

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

2-Oxa-1,2-dihydrodicyclopentadiene<sup>1</sup>

BY CHICITA F. CULBERSON, JOHN H. SEWARD AND PELHAM WILDER, JR.

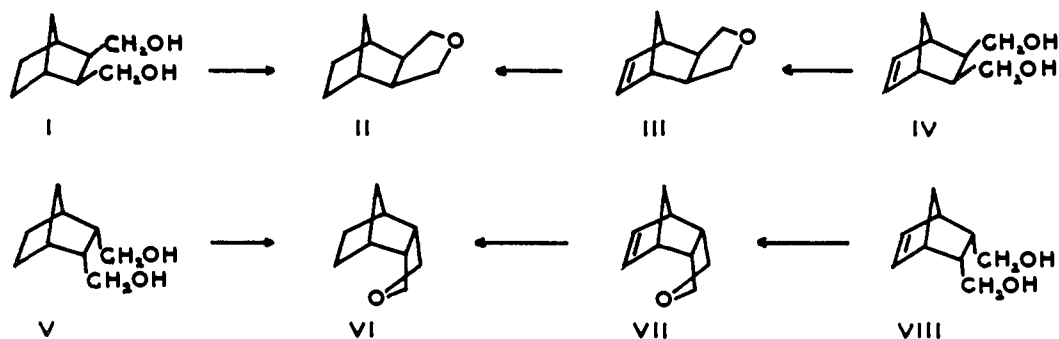
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In contrast to the behavior of *endo*-dicyclopentadiene, known to undergo rearrangement to the less hindered *exo* form upon treatment with acidic reagents, 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene yields primarily unrearranged derivatives. Since the steric course of the reactions of 2-oxa-1,2-dihydro-*exo*-dicyclopentadiene is analogous to that of *exo*-dicyclopentadiene, the resistance to rearrangement in the *endo* system is attributed to the proximity of the ether oxygen and the norbornylene double bond.

In 1954, Alder and Roth<sup>2</sup> noted the formation of 2-oxatetrahydro-*exo*-dicyclopentadiene (II) as a by-product in the synthesis of the ditosylate of *exo-cis*-bicyclo[2.2.1]heptane-2,3-dimethylol (I). Subsequently the same authors<sup>3</sup> recovered similar cyclic ethers during the tosylation of the corresponding unsaturated diol IV and of the saturated and unsaturated *endo-cis*-diols V and VIII. The unsaturated ethers III and VII readily formed adducts with phenyl azide and could be converted to the saturated ethers II and VI by catalytic reduction. The *endo* unsaturated ether, 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene (VII), has been synthesized by Eliel and Pillar<sup>4</sup> by a method similar to that of Alder and Stein and is attributed by Brace<sup>5</sup> to be a product of the Diels-Alder addition of 2,5-dihydrofuran and cyclopentadiene.

Roth's<sup>3</sup> method which is similar to the procedure of Eliel and Pillar<sup>4</sup> While Alder and Roth used two equivalents of *p*-toluenesulfonyl chloride and obtained some ditosylate of the diol, one equivalent is sufficient for the cyclization reaction and no ditosylate is isolated. Alder and Roth note that ether formation is entirely repressed if a pyridine solution of the diol is added to excess *p*-toluenesulfonyl chloride in pyridine.

The *exo*-ether is readily distilled, but the solid *endo*-ether is extremely difficult to purify. Alder and Roth<sup>3</sup> found that the *endo*-ether could be partially purified by sublimation, but attempts to recrystallize the waxy solid failed and no elemental analysis is reported. Eliel and Pillar<sup>4</sup> experienced similar difficulties and obtained a solid product after sublimation but they were unable to prepare a



The present investigation concerns the stereochemical course of certain addition reactions of 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene (VII). This heterocyclic system is structurally similar to both *endo*-dicyclopentadiene which readily undergoes Wagner-Meerwein rearrangements upon addition of acidic reagents<sup>6,7</sup> and the cyclopentadiene-maleic anhydride adduct which appears to react without rearrangement.<sup>8-11</sup>

The *endo* and *exo* isomers of 2-oxa-1,2-dihydrodicyclopentadiene were prepared from the *endo-cis*- and the *exo-cis*-diols by a modification of Alder and

satisfactory analytical sample. Brace,<sup>5</sup> who synthesized the ether by a Diels-Alder reaction rather than by cyclization of the *endo-cis*-diol, obtained a liquid product which was readily purified by distillation. The elemental analysis of this product agrees with the formula C<sub>9</sub>H<sub>12</sub>O. It seems highly probable, however, that the Diels-Alder adduct has the *exo* rather than the *endo* configuration since the physical properties (b.p. 65-70° (7.0 mm.), *n*<sub>D</sub><sup>25</sup> 1.5000 and b.p. 85.5-88° (25 mm.)) reported by Brace agree more closely with the constants found for the *exo*-ether; b.p. 82° (24 mm.), *n*<sub>D</sub><sup>20</sup> 1.4973 reported by Alder and Roth<sup>3</sup> and 86-88° (25 mm.), *n*<sub>D</sub><sup>20</sup> 1.4960 observed in the present study.

Because of the difficulties encountered in the purification of the *endo*-ether, crude material was used in several of the reactions reported in this study. The 75% yield obtained in the preparation of the nitroso chloride dimer XIV indicates that the crude starting material must have been at least 75% pure. In some reactions the *endo*-ether was partially purified by distilling with steam or by distilling under vacuum, the resulting solid product

(1) Taken in part from the M.A. Thesis of J. H. Seward and the Ph.D. Dissertation of Chicita F. Culberson, Duke University, 1958 and 1959, respectively.

(2) K. Alder and W. Roth, *Ber.*, **87**, 161 (1954).

(3) K. Alder and W. Roth, *ibid.*, **88**, 407 (1955).

(4) E. L. Eliel and C. Pillar, *THIS JOURNAL*, **77**, 3600 (1955).

(5) N. C. Brace, *ibid.*, **77**, 4157 (1955).

(6) P. D. Bartlett and A. Schneider, *ibid.*, **68**, 6 (1946).

(7) H. A. Bruson and T. W. Riener, *ibid.*, **67**, 723, 1178 (1945); **68**, 8 (1946).

(8) K. Alder and G. Stein, *Ann.*, **514**, 1 (1934).

(9) J. A. Berson, *THIS JOURNAL*, **76**, 4069 (1954).

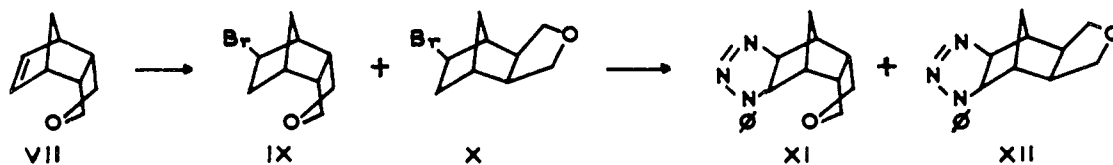
(10) H. Kwart and L. Kaplan, *ibid.*, **76**, 4078 (1954).

