

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

Bridged Polycyclic Compounds. VIII. The Bromination of Bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic Acid^{1,2}

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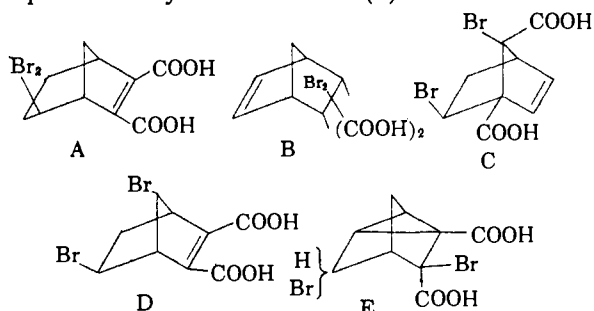
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The bromination of bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic acid (I) in the dark gave a dibromide. This was hydrogenated to a saturated dibromide which in turn was transformed into an anhydride, a bromolactonic acid and a methyl ester. The saturated dibromide was debrominated to give bicyclo[2,2,1]hept-5-ene-*endo-cis*-2,3-dicarboxylic acid. The bromolactonic acid was converted to the known γ -lactone of *endo*-5-hydroxybicyclo[2,2,1]heptane-*endo-cis*-2,3-dicarboxylic acid. These transformations suggest that the bromination product is *trans*-5,6-dibromobicyclo[2,2,1]hept-2-ene-2,3-dicarboxylic acid.

In connection with a study of the bromination of quadricycloheptane - 2,3 - dicarboxylic acid,¹ it seemed interesting to investigate the bromination of its valence-bond tautomer, bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic acid (I), the reactant from which quadricycloheptane-2,3-dicarboxylic acid was obtained.³

The bromination of I was carried out in precisely the same manner as was the bromination of its isomer, *i.e.*, in the dark and in a mixed solvent of ethyl acetate and carbon tetrachloride. The bromination gave a solid, m.p. 242°, (II) in 47% yield. This material had a satisfactory analysis for C₉H₈Br₂O₄.

The addition of bromine to I may occur in any of the following theoretically possible ways for which analogies are known. (i) Addition of bromine to the Δ^5 -double bond would result in the formation of one or more of the stereoisomeric dibromides represented by structure A. (ii) Addition to the



Δ^2 double bond would result in those dibromides represented by structure B. Addition of bromine to the Δ^2 -double bond was considered the least likely as addition of bromine to double bonds which are conjugated with electron-withdrawing groups, such as carboxylic acid groups, is known to proceed with difficulty compared to the addition of bromine to ethylene or to a double bond which is flanked by an electron-donating group.⁴ (iii) Bromination with a normal Wagner-Meerwein rearrangement⁵ would

(1) Previous paper in series: S. J. Cristol and R. T. LaLonde, *THIS JOURNAL*, **80**, 4355 (1958).

(2) This paper was presented at the Sixteenth International Congress of Pure and Applied Chemistry, Paris, France, July, 1957.

(3) S. J. Cristol and R. L. Snell, *THIS JOURNAL*, **76**, 5600 (1954); **80**, 1950 (1958).

(4) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 211.

(5) See for example the formation of: (a) the γ -lactone of *anti*-7-bromo-*endo*-5-hydroxy-6-oxabicyclo[2,2,1]heptane-*endo-cis*-2,3-dicarboxylic acid from 7-oxabicyclo(2,2,1)-5-heptene-*exo-cis*-2,3-dicarboxylic acid [R. B. Woodward and H. Baer, *THIS JOURNAL*, **70**, 1161 (1948)]; (b) *syn*-2,7-dibromobicyclo[2,2,1]heptane from norbornene [H. Kwart

give the dibromides which are represented by structures C and D. (iv) Addition may occur in a manner analogous to the addition of bromine to bicyclo[2,2,1]heptadiene⁶ which gives, in part, *cis*- and *trans*-3,5-dibromonortricyclenes. The resulting dibromide from the bromination of I would be E.

The 242° dibromide was unsaturated toward potassium permanganate, reacted with silver nitrate only at the boiling point of the ethanol solvent, and was inert toward sodium iodide in acetone.

In the infrared absorption spectrum of the dibromide was found an absorption peak at 5.83 μ , which was assigned to the carboxylic acid carbonyl absorption,⁷ and absorption peaks at 6.04 and 6.20 μ . The latter two peaks are in the region of carbon-carbon double bond absorption.⁸

The positive test for unsaturation and the appearance of carbon-carbon double bond absorption in the infrared spectrum is evidence which definitely establishes that the dibromide is not represented by structure E.

