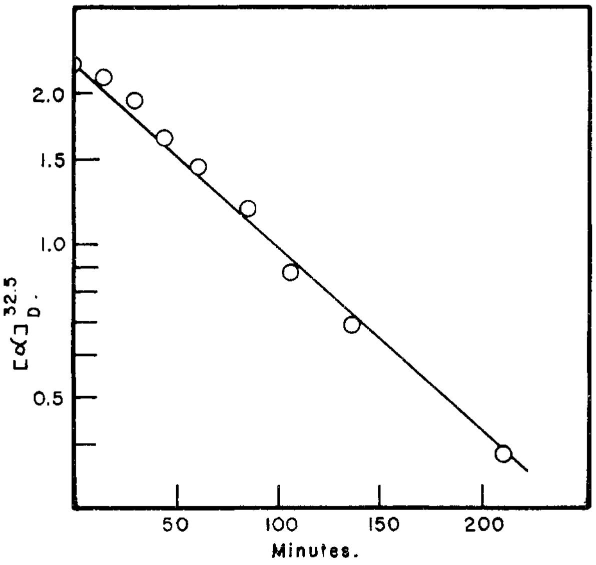

Fig. 2.—Racemization of (+)-6,6-dicarbethoxydibenzo-[a,c][1,3]cycloheptadiene (XV).

m.p. 110–112°. The ether was then completely evaporated and the residue was extracted with boiling cyclohexane which dissolved the diamine but not the dark impurity. Again evaporation of this solution gave a series of active crops of crystalline product. A total of 5.3 g. (50%) of the diamine was obtained, m.p. 111–113°, $[\alpha]^{32}D$ −25.4° (*l* 1 dm., *c* 1.062, 95% ethanol). The racemic diamine melted at 122–124°.

*Anal.* Calcd. for $C_{21}H_{24}N_2O_2$: C, 68.45; H, 6.57; N, 7.60. Found: active, C, 68.33; H, 6.42; N, 7.60; racemic, C, 68.44; H, 6.38; N, 7.64.

**Preparation of (+)-6,6-Dicarbethoxydibenzo[a,c][1,3]-cycloheptadiene (+XV).**—One and three-tenths grams of cuprous oxide was added to 2.20 g. (0.006 mole) of the (−)-diamino-diester dissolved in 67 ml. (0.64 mole) of 50% hypophosphorous acid. The mixture was cooled to −15° and 1.1 g. (0.016 mole) of sodium nitrite dissolved in 5 ml. of water were added dropwise with stirring; the addition required 0.5 hour. Stirring was continued for two hours at this temperature after which the following operation were completed as quickly as possible. The mixture was warmed to 5° and extracted with cyclohexane. This solution (at 5–10°) was washed twice with 15 ml. of 5% sodium hydroxide, water and then dried. After noting the presence of optical activity, the solution was passed through a 1.5 × 7 cm. column of alumina and the product was eluted with a 2% solution of absolute ethanol in cyclohexane. The colorless eluate quickly was concentrated below room temperature by vacuum evaporation and yielded 0.80 g. of 6,6-dicarbethoxydibenzo[a,c][1,3]cycloheptadiene (40%), m.p. 64–66°. The entire sample was redissolved in 20 ml. of cyclohexane: $\alpha^{32.5}D$ +0.18° (*l* 2 dm.), $[\alpha]^{32.5}D$ +2.25°. This portion of the solution was left in the polarimeter tube to follow the racemization which was complete in approximately five hours (*cf.* Fig. 2). The half-life period for the racemization process under these conditions was found graphically to be 80 min. The ultraviolet absorption spectrum of a second portion of this cyclohexane solution was obtained before the racemization was complete and was found to be identical with that obtained previously with the racemic diester prepared from diphenic acid. The solution contained in the polarimeter tube, above, was evaporated under vacuum and the racemized diester melted at 64–66°. (A mixture of a sample of (+)-diester and racemic di-ester melted at 62–66°.) Elemental analysis and infrared spectrum of the racemized diester isolated by vacuum evaporation of the solvent from the solution used in the racemization measurement were obtained. The infrared spectrum was identical to that produced by the separately prepared racemic diester.