(11) T. F. West, *J. Chem. Soc.*, 140 (1941).

being recovered from the condenser. The melting point range of material so purified was 85–90° as compared to carefully purified samples obtained by Alder and Roth,<sup>3</sup> m.p. 94°, and by Eliel and Pillar,<sup>4</sup> m.p. 91°. The melting point depression observed for the partially purified ether could result from only slight contamination since norbornyl compounds have high cryoscopic constants.

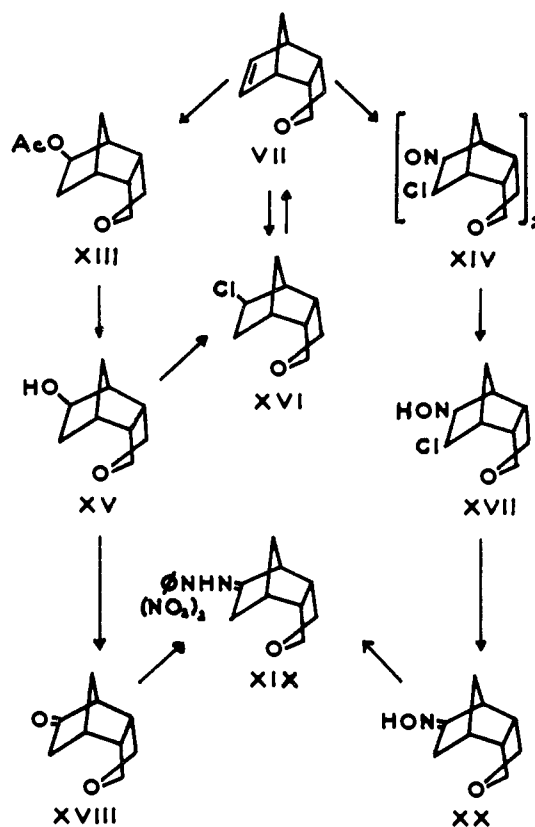
A number of acidic reagents reported to add to the norbornylene double bond of *endo*-dicyclopentadiene were used in the present study of the stereochemical course of the reactions of 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene. While addition of such reagents as hydrobromic acid, hydrochloric acid, acetic acid, sulfuric acid and methyl alcohol in the presence of a sulfuric acid catalyst to *endo*-dicyclopentadiene leads to the formation of 9-substituted derivatives of *exo*-dicyclopentadiene,<sup>7</sup> the 2-oxa system is found to resist rearrangement to the *exo* configuration with all of these reagents.

Addition of hydrobromic acid to the *endo*-ether VII yielded a product which, when purified by distillation, gave, upon dehydrohalogenation, only unrearranged *endo*-ether as identified by its phenyl azide adduct. When the reaction with hydrobromic acid was repeated without purification of the product, dehydrohalogenation yielded a crude material which gave a mixture of crystalline phenyl azide adducts, of which 17% was adduct XII of the *exo*-ether. Thus hydrobromic acid adds to the *endo*-ether to give a mixture of 9-*exo*-bromo-2-oxatetrahydro-*endo*-dicyclopentadiene (IX) and 9-*exo*-bromo-2-oxatetrahydro-*exo*-dicyclopentadiene (X), the *endo* isomer predominating to such an extent that the *exo* isomer is readily eliminated during purification. The principal product of the addition of



hydrochloric acid to the *endo*-ether VII is shown to be 9-*exo*-chloro-2-oxatetrahydro-*endo*-dicyclopentadiene (XVI) by dehydrohalogenation. The *exo*-ether III reacts with hydrobromic acid to give a bromide X, proved to have the *exo* configuration by dehydrohalogenation to starting material.

When 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene was treated with acetic acid in the presence of a catalytic amount of sulfuric acid, the unrearranged acetate XIII was isolated along with a small amount of starting material. 9-*exo*-Hydroxy-2-oxatetrahydro-*endo*-dicyclopentadiene (XV), obtained by alkaline hydrolysis of this acetate, can be converted to the chloride XVI already shown to have the *endo* configuration. Oxidation of the alcohol XV yields a ketone which forms a 2,4-dinitrophenylhydrazone (XIX). The *endo* configuration of this derivative is verified by synthesis from the dimeric nitroso chloride XIV of the *endo* ether. Zinc and acetic acid reduction of the chloro oxime XVII obtained by thermal decomposition of the nitroso chloride dimer yields a crude residue which reacts with 2,4-dinitrophenylhydrazine to give the

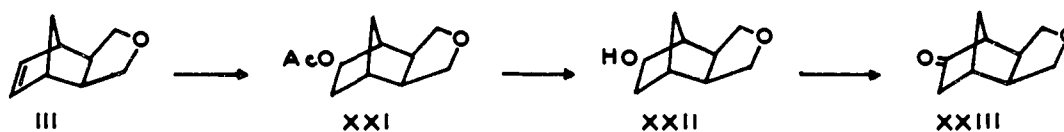


desired derivative of known *endo* configuration. This derivative is identical to the 2,4-dinitrophenylhydrazone of the ketone XVIII. Assignment of the *endo* configuration to the nitroso chloride dimer

XIV is consistent first with the fact that the *endo*- and the *exo*-ethers give isomeric nitrosyl chloride addition products and second that no case of rearrangement on the addition of this reagent to a norbornylene-type system has been reported. 2-Oxa-1,2-dihydro-*exo*-dicyclopentadiene (III) reacts with glacial acetic acid to form the *exo*-ring acetate XXI. Hydrolysis of the acetate yields the *exo*-ring alcohol XXII, distinguished from the corresponding *endo* isomer by comparison of their *p*-nitrobenzoates. Oxidation of the alcohol XXII yields 9-keto-2-oxatetrahydro-*exo*-dicyclopentadiene XXIII which readily forms a 2,4-dinitrophenylhydrazone derivative shown to be different from the previously prepared *endo* derivative XIX.

A comparison of the reactions of formic acid with *endo*-dicyclopentadiene and with the *endo*-2-oxa system illustrates a contrast in reactivity. Bergmann and Japhe<sup>12</sup> showed that *endo*-dicyclopentadiene reacts with formic acid in the absence of a sulfuric acid catalyst to yield 9-formoxy-9,10-dihydro-*exo*-dicyclopentadiene. The nearly complete

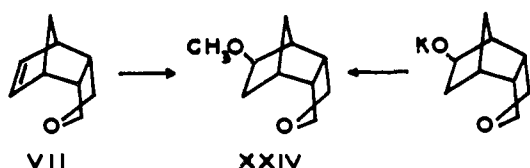
(12) F. Bergmann and H. Japhe, THIS JOURNAL, 69, 1826 (1946).



