (1955).

ether gave 4.8 g. (40%) of XIa, m.p. 103–105°; XIa crystallized as colorless cubes, m.p. 107.5–108.0°, from absolute ethanol; infrared spectrum (KBr): 5.70, 6.16, 6.30, 11.71 μ.

Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.97; H, 5.16.

Acetolysis of XIa (XIIa).—One gram of XIa was dissolved in 25 ml. of glacial acetic acid and a small crystal of *p*-toluenesulfonic acid and 1 ml. of acetic anhydride were added. The mixture was heated for 2 hours at 100° on a water-bath. After cooling, it was poured into water. On standing for two days, white crystals slowly formed. Recrystallization from absolute ethanol yielded colorless prisms, m.p. 151.3–151.8°; infrared spectrum ($CHCl_3$): 2.81, 5.71, 6.12, 6.27 μ.

Anal. Calcd. for $C_{17}H_{18}O_7$: C, 61.07; H, 5.43. Found: C, 61.21; H, 5.69.

Acetylation of XIIa (XIIIa).—A sample of XIIa was treated with acetic anhydride and pyridine in the usual way. Recrystallization of the product from absolute alcohol yielded colorless, prismatic needles, m.p. 141.5–142.0°; infrared spectrum ($CHCl_3$): 2.81, 5.67–5.77, 6.12, 6.21 μ.

Anal. Calcd. for $C_{19}H_{20}O_8$: C, 60.63; H, 5.36; acetyl, 46.7. Found: C, 60.47; H, 5.27; acetyl, 45.64.

***exo*-3',6'-Diacetoxybenzo-2-acetoxynorbornene.**—Three grams of lithium aluminum hydride was slurried in 100 ml. of dry ether with good agitation. After 0.5 hour 2.0 g. of epoxide XIa in 150 ml. of ether was added slowly. The mixture was stirred for 48 hours. Excess acetic anhydride was added followed by a little acetyl chloride. After stirring overnight the solid was filtered off and washed thoroughly with ether. The filtrate was evaporated in vacuum and the residue crystallized from absolute ethanol. Colorless needles were obtained, m.p. 120.7–121.3°; infrared spectrum (KBr): 5.69, 5.79, 6.12 μ.

Anal. Calcd. for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 64.55; H, 5.49.

Alkaline Hydrolysis of XIa.[15]—A mixture of 1.1 g. of XIa and 24 ml. of 2 *N* sodium hydroxide was refluxed in a nitrogen atmosphere for ten minutes, cooled in an ice-bath, and treated with 3.2 ml. of acetic anhydride. After dropwise addition of the anhydride the reaction mixture was diluted with water and extracted with methylene chloride. The organic extract was washed with water and sodium bicarbonate solution, and dried over magnesium sulfate. The crude product, obtained by evaporation of the methylene chloride solution, showed no 11.7 μ absorption characteristic of the epoxide grouping in the starting material. It did, however, show some hydroxylic absorption, and it was therefore reacetylated in the usual way, using pyridine and acetic anhydride. The crude acetylated product was dissolved in ethanol, decolorized with charcoal, and allowed to stand at room temperature for 10 days. During this period 0.3 g. of crystalline XIIIa, m.p. 130–132° with sintering at 103–105°, was deposited. Recrystallization from absolute ethanol gave XIIIa as colorless crystals, m.p. 137–138° with sintering at 115–117°. Cooling and remelting of the sample gave m.p. 140.0–140.5° without preliminary sintering. A mixture melting point with authentic XIIIa was undepressed (139–140°), and infrared spectra were indistinguishable.

***exo-cis*-2,3,3',6'-Tetraacetoxybenzonorbornene (XIVa.)**—A 0.5-g. sample of VIIIa was dissolved in 625 ml. of 40% (by volume) purified dioxane in water. One equivalent of potassium carbonate (0.27 g.) was added and the solution cooled to 5°. Hydrion paper indicated that the *p*H of the solution was between 8 and 9. A solution of 0.611 g. of potassium permanganate (2 molar equivalents) in 100 ml. of water was added rapidly and the solution held between 8 and 11° for 10 minutes. Sodium bisulfite was then added to decolorize the mixture, and the solution filtered. The filtrate was saturated with sodium chloride, extracted with ether, the ether layer dried over sodium sulfate and evaporated. The brown oil which remained was acetylated using acetic anhydride and pyridine in the customary manner. After recrystallization from ethanol, colorless needles, m.p. 137–138°, were obtained; infrared spectrum (KBr): 5.70, 6.15 μ as well as bands at 8.97, 10.32 and 10.43 μ which correspond to minima in the spectrum of XIIIa.