The elimination of structures B and C can be made from the observation that the characteristic *cis*-disubstituted carbon-carbon double bond absorptions in the regions of 6.35 and 14.2 μ ⁹ are absent, as well as from the ultraviolet absorption spectrum of the 242° dibromide. An absorption maximum at 250 m μ , log ϵ 3.74, demonstrates that the Δ^5 -double bond was brominated rather than the Δ^2 -double bond, since only a carbon-carbon double bond in conjugation with the carboxylic acid carbonyl groups would give rise to strong absorption in this region.¹⁰

For the general structure A, we may write now three specific structures A_I-A_{III} which in addition to structure D gives a total of four structures to consider for the dibromide. Of the four probable

and L. Kaplan, *ibid.*, **76**, 4072 (1954); (c) the γ -lactone of *anti*-7-bromo-*endo*-5-hydroxybicyclo[2,2,1]heptane-*endo-cis*-2,3-dicarboxylic acid [C. D. Ver Nooy and C. S. Rondstedt, Jr., *ibid.*, **77**, 3583 (1955)]; (d) *syn*-5,7-dibromobicyclo[2,2,1]-2-heptene from bicyclo[2,2,1]heptadiene [S. Winstein and M. Shatavsky, *Chemistry & Industry*, 56 (1956)].

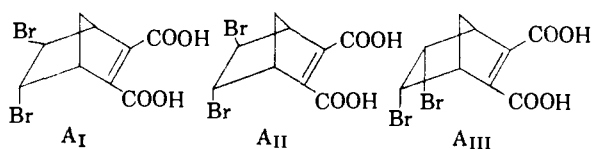
(6) (a) S. Winstein and M. Shatavsky, *ibid.*, 56 (1956); (b) L. Schmerling, L. P. Luvisi and R. W. Welch, *THIS JOURNAL*, **78**, 2819 (1956).

(7) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 143.

(8) L. J. Bellamy, *ibid.*, pp. 32-34.

(9) P. R. Schleyer, Abstracts of the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956, p. 29-O.

(10) (a) E. A. Braude and F. C. Nachod, "Determinations of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, pp. 147-148. (b) The corresponding bicyclo[2,2,1]-2-heptene-2,3-dicarboxylic acid has λ_{max} 247 m μ , log ϵ 3.96.



structures, A_{III} was considered the least probable on the basis of preferred *exo*-addition of reagents to bicyclic olefins.¹¹ *trans*-Bromination leading to the dibromide represented by structure A_I is the generally observed result for an ionic mode of addition which proceeds through a bromonium-ion intermediate.¹² The dibromide which is represented by structure A_{II} would arise by *cis*-bromination, a result which is uncommon when bromine adds to a double bond by an ionic mode of addition but which is reported to occur for a free-radical bromination of a bicyclic olefin.¹³

When the 242° dibromide was hydrogenated in ethanol with platinum oxide catalyst, one mole of hydrogen was absorbed per mole of dibromide to give III, m.p. 193°, anal. $C_9H_{10}Br_2O_4$; III gave a negative potassium permanganate unsaturation test and reacted immediately at room temperature with a 2% ethanolic silver nitrate solution.

The hydrogenation of the dibromide II should proceed in accordance with the *exo*-addition rule to give a saturated dibromodicarboxylic acid, III, in which the carboxylic acid groups are both *endo*. The validity of the *exo*-addition rule is well established for analogous hydrogenations of bicyclic olefins.¹⁴ However, as will be discussed below, the stereochemistry of the hydrogenation is demonstrated in this paper to be in accordance with the *exo* addition rule, and it does not depend upon analogy.

Treatment of the 193° solid (III) with acetic anhydride produced a solid, m.p. 139°, which gave a satisfactory analysis for an anhydride, $C_9H_8Br_2O_5$, IV. The presence of the anhydride function was confirmed by noting two carbonyl absorption peaks at 5.60 and 5.37 μ . These absorptions may be compared to the carbonyl absorptions of succinic anhydride which are found at 5.61 and 5.36 μ .¹⁵

The saturated dibromide III, when treated with warm water, gave a solid, m.p. 254°, which has a satisfactory analysis for a bromolactonic acid $C_9H_9BrO_4$, V. The infrared absorption spectrum of this compound exhibited a strained γ -lactone-carbonyl absorption at 5.59 μ ¹⁶ and a carboxylic acid-carbonyl absorption at 5.83 μ .¹⁷

Treatment of this dibromide with diazomethane

(11) K. Alder and G. Stein, *Ann.*, **515**, 185 (1935); **525**, 183 (1936). For further references see S. J. Cristol and R. P. Arganbright, *THIS JOURNAL*, **79**, 6039 (1957).