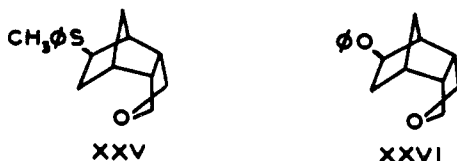
conversion, 99.9% after 5 hours reflux of a 1:3 molar ratio of *endo*-dicyclopentadiene and formic acid, affords a quantitative method for the determination of dicyclopentadiene.<sup>13</sup> Compared to the quantitative conversion in the case of dicyclopentadiene, the 2-oxa system yields only 23% addition product after refluxing for 20 hours. The stereochemistry of the formoxy derivative was not determined.

A study of the hydration of the *endo*-ether VII with 25% sulfuric acid shows that *endo* product predominates. After one distillation the product formed a *p*-nitrobenzoate identical to that of the *endo* alcohol XV, but upon oxidation of the crude alcohol a small amount of a 2,4-dinitrophenylhydrazone, identical to the derivative of the *exo*-ketone, was obtained. Conversion of the crude hydration product to the corresponding chloride with thionyl chloride followed by dehydrohalogenation regenerates the *endo*-ether VII from which no phenyl azide adduct of the *exo* isomer could be isolated.

The methoxy derivative XXIV was obtained by direct addition of methyl alcohol to the *endo*-ether VII in the presence of a sulfuric acid catalyst and the *endo* configuration of the product is proved by synthesis through reaction of methyl iodide with the potassium salt of the *endo*-alcohol XV.

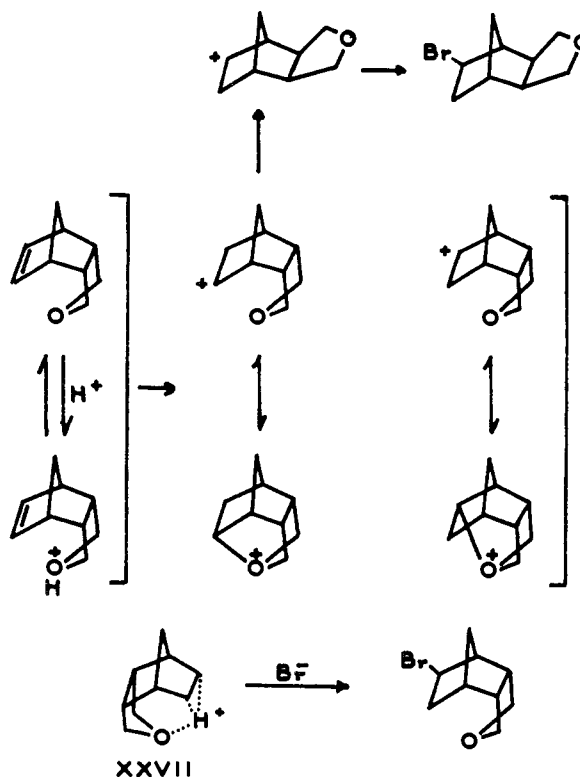


Three additional derivatives were prepared but their stereochemical structures were not proved. Like *endo*-dicyclopentadiene,<sup>7,14</sup> both *p*-thiocresol and phenol react with the *endo*-ether, but by analogy with the previously described reactions the products probably have the *endo* configuration shown in formulas XXV and XXVI. The 9-*p*-thiocresyl derivative was oxidized in high yield by hydrogen peroxide to a sulfone. Addition of bromine to the *endo*-ether yielded a crude material, possibly a mixture of bromides, from which only one product was isolated in pure form. Initial attempts to prove the structure of this solid dibromo ether were unsuccessful.



Since *endo*-dicyclopentadiene is known to rearrange with acidic reagents, any mechanism proposed for the reactions of 2-oxa-1,2-dihydro-*endo*-

dicyclopentadiene yielding unrearranged products must involve the oxygen in the 2-position. The scheme below illustrates tautomeric and resonance forms in which the oxygen atom in the 2-position contributes to resonance stabilization of the carbonium ion formed by addition of a proton to the norbornylene double bond. The non-classical, symmetrically bridged ion XXVII illustrates the possibility of an interaction between the  $\pi$ -cloud of the olefinic center, a proton and the unbonded 2p-orbital of the ether oxygen. Attack of bromide ion at C<sup>9</sup> or C<sup>10</sup> neutralizes the positive charge and the bridged ion collapses yielding the bromide in which the *endo* configuration is retained. Initial protonation of the ether oxygen might account for the lessened reactivity in the ether series because approach of a second proton to the site of the double bond would be discouraged by the existing positive charge in the molecule. The steric possibility of interaction between C<sup>9</sup> or C<sup>10</sup> and the oxygen in the 2-position has been demonstrated by an internal cyclization of 2-aza-1,2-dihydro-*endo*-dicyclopentadiene.<sup>15</sup>



The accepted mechanism of the rearrangement of *endo*-dicyclopentadiene to a 9-substituted *exo* derivative requires an *exo* configuration of the 9-substituent.<sup>6</sup> In the products of the addition reactions of 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene, the 9-substituent must have the *exo* configura-

(13) F. Bergmann and H. Japhe, *Anal. Chem.*, **20**, 146 (1948).

(14) H. A. Bruson and T. Riener, U. S. Patent 2,376,340 (1945).

(15) P. Wilder, Jr., and C. F. Culbertson, *THIS JOURNAL*, **81**, 2027 (1959).

tion not only in the rearranged portion of the product, but also in the unrearranged product. If the reaction proceeding without rearrangement follows the mechanism suggested above, then the nucleophilic group must approach the bridged ion XXVII from the top, yielding 9-*exo*-substituted unrearranged derivatives.

### Experimental<sup>16</sup>

**Preparation of *endo-cis*-Bicyclo[2.2.1]-5-heptene-2,3-dimethylol (VIII).**—The cyclopentadiene-maleic anhydride adduct was reduced with lithium aluminum hydride according to the method of Winston.<sup>17</sup> From 65.6 g. (0.40 mole) of the adduct, 65.7 g. of crude product was obtained which was recrystallized from nitroethane yielding 45.3 g. (74%) of the diol VIII. A small sample was recrystallized from ether, m.p. 85–86° (reported<sup>2</sup> 86°).

The diol readily formed a phenyl azide adduct XXVII, m.p. 165.5–167° (reported<sup>2</sup> 168°).

A ditosylate was prepared according to the method of Winston,<sup>17</sup> m.p. 90–90.5° (reported<sup>2</sup> 90–91°).

A dibrosylate was prepared from 1.5 g. (0.0098 mole) of pure diol VIII, 25 ml. of anhydrous pyridine and 5 g. (0.02 mole) of *p*-bromobenzenesulfonyl chloride. The solution was warmed on a steam-bath for 4 hours, diluted to 250 ml. with water and extracted three times with ether. The extract was dried over magnesium sulfate. Removal of the ether yielded a dark red residue which was recrystallized from ethanol-water, m.p. 138.5–139°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>20</sub>Br<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C, 42.69; H, 3.43. Found: C, 42.69; H, 3.59.