Anal. Calcd. for $C_{19}H_{20}O_8$: C, 60.63; H, 5.36. Found: C, 61.01; H, 5.27.

Lead Tetraacetate Oxidation of VIIIa.—One gram of VIIIa was dissolved in 100 ml. of glacial acetic acid which was saturated with lead tetraacetate and to which 10 ml. of water had been added. After standing for 48 hours in the dark, the mixture still oxidized starch-potassium iodide paper. It was poured into twice its volume of water containing a little oxalic acid. A white precipitate appeared. The mixture was extracted with ether and the ethereal solution washed with water and with 10% sodium hydroxide solution. After drying over sodium sulfate and boiling off solvent, a white solid was left. This material appeared, from its infrared spectrum, to be a mixture of XIIa and XIIIa (weak hydroxylic stretching frequency). It recrystallized easily from absolute ethanol as clumps of colorless needles, m.p. 110–135°. Acetylation in the usual way with acetic anhydride and pyridine gave XIIIa, identified by melting point, mixture melting point, and infrared spectrum. The over-all yield for the transformation was good.

3',6'-Dihydroxybenzonorbornadiene (VIIIb).—A sample of VIIIa was reduced with lithium aluminum hydride in the usual way, and the ethereal solution of the product dried over sodium sulfate. Upon removal of the ether, a viscous oil was obtained which crystallized (with some difficulty) from ethyl acetate-cyclohexane as colorless prisms, m.p. 144.0–144.5°; infrared spectrum ($CHCl_3$): 2.76, 2.97, 6.11, 6.21 μ.

Anal. Calcd. for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 75.82; H, 5.89.

Acetylation of VIIIb.—A sample of VIIIb was treated with excess acetic anhydride and pyridine at room temperature for 24 hours. The product was isolated in the usual way and recrystallized from absolute ethanol. Melting point, mixture melting point and infrared spectra showed the product to be identical to authentic VIIIa.

Dehydrocyclopentadiene-quinone (XVIII).—A 0.2-g. sample of VIIIb was dissolved in absolute benzene and agitated with 1 g. of dry, finely divided silver oxide plus 1 g. of sodium sulfate. The solution turned yellow almost immediately. After 0.5 hour, the mixture was filtered and the benzene evaporated. Bright yellow crystals remained in essentially quantitative yield. Recrystallization from 30–60° petroleum ether gave bright yellow prismatic rods, m.p. 66–67° (lit.[5,6] 70°); infrared spectrum ($CHCl_3$): 2.81, 3.03, 3.07, 6.01, 6.06, 6.29, 6.41 μ.

3',6'-Dimethoxybenzonorbornadiene (VIIIc).—To a slurry of 32 g. of lithium aluminum hydride in 300 ml. of anhydrous ether was added 108 g. of VIIIa in 900 ml. of ether. The mixture was stirred for 24 hours using a powerful motor (a gummy precipitate was formed). The reaction mixture was poured cautiously into 2 l. of 10% sulfuric acid and cracked ice, and extracted several times with ether. The combined ethereal solutions were washed with aqueous sodium bicarbonate followed by water, and then concentrated to a small volume. The resultant mobile oil (crude VIIIb) was added to a solution of 50.3 g. of sodium hydroxide (three times the calculated amount) in 500 ml. of water through which a stream of nitrogen previously had been bubbled. The remainder of the reaction was carried out in an atmosphere of nitrogen. The mixture was cooled to 0–5° and 157.9 g. of dimethyl sulfate (equivalent to the amount of sodium hydroxide) was added over a half-hour period with rapid stirring. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. At this point the mixture was no longer alkaline, and second portions of dimethyl sulfate and sodium hydroxide were added in half the original amounts. Stirring was continued until the alkalinity disappeared, excess 20% aqueous sodium hydroxide was added, and the mixture stirred overnight. The white precipitate which had formed in the reaction mixture was taken up in ether and dried over sodium sulfate. Evaporation of the ether gave 74.0 g. (88%) of an off-white solid. This material crystallized from acetone in stout, colorless prisms, m.p. 78.5–79.0°; infrared spectrum: 6.42 μ; ultraviolet spectrum: λ_{max}^{EtOH} 295 mμ (3.49).

Anal. Calcd. for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.31; H, 6.71.