*Anal.* Calcd. for $C_{21}H_{22}O_4$: C, 74.53; H, 6.57. Found: C, 74.51; H, 6.57.

In three other similar deaminations, the optically active product was obtained having identical properties. In a fifth deamination, because of delay in obtaining the polarimeter measurements, only racemic diester was isolated.

It was noted that racemization occurs either very slowly or not at all in the crystalline state. A 0.41-g. sample of the active diester having an initial $[\alpha]^{32}D$ +2.90° was stored at room temperature. The rotation was periodically redetermined as quickly as possible by dissolving the sample in 20 ml. of cyclohexane, making the polarimeter measurement and then by vacuum evaporating the solvent below room temperature. At 200 hours there was obtained: $\alpha^{32}D$ +0.10° (*l* 2 dm., *c* 2.05, assuming no weight loss in the course of previous measurements), $[\alpha]^{32}D$ +2.4°.

MORGANTOWN, W. VA.

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

# Bridged Polycyclic Compounds. VI. The Photoisomerization of Bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic Acid to Quadricyclo[$2,2,1,0^{2,6},0^{3,5}$]heptane-2,3-dicarboxylic Acid[1,2]

BY STANLEY J. CRISTOL AND ROBERT L. SNELL

RECEIVED NOVEMBER 4, 1957

The synthesis of quadricyclo[$2,2,1,0^{2,6},0^{3,5}$]heptane-2,3-dicarboxylic acid (III) by irradiation of bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic acid (IV) is described. This represents the first compound reported with this ring system. Certain reactions and properties of III are described, which lead to the assignment of structure to the irradiation product.

So far as we are aware, the synthesis or isolation of any derivative of quadricyclo[$2,2,1,0^{2,6},0^{3,5}$]-heptane (I) has not heretofore been accomplished, although several unsuccessful attempts have been recorded in the literature.[3,4] Such compounds might be expected to have unusual physical and chemical properties, in view of the large number of condensed rings in the system. Previous attempts[3,4] to prepare derivatives of I all started with derivatives of nortricyclene (II) and attempts were made to close the second cyclopropane ring. The present paper describes the preparation of III, the dicarboxylic acid of I, by isomerization of IV, some of the properties and reactions of III, and the evidence for the structural assignment of III.

This research was undertaken on the considera-

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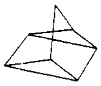
[1] Previous paper in series: S. J. Cristol, G. D. Brindell and J. A. Reeder, THIS JOURNAL, **80**, 635 (1958).

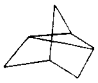
[2] Preliminary communication, S. J. Cristol and R. L. Snell, *ibid.*, **76**, 5600 (1954).

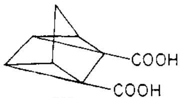
[3] M. Lipp, *Ber.*, **74**, 1 (1941).

[4] T. Hasselstrom and E. M. Falasco, Abstracts of Papers, 125th Meeting of the American Chemical Society, Kansas City, Missouri, March, 1954, p. 39-N.

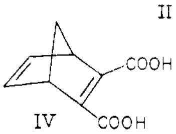
tion that irradiation of IV with ultraviolet light would activate one of the carbon–carbon double bonds in IV and that this photoactivated bond could react with the other double bond to give III. The possibilities that IV might dimerize or polymerize also were considered.


I

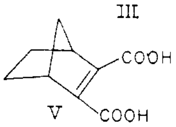

II



III



IV



V

A solution of bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic acid[5] (IV) in ethyl ether was irradiated with an ultraviolet light source. This gave a white crystalline solid acid (III), m.p. 225° dec., which was isomeric with IV. The 225° product was shown to be a dicarboxylic acid by base titration[6] and by conversion to a dimethyl ester with diazomethane. A Rast molecular-weight determination on the dimethyl ester indicated that the product was monomeric, and that neither dimerization nor polymerization had occurred.

