

The ester gave, with 2,4-dinitrophenylhydrazine reagent, the 2,4-dinitrophenylhydrazone which was recrystallized from ethanol; m.p. 101°.

*Anal.* Calcd. for  $C_{15}H_{17}FN_4O_5$ : C, 45.0; H, 4.3; N, 14.0. Found: C, 44.9; H, 4.4; N, 13.8.

**Triethyl Fluoroisocitrate.**—Triethyl fluorooxalosuccinate (5.84 g.), dissolved in anhydrous ethanol (25 ml.), was added dropwise to a cooled (−10 to 0°) suspension of potassium borohydride (1.08 g. in anhydrous ethanol, 50 ml.). The addition was completed in 1.5 hr. while the temperature was maintained between −10 and 0°. The reaction mixture was then put into the deep freeze (−5°) for 10 hr. Glacial acetic acid was then added to decompose excess borohydride, and the solvent was distilled under vacuum (bath 30°). Water (20 ml.) was added to the residue and the mixture was extracted twice with ether (50 ml.). The ether was washed with dilute sodium bicarbonate and dried with  $Na_2SO_4$ . Distillation gave triethyl fluoroisocitrate: 2.2 g., b.p. 143° (1 mm.). Redistillation for analysis gave 2 g. (34%), b.p. 135–140° (0.75 mm.).

*Anal.* Calcd. for  $C_{15}H_{19}FO_7$ : C, 49.0; H, 6.5; F, 6.5. Found: C, 49.2; H, 6.3; F, 6.4.

The infrared spectrum showed strong OH stretching absorption at 3450  $cm^{-1}$ . A 3,5-dinitrobenzoate of the alcohol was prepared with 3,5-dinitrobenzoyl chloride in pyridine. When recrystallized from ethanol, it melted at 118°.

*Anal.* Calcd. for  $C_{10}H_{21}FN_2O_2$ : C, 46.72; H, 4.34; N, 5.74. Found: C, 46.94; H, 4.53; N, 5.56.

**Diethyl  $\alpha$ -Fluoro- $\gamma$ -hydroxyglutarate.**—Diethyl fluoromalonate (9.3 g.) was added to a solution of sodium (0.2 g.) in absolute alcohol (100 ml.). After stirring this solution for 5 min., ethyl  $\alpha$ -acetoxyacrylate (7.9 g.) was added dropwise while the stirring continued. After addition, the reaction mixture was left at room temperature for 12 hr. and then neutralized with glacial acetic acid. The solvents were removed under vacuum, and the residue was extracted into ether. Filtration and vacuum distillation of the ether left a yellow oil (12.8 g.). This oil was mixed with 20% HCl (100 ml.) and heated under reflux for 4 hr. The solvent was removed under vacuum and the remaining sirup was taken up in anhydrous ethanol (100 ml.) containing *p*-toluenesulfonic acid (0.5 g.). This ethanolic solution was heated under reflux for 24 hr. Ethanol was then removed under vacuum and the residue was extracted into ether. The ether solution was washed with dilute sodium bicarbonate, separated, and dried with anhydrous  $Na_2SO_4$ . After removal of ether, distillation gave diethyl  $\alpha$ -fluoro- $\gamma$ -hydroxyglutarate: 1.8 g., 16%, b.p. 130–135° (4 mm.).

*Anal.* Calcd. for  $C_9H_{15}FO_5$ : C, 48.8; H, 6.8; F, 8.5. Found: C, 48.7; H, 6.8; F, 8.4.

The infrared spectra showed OH and C=O stretching absorption at 3450 and 1750  $cm^{-1}$ , respectively. When treated with 3,5-nitrobenzoyl chloride, a dinitrobenzoate was obtained as an oil. Its infrared spectra showed the disappearance of OH absorption at 3450  $cm^{-1}$  and the appearance of aromatic C–H absorption at 3100, 725, and 730  $cm^{-1}$ , and C=O absorption at 1625  $cm^{-1}$ .

**1-Fluoropropane-2,3-diol.**—A mixture of 4-fluoromethyl-2,2-dimethyl-1,3-dioxalane<sup>17</sup> (29.8 g.) in water (36 ml.) and 37% hydrochloric acid (11 ml.) was heated under reflux for 0.5 hr. The solvents were removed under vacuum and water was added to the residue. This water was again removed under vacuum and the remaining sirup was taken up in ethanol (50 ml.). The ethanol solution was treated with solid sodium bicarbonate and filtered. Distillation gave pure 1-fluoropropane-2,3-diol: 14.3 g., 68%, b.p. 100–102° (10 mm.) or 117° (30 mm.),  $n_D^{20}$  1.4225; lit.<sup>18</sup> b.p. 117° (30 mm.),  $n_D^{20}$  1.4230.