***exo*-3',6'-Dimethoxybenzonorbornadiene Epoxide (XIc).** Five grams of VIIIc was dissolved in 50 ml. of chloroform and 12 g. of anhydrous sodium acetate was added. The mixture was cooled to 0°, and 50 ml. of 40% peracetic acid was added over a 15-minute period with vigorous stirring. Precisely at the end of an additional 1.75 hours, the reaction mixture was made alkaline with 40% sodium hydroxide solution, taking care to keep the mixture below room temperature. After the addition of more water and chloroform, the layers were separated. The chloroform solution was washed with water and dried over sodium sulfate. Evaporation of the solvent gave a mixture of epoxide and the corresponding hydroxy acetate XIIc, from which the epoxide, m.p. 119.5–120.0°, could be obtained as colorless rods by several recrystallizations from absolute ethanol; infrared spectrum ($CHCl_3$): 6.24, 11.83 μ.

Anal. Calcd. for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.56; H, 6.69.

exo-anti-**2-Acetoxy-3′,6′-dimethoxybenzonorbornen-7-ol (XIIc).**—This compound was the sole product when the peracetic acid treatment of VIIIc was allowed to proceed at room temperature for 24 hours. It crystallized from ethanol–isoöctane as powdery, white rosettes, m.p. 97.5–98.5°; infrared spectrum ($CHCl_3$): 2.81, 5.70–5.81, 6.22 μ.

Anal. Calcd. for $C_{15}H_{18}O_4$: C, 64.73; H, 6.52. Found: C, 62.05; H, 6.31.

exo-**3′,6′-Dimethoxybenzonorbornen-2-ol (XX).**—A sample of XIc was dissolved in anhydrous ether and allowed to react for 24 hours with excess lithium aluminum hydride. After working up in the usual way, the product was recrystallized from ethyl acetate–cyclohexane to yield colorless prisms, m.p. 110.5–111.0°; infrared spectrum ($CHCl_3$): 2.78, 2.91, 6.23 μ.

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.62; H, 7.52.

Acetolysis of XIc.—A 0.1-g. sample of the epoxide XIc was heated with 1 ml. of glacial acetic acid and a small crystal of *p*-toluenesulfonic acid on a water-bath for 2.5 hours. After cooling, the mixture was poured into 5% sodium carbonate solution, extracted with ether, and the ethereal solution dried over sodium sulfate. The ether was evaporated and the residue (crude XIIc) acetylated in the usual way to give the 2,7-diacetoxy compound XIIIc, as indicated by its melting point and infrared spectrum.

exo-anti-**2,7-Diacetoxy-3′,6′-dimethoxybenzonorbornene (XIIIc). A. Acetylation of XIIc.**—A sample of XIIc was dissolved in excess acetic anhydride and pyridine and allowed to stand at room temperature for 24 hours. It was worked up in the usual way and crystallized as colorless needles, m.p. 114.5–115.0° from absolute ethanol; infrared spectrum ($CHCl_3$): 5.76, 6.19 μ.

Anal. Calcd. for $C_{17}H_{18}O_6$: C, 63.74; H, 6.29. Found: C, 63.85; H, 6.15.

B. Acetylation of XIX.—The 2,7-diol XIX was acetylated and worked up as described above. The melting point and infrared spectrum were identical with those of authentic XIIIc. (The melting point became unsharp, 110–120°, after grinding, so that a mixture melting point was not useful.)

exo-anti-**3′,6′-Dimethoxybenzonorbornen-2,7-diol (XIX). A. Reductive Cleavage of XIIc.**—A sample of the hydroxy acetate XIIc was dissolved in absolute ether and excess lithium aluminum hydride solution was added. After standing for one hour, the reaction mixture was worked up in the usual way to give a product which crystallized from ethyl acetate in thick, white prisms, m.p. 147.5–148°; infrared spectrum ($CHCl_3$): 2.84 (broad), 6.20 μ. The yield was nearly quantitative.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 65.92; H, 6.92.

B. Reductive Cleavage of XIIIc.—Lithium aluminum hydride reduction of XIIIc gave a product identical in all respects with XIX obtained as described above.

