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The Maleic Anhydride Adducts of Sorbic Acid and Methyl Sorbate

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The methyl sorbate–maleic anhydride and the deuterated sorbic acid–maleic anhydride adducts were prepared. These compounds and the previously known sorbic acid–maleic anhydride adduct were assigned the *cis,cis,cis,cis*-configuration on the basis of the Alder orientation rules. A tricarboxylic acid from the sorbic acid adduct appeared to be the initial hydrolysis product and was assigned the structure of *cis*-4-methyl-5-cyclohexene-*cis,cis,cis*-1,2,3-tricarboxylic acid. This acid was less acidic at 100° than at 0°. It rearranged under the influence of alkali to two sharply tribasic acids whose structures were tentatively assigned. These acids were also obtained by the hydrolysis of the methyl sorbate adduct and one of them was obtained by rearrangement of the adduct with dibutylaniline followed by hydrolysis. The reaction of the sorbic acid adduct with sodium methylate formed a product identical to that secured from the isomerization and hydrolysis of the methyl sorbate adduct. This and the other chemistry of the sorbic acid adduct can be explained on the basis of mesohydric tautomerism. It is proposed that formula Ib be retained for the adduct.

The finding that the sorbic acid–maleic anhydride adduct (I), only one form of which has been isolated, decarboxylates to 4-methyl-3,4,5,6-tetrahydrophthalic anhydride[1] (II) indicates that the previously proposed structure Ia may be in question. This paper, accordingly, describes a further study of the hydrolysis and other chemistry of I and includes the pertinent study of the methyl sorbate adduct VI.

The hydrolysis products of I have been variously reported to melt at 198° by Diels and Alder,[2] 194° by Farmer and Warren,[3] and 224–230° by Wicks, Daly and Lack.[4] Korolev and Mur[5] reported 180° for the melting point of (−)4-methyl-5-cyclohexene-1,2,3-tricarboxylic acid. Wheeler[6] found that the initial hydrolysis product of I rearranged to a new acid under the influence of alkali. He reported no analyses or properties of either substance except extinction data and the fact that the rearranged acid was tribasic. His ultraviolet absorption study confirmed Wicks' assignment[4] of the double bond in I to the five position.

The present study shows that the acidification of an unheated alkaline solution of I or the short contact of it with boiling water leads to the initial hydrolysis product III which is an acid melting at 225–227°. This acid displays peculiar titration behavior in that it requires more base at 0° than at 100°. Toward one-tenth normal alkali at 100° it is dibasic. It thus falls in the class of polycarboxylic acids reported on by Jones and Soper.[7] These acids are more acidic cold than hot. The effect seems to be evident where the COOH groups are held more or less rigidly near each other. Thus *cis*-caronic acid shows the effect, but the *trans*-isomer does not and is sharply dibasic both cold and hot.

On the basis of the titration behavior of III and the Alder orientation rules[8] applied to the formation of I, the structure including configuration assigned to III is that of *cis*-4-methyl-5-cyclohexene-*cis,cis,cis*-1,2,3-tricarboxylic acid. Application of the Alder rules here is possible since sorbic acid must have the *trans,trans*-configuration.[9]

When adduct I or its acid III are briefly heated with excess five normal alkali and the mixture cooled and acidified, two new acids are formed. Both are tribasic cold and only slightly less acidic hot.

One, which is nearly insoluble in hot water, melts at 240–243° and is provisionally assigned structure V. The other can be crystallized from hot water, melts at 235–237° and provisionally is assigned structure IV. About five parts of V to one of IV are formed by short boiling of I with excess caustic. Long boiling of V with caustic forms IV in appreciable amounts, but this treatment of IV does not form V. Acids III, IV and V on melting form water, carbon dioxide and II. This behavior toward heat is similar to that of aconitic acid which easily decarboxylates to itaconic acid. Acids III, IV and V by shifting of the double bond can form cyclic analogs of aconitic acid as suggested by Wicks.[4]