(12) I. Roberts and G. E. Kimball, *ibid.*, **59**, 947 (1937).

(13) J. A. Berson and R. Swidler, *ibid.*, **76**, 4060 (1954).

(14) Some examples of the preference of *exo*-addition of hydrogen, in the presence of a catalyst, to bicyclic olefins are as follows: (a) bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylic acid gave bicyclo[2.2.1]heptane-*endo-cis*-2,3-dicarboxylic acid [K. Alder and G. Stein, *Ann.*, **525**, 183 (1936)]; (b) bicyclo[2.2.1]hept-2-ene-2-carboxylic acid gave bicyclo[2.2.1]heptane-*endo*-2-carboxylic acid [K. Alder and G. Stein, *ibid.*]; (c) 2,3-dimethylbicyclo[2.2.1]hept-2-ene gave *endo-cis*-2,3-dimethylbicyclo[2.2.1]heptane [E. Deussen, *J. prakt. Chem.*, [2] **114**, 113 (1936), and K. Alder and W. Roth, *Ber.*, **87**, 161 (1945)].

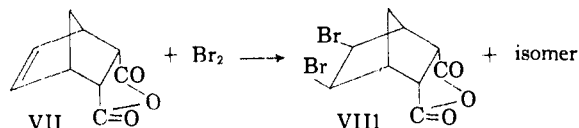
(15) L. J. Bellamy, ref. 7, p. 111.

(16) J. A. Berson, *THIS JOURNAL*, **76**, 4975 (1954).

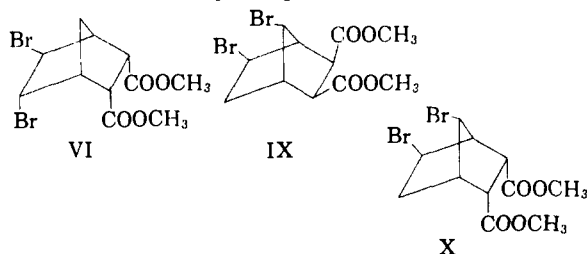
(17) L. J. Bellamy, ref. 7, p. 143.

gave a solid dimethyl ester, $C_{11}H_{14}Br_2O_4$ (VI), which melted at 125°.

The bromination of the olefin, bicyclo[2,2,1]-hept-5-ene-*endo-cis*-2,3-dicarboxylic anhydride (VII), when carried out in ethyl acetate, has been reported to give two products.¹⁸ In addition to *exo-cis*-5,6-dibromobicyclo[2,2,1]heptane-*endo-cis*-2,3-dicarboxylic anhydride (VIII), a second isomer was isolated by conversion to its methyl ester,



m.p. 119°. From what is known of the course of addition of bromine to bicyclic olefins, it was likely that this ester was either the *trans*-5,6-dibromo-*endo-cis*-2,3-dicarbomethoxy compound VI or the product of a normal Wagner-Meerwein rearrangement, that is, the *exo*-5-*anti*-7-dibromo-*exo-cis*-2,3-dicarbomethoxy compound IX.



Consideration of the method of preparation suggested that our methyl ester, m.p. 125°, was the same *trans*-5,6-dibromo compound VI or the different rearranged 5,7-dibromo-*endo-cis*-2,3-dicarbomethoxy compound X.

In a mixed melting point determination of our dibromo methyl ester with that obtained by Berson and Swidler,¹⁸ a melting point of 90° was obtained. Thus the two dibromo methyl esters are not the same. If that dibromo methyl ester which was obtained by Berson and Swidler is either of the two probable structures which we have written for it, then the proof (see below) that our methyl ester is the *trans*-5,6-dibromo methyl ester VI demonstrates that the Berson and Swidler dibromo methyl ester must be represented by the rearranged structure IX.

The conversion of the 193° dibromide III to a 139° anhydride IV, a 254° bromolactonic acid V, and a 125° methyl ester VI makes it permissible to eliminate all but structure A_I as possible structures for the 242° unsaturated dibromide, II. The elimination of structure A_{II} may be made conclusively, as the hydrogenation of this dibromide would lead to the known *exo-cis*-5,6-dibromobicyclo[2,2,1]heptane-*endo-cis*-2,3-dicarboxylic acid, m.p. 188°,¹⁹ and the subsequent transformations of this acid would have led to the corresponding known anhydride, m.p. 205-206°,^{13,19,20} the corresponding γ -lactone of *exo*-6-bromo-*endo*-5-hydroxybicyclo[2,2,1]heptane-*endo-cis*-2,3-dicarboxylic acid, m.p. 157-159°^{18,20} and the corresponding dimethyl ester, m.p. 81.5°.²¹

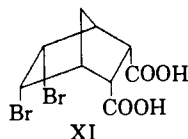
(18) We are indebted to Professor Berson for this material.

