ties at four selected temperatures were determined by procedures previously referenced.[7] The values of the purity were determined by the method of Glasgow, *et al.*[8]

Experimental

Naphthalenes.—The 1-alkylnaphthalenes were prepared by the condensation of appropriate reagents with 1-naphthylmagnesium bromide to yield the desired hydrocarbon or an intermediate which could easily be converted to the hydrocarbon. Dimethyl and diethyl sulfate were employed for the synthesis of 1-methyl- and 1-ethylnaphthalene as reported in reference 9. 1-Isopropylnaphthalene was synthesized by using acetone as the condensing agent, dehydration of the intermediate carbinol, and catalytic hydrogenation of the resulting olefin. 1-Isobutylnaphthalene was prepared by the hydrogenation of the olefin resulting from the condensation of methallyl chloride with the Grignard reagent. Several methods were used for the synthesis of 1-propyl-, 1-butyl- and 1-pentylnaphthalene; the most successful was the use of the appropriate nitrile for the condensing agent, hydrolysis to the ketone, and an atmospheric pressure Wolff–Kishner reduction[10] of the ketone to the hydrocarbon.

Each of the alkylnaphthalenes was found to be contaminated with a hydrocarbon impurity presumed to be the 2-isomer. The impurity, in the case of 1-ethylnaphthalene, was identified as the 2-isomer by infrared analysis.[6] It was found that the desired 1-isomer could be purified by fractional distillation in all cases, but purification was extremely difficult with the propyl compounds. The 2-isomers of methyl- and ethylnaphthalene have lower boiling points than the corresponding 1-isomers[3] and are removed in the forerun of the distillation. However, the 2-isomers of the propyl- and butylnaphthalenes have boiling points higher than those of the corresponding 1-isomers,[3] and are therefore concentrated in the undistilled portion of the charge. Thus, the mole fraction of the impurity is constantly increasing in both the liquid and vapor phases, making the purification increasing difficult as the distillation progresses. Several fractional distillations of 1-propylnaphthalene and 1-isopropylnaphthalene were required before the desired purity was attained.

Tetralins.—The 1- and 5-alkyltetralins were prepared by catalytic hydrogenation of purified 1-alkylnaphthalenes. The quantity of each hydrocarbon hydrogenated varied according to the amount available for such use. The hydrogenations were carried out in a 4.5-liter rocking autoclave at 1500–2000 p.s.i. and 195–225° in the presence of approximately 10% by weight of a barium-promoted copper chromite catalyst. Essentially quantitative yields of product were obtained after de-adsorption of the catalyst with boiling ethanol.

The isomers were separated by fractional distillation in 6-ft. Podbielniak columns at 100 mm. for the methyl and ethyl compounds and at 20 mm. for the butyl compounds. The ratio of the amounts of 1-isomer and 5-isomer formed in the hydrogenation was 1.3 in every instance except for the ethyl derivative. After 1-ethyl-1,2,3,4-tetrahydronaphthalene had been distilled from the mixture, the distillation column flooded over, and an undetermined amount of the 5-isomer was lost. The ratio of 1.3 was calculated on the basis of the amounts of constant $n^{20}D$ material obtained plus an estimation of the amounts of each isomer in the intermediate fractions of the distillation based on the assumption that refractive indices are volume additive. The percentage yield of constant $n^{20}D$ material of each compound is given in the table.

Cleveland, Ohio

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[7] I. A. Goodman and P. H. Wise, This Journal, **72**, 3076 (1950).

[8] A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945).

[9] H. Gilman and R. E. Hoyle, This Journal, **44**, 2621 (1922).

[10] (a) M. D. Soffer, M. B. Soffer and K. W. Sherk, *ibid.*, **67**, 1435 (1945); (b) C. H. Herr, F. C. Whitmore and R. W. Schiessler, *ibid.*, **67**, 2061 (1945).

