[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WEST VIRGINIA UNIVERSITY]

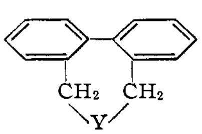
A Biphenyl Whose Optical Activity Is Due to a Three-carbon Bridge Across the 2,2'-Positions[1]

BY DON C. IFFLAND[2] AND HERBERT SIEGEL

RECEIVED NOVEMBER 29, 1957

The preparation and properties of *d*-6,6-dicarbethoxydibenzo[a,c][1,3]cycloheptadiene (XV) are described. Asymmetry is maintained in this biphenyl system by the 2,2'-three-carbon-atom bridge.

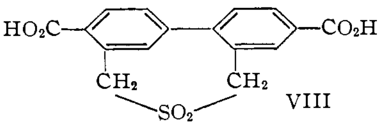
Molecular models indicate that the 2,2'-three-atom-bridged biphenyls are non-planar. The angle of twist between the planes of the benzene rings in the dibenzoxepin I has been variously estimated from *ca.* 20°[3] to 50.[4] As a consequence of this non-planar configuration these compounds should exhibit enantiomorphism. Accordingly, numerous attempts have been made to resolve 2,2'-three-atom-bridged biphenyls. In 1952, Beaven and coworkers[4] described unsuccessful attempts to resolve II and III and this was closely followed by Bell's[5] report that resolution of IV had failed.



I, Y = $>O$
II, Y = $>N^+(CH_2CH_2)_2CH_2,Br^-$
III, Y = $>N^+(CH_2CH_2)_2CHC_6H_5,Br^-$
IV, Y = $>CHCO_2H$
V, Y = $>CHCH_2OH$
VI, Y = $>CHCO_2CH_3$
VII, Y = $>C(CO_2H)_2$

The postulation of a non-planar configuration for 2,2'-three-atom-bridged biphenyls, based on rigid models, has been strongly questioned by Braude[3,6] who preferred to place reliance upon ultraviolet spectra as a means to determine configuration; he maintained that a bridged biphenyl such as I must be nearly uniplanar with an angle between the phenyl groups but little greater than in biphenyl itself.

Nevertheless, a non-planar configuration for the 2,2'-three-atom-bridged biphenyls continued to receive consideration. Beaven and his group[7] in 1955 described attempts to resolve IV and V and to demonstrate optical activity in VI and VII, again without success. Truce and Emrick[8] have reported that optically active solutions containing VIII were obtained, but they did not isolate or describe properties of the optically active substance.



VIII

We now wish to describe the successful synthesis and properties of optically active XV, the first active biphenyl with only a 2,2'-three-carbon-atom bridge.[9] Starting from optically active 6,6'-dinitrodiphenic acid the sequence of reactions indicated by IX → XV was carried out. The properties and analyses of both racemic and active intermediates are included in the experimental section.

This synthetic approach avoids an empirical resolution process which has left uncertain the results of the earlier investigators. The 6,6'-nitro groups maintained non-planarity in the biphenyl system during the formation of the 2,2'-bridge. Removal of these blocking groups *via* reduction and hypophosphorous acid deamination was well suited for a rapid and low temperature isolation of the active product.

The conversion of the di-acid chloride X to the 6,6'-dinitro-2,2'-dihydroxymethylbiphenyl (XI), was successfully achieved in a 56% yield by sodium trimethoxyborohydride reduction of the di-acid chloride. Initially, reduction of the di-acid chloride using sodium borohydride, as described by Chaikin and Brown,[10] was attempted but resulted only in a high recovery of the acid derived from hydrolysis of the di-acid chloride.

In the deamination step (XIV → XV), initial experiments employing only hypophosphorous acid[11] and sodium nitrite with the diamine produced no deamination product; only colored mixtures presumed to contain a bridged benzocinnoline[12] were obtained. As the desired deamination process has been shown to proceed *via* a free radical sequence,[13] cuprous oxide was added with the hope to catalyze the desired reaction. In this manner, at least 40% yields of pure di-ester XV were realized readily.