C. Reaction of VIIIc with Trifluoroperacetic Acid.—A solution of trifluoroperacetic acid in methylene chloride was prepared according to the method of Emmons and Pagano,[16] and a 50% excess of this reagent was dropped into a rapidly stirred mixture of 1.5 g. of VIIIc in methylene chloride and 3.80 g. of anhydrous sodium carbonate. The mixture became warm and darkened during the addition. After three hours of stirring the solids were separated by centrifuging. The methylene chloride solution was washed with 10% sodium hydroxide solution, water, and then dried over sodium sulfate and evaporated. After standing for several days in ethanol to hydrolyze the trifluoroacetate ester, a crude product was obtained which failed to crystallize from ethanol (however, its spectrum was very similar to that of authentic XIX). It was positively identified by acetylation and direct comparison with authentic XIIIc.

Reaction of XIc with Sodium Methoxide (XXI).—A 0.55-g. sample of XIc was mixed with 8 ml. of 2.4 *M* sodium methoxide solution and 20 ml. of absolute methanol. A sample withdrawn and worked up after 48 hours showed characteristic epoxide absorption in its infrared spectrum. After 96 hours the reaction seemed complete. The mixture was then cooled, diluted with water and extracted with methylene chloride. After drying over sodium sulfate and evaporating the solvent a moderate yield of yellow oil remained. This was converted into a *p*-nitrobenzoate, m.p. 154.5–155.5°; infrared spectrum ($CHCl_3$): 5.79, 6.21 μ.

Anal. Calcd. for $C_{21}H_{21}O_7N$: C, 63.15; H, 5.30; N, 3.51. Found: C, 63.72; H, 5.13; N, 3.88.

The free alcohol XXI was quantitatively regenerated by lithium aluminum hydride reduction. It could not be obtained in crystalline form; infrared spectrum (neat liquid): 2.88, 6.17 μ.

exo-cis-**3′,6′-Dimethoxybenzonorbornen-2,3-diol (XIVc).**—A variety of conditions for the oxidation of VIIIc by permanganate were investigated. There was a marked tendency for the consumption of irrationally large amounts of oxidizing agent. In several cases, complex products, which have not been fully characterized, were obtained. One typical experiment leading to 2,3-diol is described below.

A solution of VIIIc in acetone or tetrahydrofuran was allowed to react with an aqueous solution of sodium permanganate at 5°. A rapid stream of CO_2 was continually passed through the mixture. Approximately the theoretical amount of reagent for conversion of VIIIc to the diol was consumed. Upon decolorizing with SO_2, saturating with ammonium sulfate and extracting with methylene chloride, a yellow organic layer was obtained. Further working up in the usual way gave a neutral fraction, as a yellow-orange oil, in about 50% yield. The infrared spectrum of this material showed carbonyl absorption at 5.80 μ. The desired diol could be obtained in crystalline form from this mixture only with difficulty. Recrystallized from chloroform, it appeared as colorless cubes, m.p. 142.0–142.5°. About a 20% yield of XIVc could be obtained; infrared spectrum ($CHCl_3$): 2.77, 2.83 (broad), 6.22, 6.29 μ. It reacted rapidly with periodic acid (see below).

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.08; H, 6.83. Found: C, 66.12; H, 6.99.

exo-cis-**2,3-Diacetoxy-3′,6′-dimethoxybenzonorbornene.**—A sample of the above diol (XIVc) was acetylated in the usual way using acetic anhydride and pyridine. Recrystallization from alcohol yielded colorless needles, m.p. 142.8–143.0°; infrared spectrum ($CHCl_3$): 5.75, 6.21 μ.

Anal. Calcd. for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29; acetyl, 27.7. Found: C, 63.98; H, 6.39; acetyl, 27.91.

Lead Tetraacetate Oxidation of VIIIc.—Three grams of VIIIc was dissolved in 500 ml. of glacial acetic acid which was saturated with lead tetraacetate and to which 25 ml. of water had been added. After standing in the dark for 18 hours, the mixture still oxidized starch–potassium iodide paper. It was worked up just as described above for the analogous oxidation of VIIIa. The crude product showed a small amount of hydroxyl absorption, but upon recrystallization from absolute ethanol, the only product isolated was the 2,7-diacetoxy compound (XIIIc), identified by its melting point and infrared spectrum.

Periodic Acid Tests.—Qualitative tests for vicinal diols were carried out as described by Shriner and Fuson.[17] Slight precipitates were obtained with such compounds as the alcohol XX, but these were distinguished easily from true positive tests. Unprotected hydroquinone rings reduced the reagent, giving misleading results for compounds of the type VIIIb. Hydroquinone and catechol reduced the reagent and gave yellow and red colors (presumably the corresponding quinones), respectively.

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[17] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., New York, N. Y., John Wiley and Sons, Inc., 1948.

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