[Contribution from the Department of Chemistry of the University of Michigan]

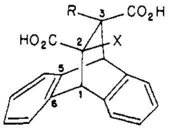
Reactions of Hindered α-Substituted Succinic Acids. II. Structure of the Rearranged Acids[1]

By Wyman R. Vaughan, Marvin V. Andersen, Jr., and Randel Q. Little, Jr.[2]

Received October 14, 1953

Evidence for the structures and configurations of the products of the acid-induced rearrangement of 2-hydroxy-3-methyldibenzo[2,2,2]bicycloöctadiene-*trans*-2,3-dicarboxylic acid (I) and the alkali-induced rearrangement of 2-bromodibenzo[2,2,2]-bicycloöctadiene-*trans*-2,3-dicarboxylic acid (II) is presented. It is also shown that silver nitrate can effect an analogous rearrangement of II with the production of a lactone acid similar to that produced from I. The elimination of bromide with the β-carboxyl accompanies the silver nitrate induced rearrangement, though to a lesser extent than observed in the alkali-induced rearrangement.

In a previous paper[3] there was reported the anomalous behavior of 2-hydroxy-3-methyldibenzo[2,2,2]bicycloöctadiene-*trans*-2,3-dicarboxylic acid (I) with hot 48% hydrobromic acid and of 2-bromodibenzo[2,2,2]bicycloöctadiene-*trans*-2,3-dicarboxylic acid (II) with alkali. Evidence was presented to support the hypothesis that any external nucleophilic attack upon carbon 2 was highly improbable, if not actually impossible, owing to steric factors. Thus any displacement of a group attached at this position must be a consequence of intramolecular nucleophilic attack. The formation of dibenzo[2,2,2]bicycloöctatriene-2-carboxylic acid from II by treatment with alkali was explained on this basis. However, speculation as to the nature of the hydroxy dibasic acid IV produced simultaneously and of the lactone acid III, which was the only product obtained upon reaction of I with 48% hydrobromic acid at 100°, was deferred until additional evidence was available. It was, however, remarked that anthraquinone was produced upon permanganate oxidation of IV while no anthraquinone was obtained from III under similar conditions. On the basis of these data it was suggested that Wagner–Meerwein rearrangements had occurred in both reactions, since both III and IV were oxidizable under relatively mild conditions whereas I and II were not; and it was further suggested on the



I, X = OH, R = CH_3
II, X = Br, R = H

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[1] Abstracted in part from a portion of the Ph.D. dissertation of Randel Q. Little, Jr., University of Michigan, 1953.

[2] American Brake Shoe Company Fellow, 1952–1953.

[3] W. R. Vaughan and K. M. Milton, This Journal, **74**, 5623 (1952).

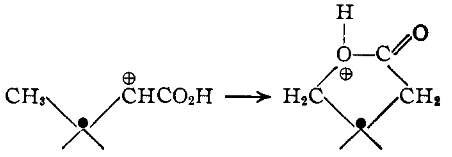
basis of anthraquinone formation from IV that the anthracene skeleton remained intact in IV. Failure to obtain anthraquinone from III was interpreted to mean alteration in the anthracene skeleton in III.

A careful reinvestigation of the oxidation of IV now makes it possible to attribute the formation of anthraquinone to contamination of the sample with traces of unrearranged II or possibly with the corresponding hydroxy acid, isomeric with IV. Thus an oxidation of IV or a derived substance does not afford anthraquinone, and it may be concluded that in IV, as in III, the anthracene skeleton has been destroyed by rearrangement.

Bearing in mind the stereospecific character of the Wagner–Meerwein rearrangement, it becomes apparent that three possibilities must be considered: migration of R from carbon 3 to carbon 2 with attendant inversion on both carbons; migration of carbon 4 from carbon 3 to carbon 2 with contraction of the *endo*-ethylene bridge to an *endo*-methylene bridge; and migration of carbon 6 from carbon 1 to carbon 2 with transformation of the [2,2,2]-bicyclooöctadiene system to a [3,2,1]bicyclooöctadiene system.

The first possibility may be discounted at once, since the result would be observable only where I or II was present as an optically active modification, in which case racemization would result. Such a process is, of course, a possible precursor or competitor to either of the other processes; but at present no evidence is at hand to establish this as fact, since neither I nor II has been resolved.

