

Acknowledgments.—This research was supported by grants from the National Science Foundation and the Wisconsin Alumni Research Foundation. We wish to

thank Drs. F. A. Miller, W. G. Fateley, and G. L. Carlson for their kind assistance in determining Raman and infrared spectra.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN, MADISON, WIS.]

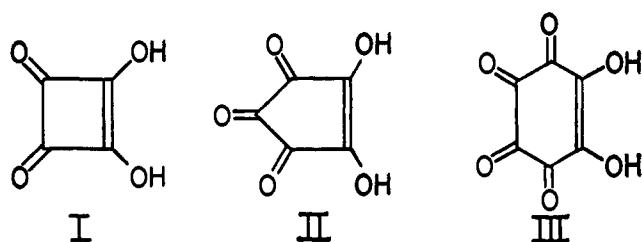
New Aromatic Anions. V. The Synthesis of Diketocyclobutenediol and its Conversion to Octahydroxycyclobutane

BY ROBERT WEST, HSIEN YING NIU, AND MITSUO ITO

RECEIVED FEBRUARY 22, 1963

Mild oxidation of diketocyclobutenediol (I) with nitric acid at 0° yields the compound octahydroxycyclobutane IV. The infrared and Raman spectra of IV and its octadeuterio analog indicate that it has the planar D_{4h} structure. The preparation of I from 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene is also discussed, and structures are presented for intermediate compounds in this synthesis.

Following publication of the synthesis of diketocyclobutenediol ("squaric acid," I) by Cohen, Lacher, and Park,¹ the relationship of this substance to the five- and six-ring compounds croconic acid (II) and rhodizonic acid (III) was pointed out and it was suggested

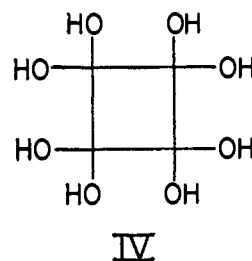


that the dianions of these enols represent a series of totally delocalized aromatic anions.² Compounds II and III, when treated with nitric acid, give rise to the interesting oxidation products leuconic acid, $C_5O_5 \cdot 5H_2O$,³ and triquinoyl octahydrate, $C_6O_6 \cdot 8H_2O$.⁴ The structure of these substances has been controversial for many years.^{5,6} Person and Williams found no absorption in the carbonyl region of the infrared spectra of leuconic acid and triquinoyl, and on that basis favored totally hydroxylated structures for these compounds.⁷

In view of the relationship of diketocyclobutenediol (I) to II and III, it was of interest to determine whether compound I would yield a related oxidation product. Treatment of I with nitric acid or bromine at room temperature or above converted it to carbon dioxide and oxalic acid. At 0°, however, brief treatment with dilute nitric acid or bromine oxidized I smoothly to a colorless crystalline substance with the composition $C_4H_8O_8$. This compound could be reduced back to I by sulfur dioxide.

A study of the infrared spectrum of solid $C_4H_8O_8$ and the Raman spectrum of its acidic aqueous solution was undertaken to determine its structure. The octadeuterio analog $C_4D_8O_8$, obtained by oxidation of deuterated I with bromine, was also studied by these tech-

niques. The results and tentative assignments are shown in Table I. The data indicate that $C_4H_8O_8$ has the octahydroxycyclobutane structure IV, with a planar or nearly planar ring configuration. No ab-



sorption bands other than the O-H stretching mode appear above 1300 cm^{-1} so the compound cannot have a free carbonyl group either in the solid or in aqueous acidic solution. The infrared spectra are extremely simple, showing only five bands above 400 cm^{-1} , of which three are associated with the motion of the hydrogen atoms. There are no coincidences between the Raman and infrared spectra, indicating by the rule of mutual exclusion that the molecule has a center of symmetry. Two polarized Raman lines are found in the expected region.⁸ The findings are all consistent with a planar symmetrical D_{4h} model, but a slight torsional deformation of the ring cannot definitely be excluded.

TABLE I
VIBRATIONAL FREQUENCIES IN CM^{-1} FOR OCTAHYDROXYCYCLOBUTANE^a

$C_4(OH)_8$	$C_4(OD)_8$	Assignment (D_{4h} model)
165 R	166 R	
405 R,p	390 R,p	OCO scissoring, A_{1g}
465 R,d	455 R,d	
707 R,p	682 R,p	C-C stretching, A_{1g}
900 IR	805 IR	O-H deformation
1080 IR,s	1065 IR,s	C-O stretching, A_{2u} or E_u
1160 IR,s	1150 IR,s	C-O stretching, A_{2u} or E_u
1215 R	1225 R	C-O stretching
1300 IR	960 IR	O-H deformation
3250 IR,s	2450 IR,s	O-H stretching

^a R = Raman, IR = infrared, s = strong, p = polarized, d = depolarized.