Acids IV and V, without III, are formed in a ratio of about ten parts of IV to one of V by the hydrolysis of the methyl sorbate–maleic anhydride adduct VI, m.p. 113–114°. This adduct results in about 85% yield at 100° and is assigned the *cis,cis,cis,cis*-configuration for reasons similar to those for the assignment of the same configuration to I. Reaction of I with diazomethane gave a mixture from which no VI could be isolated. Hydrolysis of VI yields the acid ester VIII, m.p. 192–193°. The heating of VI with dibutylaniline presumably effects rearrangement as in the case of the piperylene adducts.[8] The product, an oil, is a mixture and is believed to contain VII since hydrolysis forms an isomer of VIII. This isomer, m.p. 195–196°, is assigned structure IX. By alkaline hydrolysis IX forms IV but not V. Acid ester IX is also formed by a rather slow reaction of I with sodium methylate.[10] The fact that IX rather than VIII is the product shows that the alkoxide is an epimerizing

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[1] D. Craig, THIS JOURNAL, **72**, 3732 (1950).

[2] O. Diels and K. Alder, *Ann.*, **470**, 62 (1929).

[3] E. H. Farmer and F. L. Warren, *J. Chem. Soc.*, 897 (1929).

[4] Z. W. Wicks, O. W. Daly and H. Lack, *J. Org. Chem.*, **12**, 713 (1947).

[5] A. Korolev and V. Mur, *Doklady Akad. Nauk S.S.S.R.*, **59**, 251 (1948); *C. A.*, **42**, 6776 (1948).

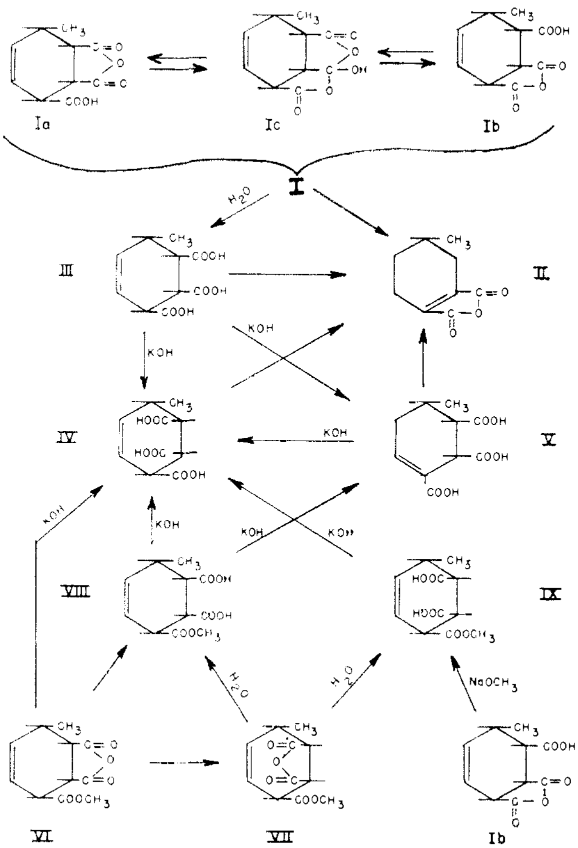
[6] O. H. Wheeler, THIS JOURNAL, **70**, 3468 (1948).

[7] I. Jones and F. G. Soper, *J. Chem. Soc.*, 134 (1936).

[8] D. Craig, THIS JOURNAL, **72**, 1678 (1950).

[9] This follows Alder and co-workers (*Ann.*, **564**, 84, 121 (1949)) who assigned the *trans* structure to piperylene (compare THIS JOURNAL, **65**, 1006 (1943) for more convincing evidence) as a result of its having been made from crotonaldehyde (mainly *trans*) and who assigned the *trans* structure to vinylacrylic acid on the basis of its oxidation to racemic acid. Sorbic acid is readily prepared from crotonaldehyde, and permanganate oxidation of sorbic acid, according to Doebner (*Ber.*, **23**, 2376 (1890)), forms racemic acid. Compare also Alder, *et al.*, *Ann.*, **570**, 234 (1950).

[10] D. M. Smith and W. M. D. Bryant, THIS JOURNAL, **58**, 2452 (1936).



agent as well as an agent for opening the anhydride ring. The action of the alkoxide supports Ib rather than Ia.