The second possibility may be discounted on the following grounds. Studies on *endo*-methylene systems of the type which would be produced, which are currently in progress in this Laboratory,[4] show that they readily afford anthraquinone upon oxidation. Secondly, the lactone system of III appears to involve a 5-membered ring,[3] and such would not seem to be derivable by simple rearrangement of I, although a secondary rearrangement involving hydride migration from the methyl group to the adjacent carbon with subsequent γ-lactone formation is not unimaginable



However, evidence that oxidation of III proceeds no farther than the removal of two hydrogens renders this hypothesis untenable, since the postulated γ-lactone would be derived from a primary alcohol and thus would consume two equivalents of oxygen instead of one.

There remains the third possibility, and all available experimental data support this hypothesis. Both III and IV are smoothly oxidized by alkaline permanganate to dibasic acids which possess a carbonyl group; and although no carbonyl derivatives can be conveniently prepared, failure to undergo further oxidation under comparatively vigorous conditions plus the presence of a strong absorption band at 5.9 μ are ample to establish the ketonic nature of the oxidation products. That the ketonic function is conjugated with an aromatic ring is indicated by the ultraviolet spectra of both the oxidation product from III (V) and the oxidation product from IV (VI).

The absence of a strong absorption band in the 2400–2450 Å. region often associated with the aromatic ketone structure[5a,b] is not surprising, since this band fails to appear in the spectra of 1-indanone,[5c] 1-tetralone[5b,c] and 2,3-benz-1-suberone[5c] which group of compounds most nearly approximates the present cyclic ketonic system. Furthermore, there is a suggestion of absorption in this region for the present compounds which discloses itself by the presence of a slight inflection in the curve at the appropriate wave length.

A comparison of the spectra of V and VI taken in ethanol and in concentrated sulfuric acid (Figs. 1 and 2) (from which each substance may be recovered unchanged by dilution with water) shows increased band intensities and shifts of 300–500 Å. toward the visible region in the sulfuric acid solutions. These changes are of the order of magnitude observed by Anderson and Gooding to occur with aromatic ketones.[5a]

The correspondence in structure of chromophoric systems of V and VI is demonstrable by the superimposability of their ultraviolet spectra, and the similarity in gross structure is revealed by the very similar nature of the infrared spectra of the two methyl esters (Fig. 3).

The final evidence is afforded by oxidative degradation. Both V and VI proved extremely resistant to the usual oxidizing agents; acidic or alkaline permanganate decomposed without affecting the organic substances as did chromic–sulfuric acid solutions, and all attempts to use nitric acid, with or without vanadium pentoxide catalyst, of concentrations from 10% to red fuming acid met with failure. At best, nitrogen was introduced in the substances and unidentifiable mixtures were obtained. Finally it was found that a suspension of excess manganese dioxide in 70% sulfuric acid would effectively oxidize both substances to 3,3′-spirobiphthalide (the anhydro derivative of benzophenone-2,2′-dicarboxylic acid) the identity of which was established by comparison with an authentic sample prepared for the purpose by permanganate oxidation of 2-(*o*-toluyl)-benzoic acid.[6] To be sure the yields of the spirobiphthalide were not high, but this is understandable since it has been shown that the acid from which it is derived is slowly oxidized to phthalic acid in alkaline permanganate.[7] In order to substantiate this explanation of low yield, it was shown that the spirobiphthalide is attacked at an appreciable rate by the oxidizing agent used in the degradation.

Bearing in mind the proposed nature of the rearrangements whereby III and IV are produced, it now becomes possible to assign structures, for

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[4] W. R. Vaughan and M. Yoshimine, unpublished results.

[5] (a) L. C. Anderson, THIS JOURNAL, **55**, 2095 (1933); L. C. Anderson and C. M. Gooding, *ibid.*, **57**, 999 (1935); (b) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951; (c) P. Ramart-Lucas and J. Jock, *Bull. soc. chim.*, [5] **2**, 327 (1935); **5**, 848 (1938).

[6] M. S. Newman and C. D. McCleary, THIS JOURNAL, **63**, 1541 (1941).

[7] C. Graebe and P. Julliard, *Ann.*, **242**, 243 (1887).