**Catalytic Reduction of the Diol VIII. Preparation of *endo-cis*-Bicyclo[2.2.1]heptane-2,3-dimethylol (V).**—A solution of 30.8 g. (0.20 mole) of the unsaturated diol in 250 ml. of absolute ethanol was reduced with Adams catalyst at an average hydrogen pressure of 40 p.s.i. Exactly 0.20 mole of hydrogen was absorbed and removal of the ethanol from the filtered solution yielded a viscous liquid which crystallized on cooling in an ice-bath for 2 hours. The product was recrystallized from ether yielding 30.2 g. (97%) of the dihydro diol V, m.p. 65–66° (reported<sup>2</sup> 62°).

A dibrosylate was prepared by the same method used to obtain the dibrosylate of the unsaturated diol VIII. Twenty grams (0.13 mole) of the saturated diol and 70 g. (0.27 mole) of *p*-bromobenzenesulfonyl chloride in 350 ml. of anhydrous pyridine yielded 30.7 g. (40%) of crude product. A sample was purified by recrystallization from ethanol-water, m.p. 162–162.5°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>22</sub>Br<sub>2</sub>O<sub>6</sub>S<sub>2</sub>: C, 42.43; H, 3.73. Found: C, 42.43; H, 3.90.

**Preparation of 2-Oxa-1,2-dihydro-*endo*-dicyclopentadiene (VII).**—The *endo* ether was prepared by a modification of the method of Alder and Roth.<sup>8</sup> A solution of 15.4 g. (0.10 mole) of the diol VIII in 50 ml. of anhydrous pyridine was treated with 20 g. (0.11 mole) of *p*-toluenesulfonyl chloride. After 15 hours the reaction mixture was warmed on a steam-bath for 1 hour, poured over about 200 g. of ice neutralized with 10% hydrochloric acid and extracted with ether. The extract was dried over magnesium sulfate and the ether removed under diminished pressure yielding 11.8 g. (88%) of a residue which partially solidified upon standing.

The phenyl azide adduct XI was prepared and recrystallized from absolute ethanol, m.p. 174–176° (reported<sup>3</sup> 178°).

**Preparation of *exo*-Bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic Acid Anhydride.**—The *endo*-anhydride was rearranged thermally according to the method of Craig<sup>18</sup> to give the *exo* isomer, m.p. 142–143° (reported<sup>18</sup> 140–142°).

**Preparation of *exo-cis*-Bicyclo[2.2.1]-5-heptene-2,3-dimethylol (IV).**—The *exo*-diol was prepared by reduction of the *exo*-anhydride with lithium aluminum hydride by the same method used to obtain the *endo*-diol VIII, except that the solid anhydride was added slowly through a Gooch tube rather than being extracted from a Soxhlet thimble. Reduction of 32.8 g. (0.20 mole) of the anhydride with 10 g. of

lithium aluminum hydride in 600 ml. of anhydrous ether yielded 24 g. (89%) of a clear liquid. A sample was distilled, b.p. 114–116° (0.6 mm.) (reported<sup>3</sup> b.p. 95° (0.035 mm.)).

**Preparation of 2-Oxa-1,2-dihydro-*exo*-dicyclopentadiene (III).**—The *exo*-ether was synthesized from the *exo*-diol IV by the same procedure described for the preparation of the *endo*-ether. From 46.2 g. (0.30 mole) of the diol there was obtained a crude product which on distillation yielded 20.5 g. (50%) of pure *exo*-ether, b.p. 86–88° (25 mm.), *n*<sub>D</sub><sup>20</sup> 1.4960 (reported<sup>3</sup> b.p. 82° (24 mm.), *n*<sub>D</sub><sup>20</sup> 1.4973).

The phenyl azide adduct XII recrystallized as prisms from acetone, m.p. 126–127° (reported<sup>3</sup> 127°).

**Addition of Hydrobromic Acid to 2-Oxa-1,2-dihydro-*endo*-dicyclopentadiene. Preparation of 9-*exo*-Bromo-2-oxatetrahydro-*endo*-dicyclopentadiene (IX).**—A solution of 6.8 g. (0.05 mole) of crude *endo*-ether VIII in 6 ml. of hexane<sup>19</sup> was stirred and refluxed for 3 hours with 17.1 ml. (0.15 mole) of 47.8% hydrobromic acid. Solid sodium carbonate was added to neutralize excess acid and the reaction mixture was extracted with ether. The ether was washed with water, dried over magnesium sulfate and removed. Distillation of the residue yielded 5.4 g. (50%) of the bromide IX, b.p. 83–84° (0.5 mm.), *n*<sub>D</sub><sup>25</sup> 1.5361.

*Anal.* Calcd. for C<sub>9</sub>H<sub>13</sub>BrO: C, 49.79; H, 6.03. Found: C, 49.96; H, 6.21.

**Dehydrohalogenation of 9-*exo*-Bromo-2-oxatetrahydro-*endo*-dicyclopentadiene (IX).**—A solution of 2.17 g. (0.01 mole) of pure bromide IX and 2.24 g. (0.04 mole) of potassium hydroxide in 10 ml. of absolute ethanol was refluxed with stirring for 12 hours. The mixture was diluted with water and extracted three times with ether. The combined extracts were washed with water, dried over magnesium sulfate, filtered, and treated with 1.5 g. (0.13 mole) of phenyl azide. After 2 days the precipitate was separated by filtration and washed with ether, yielding 1.2 g. (47%) of crude adduct, m.p. 177.5–179°. The product was recrystallized from ethanol, m.p. 178–179°; a mixed melting point with the adduct XI of 2-oxa-1,2-dihydro-*endo*-dicyclopentadiene showed no depression.

**Dehydrohalogenation of the Crude Product of the Addition of Hydrobromic Acid to 2-Oxa-1,2-dihydro-*endo*-dicyclopentadiene (VII).**—Addition of hydrobromic acid to 6.8 g. (0.05 mole) of the *endo*-ether VII in 6 ml. of hexane as previously described yielded 9.7 g. (0.045 mole, 90%, calculated as bromo-ether) of a dark viscous liquid. The crude product was dissolved in a solution of 10 g. (0.18 mole) of potassium hydroxide in 45 ml. of absolute ethanol and refluxed with stirring for 24 hours. The reaction was worked up as previously described and treated with 6.75 g. (0.057 mole) of phenyl azide. After 1 week 6.8 g. (0.027 mole, 54%) of a mixture of the adducts of the *endo*- and the *exo*-ethers was collected. From the total yield 1.14 g. (0.0045 mole, 17% of the product) of the *exo* derivative XII was isolated by manual separation and fractional recrystallization from acetone, m.p. 127–128° (reported<sup>3</sup> 127°); a mixed melting point with a known sample of the adduct of the *exo* isomer was undepressed.

**Preparation of 9-Bromo-2-oxatetrahydro-*exo*-dicyclopentadiene (X).**—A mixture of 3.4 g. (0.025 mole) of the *exo*-ether in 3 ml. of hexane and 8.5 ml. (0.075 mole) of 48% hydrobromic acid was refluxed with stirring for 3 hours. Excess acid was neutralized with solid sodium carbonate and the reaction mixture was extracted with ether. The ether was dried over magnesium sulfate and removed. Distillation of the residue yielded 3.1 g. (57%) of the bromide, b.p. 83–84° (0.6 mm.). The product was redistilled, b.p. 83–84° (0.6 mm.), *n*<sub>D</sub><sup>24</sup> 1.5325. Three attempts to obtain a satisfactory elemental analysis for this bromide failed. The average of these analyses is given below.