Apparently confirming the observations of Wheeler,[6] III is found to have a low molecular extinction $(\epsilon_{220\ \mathrm{m}\mu}^{0.15\ \mathrm{g./l.}}\ 265)$ in methanol and V in the same solvent is found to absorb strongly $(\epsilon_{220\ \mathrm{m}\mu}^{0.01\ \mathrm{g./l.}}\ 6600)$. Acid IV, m.p. 235–237°, absorbs weakly $(\epsilon_{220\ \mathrm{m}\mu}^{0.13\ \mathrm{g./l.}}\ 660)$ in methanol and thus may be a purer sample of the acid, m.p. 224–230°, reported by Wicks[4] who, however, found an absorption in alcohol of $E_{220\ \mathrm{m}\mu}^{1\%}$ of about 14.8 or ϵ of about 340. The methyl sorbate adduct VI and its acid VIII have essentially no ultraviolet absorption in methanol while the acid IX from the rearranged adduct absorbs weakly in this solvent $(\epsilon_{220\ \mathrm{m}\mu}^{0.148\ \mathrm{g./l.}}\ 710)$. In agreement with the proposed structures the ultraviolet absorption study indicates that I, III, IV, VI, VIII and IX, except for possible impurities in IV and IX, do not have double bonds in conjugation with carbonyl groups. It is presumed that the double bond in all these compounds must be in the five position. The absorption of V, however, shows that this acid is definitely α-unsaturated.

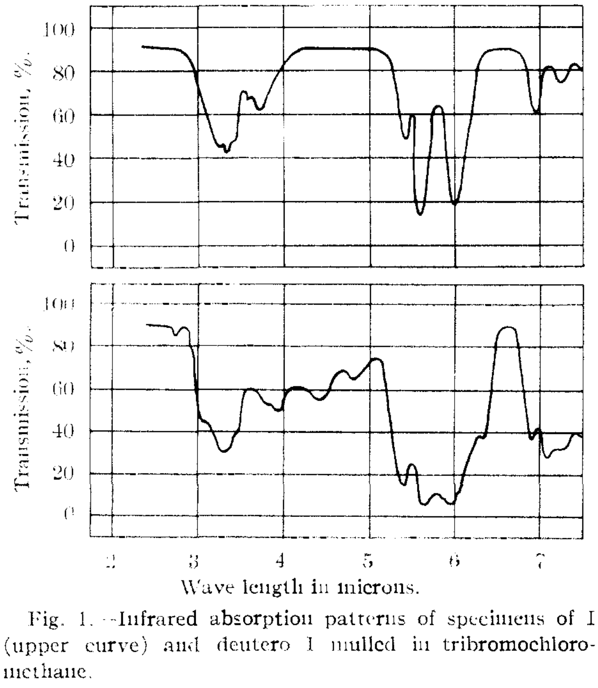
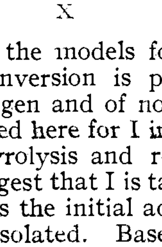


Fig. 1.—Infrared absorption patterns of specimens of I (upper curve) and deutero I mulled in tribromochloromethane.

Stuart type models of the structures in this study are of interest. The model of III indicates that the COOH groups are held near each other so that the hydrogen of any one COOH can add to the carbonyl of an adjoining COOH with the formation of a five-membered ring. Or, alternatively, seven-membered chelate rings could be formed. The extent to which such rings would be opened by the solvent would then determine the strength of III as an acid and, presumably, the effect of temperature on its titration behavior.

The models show that the strain in III can be lessened by either of two single step isomerizations. One is a shift of the double bond to a position alpha to a carbonyl group. The other is the epimerization of a carbon atom holding a carbonyl group. These reactions are of the type which is catalyzed by alkali. Either epimerization as in going from III to IV or of shifting the double bond as in going from III to V is a stabilizing effect and accordingly it might be expected that mild treatment of III would lead to IV and V.

The infrared absorption patterns for I and deutero I are shown in Fig. 1. These show that I displays the diffuse absorption in the 3 to 4 micron region characteristic of the COOH group and that substituting D for H results in the expected frequency shifts. The compound cannot therefore be a lactone such as X.



X

Consideration of the models for Ia, Ib and Ic shows that interconversion is possible with the movement of hydrogen and of no other atom and the reactions reported here for I including hydrolysis, deuterolysis, pyrolysis and reaction with sodium methylate suggest that I is tautomeric with Ia which presumably is the initial adduct. Only one form of I has been isolated. Based on the work of Hunter,[11] only one is expected since none of the possible locations of the tautomeric hydrogen is a

(11) L. Hunter, *J. Chem. Soc.*, 806 (1945).

carbon atom. Hence, this compound constitutes an instance of mesohydric tautomerism. It is proposed, however, that formula Ib be retained for I since this structure conveniently accounts for all of the behavior of the compound.