**Ethyl Fluorolactate.**—A mixture of 1-fluoropropane-2,3-diol (11.0 g.), water (36 ml.), and 70% nitric acid (50 ml.) was heated on a steam bath. When the temperature of the mixture reached 80–90°, a spontaneous reaction set in and the reaction mixture was removed from the steam bath. (Caution: the reaction can become violent.) When the reaction subsided, the mixture was maintained at 55° for 5 hr. and then left at room temperature for 12 hr., heated an additional hour at 65°, and concentrated at 65° (20–30 mm.). After addition of water (25 ml.), the distillation was repeated and continued to dryness, leaving as a sirup crude fluorolactic acid.

The sirup was heated under reflux with anhydrous ethanol (20 ml.), benzene (60 ml.), and toluenesulfonic acid (0.5 g.) while water was continuously removed by distillation. When no more water was collected, the solvents were removed and the residue was dissolved in ether (50 ml.). The ether solution was treated with solid sodium bicarbonate and filtered, and the product was isolated by distillation, yielding ethyl fluorolactate: 8.8 g., 54%, b.p. 95–98° (30 mm.); lit.<sup>17</sup> b.p. 96–98° (30 mm.).

**Fluorolactic Acid.**—Ethyl fluorolactate (8.8 g.) was dissolved in 10% hydrochloric acid (50 ml.), and the mixture was heated on a steam bath at 95° for 40 min. After standing for 12 hr. at room temperature, the solvents were removed under vacuum (60° at 20–30 mm.). Water (30 ml.) was added and the distillation was repeated and continued to dryness. The remaining sirup was purified by distillation, yielding fluorolactic acid: 4.3 g., 61%, b.p. 124° (5 mm.). A sample was distilled for analysis: b.p. 122–123° (3 mm.).

*Anal.* Calcd. for  $C_3H_5FO_3$ : C, 33.4; H, 4.6; F, 17.6; neut. equiv., 108.1. Found: C, 33.4; H, 4.6; F, 17.4; neut. equiv., 108.9.

## Configurations of Substituted 5-Cyanosorbic Acids. An Intramolecular Ritter Reaction

A. T. BALABAN, T. H. CRAWFORD, AND RICHARD H. WILEY

*Institute of Atomic Physics, Bucharest, Roumania, and the Department of Chemistry of the University of Louisville, Louisville, Kentucky*

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The ultraviolet, infrared, and n.m.r. spectra of geometric isomers of 3-alkyl-5-cyanosorbic acids (III and V) and 4-carboxy-3-methyl-5-cyanosorbic acids (VI and VII) and the configuration of the isomers is found to be in agreement with chemical data. Hydrolysis of 5-cyano-3-methylsorbic acids affords an acid for which structure X is proposed; its formation involves an intramolecular Ritter reaction.

The reaction of substituted pyrylium salts (I) with aqueous alkali cyanides<sup>1</sup> affords 5-cyanopentadienones (II) which are oxidized by hypobromite to 5-cyanosorbic acids (III). Configurations about the C-2–C-3 double bond are most likely to be those indicated in formulas II and III (*cis* position of the carbonyl and the CH=CMeCN groups) if ring cleavage of the cyclic starting compound takes place without isomerization.

On treatment with concentrated mineral acids the 2-*cis*-5-cyanopentadienones (II) undergo two reactions. They eliminate hydrogen cyanide to re-form the initial pyrylium salt (I) and they isomerize into 2-*trans*-5-cyanopentadienones (IV). These latter isomers, and their arylhydrazones, have higher melting points than the 2-*cis* isomers and, unlike them, can no longer be cyclized to pyrylium and pyridinium salts. Hypobromite oxidation of the 2-*trans*-5-cyanopentadienones (IV) leads to 2-*trans*-5-cyanosorbic acids (V). No