Octahydroxycyclobutane decomposes at about 140° with liberation of carbon dioxide. Aqueous solutions

(8) The D_{4h} model is predicted to have three polarized Raman lines; reasonable structures with lower symmetry should have a larger number of polarized Raman lines. See G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, D. Van Nostrand Co., Inc., Princeton, N. J., 1945, Chapter II.

(1) S. Cohen, J. R. Lacher, and J. D. Park, *J. Am. Chem. Soc.*, **81**, 3480 (1959).

(2) R. West, H. Y. Niu, D. L. Powell, and M. V. Evans, *ibid.*, **82**, 6204 (1960).

(3) H. Will, *Ann.*, **118**, 177 (1858).

(4) J. U. Lerch, *ibid.*, **124**, 20 (1862).

(5) R. Nietzki and T. Benckiser, *Ber.*, **18**, 499 (1885); **19**, 293 (1886); R. Nietzki and H. Rosemann, *ibid.*, **22**, 916 (1889).

(6) R. P. Temple, *Research* (London), **1**, 280 (1948); P. Souchay and F. Tatibouet, *J. chim. phys.*, **49**, C108 (1952).

(7) W. B. Person and D. G. Williams, *J. Phys. Chem.*, **61**, 1016 (1957). We find that triquinoyl octahydrate has a band of medium intensity at 1650 cm^{-1} , and that leuconic acid has a weak band at 1625 cm^{-1} . However, it is probable that these bands do not represent carbonyl stretching modes.

of IV at pH 1 or 0 are initially transparent in the ultraviolet region and are stable for several hours. Absorption bands slowly develop in the solutions, probably indicating that decomposition is taking place. At higher pH IV gives immediately a weak band at about 2350 Å., and the spectrum also changes with time. Decomposition appears to take place rapidly in basic solution.

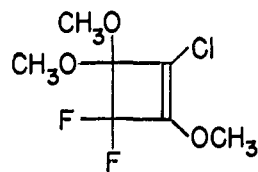
Synthesis of Diketocyclobutenediol (I).—A recent paper by Park, Cohen, and Lacher has outlined a high-yield synthesis of squaric acid from 1,2-diethoxy-3,3,4,4-tetrafluorocyclobutene.⁹ We have utilized their earlier-reported method of synthesis in two steps from the commercially available compound, 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene (V).^{1,10} For workers desiring small amounts of I, this method may still be the most convenient. Improved directions are given in the Experimental section; in particular, the use of hydrochloric acid instead of sulfuric acid in the final hydrolysis step improves the yield of I. (The over-all yield of squaric acid from V is about 60%.)

Park, Snow, and Lacher found that the action of methoxide ion in methanol on V gave a monoether, 1-methoxy-2-chloro-3,3,4,4-tetrafluorocyclobutene, and a triether. The latter was tentatively formulated as 1,3,3-trimethoxy-2-chloro-4,4-difluorocyclobutene (VI), but without definite evidence for this structure.¹⁰ Under the conditions reported in the Experimental section, no monoether was observed. The triether was the principal product, but in addition a solid tetramethoxy compound was formed. Infrared and ultraviolet spectra, along with the analytical results, showed this compound to be a saturated cyclobutane derivative of the formula $C_4ClF_2H(OCH_3)_4$.

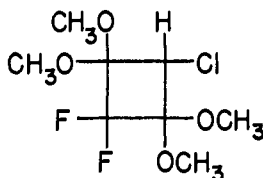
That this compound results from addition of methanol to the triether was shown by its synthesis in nearly quantitative yield from VI and methoxide. The addition of ethanol during the hydrolysis of the analogous triethoxy compound has recently been noted by Park.⁹ Acid hydrolysis of the tetraether gives squaric acid, suggesting that the addition of methanol may be reversible.