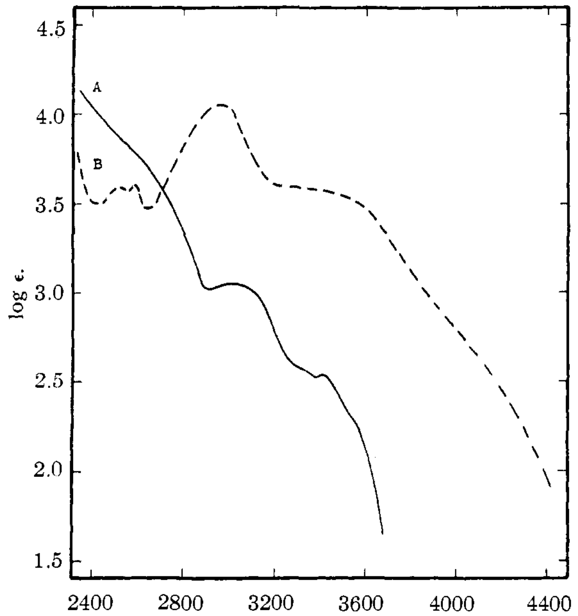


Fig. 1.—Ultraviolet spectra of V: A, solvent, 95% ethanol; B, solvent, concd. sulfuric acid.

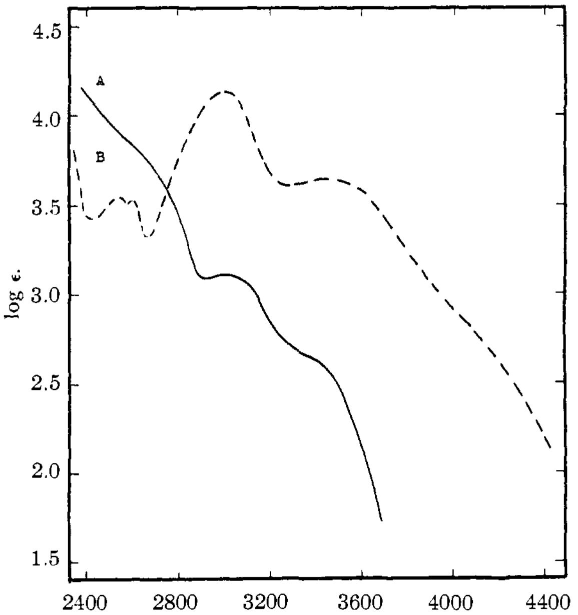
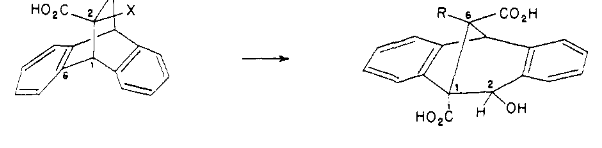


Fig. 2.—Ultraviolet spectra of VI: A, solvent 95% ethanol; B, solvent concd. sulfuric acid.

the degradation clearly demonstrates the disruption of the anthracene system. It will be seen that migration of carbon 6 from carbon 1 to carbon 2 will produce a system in which an oxygen function becomes affixed to carbon 2 of the new 3,4,7,8-dibenzo[3,2,1]bicycloöctadiene system.



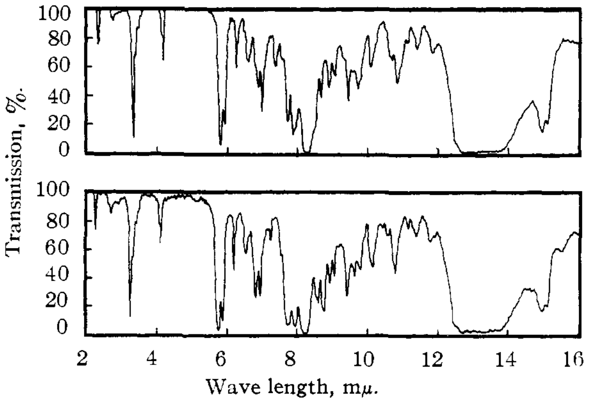
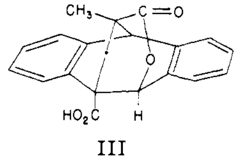


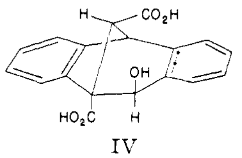
Fig. 3.—Infrared spectra of dimethyl esters in chloroform: upper curve, VI dimethyl ester; lower curve, V dimethyl ester.