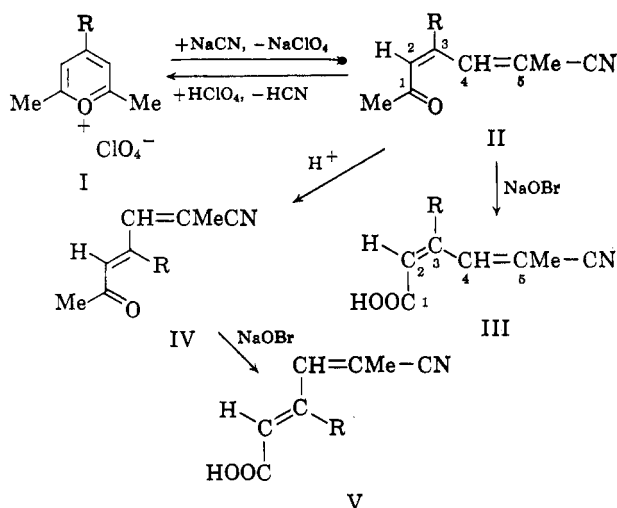
(1) A. T. Balaban and C. D. Nenitzescu, *J. Chem. Soc.*, 3566 (1961).

TABLE I  
 N.M.R. ABSORPTION DATA<sup>a</sup>

Cyano acid	M.p., °C.	Acid proton COOH	—Olefinic protons—		Methyl protons C-3 Me	—Ethyl protons—			—Ethoxy protons—	
			C-2 H	C-4 H		C-5 Me	C-3 CH <sub>2</sub> <sup>b</sup>	CH <sub>3</sub> <sup>c</sup>	CH <sub>2</sub> <sup>b</sup>	CH <sub>3</sub> <sup>c</sup>
III, R = Me <sup>d</sup>	118	-0.85	4.11	2.20	7.64	7.83	...	...	...	...
V, R = Me <sup>d</sup>	160	-1.18	3.99	3.45	7.49	7.88	...	...	...	...
III, R = Et <sup>d</sup>	59 <sup>e</sup>	+0.19	4.12	2.48	...	7.86	7.31	8.83	...	...
V, R = Et <sup>d</sup>	146	-0.40	3.96	3.51	...	7.88	7.07	8.87	...	...
VI <sup>f</sup>	161	-1.35	4.02	...	7.93	8.00	...	...	5.70	8.70
VII <sup>f</sup>	79	0.02	4.05	...	7.84	7.68	...	...	5.81	8.76

<sup>a</sup> Chemical shifts of solutions in CDCl<sub>3</sub> expressed as  $\tau$ -values.<sup>g</sup> <sup>b</sup> Center of quadruplet. <sup>c</sup> Center of triplet. <sup>d</sup> Ref. 1. <sup>e</sup> The m.p. 54° given in ref. 1 is incorrect. <sup>f</sup> Ref. 5.

direct conversion of 2-*cis*- into 2-*trans*-5-cyanosorbic acids could be produced under mild conditions. As shown in the following discussion, hot aqueous alkali causes more profound structural changes. The 2-*cis*-5-cyanosorbic acid (III, R = Me) has been obtained by Vogel from 4,6-dimethyl-2-pyrone and sodium cyanide in dimethylformamide<sup>3</sup> and the identity of the two products was established by the melting point of the mixture.



Similar isomerizations have been observed in the reaction of pyrylium salts with phenylhydrazine<sup>3</sup> and with bases<sup>4</sup>; the primary "pyranolhydrazides" and "pseudobases" formed in these reactions have been converted in both cases into isomeric forms; these were shown by physical evidence to differ by the *cis* and *trans* configurations about the C-2-C-3 double bond. The stereochemistry of the 4-carbomethoxy-5-cyano-3-methylsorbic acids (VI and VII), formed from ethyl isodehydroacetate and sodium cyanide, depends on the solvent.<sup>5</sup>

The configuration about the C-4-C-5 double bond in the 5-cyanopentadienones (II and IV), in the 5-cyanosorbic acids (III and V), and in the "pyranolhydrazides" remained unsettled. Because no isomerism attributable to this bond was observed, it was assumed<sup>1,3</sup> that the 5-CN and 5-NH-NH-Ph groups assume the most stable configuration on addition to the pyrylium salt (I). The present n.m.r. study was initiated in order to verify the structures assumed and

to obtain information on the configuration about the C-4-C-5 double bond. N.m.r. data are presented in Table I. All chemical shifts are reported as  $\tau$ -values,<sup>g</sup> and they refer to deuteriochloroform solutions.