(19) K. Alder and G. Stein, *Ann.*, **504**, 247 (1933).

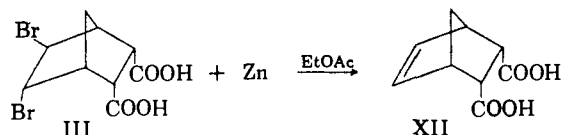
(20) H. Kwart and L. Kaplan, *THIS JOURNAL*, **76**, 4078 (1954).

(21) J. A. Berson, *ibid.*, **76**, 5748 (1954).

Elimination of structure A_{III} may be made on theoretical grounds. Hydrogenation of A_{III} would lead to XI, whose bromine atoms do not have the appropriate stereochemistry to permit ready lactonization either with participation by the carboxylate anion²² or with solvolytic assistance by carbon.²³



Structure D was eliminated on the basis that upon hydrogenation and subsequent lactonization, the known γ -lactone of *anti*-7-bromo-*endo*-5-hydroxybicyclo(2,2,1)heptane-*endo*-*cis*-2,3-dicarboxylic acid, m.p. 213°, would have been produced. However, in order to demonstrate with certainty the non-identity of the 242° dibromide with structure D, its hydrogenation product III was dehalogenated with zinc in ethyl acetate. The formation of bicyclo(2,2,1)hept-5-ene-*endo*-*cis*-2,3-dicarboxylic acid (XII) confirms the identity of the 242° dibromide II with structure A_I. As the melting point of XII is in question,²⁵ the unsaturated acid which was obtained from the



dehalogenation was converted by hydrogenation to bicyclo(2,2,1)heptane-*endo*-*cis*-2,3-dicarboxylic acid.²⁶ Treatment of the debrominated product with acetic anhydride gave a second derivative, bicyclo(2,2,1)hept-2-ene-*endo*-*cis*-2,3-dicarboxylic anhydride.²⁶

Had the 242° dibromide been the dibromide represented by structure D, it is conceivable that its hydrogenated product XIII, upon treatment with zinc in ethyl acetate, could have been dehalogenated. Such a 1,3-dehalogenation, where zinc serves as the electron source, has been reported in the conversion of pentaerythrityl tetrabromide^{27,28} and 1,1-bis-(bromomethyl)-cyclopropane²⁹ to methylenecyclobutane. However, it seems likely that such a debromination, if possible at all in the bicycloheptane ring system, would lead to the *exo*-acid XIV rather than the *endo*-acid XII, assuming the transformations shown in XIII.

It was also considered possible that the presence of zinc bromide might promote isomerization of the

(22) G. N. Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1923, p. 113.

(23) A. Streitwieser, Jr., *Chem. Revs.*, **56**, 703 (1956).

(24) C. D. Ver Nooy and C. S. Rondstedt, Jr., *ibid.*, **77**, 3583 (1955).

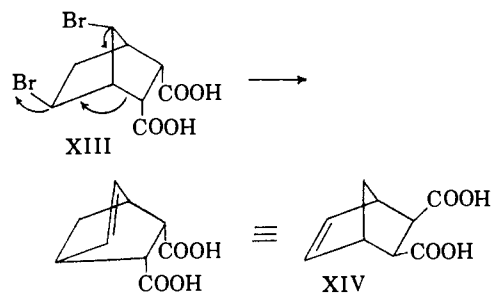
(25) A 177–179° m.p. is reported by O. Diels and K. Alder, *Ann.*, **460**, 98 (1928). A 193–194° m.p. is reported by D. Craig, *This Journal*, **73**, 4889 (1951).

(26) O. Diels and K. Alder, *Ann.*, **460**, 98 (1928).

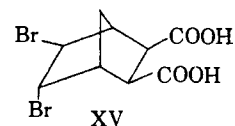
(27) W. Shand, V. Schomaker and J. R. Fischer, *This Journal*, **66**, 636 (1944).

(28) M. J. Murray and E. H. Stevenson, *ibid.*, **66**, 812 (1944).