The n.m.r. spectra of this tetramethoxy compound allow its configuration to be established unequivocally. The proton magnetic resonance spectrum of the tetramethoxy compound shows four peaks with relative intensities 1:1:12:12. The two peaks with relative intensity 12 are separated by a chemical shift, and represent two different environments for the four methoxy groups. The splitting of the peak due to the one ring proton is caused by spin-spin interaction with one fluorine atom. The fluorine n.m.r. spectrum, consisting of three peaks with relative intensity 1:1:2, confirms this interpretation. The H-F splitting constant is 7 c.p.s., too large for atoms attached to adjacent carbon atoms, but of the right magnitude for 1,3-interaction across a cyclobutane ring.¹¹

Of the possible $C_4ClF_2H(OCH_3)_4$ isomers, only structure VII is consistent with the data. If addition to the



VI



VII

triether is assumed to occur without rearrangement, its structure must indeed be VI, confirming the earlier assignment.

Experimental

Reaction of 1,2-Dichloro-3,3,4,4-tetrafluorocyclobutene with KOH in Methanol.—A solution of 200 g. (1.02 moles) of 1,2-dichloro-3,3,4,4-tetrafluorocyclobutene in 100 ml. of methanol was added dropwise to a stirred solution of 200 g. (3.56 moles) of potassium hydroxide in 500 ml. of methanol, as rapidly as possible while maintaining control of the exothermic reaction. The addition required about 3 hours, and a vigorous refluxing took place throughout this time. When the addition was complete, about 500 ml. of water was added to the mixture, causing separation into three phases: an organic layer, an aqueous layer, and a colorless solid. The three phases were separated, and the organic layer was dried and distilled, yielding 150 g. (70%) of 2-chloro-3,3-difluoro-2,4,4-trimethoxycyclobutene, b.p. 206–210°. This substance had an ultraviolet absorption band with λ_{max} 2420 Å., ϵ 1860. The fluorine n.m.r. spectrum shows a single peak at $\delta = 117.1$,¹² and in the proton n.m.r. spectrum two peaks are found at $\tau = 6.01$ and 6.53, with relative strength 1:2.

About 5 g. of solid was left as a residue. This was combined with the solid previously separated to give a total of 10 g. (4%). The solid product was recrystallized from methanol-water to give colorless crystals, m.p. 66.5–67.5°, b.p. 220–224°.

Anal. Calcd. for $C_4H_3ClF_2O_4$: C, 38.96; H, 5.31; Cl, 14.4; F, 15.4; OCH_3 , 50.3. Found: C, 39.30; H, 5.40; Cl, 14.6; F, 15.4; OCH_3 , 49.6.

The solid had no ultraviolet absorption bands. In the fluorine n.m.r. spectrum of the solid, in fluorotrichloromethane solution, three peaks were observed at $\delta = 122.8$, 123.0, and 124.1,¹² with relative strengths 1:1:2. The proton n.m.r. spectrum showed four peaks at $\tau = 5.92$, 6.06, 6.57, and 6.70 in the ratio 1:1:12:12.

Synthesis of Diketocyclobutenediol (I).—To 30 g. (0.14 mole) of 1-chloro-3,3-difluoro-2,4,4-trimethoxycyclobutene in a 250-ml. erlenmeyer flask was added 100 ml. of 12 N hydrochloric acid. The mixture was heated to boiling and allowed to evaporate to reduce the volume of liquid to about 10 ml. Colorless crystals of product formed during the evaporation. The suspension was cooled and filtered, and the product was recrystallized from water. The yield of I was 13.5 g. (85%). The compound had physical properties identical with those reported earlier for diketocyclobutenediol. Analysis showed the correct C and H percentages and neutralization equivalent.

Oxidative Hydrolysis of Tetraether to Squaric Acid.—Two grams (0.008 mole) of the solid tetraether VII and 10 ml. of 70% sulfuric acid were placed in a heavy walled Pyrex glass tube of 100-ml. capacity, which was sealed off. The tube was heated in a rocking autoclave at 100° for 12 hours. It was cooled and opened, and the white crystals which had formed were filtered off and recrystallized from water to give 0.7 g. (75%) of I.

Synthesis of Tetraether VII from Triether.—In 20 ml. of methanol was dissolved 2 g. (0.0094 mole) of 2-chloro-3,3-difluoro-2,4,4-trimethoxycyclobutene and 5 g. of potassium hydroxide. The resulting solution was heated to reflux for 2 hours and then cooled. Water was added to the solution, causing the precipitation of white crystals which were recrystallized from methanol and water; m.p. 66.5–67.5°. The product had an infrared spectrum identical with that of the solid obtained as a by-product in the synthesis of the triether. The yield was 2.2 g., 95%.