Experimental

***cis*-4-Methyl-5-cyclohexene-*cis,cis,cis*-1,2,3-tricarboxylic Acid (III).**—Two and one-tenth grams of I[3] (m.p. 178–182°) was allowed to stand with 5.0 g. of water for 30 minutes. The mixture was boiled for 3 minutes, filtered hot, and the colorless solid washed with two 3-ml. portions of water and dried. It then weighed 1.81 g. and melted at 225–227° with decomposition. The filtrate and washings were allowed to stand overnight at 25°. An additional yield of 0.13 g. of III, m.p. 223–225° dec., was thus obtained, making a total of 1.94 g. (85%). The "melting point" of this acid and the other unstable acids described here was taken by placing the m.p. tube in the previously heated bath according to Bruce's[12] method for aconitic acid.

Anal. Calcd. for $C_{10}H_{12}O_6$: C, 52.61; H, 5.30. Found: C, 51.92; H, 5.58.

A 0.2120-g. sample of III required 19.55 ml. of 0.1 *N* sodium hydroxide at 0°. Phenolphthalein was used as the indicator. The titration solution was heated to boiling. The end-point which was not very sharp deepened and 0.1 *N* hydrochloric acid was added as needed in order to maintain the end-point, 1.05 ml. being required during five minutes; calcd. for three COOH groups, neut. equiv., 76, and for two COOH groups 114. Found: neut. equiv. at 0° 108.0 and at 100° 115.0. When normal sodium hydroxide was used the neutral equivalent found at 0° was 93.5 and at 100° was 109. The neutral equivalent at 0° with 5 *N* alkali was approximately 77. Acidification of the titration solutions with hydrochloric acid caused the slow crystallization of III. After filtering and extraction with hot water the product melted at 225–227° alone or mixed with the III prepared by direct hydrolysis.

***cis*-4-Methyl-5-cyclohexene-*cis,cis,cis*-1,2,3-tricarboxylic Acid 2,3-Anhydride-1-methyl Ester (VI).**—A mixture of 6.70 g. (0.05 mole) of methyl sorbate (m.p. 10.5°) and 4.96 g. (0.0506 mole) of maleic anhydride was heated to 80° where a mild reaction set in. The temperature was adjusted to 100° for 30 minutes and finally at 130° for 15 minutes. Upon cooling, the mixture crystallized. It melted at 103–105° or at 113–114° after crystallization from an equal volume of benzene. The total yield including that recovered from the filtrate amounted to 9.8 g. (84%).

Anal. Calcd. for $C_{11}H_{14}O_6$: C, 54.52; H, 5.83. Found: C, 54.65; H, 5.83.

***cis*-4-Methyl-5-cyclohexene-*cis,trans,trans*-1,2,3-tricarboxylic Acid 1-Methyl Ester (IX).**—A mixture of 10 g. of VI and 0.10 g. of dibutylaniline was heated in a modified Claisen flask at 205° for 15 minutes to effect rearrangement. The mixture was then distilled. The main fraction distilled at 133 to 153° at 0.2 mm. and weighed 7.4 g. It was a viscous oil that failed to crystallize. Boiling with 10 ml. of water for 15 minutes, however, and then cooling resulted in the formation of crystals which amounted to 1.1 g. (12%). These melted at 185–190° and after recrystallization from water melted at 195–196° or at 180–185° when mixed with VIII.

Anal. Calcd. for $C_{11}H_{14}O_6$: C, 54.52; H, 5.83. Found: C, 54.54; H, 5.82.

Acid IX was also isolated from the titration of 0.235 g. of I with 0.095 *N* sodium methylate in methanol according to Smith and Bryant.[10] Since the reaction was slow, the titration was run in boiling methanol during one hour. Phenolphthalein was used as the indicator. Twenty-three ml. of the alcoholate solution was required. Calcd.: neut. equiv., 105. Found: neut. equiv., 107.5. The titration mixture contained crystals which were filtered off after standing overnight. They were decomposed with excess hydrochloric acid and the resulting IX separated and crystallized from water to give 0.05 g. (18%), m.p. 185–190°. The methanol filtrate was evaporated to dryness and the residue worked up as for the crystals. The acid thus obtained amounted to 0.06 g. (21%) and melted at 195–196° alone or mixed with the above sample of IX.