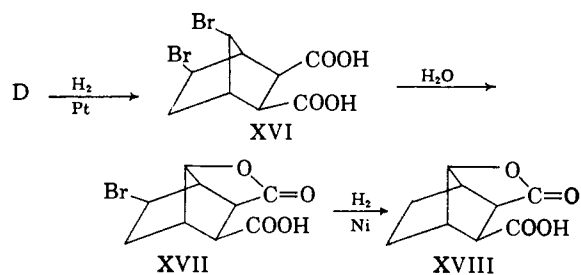
(29) I. Shaker and N. Slobodin, *J. Gen. Chem. U.S.S.R.*, **21**, 2005 (1951).



dibromodicarboxylic acid during the course of the debromination. Kwart and Kaplan have reported the nearly complete conversion of *syn*-5,7-dibromobicyclo(2,2,1)heptane to *trans*-2,3-dibromobicyclo(2,2,1)heptane in the presence of hydrogen bromide or stannic bromide.³⁰ However, had a similar Wagner–Meerwein rearrangement occurred with XIII, it would have led to the *exo*-dicarboxylic acid XV which on debromination would yield the *exo*-acid XIV rather than the *endo*-acid XII which was in fact obtained.



The work which has been reported thus far constitutes a proof that the 242° dibromide II can be represented by structure A_I only if the hydrogenation of this dibromide took place in accordance with the *exo* addition rule.^{11,14} If this were not true, then structure D might be consistent with the observations.³¹ *endo*-Hydrogenation of D would give the saturated *exo*-dicarboxylic acid XVI, and subsequent lactonization would produce the bromolactonic acid XVII. In addition, zinc-promoted dehalogenation of XVI, assuming the transformation analogous to XIII would give the *endo*-acid XII.

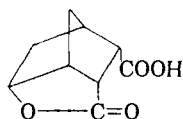


However, hydrogenolysis of the 254° bromolactonic acid V over Raney nickel catalyst gave the known γ -lactone of *endo*-5-hydroxybicyclo(2,2,1)heptane-*endo*-*cis*-2,3-dicarboxylic acid (XIX), m.p. and mixed m.p. with an authentic sample,³² 202.5–203.5°. The infrared spectra of this sample and the authentic sample were identical. Had the 254° bromolactonic acid been that bromolactonic acid represented by structure XVII, hydrogenolysis would have given the new lactonic acid XVIII rather than XIX.

(30) H. Kwart and L. Kaplan, *This Journal*, **76**, 4072 (1954).

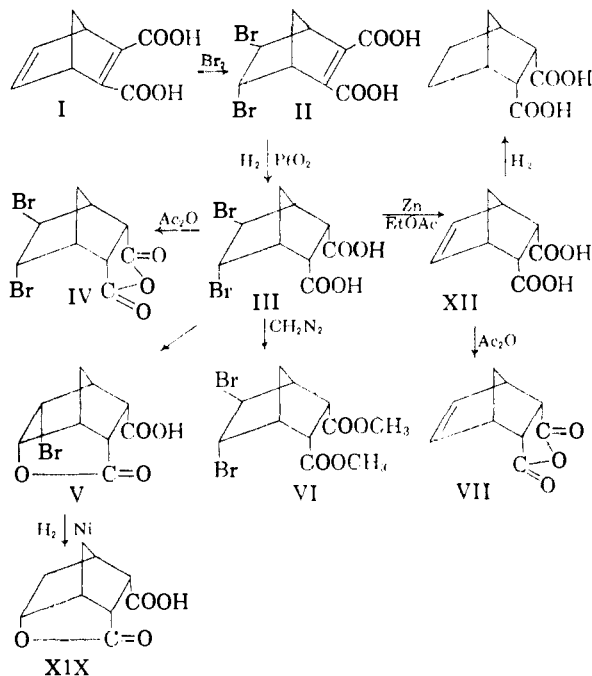
(31) It may be noted that *endo*-hydrogenation of the dibromides represented by formulas A_{II} and A_{III} would give compounds that would not yield bromolactonic acids readily.

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



XIX

The conversion of the 254° bromolactonic acid to the known lactonic acid XIX made it apparent that the hydrogenation of this dibromide had occurred according to the *exo* addition rule. Thus, we have shown that the structure of the 242° dibromide, obtained from the bromination of bicyclo(2,2,1)heptadiene-2,3-dicarboxylic acid (I), can be represented by structure A₁. The series of reactions which were carried out in order to effect this structure proof are summarized in Chart I.



The light-catalyzed bromination of I appeared to produce results different from bromination in the dark. An extremely small amount of unsaturated material which melted at 255° was obtained in addition to a lower-melting solid, m.p. 190-200°. An investigation of these products is being conducted.