Oxidation of this function will then afford the ketonic carbonyl conjugated with an aromatic ring as suggested by the spectrometric data. It should be pointed out that this expansion of a [2,2,2]bicycloöctane system has a precedent only in the rearrangement of 2-bromo[2,2,2]bicycloöctane to 2-bromo[3,2,1]bicycloöctane by treatment with silver bromide.[8]

With the exception of the hydroxyl function in IV the geometry of the new system is clear: the lactonic nature of III establishes the position of the 6-carboxyl and the 2-hydroxyl, and the structure of the remainder of the system is self-evident. The related geometry in IV was established by treating the hydroxy acid with acetic anhydride in the presence of sulfuric acid, whereupon a lactone acid (carbonyl absorption at 5.6 μ) closely resembling III was produced in about 60% yield. From the new lactone acid, IV was readily regenerated by treatment with alkali and precipitation with acid. The only point of difference between the two compounds then is the failure of IV to lactonize spontaneously. Since the only structural difference is the 6-methyl in III, this failure to lactonize must be attributed to such electronic effect as is lost when the 6-methyl is replaced by hydrogen, the geometry of the system arguing against any steric effect of the methyl group. Thus the structures may be assigned as



III



IV

Inasmuch as the acid-induced rearrangement of I to III and the base-induced rearrangement of II to IV both afford the *exo*-oxygen function at carbon 2 in the new system, it is appropriate to consider briefly the stereospecificity of the two rearrangements. The rearrangement of I does not raise any serious questions, since it may be explained in terms of a carbonium ion mechanism in which carbon 1 of I acquires a positive charge as carbon 6 migrates, possibly with the assistance of a solvent molecule

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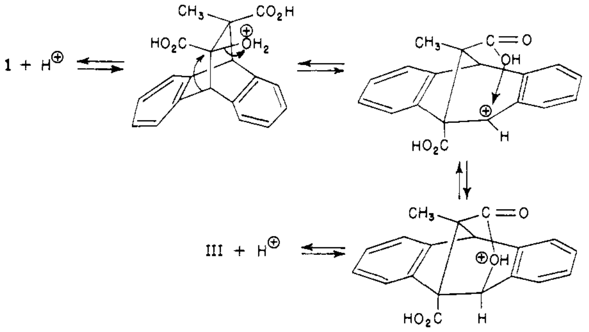
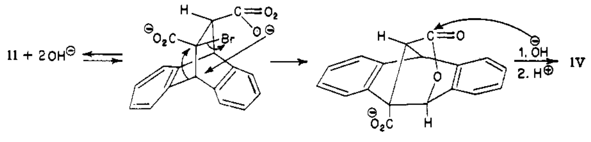
(8) W. von E. Doering and M. Farber, This Journal, **71**, 1514 (1949).

approaching from the opposite side. In its new position as carbon 2 of III, the carbonium ion may be stabilized by union with the 6-carboxyl to give the protonated lactone, which then ejects the proton to give III.



The rearrangement of II is no less easily explained



However, in order to obtain confirmation of this general picture as applied to the rearrangement of II, a further experiment was carried out: reasoning that if the rearrangement could be effected in a non-alkaline medium, the lactone would be obtained as a result of a process analogous to that outlined for the reaction III → V, an acetone solution of II was treated with an equivalent of 0.5 *M* silver nitrate. Silver bromide precipitated at once in nearly quantitative yield, and upon evaporation of the acetone from the filtrate there was obtained a viscous oil which was subsequently purified and found to be identical with the lactone produced from IV. Thus initiation of the rearrangement by electrophilic attack upon bromine, which in effect is catalytically related to the proton initiated rearrangement of III, affords the lactone acid system. It is interesting to note that the yield of IV (as the lactone acid) is 60% under these conditions, whereas with alkali the yield of IV is only 42%.[3] The yield of concomitant dibenzo[2,2,2]bicycloöctatriene-2-carboxylic acid is reduced from 25% with alkali to 14% with silver nitrate. Work on the nature of these two reactions and the general character of the Wagner–Meerwein rearrangement in this series of compounds is continuing.