The 225° product was quite stable in storage and did not appear to undergo air oxidation, although its progenitor IV darkens and suffers a depression in melting point on storage in the laboratory. A comparison of III and IV in reactions for unsaturation is of interest. Acetone solutions of IV react instantly with both bromine and potassium permanganate, while acetone solutions of III react rapidly with bromine, but only very slowly, if at all, with potassium permanganate at room temperature. On the other hand, IV does not appear to react with iodine, while a solution of III in acetone reacts rapidly with one mole of iodine to give a moderately stable diiodide. It appeared that III reacted with water rapidly and with ethanol slowly, although the products of these reactions were not characterized. The chemical reactions indicated above do not form a firm base for an assignment of structure of the 225° product, in particular with respect to the type of unsaturation present.

The fact that no skeletal rearrangement occurred in the irradiation seemed evident from two experiments. First, hydrogenation of the 225° product over palladium-on-charcoal catalyst led to bicyclo[2,2,1]hept-2-ene-2,3-dicarboxylic acid (V), which was identical with a sample prepared from IV.[5] Further, a sample of III was heated at reflux over palladium-on-charcoal catalyst for three hours in ethyl acetate solution, and it was noted that reisomerization to IV occurred. It is not clear whether the hydrogenation of III to V involves a preliminary isomerization to IV, although a test indicated that the isomerization of III to IV, even over freshly reduced catalyst, is very much slower than the hydrogenation of III.[7] In any case, the ready formation of IV and V in these experiments makes it unlikely that the 225° product could have a carbon skeleton significantly different from IV; that is, it is unlikely that any of the rings already present in the bicyclic system in IV could be broken in the isomerization.

The ultraviolet spectra of III and IV and of their dimethyl esters were measured in solution in 95% ethanol in the range above 210 mμ. Compound IV has an absorption maximum at 243 mμ (log ε 3.73) and a minimum at 216 mμ, and its methyl ester has a maximum at 237 mμ (log ε 3.60) with a minimum at 217 mμ. Compound III has a maximum at 233 mμ (log ε 3.41) and a minimum at 222 mμ, while its methyl ester has no maximum above 210 mμ, although its absorption is substantial (*e.g.*, log ε 3.41 at 229 mμ) in this region. These results suggest some type of conjugation in III. It should be noted that the spectra change rapidly,[6] presumably due to reaction with solvent.

A comparison of the infrared spectra of III and IV is of value. The diene dicarboxylic acid IV has a complex spectrum in the double-bond stretching region, having absorption peaks at 5.82, 6.07, 6.25 and 6.35 μ, while the isomer III has only two peaks in this region, at 5.98 and 6.18 μ. Presumably both these latter peaks are assignable to the carboxyl groups, and the disappearance of peaks in the isomerization results from the loss of the carbon–carbon double bonds. No absorption peak was noted in the region 12.3–12.5 μ, a region assumed to be typical of nortricyclene (II) derivatives,[1,8–10] although it has been observed recently that this peak is not present in all nortricyclene derivatives.[11] Evidence that one or more three-membered rings is present in the 225° product is revealed by a study of the spectrum in the carbon–hydrogen stretching region. This material had a peak at 3.23 μ, a value diagnostic of hydrogen atoms attached to three-membered rings.[9] There was no absorption in the 4–5 μ region characteristic of triple bonds.

The facts given above appear to be consistent with the valency tautomeric[12,13] structure quadricyclo[2,2,1,$0^{2,6}$,$0^{3,5}$]-heptane-2,3-dicarboxylic acid (III) for the 225° product. No other structures appear to be consistent with the evidence presented above. This compound, then, is the first derivative of the ring system I. In the preliminary communication on this work,[2] we suggested the name "nortetracyclene" as derived from its relationship to the *unknown* dehydroterpene tetracyclene,[3,4] but certain objections have been raised to to this name because of the similarities to tetracycline and tetracyclone. The Baeyer system

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[5] O. Diels and K. Alder, *Ann.*, **490**, 236 (1931).

[6] The authors are indebted to Dr. E. F. Hoegger for this observation.