That the bromination of I gives a dibromide different from that obtained in the bromination of quadricyclo(2,2,1,0^{2,6},0^{3,5})heptane-2,3-dicarboxylic acid,¹ is added evidence that the structures by which these two compounds are represented are not different resonance structures for one compound, but on the contrary, they represent the structures of two distinctively different chemical entities.

Acknowledgment.—The authors are indebted to the Office of Ordnance Research, U. S. Army, for support of this work.

Experimental

Bromination of Bicyclo(2,2,1)hepta-2,5-diene-2,3-dicarboxylic Acid (I).—In 100 ml. of ethyl acetate was dissolved 20.0 g. (0.111 mole) of bicyclo(2,2,1)heptadiene-2,3-dicarboxylic acid²; 2.3 l. of carbon tetrachloride was added. To

the resulting solution 18.0 g. (0.111 mole) of bromine in 100 ml. of carbon tetrachloride was added with stirring. The reaction mixture was allowed to stand at room temperature for 5 hours. This reaction was carried out in a 3-liter brown bottle which was covered with aluminum foil and which was provided with a magnetic stirrer.

The solid which had precipitated out of solution was filtered and dried; 15.2 g. of solid (40.3% yield), m.p. 232-238°, was recovered. The filtrate was distilled until only an oil remained. This oil was triturated with 170 ml. of carbon tetrachloride. In time the total quantity of oil dissolved in the carbon tetrachloride. Allowing this solution to stand overnight at room temperature resulted in the formation of 2.24 g. (7.1%) of a solid, m.p. 210-225°. Distillation of the solvent from the filtrate gave 20.8 g. of oil. An infrared absorption spectrum had a peak at 5.77 μ and in the region 6.00-6.25 μ .

Recrystallization of the solid products three times from a mixture of ethyl acetate and petroleum ether, b.p. 85-100°, produced pure *trans*-5,6-dibromobicyclo(2,2,1)-2-heptene-2,3-dicarboxylic acid, (II) m.p. 230-242°. A fourth recrystallization did not raise the melting point.

Anal. Calcd. for C₉H₈Br₂O₄: C, 31.79; H, 2.37; Br, 47.01. Found: C, 32.07; H, 2.42; Br, 46.76.

This solid decolorized an aqueous potassium permanganate solution, did not react with a 2% ethanolic silver nitrate solution at room temperature but did react with this reagent in boiling ethanol; it did not react with sodium iodide in acetone. A mixed melting point of this solid with the dibromide¹ obtained from quadricyclo(2,2,1,0^{2,6},0^{3,5})heptane-2,3-dicarboxylic acid was 185-206°.

Hydrogenation of *trans*-5,6-Dibromobicyclo(2,2,1)-hept-2-ene-2,3-dicarboxylic Acid (II).—A 100-ml. hydrogenation flask containing 40 mg. of platinum oxide catalyst and 10 ml. of ethanol was shaken under an atmosphere of hydrogen until hydrogen was no longer absorbed. To the flask was added 418 mg. of II in 20 ml. of ethanol, and hydrogenation was conducted at atmospheric pressure. In 30 minutes, 1.02 moles of hydrogen had been absorbed per mole of II. The catalyst was removed by filtration. Evaporation of the solvent from the filtrate gave 485 mg. of an oil which soon crystallized. The crude reaction product did not decolorize an aqueous solution of potassium permanganate and reacted immediately at room temperature with an ethanolic solution of silver nitrate. Recrystallization of the crude reaction product from a solvent mixture of ethyl acetate and petroleum ether gave a solid, m.p. 187-188°. A recrystallization of this material, *trans*-5,6-dibromobicyclo(2,2,1)heptane-*endo*-2,3-dicarboxylic acid (III), from a small quantity of ethyl acetate raised the melting point to 191-193°. A mixed melting point with starting material, m.p. 234-236°, showed an 11° depression in the melting point of the lower melting substance. Attempted hydrogenations of II over palladium were unsuccessful.

Anal. Calcd. for C₉H₁₀Br₂O₄: C, 31.61; H, 2.95; Br, 46.73. Found: C, 32.19; H, 3.05; Br, 45.83.

Conversion of *trans*-5,6-Dibromobicyclo(2,2,1)heptane-*endo*-*cis*-2,3-dicarboxylic Acid (III) to its Anhydride IV.—To 10 g. of freshly distilled acetic anhydride in a 50-ml. flask was added 315 mg. of III. The solution was heated at 120° for 10 minutes and then allowed to stand at room temperature overnight. The acetic anhydride was removed under a water aspirator. The last traces of acetic anhydride were removed under a vacuum pump. After 30 hours at reduced pressure, solid formation began to occur. The solid product recovered amounted to 141 mg. or 48% of the theoretical yield. The solid was recrystallized from a solvent mixture of dry acetone and petroleum ether to give *trans*-5,6-dibromobicyclo(2,2,1)heptane-*endo*-2,3-dicarboxylic anhydride (IV), m.p. 138-139°.