Octahydroxycyclobutane. a. Nitric Acid Oxidation.—To a solution of 2.0 g. (0.0175 mole) of I in 25 ml. of water at 0°, 4 ml. of 12 N nitric acid was added. The resulting solution was shaken for 30 seconds and then frozen in a -70° bath. Water and excess nitric acid were removed by freeze-drying; the white solid residue was purified by dissolving it in water and quickly reprecipitating it with acetone. The solid was then filtered off and dried under vacuum for 48 hours. The yield was 2.7 g., 84%. The product decomposed with evolution of carbon dioxide at about 140°.

Anal. Calcd. for $C_4H_8O_8$: C, 26.10; H, 4.38. Found: C, 26.00, 26.17; H, 4.55, 4.52.

b. Bromine Oxidation.—To a solution of 2.0 g. (0.0175 mole) of I in about 25 ml. of water at 0°, bromine was added dropwise until on shaking a faint yellow color persisted. The solution was then frozen in a -70° bath. Water and excess bromine were removed by freeze-drying. The white product was purified in the same way as described in a. The yield was about 2.2 g., 70%.

Octahydroxycyclobutane-*d*₈.—Five grams of diketocyclobutenediol was dissolved in 100 ml. of 50% D₂O. The solution was then frozen in a -70° bath. Both water and deuterated water were removed by freeze-drying. This process was then repeated

(9) J. D. Park, S. Cohen, and J. R. Lacher, *J. Am. Chem. Soc.*, **84**, 2919 (1962).

(10) J. D. Park, C. M. Snow, and J. R. Lacher, *ibid.*, **73**, 2342 (1951).

(11) C. M. Sharts and J. D. Roberts, *ibid.*, **79**, 1008 (1957).

(12) Referred to internal fluorotrichloromethane.

twice with 75% D₂O and finally six times with 99.7% D₂O. The deuterated I was again dissolved in 100 ml. of 99.7% D₂O and cooled to 0°. Bromine was added dropwise with shaking until a faint yellow color persisted. The solution was then frozen and the deuterated water was removed by freeze-drying to give about 6 g. of product octahydroxycyclobutane-*d*₈. The product was not analyzed, but spectral studies indicated it to be octahydroxycyclobutane with more than 97% of the hydrogen replaced by deuterium. It was free of carbonyl-containing impurities.

Reduction of Octahydroxycyclobutane to I.—In 5 ml. of water was dissolved 0.5 g. of octahydroxycyclobutane. A slow stream of sulfur dioxide was passed through the solution for 30 minutes. The solution was then evaporated to small volume, and the white crystals which formed were isolated and recrystallized from water. The product was identified as I by comparison of its ultraviolet and infrared spectra with those of an authentic sample.

Ultraviolet Spectra of Octahydroxycyclobutane Solution.—All spectra were determined using a Cary model 14 spectrophotometer. At 0.01 *M* in 1 *N* hydrochloric acid, IV showed no ultraviolet bands except for some end absorption below 2100 Å. A very weak band at about 2900 Å. became noticeable after several hours, and later a band with λ_{\max} 2350 Å. appeared. The latter grew steadily and after 2 days had ϵ_{app} 100. A solution of IV at pH 1 was also initially transparent, but absorption developed somewhat more rapidly, leading to bands at about 2450 and 2750 Å. In pure water IV gave a weakly acidic solution which showed initially a band with λ_{\max} 2450 Å., ϵ_{app} 40.

A shoulder gradually appeared at about 2750 Å., and both peaks increased with time. Some of the maxima are close to those for diketocyclobutene in acid solution,¹³ suggesting that compound I may be one of the decomposition products of IV. In a strongly basic solution of IV all of the ultraviolet bands disappeared except for very strong end absorption, and octahydroxycyclobutane was found not to be present when the solution was acidified.

Infrared and Raman Spectra.—Infrared spectra were determined on solid octahydroxycyclobutane and octahydroxycyclobutane-*d*₈ as mulls in Stanolind white petroleum oil and as pressed disks in KBr. A Baird model S spectrophotometer was used for the 650–4000 cm.⁻¹ and a Perkin-Elmer model 112 instrument with a cesium bromide prism was used for the 400–650 cm.⁻¹ region. For the Raman spectra, a 12% solution in 1 *N* hydrochloric acid was used for the protium compound, and a 15% solution in 1–2 *N* DCl in D₂O was used for the octadeuterio compound. The spectra were determined on a Cary model 44 automatic recording Raman spectrometer at the Argonne National Laboratory.