The assignment of the methyl peaks of 5-cyanosorbic acids was made on the basis of the behavior in deuteriochloroform and pyridine (see iii below). In the spectra of compounds with R = Et, the ethyl group is particularly easy to identify and assists in the assignment of the olefinic proton peaks. The peak of the C-2 proton is split into a triplet in these cases by the C-3 methylene group just as that of the C-4 proton is split in all cases into a quadruplet by the C-5 methyl group. These olefinic proton splittings were observed at low sweep rates.

The n.m.r. spectra presented in Table I confirm the previously assigned configuration at the C-2-C-3 double bonds. Essential points follow: (i) The C-3 methyl peak in V (R = Me) and the C-3 methylene quadruplet in V (R = Et) are at lower field than those in III (R = Me and Et, respectively). This indicates a deshielding by the carboxyl group and requires a 2-*trans* configuration in V. The deshielding,  $\Delta\tau = -0.15$  and  $-0.24$  p.p.m., is a little smaller than the literature values for a  $\beta$ -methyl *cis* to a carbomethoxy group.<sup>7,8</sup> (ii) The C-4 olefinic protons in III (R = Me and Et) are at lower field than those of V (R = Me and Et). This indicates a deshielding by the carbonyl group and requires a 2-*cis* configuration in III. The deshielding  $\Delta\tau = -1.25$  and  $-1.03$  p.p.m. is a little larger than literature values<sup>7</sup> for a  $\beta$ -olefinic (C-3) proton *cis* to a carbomethoxy group. (iii) The C-3 methyl peak of V (R = Me) which in deuteriochloroform is at  $\tau$  7.49, shifts to lower field ( $\tau$  7.34) in pyridine, as expected for a  $\beta$ -methyl *cis* to a carbonyl.<sup>8</sup> The 3-methyl of III (R = Me) in pyridine shows a slight shift to higher field. This indicates that it is not the 2-*trans* isomer. (iv) The C-2 protons of V (R = Me and Et) appear at a lower field than the C-2 protons of III (R = Me and Et). In V, but not in III, the C-4-C-5 double bond is in a position to deshield the C-2 protons. The deshielding is  $\Delta\tau = -0.12$  and  $-0.16$  p.p.m., respectively.

Because of the shifts described in (ii) and (iv), the olefinic proton bands are much closer to one another in the 2-*trans* (V) than in the 2-*cis*-5-cyanosorbic acids (III). The C-5 methyl group is at a practically constant field, and, for the reason noted in (i), the distance between the 5-methyl and the 3-methyl or 3-methylene

(2) G. Vogel, *Chem. Ind. (London)*, 1829 (1962).

(3) A. T. Balaban, P. T. Frangopol, G. D. Mateescu, and C. D. Nenitescu, *Bull. soc. chim. France*, 298 (1962).

(4) G. Rio and J. Fellion, *Tetrahedron Letters*, 1213 (1962).

(5) G. Vogel, Abstracts of Papers, 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1963, p. 47M.

(6) G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

(7) L. M. Jackman and R. H. Wiley, *J. Chem. Soc.*, 2881, 2886 (1960).

(8) R. H. Wiley, T. H. Crawford, and C. E. Staples, *J. Org. Chem.*, **27**, 1535 (1962).

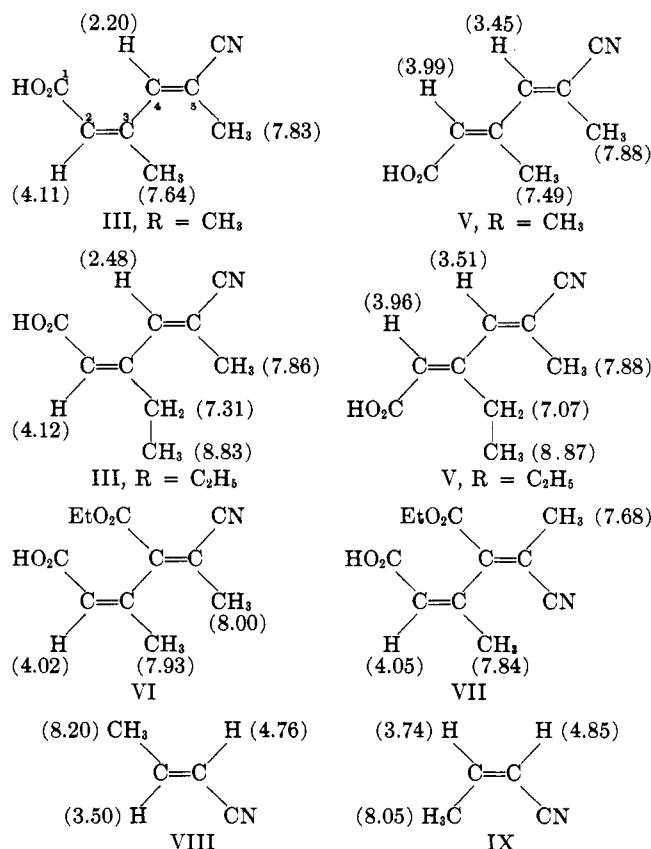
peak is less in the *cis* cyano acids (III) than in the *trans* isomers (V).