For comparison purposes, racemic XV was prepared from diphenic acid. An analogous sequence of reactions was employed to form the 2,2'-bridge except, as in this sequence the reducible 6,6'-nitro groups were absent, lithium aluminum hydride was used in the conversion of the di-acid chloride to the 2,2'-dihydroxymethylbiphenyl.

Active XV obtained from (+)-IX and racemic XV obtained from diphenic acid had identical ultraviolet and infrared spectra. Interestingly, although both the active and racemic XV melt at 64–66°, the mixed melting point was depressed: 62–66°. The mixed melting point of racemized XV

---

[1] Based on the thesis submitted by Herbert Siegel in partial fulfillment of the requirements for the Ph.D. degree in the Faculty of the Graduate School, West Virginia University, August, 1956.

[2] Department of Chemistry, Western Michigan University, Kalamazoo, Mich.

[3] E. A. Braude and W. F. Forbes, *J. Chem. Soc.*, 3776 (1955).

[4] G. H. Beaven, D. M. Hall, M. S. Lesslie and E. E. Turner, *ibid.*, 854 (1952).

[5] F. Bell, *ibid.*, 1527 (1952).

[6] E. A. Braude and E. S. Waight, "Progress in Stereochemistry," W. Klyne, editor, Academic Press, Inc., New York, N. Y., 1954, p. 142.

[7] G. H. Beaven, G. R. Bird, D. M. Hall, E. A. Johnson, J. E. Ladbury, M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 2708 (1955).

[8] W. E. Truce and D. D. Emrick, THIS JOURNAL, **78**, 6130 (1956).

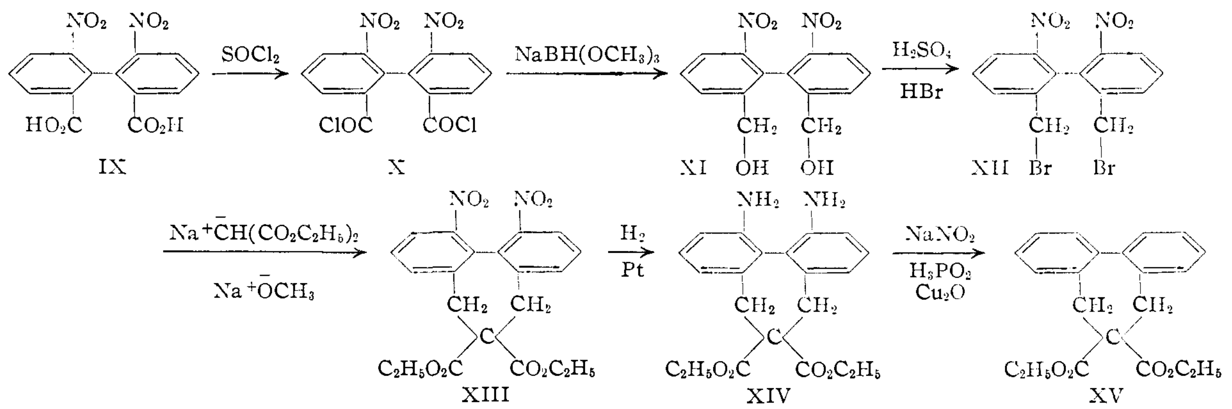
[9] A preliminary description of part of this work was published earlier: D. C. Iffland and H. Siegel, *J. Org. Chem.*, **21**, 1056 (1956).

[10] S. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 122 (1949).

[11] N. Kornblum and D. C. Iffland, *ibid.*, **71**, 2137 (1949).

[12] R. C. Elderfield, "Heterocyclic Compounds," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 175.

[13] N. Kornblum, G. D. Cooper and J. E. Taylor, THIS JOURNAL, **72**, 3013 (1950).



obtained from (+)-IX and racemic XV obtained from diphenic acid showed no depression.

This correspondence of physical properties, along with excellent elemental analysis, can leave no question regarding the structure of the deamination product. Similar rates of racemization of the several preparations of the diester as well as the complete racemization in each instance attest to the purity of the product obtained by this synthesis.