Anal. Calcd. for C₉H₈Br₂O₃: C, 33.36; H, 2.49. Found: C, 33.27; H, 2.64.

Preparation of Methyl *trans*-5,6-Dibromobicyclo(2,2,1)-heptane-*endo*-*cis*-2,3-dicarboxylate (VI).—In 50 ml. of anhydrous ether in a 125-ml. flask, which was provided with a magnetic stirrer, was dissolved 68 mg. of *trans*-5,6-dibromobicyclo(2,2,1)heptane-2,3-dicarboxylic acid (III). To this solution an ethereal solution of diazomethane was added until the yellow color of diazomethane persisted. By evaporation of the solvent under an aspirator, 75 mg. of a solid, m.p. 112-122°, was obtained. Recrystallization from ethyl

(33) O. Diels and K. Alder, *Ann.*, **490**, 286 (1931).

acetate-petroleum ether gave methyl *trans*-5,6-dibromobicyclo(2,2,1)heptane-*endo-cis*-2,3-dicarboxylate (VI), m.p. 123.5–125.0°.

Anal. Calcd. for $C_{11}H_{14}Br_2O_4$: C, 35.70; H, 3.81. Found: C, 35.46; H, 3.57.

In a mixed melting point determination of this methyl ester with a methyl ester (m.p. 117–118°) of the same empirical formula but which had been prepared by a different synthesis scheme,^{13,18} a depression of 27° in the melting point of the lower-melting isomer was observed.

Preparation of the γ -Lactone of *endo*-6-Bromo-*endo*-5-hydroxybicyclo(2,2,1)heptane-*endo-cis*-2,3-dicarboxylic Acid (V).—To 100 ml. of water in a round-bottom flask which was provided with a magnetic stirrer, heating mantle and reflux condenser, was added 437 mg. (1.28 mmoles) of III. After two hours of stirring at 95°, the solid went into solution. After 2.75 hours a 5-ml. sample was withdrawn and titrated for the amount of bromide ion present. The determination showed that 88% of one mole of bromide ion had been liberated. Heating was continued for 1.5 hours. The solvent was then partially evaporated under a stream of dry air. Further evaporation of water, under a vacuum pump, reduced the volume of water to 10 ml. From this solution 313 mg. (92%) of the lactone crystallized. Recrystallization and treatment of the crude lactone with decolorizing charcoal gave a crystalline solid which melted at 250–254°.

Anal. Calcd. for $C_9H_9BrO_4$: C, 41.40; H, 3.47. Found: C, 41.25; H, 3.62.

Bicyclo(2,2,1)hept-5-ene-*endo-cis*-2,3-dicarboxylic anhydride and acid were prepared according to the method of Diels and Alder.²⁵ The anhydride melted at 160–164° and the dicarboxylic acid at 192–193°. Diels and Alder have reported²⁵ the melting point of the dicarboxylic acid to be 177–179°. Craig was unable to duplicate this melting point but reported that the melting point was 193–194°.²⁶

Debromination of *trans*-5,6-Dibromobicyclo(2,2,1)heptane-*endo-cis*-2,3-dicarboxylic Acid (III).—In a 100-ml. round-bottom flask which was provided with a reflux condenser, heating mantle and a magnetic stirrer was dissolved 2.76 g. of the dibromodicarboxylic acid III in 40 ml. of ethyl acetate. To this solution was added an excess of zinc powder. The contents of the flask were heated at reflux and stirred for 12 hours. The contents of the flask were then cooled; the solids were removed by filtration, and the ethyl acetate was evaporated under reduced pressure. The oil which remained was triturated with a small quantity of ethyl acetate to give more solid. By this procedure was obtained 680 mg. (46% yield) of impure solid, which upon recrystallization from water melted at 188–189°. This material decolorized an aqueous solution of potassium permanganate. A mixed melting point with an authentic sample of bicyclo(2,2,1)hept-5-ene-*endo-cis*-2,3-dicarboxylic acid (m.p. 192–193°) (XI)²⁵ showed no depression, and the infrared spectra of the two samples were identical.