*Anal.* Calcd. for C<sub>9</sub>H<sub>13</sub>BrO: C, 49.79; H, 6.03. Found: C, 51.27; H, 6.61.

**Dehydrohalogenation of 9-Bromo-2-oxatetrahydro-*exo*-dicyclopentadiene (X).**—A solution of 2.17 g. (0.010 mole) of bromide and 2.24 g. (0.040 mole) of potassium hydroxide in 10 ml. of absolute ethanol was refluxed with stirring for 12 hours. The mixture was poured into an excess of water and extracted with ether. The extract was washed with water, dried over magnesium sulfate and filtered. An ether solu-

(16) Melting points and boiling points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer model 21 double beam recording spectrophotometer. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(17) A. Winston, Ph.D. Thesis, Duke University, 1955.

(18) D. Craig, THIS JOURNAL, 73, 4889 (1951).

(19) The hexane used in many of these reactions prevented the *endo*-ether from collecting on the walls of the reflux condenser.

tion of phenyl azide was added and after 3 days 1.35 g. (53%) of solid adduct had formed. The product recrystallized from acetone in the form of prisms, m.p. 126–127°; a mixed melting point with the adduct of the *exo*-ether was not depressed.

**Preparation of 9-*exo*-Chloro-2-oxatetrahydro-*endo*-dicyclopentadiene (XVI).**—To 13.6 g. (0.1 mole) of the crude *endo*-ether VII was added 15 ml. of hexane and 20 g. (0.2 mole) of concentrated hydrochloric acid. The mixture was stirred and refluxed for 5 hours and then poured into 200 ml. of water. Excess acid was neutralized with sodium carbonate and the ethereal extract was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the ether and distillation of the residue yielded 9.5 g. (55%) of the chloride, b.p. 90.0–92.0° (3.25 mm.),  $n_D^{25}$  1.5135.

*Anal.* Calcd. for  $C_9H_{11}ClO$ : C, 62.61; H, 7.59. Found: C, 62.66; H, 7.65.

**Dehydrohalogenation of 9-*exo*-Chloro-2-oxatetrahydro-*endo*-dicyclopentadiene (XVI).**—A solution of 7.5 g. of potassium hydroxide in 35 ml. of absolute ethanol was added to 5.2 g. (0.03 mole) of the purified chloro ether. The mixture was heated under reflux for 23 hours, poured into an excess of water and extracted with ether. The extract was washed with water until the aqueous solution was no longer basic and was dried over anhydrous magnesium sulfate. The ether was removed and then to the residue was added 6 g. of phenyl-azide in an ether solution. Upon standing, crystals were deposited, which on recrystallization from absolute ethanol gave 0.5 g. (7%), m.p. 176–178°. A mixed melting point with the adduct of the *endo*-ether was not depressed.

**Preparation of 9-*exo*-Acetoxy-2-oxatetrahydro-*endo*-dicyclopentadiene (XIII).**—To 20 ml. of hexane, 0.8 g. of sulfuric acid (98%) and 50 ml. of glacial acetic acid was added 20.0 g. (0.15 mole) of purified *endo*-ether. The mixture was heated under reflux with stirring for 5 hours. The reaction mixture was then diluted with water and neutralized with sodium bicarbonate. The mixture was extracted with ether and the ether extract was washed with water and dried over anhydrous magnesium sulfate. Upon removal of the ether, the residue, distilled at reduced pressure, yielded 20.2 g. (70%) of the acetate, b.p. 109–110° (3 mm.), and 1.0 g. (5%) of unreacted starting material which was identified through its phenyl azide derivative, m.p. 176–177°. An analytical sample of the acetate was prepared; b.p. 110–112° (3 mm.),  $n_D^{25}$  1.4871.

*Anal.* Calcd. for  $C_{11}H_{15}O_3$ : C, 67.32; H, 8.22. Found: C, 67.13; H, 8.48.

**Hydrolysis of the Acetate XIII. Preparation of 9-*exo*-Hydroxy-2-oxatetrahydro-*endo*-dicyclopentadiene (XV).**—To a solution of 28 g. (0.5 mole) of potassium hydroxide in 50 ml. of 95% ethanol and 50 ml. of water was added 11.8 g. (0.06 mole) of the acetoxy derivative XIII. The mixture was heated to boiling and then was allowed to stand overnight. The mixture was poured into 100 ml. of water and extracted three times with ether. The ether solution was dried over anhydrous magnesium sulfate. Removal of ether and ethanol and distillation of the residue yielded 6.5 g. (70%) of the hydroxy derivative XV, b.p. 100–102° (0.4 mm.), 104–106° (0.5 mm.). The product solidified in the condenser and became a viscous liquid upon exposure to air. The elemental analysis of 9-*exo*-hydroxy-2-oxatetrahydro-*endo*-dicyclopentadiene (XV) is given in a later paragraph.

A *p*-nitrobenzoate was prepared and purified by recrystallization from methanol, m.p. 150.5–152.5°.

*Anal.* Calcd. for  $C_{10}H_{13}O_4N$ : C, 63.35; H, 5.65. Found: C, 63.12; H, 5.52.

**Preparation of 9-*exo*-Chloro-2-oxatetrahydro-*endo*-dicyclopentadiene (XVI) from 9-Hydroxy-2-oxatetrahydro-*endo*-dicyclopentadiene (XV).**—To 5.2 g. (0.03 mole) of the bicyclic alcohol XXI was added slowly 9.0 g. (0.25 mole) of thionyl chloride. When the heat of reaction had subsided, the mixture was refluxed on a steam-bath for 1 hour. Excess water was added cautiously, and the mixture was extracted with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. Removal of ether and distillation of the residue at reduced pressure yielded the chloro derivative XVI, b.p. 89–90° (3.25 mm.),  $n_D^{25}$  1.5121. The infrared spectrum of this product was identical with that of the chloride obtained by direct addition of hydrochloric acid to the *endo*-ether, previously described.

**Oxidation of the Alcohol XV Obtained by Hydrolysis of the Acetate XIII. Preparation of 9-Keto-2-oxatetrahydro-*endo*-dicyclopentadiene (XVIII) and the 2,4-Dinitrophenylhydrazones XIX.**—A solution of 13 g. (0.084 mole) of the alcohol XV in 25 ml. of glacial acetic acid was treated dropwise with stirring with 8.0 g. (0.08 mole) of chromic acid in 25 ml. of glacial acetic acid and 100 ml. of water. The temperature was maintained at about 40° during the addition and the reaction mixture was allowed to stand overnight at room temperature. After warming on a steam-bath for 1 hour the solution was poured into 1 liter of water and extracted with ether. The extract was washed with aqueous sodium carbonate and with water and dried over magnesium sulfate. Removal of the ether yielded 8.0 g. (62%) of crude ketone. Attempts to distill the product failed because of solidification of the distillate in the condenser, b.p. 105–106° (3 mm.). The product could not be sublimed satisfactorily nor recrystallized from any of the common solvents or nitroethane. An infrared spectrum of material scraped from the condenser after attempted distillation showed the expected carbonyl peak at 5.72  $\mu$  and also some hydroxyl impurity.