The configuration about the C-4-C-5 double bond can be assigned, but with less confidence, on the basis of the position of the C-4 proton band. A deshielding, for a proton  $\beta$  to a cyano group in a *cis* relationship, of  $\Delta\tau = -0.15$  to  $-0.25$  p.p.m. is observed in the n.m.r. data of crotononitrile (VIII) and isocrotononitrile (IX).<sup>9</sup> The value  $\tau$  3.50 for the *cis*- $\beta$ -proton in isocrotononitrile is in good agreement with the values  $\tau$  3.45 and 3.51 for the similar protons bonded to C-4 in V (R = Me and Et). The values for the C-4 proton in III ( $\tau$  2.20, 2.48) indicate deshielding both by the cyano and the carboxy group. It is to be noted, however, that the orientation of the C-5 methyl and cyano groups is not firmly established by the n.m.r. data in the absence of data for both isomers.

The infrared and ultraviolet spectra of the cyano acids (III and V, R = Me) are in agreement with the assigned structures. Both present infrared bands at 2212 ( $\nu$  C $\equiv$ N conjugated), 1688 ( $\nu$  HOC=O conjugated), a band at 1620 which is stronger in III than in V in agreement with the *cis* structure of III, and two strong bands at 1290 and 1223 in III, and at 1268 and 1200  $\text{cm}^{-1}$  in V. The ultraviolet band at 269  $\text{m}\mu$  ( $\log \epsilon$  4.05) in III has a lower molar absorptivity than in V [270  $\text{m}\mu$  ( $\log \epsilon$  4.14)] in agreement with the *trans* structure of V.<sup>10</sup> This is also observed in the ultraviolet spectra of III (R = Et) [269  $\text{m}\mu$  ( $\log \epsilon$  4.04)] and of V (R = Et) [272  $\text{m}\mu$  ( $\log \epsilon$  4.14)].

The methyl peaks of the isomeric 4-carbomethoxy-5-cyanosorbic acids (VI and VII)<sup>5</sup> are differentiated by the broadening effects due to the spin coupling between the C-3 methyl protons and the C-2 proton ( $J = 1.3$ – $1.5$  c.p.s.); thus the C-3 methyl protons are found to give peaks at  $\tau$  7.93 and 7.84 in the two isomers. The peak of the C-3 methyl in VI is at  $\tau$  7.93, a normal value for an unshielded olefinic methyl; the lower value ( $\tau$  7.84) for this peak in VII may be attributed to deshielding by the cyano group. The C-5 methyl peak is at higher field ( $\tau$  8.00) than the C-3 methyl in VI ( $\tau$  7.93) which is the normal position for an olefinic methyl  $\beta$  to a carbonyl group but not deshielded by it. In VII, the C-5 methyl peak is at lower field ( $\tau$  7.68) than the C-3 methyl ( $\tau$  7.84). This is attributed to deshielding due to a configuration VII at the C-4-C-5 double bond which places the C-5 methyl in the region of the carbomethoxy group. The configuration about the C-2-C-3 double bond follows from a comparison between values for VI and VII and for III and V. The C-2 olefinic proton and the C-3 methyl protons have values in the normal range.