[7] The difficulty with such comparisons in rate is that the hydrogenation experiment may involve rapid isomerization of III to IV, followed by hydrogenation to V and desorption of the monoölefin V from the catalyst surface, while the isomerization experiment would require desorption of the diene IV from the catalyst surface.

[8] J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, THIS JOURNAL, **72**, 3116 (1950).

[9] E. R. Lippincott, *ibid.*, **73**, 2001 (1951).

[10] A. Winston and P. Wilder, Jr., *ibid.*, **76**, 3045 (1954).

[11] S. J. Cristol and R. T. LaLonde, unpublished work.

[12] J. W. Baker, "Tautomerism," George Routledge and Sons, London, 1934, pp. 201–206.

[13] A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, THIS JOURNAL, **74**, 4867 (1952).

utilizes the name quadricycloheptane[14] for such ring systems, and we are inclined to use the coined name "quadricyclene" for I.

The high reactivity of the quadricyclene ring system to such reactions as catalytic hydrogenation, bromination, iodination and reaction with other ionic reagents contrasts with the greater stability of nortricyclenes[1,8,10,15] or simple cyclopropane derivatives[16] or cyclobutane derivatives.[16] Turner and his colleagues[17] have shown that the bicyclo-[2,2,1]hepta-2,5-diene ring system is an extremely strained system, the heat of hydrogenation being about 14 kcal./mole greater than twice that of cyclohexene (27 kcal./mole). The evidence that IV is converted to III by irradiation, a process in which considerable energy may be absorbed, and that III is reisomerized to IV over a hydrogenation catalyst, indicates that III is less stable than IV, and therefore that the strain in the quadricyclene ring system I is very large. This strain, resulting from the fusion of so many small rings in I, would appear to account for the high reactivity of III.

**Acknowledgments.**—The authors wish to acknowledge financial support of this work under a contract between the University of Colorado and the Office of Naval Research. The infrared spectra were kindly determined by Mr. Jack L. Bitner and Dr. Ernest Silversmith, and analyses were performed by Galbraith Laboratories. We are further indebted to Mrs. Patricia S. Ramey for technical aid.

## Experimental

**Isomerization of Bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic Acid (IV) to Quadricyclo[2,2,1,$0^{2,6}$,$0^{3,5}$]heptane-2,3-dicarboxylic Acid (III).**—A solution of 3.0 g. of IV[5] in 200 ml. of anhydrous ethyl ether was placed in a Vycor flask equipped with a magnetic stirrer and a reflux condenser. The solution was irradiated for eight hours with a General Electric AH-4 mercury vapor lamp. During this period 1.41 g. of III (47%) crystallized from solution as it was formed. Concentration of the ethereal solution gave impure material, from which additional III could be crystallized from dry acetone.

*Anal.* Calcd. for $C_9H_8O_4$: C, 60.00; H, 4.48. Found: C, 59.80; H, 4.57.

The quadricyclene acid III is a white crystalline solid, which does not have a definite melting point, but which does have a characteristic behavior upon melting. The solid begins to soften between 220° and 235°, depending upon the rate of heating, then it begins to expand with foaming to 2–3 times its original volume. By 260–270° the foaming stops and a tan powder remains which is acid to litmus and which does not melt below 300°. This m.p. behavior is in striking contrast with the diene acid IV, which melts at about 170° with decomposition to a black liquid; addition of a small amount of III to IV lowers its m.p. significantly.

The diene IV and quadricyclene III have differences in solubility that probably parallel the differences in melting points. IV is soluble in ether, chloroform, ethanol, acetone, ethyl acetate and water and slightly soluble in carbon tetrachloride, while III is moderately soluble in acetone, ethyl acetate and ethanol, slightly soluble in water, less soluble in ether and insoluble in chloroform and carbon tetrachloride.