A sample was used to prepare a 2,4-dinitrophenylhydrazone which formed slowly and was recrystallized from 95% ethanol-ethyl acetate, m.p. 181.5–182°; mixed melting point with the derivative obtained through the nitroso chloride dimer XIV, 181.5–182°; mixed melting point with a sample of the derivative of the *exo*-ketone, 145–164°.

*Anal.* Calcd. for  $C_{10}H_{12}N_4O_6$ : C, 54.21; H, 4.85. Found: C, 54.01; H, 4.74.

**Preparation of the Dimeric Nitroso Chloride XIV of 2-Oxa-1,2-dihydro-*endo*-dicyclopentadiene.**—A solution of 1.36 g. (0.010 mole) of the *endo*-ether, 1.25 g. (0.011 mole) of isoamyl nitrite, 1 ml. of glacial acetic acid and 1 ml. of 95% ethanol was cooled in an ice-bath and treated dropwise with a solution of 1 ml. of concentrated hydrochloric acid in 1 ml. of 95% ethanol with vigorous stirring. The solid product was collected by filtration and washed with 95% ethanol and with ether. The compound could not be recrystallized without decomposition, but a sample was prepared by trituration with 95% ethanol yielding 1.5 g. (75%) of the nitroso chloride XIV, m.p. 187.5–188.5°.

*Anal.* Calcd. for  $C_{18}H_{24}Cl_2N_2O_4$ : C, 53.60; H, 6.00. Found: C, 53.83; H, 6.16.

**Preparation of the Dimeric Nitroso Chloride of the *exo*-Ether.**—The nitroso chloride was prepared by the same method used to prepare the nitroso chloride of the *endo*-ether. The product could not be recrystallized without decomposition, but again a sample was purified by trituration with 95% ethanol, m.p. 169–170°.

*Anal.* Calcd. for  $C_{18}H_{24}Cl_2N_2O_4$ : C, 53.60; H, 6.00. Found: C, 53.82; H, 5.91.

**Monomerization of the Dimeric Nitroso Chloride XIV. Preparation of 10-Chloro-9-keto-2-oxatetrahydro-*endo*-dicyclopentadiene Oxime (XVII).**—A suspension of 30 g. (0.15 mole) of the dimeric nitroso chloride in 200 ml. of *n*-amyl alcohol was refluxed with vigorous stirring until all of the solid had dissolved. After removal of *n*-amyl alcohol under diminished pressure the black viscous liquid residue was boiled in ligroin (90–120°) and treated several times with Norite. Upon cooling, 11.5 g. (38%) of the monomeric material was precipitated, m.p. 138–140°. A sample was further purified by recrystallization from chloroform, m.p. 145–147°.

*Anal.* Calcd. for  $C_9H_{12}ClNO_2$ : C, 53.60; H, 6.00. Found: C, 53.56; H, 6.19.

**Preparation of 9-Keto-2-oxatetrahydro-*endo*-dicyclopentadiene 2,4-Dinitrophenylhydrazone (XIX) from the Dimeric Nitroso Chloride XVII.**—A suspension of 10 g. (0.025 mole) of the dimeric nitroso chloride in 80 ml. of *n*-amyl alcohol was refluxed with vigorous stirring for 2 hours. After cooling the brown solution, 25 ml. of absolute ethanol, 12.5 ml. of glacial acetic acid and 6.0 g. (0.13 g. atom) of zinc were added and the mixture was refluxed for 5 hours. The reaction stood overnight and then ethanol and some *n*-amyl alcohol were removed under diminished pressure. The residue was poured into 250 ml. of ether and the pale yellow ether solution decanted from a viscous insoluble mass which settled to the bottom of the flask. The ether was washed with water, dried over magnesium sulfate and removed. The residue consisted primarily of *n*-amyl alcohol which was removed under reduced pressure. All materials boiling

over 100° (10 mm.) were collected yielding a crude distillate of 0.7 g. (9.2%) which was treated directly with a 2,4-dinitrophenylhydrazine reagent. After 12 hours a precipitate was formed which yielded upon recrystallization from 95% ethanol-ethyl acetate 0.7 g. of a mixture of slender yellow needles and small red prisms. A few crystals were separated manually, m.p. yellow needles 180–182°, red prisms 182–185°, mixed m.p. 184–185°.

**Preparation of 9-Acetoxy-2-oxatetrahydro-*exo*-dicyclopentadiene (XXI).**—A mixture of 10.8 g. (0.080 mole) of the *exo*-ether, 25 ml. of glacial acetic acid and 1 g. of concentrated sulfuric acid was refluxed for 15 hours. After being cooled the reaction mixture was poured into about 100 ml. of cold water and excess acid was neutralized with solid sodium carbonate. Organic materials were separated by extraction with ether. The extract was washed with water and dried over magnesium sulfate and the ether was removed. The residue was distilled under reduced pressure yielding 13.3 g. (87%) of the acetate XXI, b.p. 85–86° (0.35 mm.),  $n_D^{25}$  1.4858.

*Anal.* Calcd. for  $C_{11}H_{16}O_3$ : C, 67.32; H, 8.22. Found: C, 67.38; H, 8.06.

**Hydrolysis of the Acetate XXI. Preparation of 9-Hydroxy-2-oxatetrahydro-*exo*-dicyclopentadiene (XXII).**—Seventeen grams (0.087 mole) of the acetate, 50 ml. of 95% ethanol, 50 ml. of water and 25 g. of potassium hydroxide were mixed and heated to boiling. The solution was allowed to stand overnight and then some of the alcohol was removed under diminished pressure. The residue was taken up in ether and water and the aqueous portion extracted with ether. The extract was washed with water and dried over magnesium sulfate. Removal of the ether and distillation of the residue yielded 10.0 g. (75%) of the alcohol, b.p. 95–97° (0.7 mm.). A sample was further purified by redistillation, b.p. 95–97° (0.7 mm.),  $n_D^{25}$  1.5120.

*Anal.* Calcd. for  $C_9H_{14}O_2$ : C, 70.10; H, 9.15. Found: C, 70.41; H, 9.21.

A *p*-nitrobenzoate was prepared from this alcohol, m.p. 122–124°.

*Anal.* Calcd. for  $C_{16}H_{17}NO_2$ : C, 63.35; H, 5.65. Found: C, 63.42; H, 5.70.