While the diester XV, in cyclohexane solution, loses half of its activity in 80 minutes (*cf.* Fig. 2), the compound is optically stable in the crystalline state. No significant loss of activity was observed after about 200 hours in the solid state. Thus, the forces holding the molecule in the crystal lattice must reinforce the steric forces resulting from the three-carbon-atom bridge and the repulsive forces of the 1,11-hydrogen atoms.

The results of these experiments support the view of Beaven, *et al.*,[8] and Bell[9] that compounds of type I to VII should exhibit enantiomorphism. In addition, the relatively short half-life period for the activity of XV suggests the explanation for the failure of their resolution attempts.

The observed optical activity of XV is unquestionably a consequence of the steric requirement of the three-carbon-atom bridge maintaining the benzene rings in a non-planar configuration. In addition, the diester XV has an ultraviolet absorption maximum at 249 mμ as is also found in biphenyl itself and numerous other 2,2'-bridged biphenyls. This "250 mμ" or biphenyl band[14] has been interpreted as related to inter-ring conjugation[15] which is expected to be greatest with a coplanar biphenyl configuration.[16,17]

The simultaneous observation of optical activity and the biphenyl absorption band in XV may be a consequence of XV existing as a mixture of optically active non-planar molecules and higher energy planar molecules having a very high ultraviolet absorption at 249 mμ. However, the high extinction coefficient value of E 16,980 for XV as compared to E 19,000 for fluorene, which is considered too highly strained to be truly planar,[3] suggests that an alternate interpretion as discussed by Suzuki[17] is more reasonable, *i.e.*, conjugation does not necessitate coplanarity. Finally, the conclusion expressed by Beaven[4] that "the ultraviolet absorption spectrum of a substituted diphenyl must be used with considerable reserve as a criterion of coplanarity or otherwise," must be reemphasized.

Experimental[18]

Preparation of (±)-6,6'-Dicarbethoxydibenzo[a,c][1,3]-cycloheptadiene (±XV).—Sixteen grams (0.1 mole) of diethyl malonate dissolved in 150 ml. of ether was mixed with a sodium ethoxide solution prepared by reaction of 4.6 g. (0.2 g. at. wt.) of sodium with 60 ml. of absolute ethanol. Thirty grams (0.09 mole) of 2,2'-bis-(bromomethyl)-biphenyl[19] dissolved in 220 ml. of ether was added while refluxing the mixture. Heating was continued for 3 hours. The mixture was filtered and the solvents were removed by distillation. The product was distilled (192–194° at 1 mm.) and crystallized from 35–37° petroleum ether. There was obtained 21.5 g. (72%) of the diester, m.p. 64–66° (lit.[20] 64°). The ultraviolet absorption spectra for ethanol and cyclohexane solutions of the product were determined using a Beckman model DU spectrophotometer. The spectrum for a 5×10^{-5} *M* solution (95% ethanol) is found in Fig. 1; λ_{max} 249 mμ, E 16,980.

3-Nitro-2-iodobenzoic Acid.—3-Nitrophthalic acid (Matheson, Coleman and Bell, no. 5859) was converted to anhydro-2-hydroxymercuri-3-nitrobenzoic acid[21] and without drying allowed to react with potassium iodide–iodine solution.[22] 3-Nitro-2-iodobenzoic acid, m.p. 210–212° (lit. 204–206°) was obtained in 52% yield.

Methyl 3-Nitro-2-iodobenzoate.—Dry hydrogen chloride was bubbled for 3 hours into 455 g. (1.55 moles) of 3-nitro-2-iodobenzoic acid dissolved in 4000 ml. of methanol. After refluxing for 21 hours, the mixture was diluted with ice-water and the liquid decanted from the precipitate. The product was recrystallized from methanol to yield 455 g. (93%) of the methyl ester, m.p. 64–66°.

Anal. Calcd. for $C_8H_6NO_4I$: N, 4.56. Found: N, 4.51.

---

[14] The position of this biphenyl band has been variously reported as having λ_{max} between 249 and 251 mμ.

[15] E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 151.

[16] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 157.

[17] The relationship between configuration of biphenyl and 2,2'-bridged biphenyls and ultraviolet absorption spectra has been discussed in detail by Beaven, *et al.*,[4] Braude[6] and H. Suzuki (*Bull. Chem. Soc., Japan*, **27**, 597 (1954)).