Acid IV, m.p. 235–237°, and Acid V, m.p. 240–243°.—Five grams (0.0238 mole) of I and 16.05 ml. of 5 *N* potassium hydroxide were refluxed for 10 minutes. The solution was then cooled and acidified with 80.25 ml. of 1 *N* hydrochloric acid. The solid which formed was filtered off after 30 minutes and dried. It weighed 3.17 g. and melted at 208–210°. Extraction with 30 ml. of boiling water in a beaker and filtering left undissolved 2.42 g. (45%) of colorless powder. This melted at 228–232° and is nearly pure V. Further extraction with boiling water raised the m.p. to 240–243°. This acid was sharply tribasic toward tenth normal NaOH.

Anal. Calcd. for $C_{10}H_{12}O_6$: C, 52.61; H, 5.30. Found: C, 52.59; H, 5.30.

The filtrate from the crude acid, m.p. 208–210°, was extracted with three 75-ml. portions of ether. The extracts were united and evaporated to dryness. Recrystallization of the residue (0.79 g.) from water provided 0.48 g. (9%) of acid IV which melted at 231–234° or at 220–223° when mixed with either V or III.

Anal. Calcd. for $C_{10}H_{12}O_6$: C, 52.61; H, 5.30. Found: C, 52.59; H, 5.30.

The use of III instead of I under the same conditions resulted in a 50% yield of V and a 6.5% yield of IV.

Acids IV and V were also obtained from the titration of 2.24 g. of VI with 5 *N* potassium hydroxide. The end-point which was not sharp required 4.05 ml. Calcd.: neut. equiv., 111. Found: neut. equiv., 112. An additional volume of 2.65 ml. of 5 *N* potassium hydroxide was added and the solution boiled for ten minutes, cooled, and acidified. The 1.53 g. of crude acid filtered off melted at 207–210°. By extraction with 15 ml. of hot water a yield of 0.145 g. of insoluble acid V was obtained. This melted at 231–235° alone or at 235–238° mixed with the V prepared from III. The filtrate on cooling deposited 0.945 g. of IV, m.p. 226–228°. Acid IV was secured in a purer form, m.p. 235–237°, when prepared from the similar hydrolysis of IX. The yield from 0.61 g. of IX amounted to 0.19 g. (33%). This acid was sharply tribasic toward tenth normal NaOH.

The decomposition of acids III, IV or V under the conditions used for the previously described pyrolysis[1] of I formed water and carbon dioxide in nearly theoretical yield. The anhydride II which also was formed in nearly theoretical crude yield was identified by conversion to the acid,[1] m.p. 125–126° alone or mixed with an authentic specimen.

Sorbic acid (5.6 g.), m.p. 132–134°, was distilled with 1.9 g. of 99.87% D_2O and 30 ml. of benzene until dry. A second portion of 1.4 g. and a third of 1.7 g. of D_2O were added and the mixture distilled until dry with benzene being added as needed. The deuterosorbic acid in the remaining benzene was found to melt at 132–134°. Maleic anhydride (4.9 g.) was added to the benzene solution, most of the benzene was evaporated and reaction was effected at 95 to 125° during 25 minutes. The yield of deuterated sorbic acid adduct, m.p. 177–181°, was 8.5 g. (84%). Deuterolysis gave the slightly impure tribasic acid, m.p. at about 220° alone or mixed with III, or with the deuterolysis product of I.

The deuterated sorbic acid adduct was decarboxylated as for I and the product found to melt at −5 to −3° alone or mixed with II.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.05; H, 6.07; O, 28.88. Calcd. for $C_9H_9DO_3$: C, 64.66; H, 5.42; D, 1.21; O, 28.71. Found: C, 64.53, 64.43, 64.53; (H_2O and D_2O were weighed together and calcd. as H_2) H, 6.09, 6.14, 6.03, average 6.09; assuming one D atom for nine H atoms and that one D equals two H atoms in wt. the corrected found value for H + D is $6.09 \times 11/10 = 6.70$.

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[12] W. F. Bruce, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 12.