**Oxidation of the Alcohol XXII. Preparation of 9-Keto-2-oxatetrahydro-*exo*-dicyclopentadiene (XXIII).**—A solution of 7.7 g. (0.05 mole) of the alcohol in 12.5 ml. of glacial acetic acid was treated dropwise with stirring with 4.0 g. of chromic acid in 12.5 ml. of glacial acetic acid and 25 ml. of water. The temperature was maintained below 40° during the addition and then the solution was allowed to stand at room temperature overnight. After being warmed on a steam-bath for two hours, the mixture was neutralized with 10% sodium hydroxide. An attempt to remove the ketone by steam distillation failed. The aqueous solution was extracted with ether and the extract was washed with water and dried over magnesium sulfate. Removal of the ether and distillation of the residue yielded 1.9 g. (25%) of the ketone, b.p. 79–80° (0.6 mm.),  $n_D^{25}$  1.5032.

*Anal.* Calcd. for  $C_9H_{12}O_2$ : C, 71.02; H, 7.95. Found: C, 70.85; H, 8.09.

A 2,4-dinitrophenylhydrazone was prepared. Addition of the reagent to an alcoholic solution of the *exo*-ketone caused immediate precipitation of a yellow, finely crystalline product which was purified by recrystallization from 95% ethanol, m.p. 186–187°.

*Anal.* Calcd. for  $C_{15}H_{15}N_4O_6$ : C, 54.21; H, 4.85. Found: C, 54.34; H, 4.78.

**Addition of Formic Acid to the *endo*-Ether. Preparation of 9-Formoxy-2-oxatetrahydrodicyclopentadiene.**—A solution of 7.5 g. (0.055 mole) of partially purified *endo*-ether in 5 g. of 98% formic acid was refluxed with stirring for 20 hours. The reaction mixture was distilled directly under reduced pressure. After excess formic acid was removed, unreacted starting material sublimed. When the temperature began to rise the distillation was stopped and the *endo*-ether which had solidified in the condenser was removed. Then the formoxy derivative was collected; b.p. 84–85° (0.1 mm.),  $n_D^{27.5}$  1.5046. The yield of ester slightly contaminated with starting material was 2.34 g. (23.2%). In another run an analytical sample was obtained after repeated distillation; b.p. 92–94° (0.25 mm.),  $n_D^{28.5}$  1.4941.

*Anal.* Calcd. for  $C_{10}H_{14}O_3$ : C, 65.91; H, 7.74. Found: C, 65.66; H, 7.52.

**Hydration of the *endo*-Ether VII. Preparation of 9-*exo*-Hydroxy-2-oxatetrahydro-*endo*-dicyclopentadiene (XV).**—To 3.4 g. (0.025 mole) of the *endo*-ether in 3 ml. of hexane was added a solution of 2.5 g. (0.025 mole) of concentrated sulfuric acid in 7.5 ml. of water. The mixture was stirred under reflux for 5 hours, cooled, and extracted with ether. The ether solution was washed with aqueous sodium bicarbonate, dried over magnesium sulfate and the organic solvents removed under diminished pressure yielding 2 g. (52%) of crude product. Distillation of the viscous yellow liquid yielded 1.5 g. (49%) of a semi-solid, b.p. 100–108° (0.4–0.35 mm.). The product was redistilled, b.p. 102–103° (0.4 mm.).

*Anal.* Calcd. for  $C_9H_{14}O_2$ : C, 70.10; H, 9.15. Found: C, 70.32; H, 9.25.

**Reactions of the Crude Hydration Product. Preparation of the *p*-Nitrobenzoate of the *endo*-Alcohol. Preparation of the 2,4-Dinitrophenylhydrazone of 9-Keto-2-oxatetrahydro-*exo*-dicyclopentadiene.**—A sample of the hydration product of the *endo*-ether which had been distilled once was used to prepare a *p*-nitrobenzoate, m.p. 149–151°.

Part of the same sample of hydration product was oxidized to the ketone. A 2.5-g. (0.016 mole) sample of the hydration product was dissolved in 5 ml. of glacial acetic acid and a solution of 1.6 g. (0.016 mole) of chromic acid in 5 ml. of glacial acetic acid and 10 ml. of water was added slowly with vigorous stirring at a temperature of about 40°. The reaction stood overnight and then was warmed on a steam-bath for 1 hour. The solution was cooled, diluted to 200 ml. with water and extracted with ether. The extract was dried over magnesium sulfate and removal of the ether yielded 0.5 g. (20%) of a pale yellow liquid which was dissolved in 20 ml. of 95% ethanol. Addition of 2,4-dinitrophenylhydrazine reagent caused an immediate precipitation. The solid was separated by filtration within 0.5 hour and recrystallized from 95% ethanol-ethyl acetate. After two recrystallizations, two crystal forms were observed and these were separated manually, m.p. light yellow needles 186–187°, m.p. darker prisms 182–184°, mixed melting point of needles and prisms 184–185.5°; a mixed melting point with a sample of the derivative of the *exo*-ketone was not depressed; mixed melting point with the *endo* derivative obtained from the nitroso chloride, 151–174°.

**Preparation of 9-*exo*-Chloro-2-oxatetrahydrodicyclopentadiene (XVI)**—A sample of the hydration product which had been distilled once to remove unreacted *endo*-ether was converted to the chloride. Seven grams (0.045 mole) of the alcohol, treated with 10 ml. of thionyl chloride, yielded 7.1 g. (84%) of crude chloride which was used directly in the next reaction without purification.

**Dehydrohalogenation of 9-*exo*-Chloro-2-oxatetrahydrodicyclopentadiene (XVI).**—A solution of 7.1 g. (0.041 mole) of the crude chloride obtained above, 10 g. (0.18 mole) of potassium hydroxide and 40 ml. of absolute ethanol was refluxed with stirring for 24 hours. The mixture was then poured into excess water, extracted thoroughly with ether and the extract was washed with water and dried over magnesium sulfate. The solution was concentrated to about 25 ml. under diminished pressure and 2.5 g. (0.042 mole) of phenyl azide in ether solution was added. Solid which formed was collected over a period of one week yielding 1.81 g. (23%) of crude adduct. Recrystallization from acetone gave 1.65 g. (18%) of colorless needles which was entirely the phenyl azide adduct of the *endo*-ether, m.p. 176–177°.

**Addition of Methanol to 2-Oxa-1,2-dihydro-*endo*-dicyclopentadiene (VII). Preparation of 9-*exo*-Methoxy-2-oxatetrahydro-*endo*-dicyclopentadiene (XXIV).**—To 6.5 g. of methanol, cooled in an ice-bath, was added with stirring 3.0 g. of 98% sulfuric acid so that the temperature remained between 5–20°. After slowly adding 13.6 g. (0.1 mole) of crude *endo*-ether, the mixture was heated under reflux with stirring for 5 hours. The reaction was poured into 200 ml. of water, neutralized with sodium carbonate, and extracted three times with ether. The ether extract was washed with water and dried over anhydrous magnesium sulfate. Removal of the ether and distillation of the residue yielded 11.8 g. (70.5%) of methoxy derivative, b.p. 99–101° (8.0 mm.),  $n_D^{25}$  1.4880.

*Anal.* Calcd. for  $C_{10}H_{16}O_2$ : C, 71.39; H, 9.59. Found: C, 71.48; H, 9.44.