Acknowledgments.—The authors are grateful to personnel of the Argonne National Laboratory for making the Raman spectrometer available for their use and to the National Science Foundation and the Wisconsin Alumni Research Foundation for financial support.

(13) H. Y. Niu, Thesis, University of Wisconsin, 1961.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

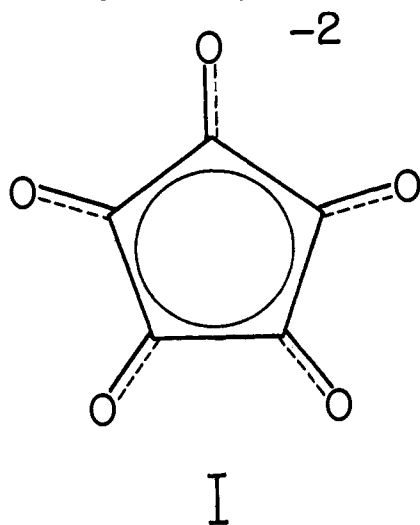
New Aromatic Anions. VI. Complexes of Croconate Ion with Some Divalent and Trivalent Metals

BY ROBERT WEST AND HSIEN YING NIU

RECEIVED FEBRUARY 22, 1963

Complexes of croconate ion with the divalent metal ions Cu, Fe, Zn, Ni, Mn, Co, and Ca and trivalent Al, Fe, and Cr have been prepared and characterized by means of analysis, infrared spectroscopy, powder X-ray diffraction, and magnetic studies. All of the divalent metal complexes have the general formula $\text{MC}_5\text{O}_5 \cdot 3\text{H}_2\text{O}$. The divalent transition metal compounds are all high-spin complexes, and all have the same polymeric structure (Fig. 1), determined from a single-crystal X-ray analysis of the copper(II) compound. The trivalent metal complexes have more complicated formulas containing hydroxyl groups, and those of Fe(III) and Cr(III) show paramagnetism lower than that expected for high-spin complexes.

Although copper(II) and silver derivatives of croconate ion ($\text{C}_5\text{O}_5^{-2}$, I) have been known for over a hundred years,^{1,2} no general study of transition metal cro-



conates has been reported. The present investigation was initiated because it seemed likely that the planar, symmetrical croconate ion^{2,3} (I) might show unusual

properties as a complexing agent. In particular, sandwich complexes with ring-bonding to transition metal ions were thought to be possible. Such π -complexes of the sandwich type were not found; instead, the croconate ion bonds to metals through oxygen, serving both as a monodentate and bidentate ligand toward divalent transition metals. The resulting metal complexes form an interesting new class of inorganic coordination polymers.

Divalent Transition Metal Croconates.—The croconate derivatives of Mn(II), Fe(II), Cu(II), Ni(II), Co(II), Ca(II), and Zn(II) were all prepared from aqueous solutions of salts of the divalent cations and of dipotassium croconate. All of the compounds were trihydrates with general formula $\text{MC}_5\text{O}_5 \cdot 3\text{H}_2\text{O}$, and all of the divalent transition metal croconates had closely similar powder X-ray diffraction patterns, differing only slightly in interplanar *d*-spacing. Representative data are shown in Table I. The croconate derivative of the nontransition metal calcium is also a trihydrate, but it has a quite different X-ray pattern and hence probably a different structure.

Preliminary single-crystal X-ray work on copper croconate trihydrate was carried out previously by Takehara and Yokoi,⁴ who found that the crystals are orthorhombic with eight molecules per unit cell. The lattice parameters reported were $a = 15.1$ Å., $b = 11.4$ Å., and $c = 7.83$ Å. Redetermination of the lattice

(1) L. Gmelin, *Ann.*, **37**, 58 (1841); H. Wüll, *ibid.*, **118**, 177 (1861).

(2) K. Yamada, N. Mizuno, and Y. Hirata, *Bull. Chem. Soc. Japan*, **31**, 543 (1958).

(3) M. Ito and R. West, *J. Am. Chem. Soc.*, **85**, 2580 (1963); R. West, H. Y. Niu, D. L. Powell, and M. V. Evans, *ibid.*, **82**, 6204 (1960).

(4) A. Takehara and M. Yokoi, *Shinshu Daigaku Sen Igakubu Kenkyu Hokoku*, **8**, 108 (1958).