Experimental[9]

2-Hydroxy-3-methyldibenzo[2,2,2]bicycloöctadiene-*trans*-2,3-dicarboxylic Acid (I).—This substance was prepared according to the directions of Vaughan and Milton.[3]

2-Bromodibenzo[2,2,2]bicycloöctadiene-*trans*-2,3-dicarboxylic Acid (II).—This substance was prepared according to a modification of the procedure of Vaughan and Milton.[3] A mixture of 7.9 g. (0.027 mole) of dibenzo[2,2,2]bicyclooctatriene-2,3-dicarboxylic acid[10] and 75 ml. of 30% hydrogen bromide–acetic acid was shaken in a closed flask for 24 hr. The precipitate of II which separated was filtered and washed with acetic acid; yield 8.5 g. (85%), m.p. 217.0–217.5° dec. An additional crop weighing 1.0 g. (10%) was obtained by concentration of the filtrate from the original reaction. One recrystallization from nitromethane afforded material melting at 219.3–220.0° dec., previously reported 221.6–222.0° dec., cor.[3]

The methyl ester was prepared by means of diazomethane and was recrystallized from methanol, m.p. 141.8–143.3°.

Anal. Calcd. for $C_{20}H_{17}BrO_4$: C, 59.86; H, 4.27; Br, 19.92. Found[11]: C, 59.81; H, 4.48; Br, 20.08.

2-*exo*-Hydroxy-6-methyl-3,4,7,8-dibenzo[3,2,1]bicyclooctadiene-1-*cis*-6-dicarboxylic Acid-2,6-lactone (III).—This substance was prepared by heating I with 48% hydrobromic acid according to the directions of Vaughan and Milton.[3] The methyl ester was prepared by means of diazomethane, and was recrystallized from methanol, m.p. 153.0–154.5°.

Anal. Calcd. for $C_{20}H_{16}O_4$: C, 74.98; H, 5.04. Found[12]: C, 74.83; H, 5.01.

2-*exo*-Hydroxy-3,4,7,8-dibenzo[3,2,1]bicyclooctadiene-1-*cis*-6-dicarboxylic Acid (IV).—This substance was prepared by treatment of II with alkali according to the directions of Vaughan and Milton.[3] The dimethyl ester was prepared by means of diazomethane and was recrystallized from methanol–water, m.p. 107.8–108.5°.

Anal. Calcd. for $C_{20}H_{18}O_5$: C, 70.99; H, 5.36. Found[12]: C, 70.83; H, 5.45.

Reaction of II with Silver Nitrate.—A 0.502-g. (0.00135 mole) sample of II was dissolved in 5 ml. of acetone and 2.7 ml. of 0.5 *M* aqueous silver nitrate solution was added. A yellow precipitate of silver bromide appeared immediately, and after a few minutes of shaking, it was filtered off and washed with acetone. In order to remove traces of unprecipitated silver ion from the filtrate, it was treated with 1 ml. of 5% potassium bromide solution and then was refiltered. The acetone was evaporated from the filtrate by means of an air stream at room temperature, whereupon a viscous colorless oil separated. The aqueous phase was decanted, and the residual oil was washed with 25-ml. portions of water. Next, toluene was added, and the residual water was removed by azeotropic distillation. The dry toluene solution was diluted to 20 ml. with additional toluene, and solution was effected by heating. Upon standing, a white crystalline solid separated, m.p. 120–140°. After drying at 132° and 0.05 mm. the product weighed 0.234 g. (59.6%), m.p. 177–180°. Since the product appears to solvate rather readily with any solvent from which it may be recrystallized (*e.g.*, nitromethane, ether–petroleum ether, benzene, etc.) careful drying is essential. After three recrystallizations from toluene and drying for 5 hr. at 100° (0.05 mm.), it melted constantly at 183.5–185.5°.