Conversion of Bicyclo(2,2,1)hept-5-ene-*endo-cis*-2,3-dicarboxylic Acid (XI) to its Anhydride VII.—The unsaturated dicarboxylic acid obtained from the zinc debromination of III was transformed to its anhydride VII by the procedure described below.

In 5 ml. of acetic anhydride was dissolved 34 mg. of the dibasic acid. The solution was allowed to stand overnight at room temperature. Evaporation of the acetic anhydride under a vacuum pump gave 29 mg. of white solid. Recrystallization of this solid from petroleum ether gave a solid which melted at 159–163°. A mixed melting point with an authentic sample of the anhydride VII²⁵ (m.p. 160–164°) showed no depression in melting point.

Conversion of Bicyclo(2,2,1)hept-5-ene-*endo-cis*-2,3-dicarboxylic Acid to Bicyclo(2,2,1)heptane-*endo-cis*-2,3-dicarboxylic Acid.—The unsaturated dicarboxylic acid (298 mg.) obtained from the zinc debromination of III was added to a hydrogenation flask containing 20 mg. of 10% palladium-on-charcoal catalyst suspended in 5 ml. of 4% sodium carbonate solution. The flask and its contents were shaken under a pressure of 626 mm. for about one hour; 933 mmoles of hydrogen was absorbed for each mole of unsaturated dibasic acid. The catalyst was removed by filtration, and the filtrate was acidified with 20% sulfuric acid. The solvent was partially evaporated under a stream of dry air. By this procedure was isolated 262 mg. (87%) of a crystalline solid, m.p. 160–164°. A recrystallization from water raised the melting point to 162–164°. The reported melting point for this acid is 161°.²⁵

Hydrogenolysis of the γ -Lactone of *endo*-6-Bromo-*endo*-5-hydroxybicyclo(2,2,1)heptane-*endo-cis*-2,3-dicarboxylic Acid (V).—A suspension of 0.58 g. of Raney nickel catalyst in 5 ml. of 5% aqueous sodium carbonate solution was shaken for 2 hours under 630 mm. of hydrogen. Then 149 mg. (0.57 mmole) of V was added and the shaking was continued for 3 hours. The catalyst was then removed by filtration, and the filtrate was acidified to pH 3 with 20% sulfuric acid. The solvent was then removed and the residual solid was extracted with a small amount of ethyl acetate. Evaporation of the ethyl acetate gave 102 mg. of solid, m.p. 140–200°. Two recrystallizations from water gave pure γ -lactone of 5-hydroxybicyclo(2,2,1)heptane-*endo-cis*-dicarboxylic acid (XIX), m.p. and mixed m.p. with an authentic sample,²⁷ 202.5–203.5°.

Light-catalyzed Bromination of Bicyclo(2,2,1)heptadiene-2,3-dicarboxylic Acid.—The light-catalyzed bromination of bicyclo(2,2,1)heptadiene-2,3-dicarboxylic acid was carried out in a 125-ml. Vycor flask which was provided with a reflux condenser and which was placed adjacent to a General Electric AH-4 ultraviolet lamp. In 80 ml. of methylene chloride was dissolved 0.30 g. of the dicarboxylic acid (1.66 mmoles). The ultraviolet light was directed onto the contents of the flask and 0.30 g. of bromine (1.88 mmoles) in 10 ml. of methylene chloride was added in one portion. The bromine color diminished from a dark red to yellow in less than one minute. That color which did persist (for at least 10 minutes) was probably due to the excess quantity of bromine which was used in this reaction. A yellow oil was obtained by evaporation of the solvent under a stream of dry air. Further removal of solvent under a vacuum pump gave a tan solid (0.37 g.) which was triturated with 10 ml. of ethyl acetate. In time most of the solid went into solution; that which did not was collected and dried. About 5 mg. of this solid, which melted at 255°, was recovered; it was soluble in a 5% solution of sodium bicarbonate with the evolution of carbon dioxide, decolorized a potassium permanganate solution, but did not react with silver nitrate immediately at room temperature.

To the solution of product in ethyl acetate was added about 90 ml. of petroleum ether, b.p. 60–70°. This solution was boiled until it became turbid and then it was cooled. The solid which formed (60 mg.) was collected and dried. A recrystallization from methylene chloride gave a solid which melted at 190–200°. No further attempt was made to purify or characterize these products.

Infrared Absorption Spectra.—The infrared absorption spectra of the compounds were determined as solids in potassium bromide disks with a Perkin-Elmer model 21 spectrophotometer, except for the spectrum of the oil obtained from the bromination of bicyclo(2,2,1)heptadiene-2,3-dicarboxylic acid. This spectrum was determined in ethanol.

BOULDER, COLO.