[18] Microanalysis by Galbraith Laboratories, Knoxville, Tenn. Melting points are uncorrected. Optical activity was measured on a Hilger model 412 polarimeter and at least five readings were averaged to calculate specific rotations.

After completion of this work it was learned from Dr. Kurt Mislow, Department of Chemistry, New York University, that he and his students had independently prepared active XI and compounds XII and XIII from active IX and had observed essentially the same properties as reported herein (*cf.* P. Newman, P. Rutkin and K. Mislow, THIS JOURNAL, **80**, 465 (1958)).

[19] C. W. Muth, W. Sung and Z. B. Papanastassiou, THIS JOURNAL, **77**, 3394 (1955).

[20] J. Kenner, *J. Chem. Soc.*, **103**, 613 (1913).

[21] F. C. Whitmore, P. J. Culhane and H. T. Neher, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 56.

[22] P. J. Culhane, *ibid.*, p. 126.

6,6'-Dinitrodiphenic Acid (±IX).—Copper powder, 293 g. (4.6 g. at. wt.), was added and mixed in small portions with 606 g. (1.97 moles) of methyl 3-nitro-2-iodobenzoate heated to 160–165° in an oil-bath. The addition required 2.5 hours and heating with stirring was continued for 1 hour. The reaction mixture was cooled to 100° and poured into 2.5 l. of chloroform. The chloroform solution was filtered through Celite and most of the solvent was removed by distillation. Four crops of crystals were collected and totaled 280 g. (79%), m.p. 128–130° (lit. 129°[23] and 132–133°[24]).

The ester (0.78 mole) was dissolved in 1500 ml. of ethanol and added to 125 g. (3.12 moles) of sodium hydroxide in 1000 ml. of water. After refluxing for 13 hours, the alcohol was distilled. The aqueous solution was partially neutralized by adding 125 ml. of concd. hydrochloric acid, cooled and clarified with Norite. After acidification with excess hydrochloric acid, the crude product was recrystallized from glacial acetic acid to yield 210 g. (63% based on methyl 3-nitro-2-iodobenzoate) of dinitrodiphenic acid, m.p. 259–261°; lit. 249–253°,[25] 258°[24] and 263°[26,27].

Active 6,6'-Dinitrodiphenic Acid (+IX).—Racemic 6,6'-dinitrodiphenic acid (0.73 mole) was dissolved in acetone and resolved using (+)-α-phenylethylamine[28] according to the procedure of Ingersoll and Little.[23] The *dAdB* salt (146 g.) was obtained and after decomposition with concd. hydrochloric acid yielded 95 g. of the *d*-acid, m.p. 228–234°, $[\alpha]^{28}_{\rm D}$ 125° (*l* 1 dm., *c* 1.690, methanol); $[\alpha]^{30}_{\rm D}$ 261° (*l* 1 dm.; 0.4785 g. neutralized with 22.81 ml. of 1.264 *N* NaOH); lit.[23] m.p. 231°, $[\alpha]_{\rm D}$ 127° (methanol), $[\alpha]_{\rm D}$ 233° in sodium hydroxide.

The acetone solution containing largely the *lAdB* salt was concentrated and several crops of crystals were collected. This salt was hydrolyzed as above and produced 101 g. of *l*-acid, m.p. 248–252°, $[\alpha]^{31}_{\rm D}$ −81.5° (*l* 1 dm., *c* 1.8528, methanol).

Preparation of Di-acid Chloride from (+)-6,6'-Dinitrodiphenic Acid (+X).—A mixture of 255 g. (2.1 moles) of thionyl chloride and 71 g. (0.21 mole) of (+)-6,6'-dinitrodiphenic acid was refluxed 24 hours. After removing the excess thionyl chloride by vacuum distillation, the acid chloride was dissolved in chloroform, treated with Norite and crystallized. The yield was 72 g. (91%), m.p. 155–157°, $[\alpha]^{25}_{\rm D}$ +152° (*l* 1 dm., *c* 1.6784, methanol).