**Methyl Quadricyclo[2,2,1,$0^{2,6}$,$0^{3,5}$]heptane-2,3-dicarboxylate.**—A solution of III in absolute ethanol was treated with a slight excess of diazomethane. Distillation of the alcohol left a tan liquid, which could not be induced to crystallize. The ester was insoluble in petroleum ether and very soluble in chloroform. Distillation gave the dimethyl ester of III, b.p. 100–105° (0.5 mm.), as a water-white, odorless, viscous liquid, which appeared to be stable to air and to light, $n^{25}_D$ 1.5000, $n^{20}_D$ 1.5022.

*Anal.* Calcd. for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81; mol. wt., 208. Found: C, 63.63; H, 5.77; mol. wt. (in camphor), 208.

**Hydrogenation of Quadricyclene-2,3-dicarboxylic Acid (III).**—When 0.45 g. (2.5 mmoles) of III in 80 ml. of ethyl acetate was subjected to hydrogenation over 40 mg. of 10% palladium-on-charcoal catalyst at one atmosphere pressure, one mole of hydrogen per mole of compound was absorbed in five minutes. The catalyst was removed by filtration, and the solution was concentrated to approximately 5 ml. Addition of petroleum ether, b.p. 60–70°, gave white crystals, m.p. 210–214°, of bicyclo[2,2,1]hept-2-ene-2,3-dicarboxylic acid (V). There was no depression in m.p. when this material was admixed with authentic V,[5] m.p. 214–215°, prepared by hydrogenation of IV.

**Isomerization of Quadricyclene-2,3-dicarboxylic Acid (III) to Bicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylic Acid (IV).**—A small sample of III dissolved in ethyl acetate was heated at reflux with an equal weight of 10% palladium-on-charcoal catalyst for three hours. Removal of most of the solvent gave IV, m.p. 156–165°, mixed m.p. with authentic IV, 156–165°. The infrared spectra of both samples of IV were substantially identical.

**Iodination of Quadricyclene-2,3-dicarboxylic Acid (III).**—An acetone solution of 200 mg. (1.1 mmoles) of III was titrated with an 0.095 *N* solution of iodine in acetone. The iodine color disappeared rapidly, leaving a slightly yellow solution, the color of which obscured the end-point. The end-point appeared to be at 21.1 ml., but the calculated volume (23.3 ml.) was added and the solution was allowed to stand for six hours. The solution was concentrated by removal of solvent under reduced pressure. Addition of benzene or petroleum ether, b.p. 60–70°, gave a white solid, m.p. 170° (decomposition with evolution of iodine), which decomposed during attempts to purify it by recrystallization. This compound is formulated as a diiodide.

*Anal.* Calcd. for $C_9H_8O_4I_2$: I, 58.5. Found: I, 56.6.

**Other Reactions of Quadricyclene-2,3-dicarboxylic Acid (III).**—A solution of III in ethyl acetate rapidly decolorized a solution of bromine in carbon tetrachloride. Approximately one mole of bromine was absorbed per mole of III and substantial amounts of hydrogen bromide were not produced.[18]

The quadricyclene acid III appeared to react rapidly with water and slowly with absolute ethanol. The products of these reactions, which were different from III, were not characterized.

**Spectra.**—The ultraviolet spectra were determined in 95% ethanol with a Beckman DU spectrophotometer. The spectra in the 3 $\mu$ region were obtained with a Perkin–Elmer model 12 spectrometer using lithium fluoride cells and prisms. Other infrared spectra were determined in Nujol mulls with a Baird double-beam spectrophotometer using sodium chloride cells and prisms.

BOULDER, COLORADO

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[14] We are indebted to Dr. Louis Schmerling for his advice on nomenclature.

[15] K. Alder and F. Brochhagen, *Chem. Ber.*, **87**, 167 (1954).

[16] R. A. Raphael in E. H. Rodd, "Chemistry of Carbon Compounds," Elsevier Press, New York, N. Y., 1953, Vol. IIA, Chapters II and III.

[17] R. B. Turner, W. R. Meador and R. E. Winkler, THIS JOURNAL, **79**, 4116 (1957).

[18] For the structure of this dibromide see R. T. LaLonde, Ph.D. Thesis, University of Colorado, 1957.