Anal. Calcd. for $C_{18}H_{12}O_4$: C, 73.96; H, 4.14; neut. equiv., 292; mol. wt., 292.28. Found[12]: C, 73.68; H, 4.28; neut. equiv., 296, 295; mol. wt. (Rast), 303.

The methyl ester was prepared by means of diazomethane and was recrystallized from methanol, m.p. 183.5–185.3°. The infrared spectrum has a strong band at 5.6 μ (*cf.* spectrum of compound III, reported in ref. 3).

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found[12]: C, 74.18, 74.00, 74.16; H, 4.62, 4.59, 4.76.[13]

Hydrolysis of a small sample (0.053 g.) of the lactonized IV was achieved by dissolution in dilute alkali followed by acidification with dilute hydrochloric acid. By concentrating the filtrate from the initial precipitation, a total of 0.052 g. (93%) of IV was recovered as shown by mixed melting point determination in which no depression was observed.

The toluene filtrate was evaporated to dryness and the residue was triturated with nitromethane. There was recovered in this manner 0.046 g. (13.8%) of dibenzo[2,2,2]-bicycloöctatriene-2-carboxylic acid, m.p. 246–249° dec. No depression was observed in a mixed melting point determination with an authentic sample.[3]

Lactonization of IV.—A solution of 1.00 g. (0.00323 mole) of IV in 5 ml. of acetic anhydride containing 2 drops of concd. sulfuric acid was heated on the steam-bath for 3 hr. The solution was cooled and 5 ml. of methanol was

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[9] Melting points are uncorrected.

[10] O. Diels and K. Alder, *Ann.*, **486**, 191 (1931).

[11] Microanalysis by Clark Microanalytical Laboratory, Urbana, Ill.

[12] Microanalysis by Goji Kodama, University of Michigan.

[13] When this methyl ester was first prepared it melted at 157–158°. However, upon standing for several weeks the melting point had changed to that reported above. Subsequent preparations afforded only the higher melting form. The analytical data are for both the low and high melting modifications.

added slowly. Then, after dilution with 50 ml. of ether, the solution was washed with four 25-ml. portions of water and dried over magnesium sulfate. The yellow oil obtained upon evaporating the dried ethereal solution to dryness was triturated with a few ml. of warm toluene and allowed to stand. The crude product weighed 0.602 g. and was recrystallized from toluene and dried *in vacuo*, m.p. 179–182°. However, the melting point of a sample produced by the silver nitrate method was undepressed.

Oxidation of III to V.—A 0.154-g. (0.00503 mole) sample of III was heated on the steam-bath for 4 hr. with a solution of 5.5 ml. of 1% potassium permanganate and 20 ml. of 0.3% sodium hydroxide. The manganese dioxide was separated by filtration with good washing, and the slightly pink filtrate was acidified with dilute hydrochloric acid, and a trace of sodium bisulfite was added to destroy the slight excess of oxidizing agent remaining. The white precipitate weighed 0.161 g. (99.4%) and melted at 258–263° dec. when placed in the bath below 180°. If placed in the bath above this temperature it melted immediately, resolidified and then remelted at 258–263° dec. An analytical sample was prepared by recrystallization from acetone–benzene, m.p. 267–268° dec.

Anal. Calcd. for $C_{19}H_{14}O_5$: C, 70.80; H, 4.38. Found[12]: C, 70.79; H, 4.73.

The dimethyl ester was prepared by means of diazomethane and was recrystallized from methanol, m.p. 143.0–144.3°.

Anal. Calcd. for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found[12]: C, 71.63; H, 5.14.

Subsequently it was found that equally good results could be obtained in much shorter time by refluxing together 5.0 g. of III, 1.7 g. of sodium hydroxide and 1.85 g. of potassium permanganate in 100 ml. of water for 1 hr. The solution was filtered hot and acidified while still hot, whereupon a gummy precipitate was obtained. By digesting the hot mixture for about 20 min. on the steam-bath and then cooling, an analytically pure sample of crystalline V was obtained: 5.15 g., 98.3%, m.p. 267–268° dec.