(+)-2,2'-Bis-(hydroxymethyl)-6,6'-dinitrobiphenyl (+XI).—A suspension of 250 g. (2.0 moles) of sodium trimethoxyborohydride in 1020 ml. of dioxane was added with vigorous stirring to a solution of 72 g. (0.20 mole) of the *d*-di-acid chloride dissolved in 135 ml. of dioxane. The temperature was maintained at approximately 20°; addition required about 35 minutes. The mixture was stirred at room temperature for five hours and then acidified with hydrochloric acid. After the inorganic precipitate was filtered, the filtrate was steam distilled and finally the water was removed from the residue under reduced pressure. The solid was dissolved in chloroform and on concentration yielded 33 g. (56%) of the di-alcohol, m.p. 120–122°, $[\alpha]^{25}_{\rm D}$ +55.6° (*l* 1 dm., *c* 3.5580, methanol). The racemic di-alcohol melted at 143–145°.

Anal. Calcd. for $C_{14}H_{12}N_2O_6$: C, 55.26; H, 3.98; N, 9.21. Found: active, C, 55.25; H, 3.95; N, 9.37; racemic, C, 55.22; H, 3.81; N, 8.91.

Before the above procedure was developed, attempts were made to effect the reduction using sodium borohydride, but this resulted only in recovery of the di-acid. For example, 90 g. (0.24 mole) of the active di-acid chloride was dissolved in 150 ml. of dioxane, mixed with 92 g. (2.43 moles) of sodium borohydride and refluxed for 37 hours. After filtration, 500 ml. of 10% sodium hydroxide solution was added and the solution was steam distilled. The residue was again filtered and the filtrate was acidified to yield 78 g. (87%) of (+)-6,6'-dinitrodiphenic acid, m.p. 225–235°.

(+)-2,2'-Bis-(bromomethyl)-6,6'-dinitrobiphenyl (+XII).—Nine ml. of concd. sulfuric acid was added to 84 ml. (0.74 mole) of 48% hydrobromic acid and the solution was cooled to 0–5°. Fifteen grams (0.05 mole) of the (+)-di-alcohol was added with stirring and solution resulted on warming the mixture. After the solution was refluxed for 2.5 hours, it was cooled, poured into 300 ml. of water and the precipitate was collected and washed. This solid was dissolved in 500 ml. of benzene, clarified with Norite, filtered through Celite and dried. Concentration led to 17.5 g. (82%) of crystalline dibromide, m.p. 168–170°, $[\alpha]^{29}_{\rm D}$ +45.3° (*l* 1 dm., *c* 2.9560, dioxane). The racemic dibromide melted at 182–184°.

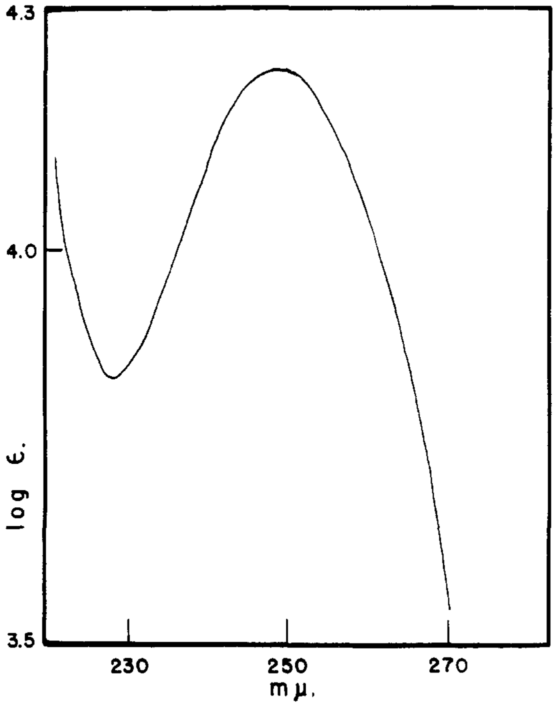


Fig. 1.—Ultraviolet spectrum of 6,6-dicarbethoxydibenzo-[a,c][1,3]cycloheptadiene (XV).

Anal. Calcd. for $C_{14}H_{10}N_2O_4Br_2$: C, 39.10; H, 2.34; N, 6.51. Found: active, C, 39.36; H, 2.52; N, 6.65; racemic, C, 39.23; H, 2.49; N, 6.59.