**Preparation of 9-*exo*-Methoxy-2-oxatetrahydro-*endo*-dicyclopentadiene (XXIV) from 9-*exo*-Hydroxy-2-oxatetra-**

hydro-endo-dicyclopentadiene (XV).—To 1.6 g. of potassium metal (0.04 g. atom) was added 30 ml. of toluene, previously dried over sodium. The mixture was heated until the potassium melted and then was allowed to cool slowly with vigorous stirring. A 5.2-g. (0.03 mole) sample of the alcohol XV in 10 ml. of dry toluene was added slowly and the mixture was refluxed for 2 hours with stirring and cooled in an ice-bath; then 6.4 g. (0.045 mole) of methyl iodide was added dropwise. The mixture was heated for an additional hour. The precipitate of potassium chloride was removed by filtration, washed with ethanol, and dissolved in water. The water was extracted with ether, and this extract was added to the toluene-alcohol mixture. The solution was dried over anhydrous magnesium sulfate, and the solvents were removed. The residue, distilled under reduced pressure, yielded 4.1 g. (81%) of product, b.p. 99–101° (8.0 mm.),  $n_D^{20}$  1.4870. The infrared spectrum of this methoxy derivative was the same as that of the product obtained by direct addition of methanol.

Addition of *p*-Thiocresol to 2-Oxa-1,2-dihydro-endo-dicyclopentadiene. Preparation of 9-*p*-Thiocresyl-2-oxatetrahydrodicyclopentadiene.—To 13.6 g. (0.1 mole) of the crude bicyclic ether VII was slowly added with stirring 12.4 g. (0.1 mole) of *p*-thiocresol. When the heat of reaction subsided, the mixture was heated to 75° and held at that temperature overnight. The mixture was distilled under vacuum to remove unreacted *p*-thiocresol (b.p. 110–113° (32 mm.)) which solidified in the condenser. The residue was distilled again yielding 20.2 g. (78%) of the thiocresyl derivative, b.p. 148–150° (0.35 mm.). The product solidified after two days and was recrystallized from methanol, m.p. 72.0–72.5°.

*Anal.* Calcd. for  $C_{16}H_{20}OS$ : C, 73.80; H, 7.74. Found: C, 73.85; H, 7.80.

In 5 ml. of acetic acid and 5 ml. of acetic anhydride at ice temperature was dissolved 2.6 g. (0.01 mole) of the thiocresyl derivative XXV. To it was added dropwise and with stirring 3 ml. of cold 30% hydrogen peroxide. When heat was no longer evolved, the mixture was heated for one hour on a steam-bath. Cooling the reaction mixture yielded crystals of the sulfone which were recrystallized from methanol. The yield was essentially quantitative, 2.8 g. (96%), m.p. 164–166°.

*Anal.* Calcd. for  $C_{16}H_{20}O_3S$ : C, 65.72; H, 6.90. Found: C, 65.52; H, 7.01.

Addition of Phenol to 2-Oxa-1,2-dihydro-endo-dicyclopentadiene. Preparation of 9-Phenoxy-2-oxatetrahydrodicyclopentadiene.—A mixture of 13.6 g. (0.1 mole) of the endo-ether and 9.4 g. of phenol was added dropwise to 2.0 g. of 98% sulfuric acid maintained at 0°. The reaction was stirred for 2 hours, and then poured into 50 ml. of hot water. The oily layer was washed with hot sodium bicarbonate solution, and distilled under reduced pressure, yielding 2 g. (9%), b.p. 122–124° (0.25 mm.). The oil solidified after one week and the product was recrystallized from methanol; m.p. 62.5–64.5°.

*Anal.* Calcd. for  $C_{15}H_{18}O_2$ : C, 78.23; H, 7.88. Found: C, 78.02; H, 7.77.

Bromination of 2-Oxa-1,2-dihydro-endo-dicyclopentadiene.—Ten grams (0.074 mole) of the endo-ether which had been purified by sublimation, m.p. 85–90°, was dissolved in 40 ml. of chloroform and treated dropwise with stirring with 12 g. (0.075 mole) of bromine in 30 ml. of chloroform. The reaction mixture was stirred overnight and excess bromine was then destroyed by shaking the chloroform solution with aqueous sodium thiosulfate. The chloroform was dried over magnesium sulfate and removed yielding 23.3 g. of a pale yellow viscous liquid which on cooling in an ice-bath gave a precipitate. More chloroform was removed under reduced pressure at room temperature and 12.5 g. (58%) of solid was obtained by cooling a slurry of the crude product in absolute ethanol. A sample was further purified by distillation, b.p. 118–120° (0.3 mm.), and recrystallization from nitroethane, m.p. 101–102°.

*Anal.* Calcd. for  $C_9H_{12}Br_2O$ : C, 36.51; H, 4.09. Found: C, 36.66; H, 4.12.

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DURHAM, N. C.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS]

## Quantitative Relationships in the Reactions of *trans*-4-X-Cyclohexanecarboxylic Acids and their Methyl Esters<sup>1</sup>

BY SAMUEL SIEGEL AND J. M. KOMARMY<sup>2</sup>

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The dissociation constants of a series of *trans*-4-X-cyclohexanecarboxylic acids (X = H, -OH, -OCH<sub>3</sub>, -Cl, -CO<sub>2</sub>CH<sub>3</sub>, -CN and =O) have been measured in water and two mixed solvents at 25°. The rate of reaction of these acids with diphenyldiazomethane and the rate of the basic hydrolysis of the methyl esters in 50% aqueous methanol were also determined, the latter at three temperatures. These data are correlated by an equation of the form  $\log k/k_0 = \rho''\sigma'$ , e.g., the Hammett equation. The dimensions of substituted cyclohexanecarboxylic acids approximate the dimensions of substituted benzoic acids and the magnitudes of the substituent effects are comparable. The difference in the effect of a substituent upon reactivity in the two series results mainly from the resonance interaction of the substituent with the aromatic ring, an effect which is obviously absent in the saturated compounds. Groups which do not interact strongly with an aromatic ring have about the same quantitative effect upon reactivity in both series. The substituent effects can be calculated with reasonable accuracy by employing the Kirkwood-Westheimer model as modified by Tanford.

A search for quantitative relationships between the structure of organic compounds and their reactivity has received considerable attention.<sup>3–6</sup> Undoubtedly, the Hammett equation correlates

(1) From the dissertation submitted by J. M. Komarmy in partial fulfillment of the requirements for the Ph.D. degree at the University of Arkansas, January, 1958. Presented in part before the Division of Organic Chemistry, 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957.

(2) Flint Community College, Flint, Mich.

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 184.

(4) G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941.

the broadest spectrum of reactions in a simple way.<sup>7</sup> The success of this equation has been attributed to the rigidity which the benzene ring imparts to the structure of substituted aromatic compounds and which holds the reactive center and the substituent at a relatively fixed distance.<sup>8</sup> In few aliphatic systems is so simple a relation-

(5) H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

(6) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(7) Reference 3, p. 186.

(8) P. D. Bartlett in "Organic Chemistry," Vol. IV, Edited by H. Gilman, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 19–20.