Oxidation of IV to VI.—To a solution of 10.0 g. (0.0322 mole) of IV in 40 ml. of 20% sodium hydroxide and 200 ml. of water was added a solution of 10 g. (0.063 mole) of potassium permanganate in 300 ml. of water. The solution was allowed to stand at room temperature for 24 hr., and then it was heated on a steam-bath for an additional 24 hr. After the reaction mixture had cooled, the manganese dioxide was filtered off and washed with water. The filtrate was acidified with hydrochloric acid and digested on a steam-bath; after cooling, 8.0 g. (81%) of VI was obtained, m.p. 249–51° dec., and after recrystallization from ethanol-water VI melted at 255.0–256.5° dec.

Anal. Calcd. for $C_{18}H_{12}O_5$: C, 70.13; H, 3.93. Found[14]: C, 69.79; H, 3.90.

The dimethyl ester was prepared by means of diazomethane and was recrystallized from methanol, m.p. 170.5–173.0°.

Anal. Calcd. for $C_{20}H_{16}O_5$: C, 71.42; H, 4.80. Found[12]: C, 71.42; H, 4.81.

In one experiment insufficient permanganate was used to effect oxidation, and a substantial quantity of IV was recovered. Unlike previous samples of IV, this material afforded absolutely no anthraquinone when subjected to vigorous permanganate oxidation. As noted,[3] prolonged refluxing of the originally prepared samples of IV with either acidic or alkaline permanganate afforded some anthraquinone. In the oxidations of V and VI, which follow, no anthraquinone was ever isolated.

Oxidations of V and VI.—Both V and VI were oxidized according to the following general procedure. To a solution of 0.503 g. (0.00163 mole) of VI in 19 ml. (35 g.) of concd. sulfuric acid was added 15 ml. of water, and while the mixture was still hot, 1.514 g. (0.174 mole) of manganese dioxide was added in 3 portions. Complete decolorization was allowed to occur between additions. Finally, the mixture was allowed to stand on the steam-bath or was refluxed for 1–3 hr. to complete the reaction. The mixture was then diluted with 50 ml. of water and digested for 2 hr. on the steam-bath, cooled, filtered, and the residue was washed with water, 10 ml. of 3% sodium bicarbonate and then again with water. From the acidified bicarbonate washings there was recovered 0.079 g. of VI (15.7%). The bicarbonate-insoluble residue was taken up in ethanol, treated with Norit, filtered and evaporated to a slightly yellowish solid which weighed 0.127 g. (30.9%), m.p. 201.5–204.0°. Under similar conditions a like quantity of V afforded 0.25 g. (61%). The crude product was recrystallized from ethanol, m.p. 205.5–206.5°. Upon being mixed with an authentic sample of 3,3′-spirobiphthalide, m.p. 205.5–207.0°, no depression in melting point was observed.

Anal. Calcd. for $C_{15}H_8O_4$: C, 71.43; H, 3.20. Found[12]: C, 71.21; H, 3.24.

3,3′-Spirobiphthalide.—A solution of 3 g. (0.02 mole) of potassium permanganate in 75 ml. of water was added to a solution of 2.01 g. (0.00836 mole) of 2-(*o*-toluyl)-benzoic acid, prepared according to the directions of Newman and McCleary,[6] in 30 ml. of 3.5% sodium hydroxide solution, and the mixture was heated overnight on the steam-bath. The manganese dioxide was removed by filtration and the filtrate was acidified. On digesting the clear solution on the steam-bath, a white precipitate appeared; 1.42 g. (67.5%), m.p. 205.0–206.5°. An additional crop of 0.37 g. (17.6%) was obtained by further digestion. The product was recrystallized from ethanol, m.p. 205.5–207.0°, previously reported 212°.[7]

Under conditions for the oxidation of V or VI, above, it was found that 3,3′-spirobiphthalide slowly reacts with manganese dioxide to give a colorless solution.

ANN ARBOR, MICHIGAN

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[14] Microanalysis by W. J. Byrd.