The infrared  $\nu$  C $\equiv$ N band at 2220  $\text{cm}^{-1}$ , the four strong bands in the 1150–1300- $\text{cm}^{-1}$  range, and the four strong bands at 1610 and 1658 ( $\nu$  C=C), 1698 ( $\nu$  HOC=O), and 1740 ( $\nu$  EtOC=O)  $\text{cm}^{-1}$  of both acids VI and VII agree with their structure. The absence of ultraviolet absorption and shift of infrared maxima to lower wave lengths is attributed to non-planar structures similar to those previously encountered in such structures.<sup>11</sup>



The available n.m.r. data for the 2,4-dimethylmuconic acid, m.p. 198°, obtained by alkaline hydrolysis of III (R = Me),<sup>1</sup> agrees with this structure; however, the insolubility in deuteriochloroform made it necessary to employ pyridine as solvent. This partially obscures the olefinic proton absorption and thus makes a determination of configuration impossible. The two methyl peaks at  $\tau$  7.81 and 7.53 have doublet splitting characteristic of the H—C=C—CH<sub>3</sub> structure. The acid proton absorbs at  $\tau$   $-2.99$ , and one olefinic proton at  $\tau$  3.77. These data appear to fit the 2,4-di-*trans* structural requirements. The presence of carboxyl groups conjugated with carbon-carbon double bonds is confirmed by the strong infrared bands at 1680 ( $\nu$  HOC=C), 1600 ( $\nu$  C=C), and 1260  $\text{cm}^{-1}$ , and by the ultraviolet band at 268  $\text{m}\mu$  ( $\log \epsilon$  4.05) with a shoulder at 235  $\text{m}\mu$  ( $\log \epsilon$  3.7) encountered in muconic acids.<sup>12</sup>

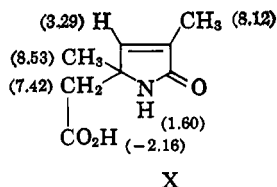
The acid with m.p. 155° obtained on alkaline hydrolysis, along with the foregoing acid from III (R = Me), and as the only product from V (R = Me),<sup>1</sup> possesses an elementary analysis and a neutralization equivalent corresponding to the formula C<sub>3</sub>H<sub>11</sub>NO<sub>3</sub>. It cannot be dimethylmuconamic acid because it presents no ultraviolet band beyond 220  $\text{m}\mu$  and cannot be hydrolyzed further in alkaline solution. The n.m.r. spectrum indicates that it possesses structure 3,5-dimethyl- $\Delta^3$ -pyrrolin-2-on-5-acetic acid (X). The saturated methyl peak at  $\tau$  8.53 is a singlet with no indications of splitting. The  $\tau$  8.12 methyl peak and the  $\tau$  3.29 olefinic peak are a doublet and a quadruplet, respectively, consistent with a H—C=C—Me structure. The quadruplet type absorption at  $\tau$  7.42 in deuteriochloroform is in fact two doublets separated

(9) G. S. Reddy, J. H. Goldstein, and L. Mandell, *J. Am. Chem. Soc.*, **83**, 1300 (1961).

(10) A. T. Nielsen, *J. Org. Chem.*, **22**, 1539 (1957).

(11) R. H. Wiley, *J. Chem. Soc.*, 3831 (1958).

(12) J. A. Elvidge, R. P. Linstead, and P. Sims, *ibid.*, 1793 (1953), and previous papers in the series.



by a small chemical shift; in pyridine this band appears as a singlet with an area corresponding to one methylene group. The NH peak at  $\tau$  1.60 is rather broad, but its area is equal to that of the olefinic and of the acid proton peaks. In the infrared spectrum of this compound in potassium bromide pellet, bands characteristic of secondary cyclic amides, double bonds, and carboxyl groups (3358 and 1652, 2500 broad, 1708, 1406, and 1302  $\text{cm}^{-1}$ ) appear.

The formation of X by alkaline hydrolysis of III and V (R = Me) followed by acidification is in fact an intramolecular Ritter reaction favored by the configuration. Should the configuration about the C-4-C-5 double bond be that shown in III and V, the formation of X appears to require isomerization about this bond. It seems probable that V forms X directly, while III must first be converted into V. Although such isomerizations are known to take place readily under the influence of hot alkali,<sup>12</sup> the readiness with which V cyclizes to X suggests that isomerization of V may not be required for the cyclization and that the C-5 methyl and cyano groups may have opposite configurations to those shown in the formulas III and V.

### Experimental

N.m.r. spectra were measured with a Varian Associates HR-4302 high-resolution spectrometer with a 60-Mc. oscillator with

super stabilizer and field homogeneity control. Samples were examined in 5–10% solution in deuteriochloroform, unless otherwise stated. Tetramethylsilane was used as internal standard and chemical shifts are reported as  $\tau$ -values<sup>8</sup>;  $\Delta\tau = \tau_{cis} - \tau_{trans}$ , where the subscripts refer to the relative positions of the carboxyl group and of the olefinic or methyl protons, and not to the configuration of the acid.