(−)-1,11-Dinitro-6,6-dicarbethoxydibenzo[a,c][1,3]cycloheptadiene (−XIII).—A solution of 3.2 g. (0.14 g. at. wt.) of sodium in 200 ml. of absolute ethanol was prepared and 11.0 g. (0.07 mole) of diethyl malonate was added. This solution was added dropwise at room temperature to a vigorously stirred solution of 20 g. (0.047 mole) of the (+)-dibromide dissolved in 50 ml. of dioxane. The addition was completed in one hour. The mixture was then stirred and heated on a steam-bath for 3 hours. Addition of ice-water to the cooled mixture gave a precipitate (reverse addition produced an oil) which was collected, washed and vacuum-dried. The di-ester product weighed 15 g. (75%), m.p. (recrystallized from ethanol) 141–143°, $[\alpha]^{32.5}_{\rm D}$ −443° (*l* 1 dm., *c* 1.1960, methanol). The racemic diester melted at 158–160°.

Anal. Calcd. for $C_{21}H_{20}N_2O_8$: C, 58.88; H, 4.71; N, 6.54. Found: active, C, 58.83; H, 4.88; N, 6.50; racemic, C, 59.26; H, 4.95; N, 6.67.

(−)-1,11-Diamino-6,6-dicarbethoxydibenzo[a,c][1,3]-cycloheptadiene (−XIV).—A mixture of 11.0 g. (0.026 mole) of the (−)-dinitro di-ester, 0.15 g. of platinum oxide catalyst, 50 ml. of ethanol and 75 ml. of glacial acetic acid was shaken with hydrogen at 2–3 atmospheres in a Parr low pressure hydrogenation apparatus. After the addition of hydrogen ceased, the solution was filtered and the solvents were removed from the filtrate by vacuum evaporation. The residue was dissolved in benzene and precipitated by adding petroleum ether (90–100°). The solid which resulted was collected and weighed 8.5 g., m.p. 105–110°.

This crude product was dissolved in ether and the solution was evaporated to yield crystals. The first crop (0.5 g.) was inactive. The second crop (2.0 g.) was active,

---

[23] A. W. Ingersoll and J. R. Little, THIS JOURNAL, **56**, 2123 (1934).

[24] J. Kenner and W. V. Stubbings, *J. Chem. Soc.*, **119**, 593 (1921).

[25] G. H. Christie, A. Holderness and J. Kenner, *ibid.*, 671 (1926).

[26] G. H. Christie and J. Kenner, *ibid.*, **121**, 614 (1922).

[27] R. Kuhn and O. Albrecht, *Ann.*, **455**, 272 (1927).

[28] A. W. Ingersoll, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 506.

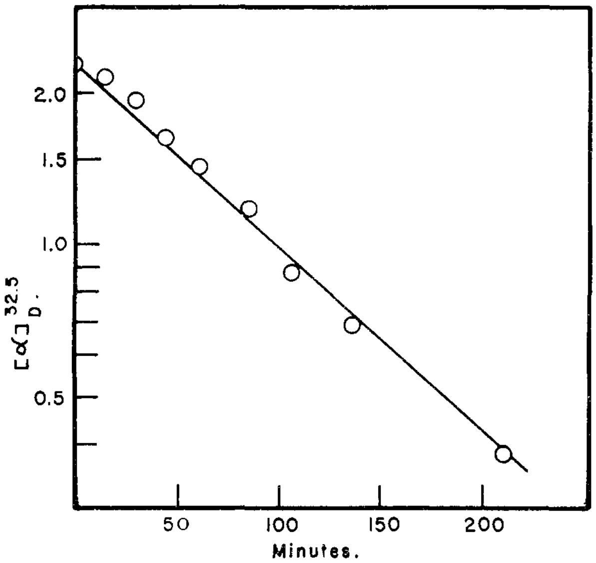


Fig. 2.—Racemization of (+)-6,6-dicarbethoxydibenzo[a,c][1,3]cycloheptadiene (XV).

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.

[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-

---

(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.