Infrared spectra were determined in Nujol mulls and in potassium bromide wafers with a double-beam Jena UR-10 spectrophotometer. Ultraviolet absorption spectra were recorded with a CF-4 Optica Milano spectrophotometer in 96% ethanol.

Cyano acids were obtained<sup>1</sup> from 2,4,6-trimethylpyrylium and 2,6-dimethyl-4-ethylpyrylium perchlorates and aqueous sodium cyanide, followed by oxidation with sodium hypobromite. Samples of 4-carbomethoxy-5-cyano-3-methylsorbic acids (VI and VII) were kindly supplied by Dr. G. Vogel.

**3,5-Dimethyl- $\Delta^2$ -pyrrolin-2-one-5-acetic Acid (X).**—Alkaline hydrolysis of 2-*cis*-5-cyano-3-methylsorbic acid (III) afforded<sup>1</sup> a 2,4-dimethylmuconic acid, m.p. 198°, and the acid X, m.p. 155°. The latter (X) is more soluble in water than the dimethylmuconic acid and was separated by fractional crystallization. It is the sole product from V.

*Anal.* Calcd. for  $\text{C}_8\text{H}_{11}\text{NO}_3$ : C, 56.79; H, 6.55; N, 8.28; neut. equiv., 169. Found: C, 57.27; H, 6.46; N, 8.38; neut. equiv., 165.

**Acknowledgment.**—We express our thanks to Dr. G. Vogel for discussions, for providing samples of compounds VI and VII, and for the determination of the mixture melting point of III (R = Me). We also thank Mrs. E. Romas and Mr. C. N. Rentea for recording the infrared spectra, Miss M. Mocanu for the ultraviolet spectra, and Mr. S. W. Thomas for the n.m.r. spectra. Final preparation of the manuscript was completed during the tenure of one of us (R. H. Wiley) as a visiting professor in the Graduate Division of the City University of New York.

## The Effect of Structure on the Rate of Disproportionation of Aromatic Sulfinic Acids<sup>1a</sup>

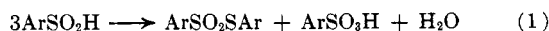
JOHN L. KICE, DAVID C. HAMPTON,<sup>1b</sup> AND ALVIN FITZGERALD

*Department of Chemistry, Oregon State University, Corvallis, Oregon*

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The rates of disproportionation of a series of aromatic sulfinic acids have been determined in acetic acid, containing small amounts of water and sulfuric acid. All of the disproportionations exhibit kinetics which are second order in sulfinic acid and show essentially the same dependence on water and sulfuric acid concentration previously found for *p*-toluenesulfinic acid. For *para*-substituted benzenesulfinic acids one finds that electron-withdrawing *para* substituents retard the disproportionation while electron-releasing ones accelerate it. This is exactly the opposite of the effect of the same substituents on the rate of decomposition of the corresponding sulfinyl sulfones I, eq. 2b, the reaction believed to be the rate-determining step in the disproportionation. This means that the observed effect of *para* substituents on disproportionation is entirely the result of their influence on the prior equilibrium between sulfinic acid and sulfinyl sulfone (eq. 2a). Evidence is also presented which indicates that the equilibrium between sulfinic acid and sulfinyl sulfone is not really too unfavorable thermodynamically to the sulfinyl sulfone, and that in favorable cases the equilibrium concentration of the sulfinyl sulfone may be as much as a few per cent of the stoichiometric concentration of the sulfinic acid.

On being heated in solution aromatic sulfinic acids undergo disproportionation to thiolsulfonate and sulfonic acid (eq. 1). An earlier detailed study<sup>2</sup> of the disproportionation of *p*-toluenesulfinic acid in acetic



(1) (a) This research supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AFOSR-106-63. (b) Participant in National Science Foundation Research Participation for College Teachers Program, Oregon State University, summer 1963.

(2) J. L. Kice and K. W. Bowers, *J. Am. Chem. Soc.*, **84**, 605 (1962).

acid-water-sulfuric acid solution indicated a mechanism (eq. 2) for the reaction involving rate-determining decomposition of an intermediate sulfinyl sulfone I, eq. 2b. Subsequent study<sup>3</sup> of sulfinyl sulfones has confirmed that they undergo thermal decomposition in a manner entirely compatible with the kinetic and stoichiometric requirements of the disproportionation

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