bromo- and iodo-benzenephosphonic acids is described and the syntheses of the related bis-(*p*-aminobenzene)-phosphinic acid and (*p*-chlorobenzene)-(*p*-aminobenzene)-phosphinic acid are presented.

DAYTON, OHIO RECEIVED MAY 26, 1948

[CONTRIBUTION FROM GENERAL MILLS, INC.]

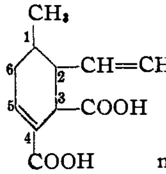
The Dimers of Methyl Sorbate

BY D. H. WHEELER

The structure of the dimer of methyl sorbate, the simplest of the conjugated diene esters, has been of interest as a model whereby structures of some probability might be assigned to the dimers formed during the thermal polymerization of drying oils and the simpler esters of the corresponding acids.

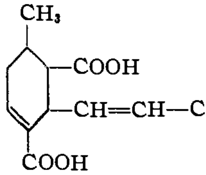
Farmer and Morrison-Jones[1] obtained dimers of methyl sorbate in 81% yield by heating the monomer at 180–230° for about three hours. By an elaborate fractionation they separated the crude dimer ester into fraction A (n^{18}_{D} 1.47720 to 1.47870) and fraction B ($n^{18}_{\mathrm{D}} > 1.4900$), estimating the percentages of A and B to be 13 and 12%, respectively, of the total dimer. By saponification of A they obtained acids from which, by fractional crystallization, they isolated four different crystalline disorbic acids. One of these acids, m. p. 216°, isolated in 2–4.5% yield (0.3 to 0.6% of total dimer), was definitely shown to have structure I, 1-methyl-2-propenyl-4-cyclohexene-3,4-dicarboxylic acid. A second acid, m. p. 191°, isolated in a similarly small yield, was shown to have structure II, 1-methyl-3-propenyl-4-cyclohexene-2,4-dicarboxylic acid. A third acid, m. p. 200°, apparently was a *cis–trans* isomer of II, and a fourth acid, m. p. 164–169°, was not characterized. They could isolate no crystalline dimeric acid from mixture B, except traces of the same acids as from A and B was not investigated further.

As was pointed out by these workers, the structures shown for these acids differ from those expected as a result of the usual Diels–Alder reaction in that the ring double bond is α-β or conjugated to the carboxy group rather than β-γ to it. Thus, the normal structure instead of I would be III, 1-methyl-2-propenyl-5-cyclohexene-3,4-dicarboxylic acid, and the normal structure instead of II would be IV, 1-methyl-3-propenyl-5-cyclohexene-2,4-dicarboxylic acid.

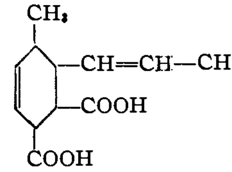


m. p. 216°

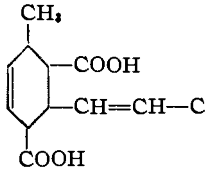
I



II



III



IV

These authors did not definitely comment upon the stage at which the shift of the double bond occurred, but they apparently believed that the esters had the same structure as the acids from which they were derived. Bradley[2] has suggested that the dimeric methyl esters had the normal structure, and that the β-γ to α-β shift of the double bond occurred during the alkaline saponification of the ester.

The present work indicates that the esters composing mixture A have the normal structure, and that mixture B is composed largely of dimers with a double bond in the α-β position to a carbomethoxy group. The conjugated acids isolated by the English workers from mixture A of the esters must therefore have been formed by a β-γ to α-β shift of the cyclic double bond during the alkaline saponification. These conclusions are based largely on considerations of the ultraviolet absorption characteristics of the dimeric methyl esters, and of the acids obtained from them by alkaline saponification.

Iodine values of the esters and acids were in accord with the indicated structures, but molecular refractions of the conjugated forms did not show as much exaltation as was expected.

The high yield of crude dimeric methyl esters reported by Farmer was confirmed. However, a single efficient fractional distillation afforded 43% of dimeric ester A, and 32.5% of dimeric ester B, corresponding in n_{D} to the fractions separated by Farmer in 13% and 12% yield, respectively. The boiling point of fraction B was 16–18° above that of fraction A. Refractionation of A afforded 47% of a lower boiling fraction, A-1, with a lower n_{D} and 27% of a higher boiling fraction, A-2, with a higher n_{D}. Fraction A-2, when crystallized from petroleum ether at −40°, yielded 25% of a crystalline dimeric ester, A-2-p, m. p. 64.5–65.5°. No crystalline methyl ester could be isolated from A-1 or B by similar treatment. Alkaline saponification of A-2-p afforded the dimer of sorbic acid m.

---

[1] Farmer and Morrison-Jones, *J. Chem. Soc.*, 1339–1346 (1940).

[2] Bradley, Symposium on Vegetable Drying Oils, Univ. of Minnesota, March 28, 1947.

p. 216° in 72.3% yield. This acid was converted to its methyl ester by action of diazomethane. The ester was a viscous liquid which could not be crystallized, even on seeding with A-2-p. Saponification of this ester afforded the original acid, m. p. 216°.

Fractions A, A-1, A-2 and A-2-p all showed low values for molecular extinction, ϵ, at 220 mμ, from 346 to 782, while the acid from A-2-p and the ester prepared from it gave high values, 6,900 and 8,720, respectively. Fraction B also had a high value for ϵ, 12,600. At longer wave lengths the absorption decreased rapidly to very low values at 260–280 mμ and beyond. These values indicate that A, A-1, A-2 and A-2-p do not have the double bond α-β to the carbomethoxy group, whereas the A-2-*p* acid, its ester, and fraction B have a double bond in this position. The non-cyclic analogs, vinylacetic acid and crotonic acid have ϵ values of about 1,200 and 8,600 respectively at 220 mμ, according to Bruylants and Castle.[3] The various values are shown in Fig. 1.

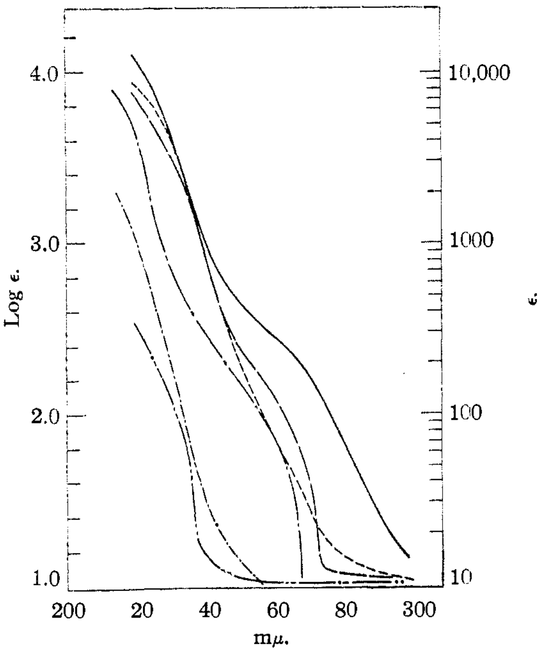


Fig. 1.—Ultraviolet absorption curves: ——, dimer ester B; — - - -, dimer ester A-2-p; — —, dimer acid from A-2-p; ------, reësterified dimer acid from A-2-p; — -, vinylacetic acid (Bruylants and Castle); — · — - — -, crotonic acid (Bruylants and Castle).

The very closely related adduct from sorbic acid and maleic anhydride apparently undergoes a similar shift of double bond upon alkaline saponification. Confirming the work of Wicks, Daly and Lack,[4] it was found that this adduct has a low molecular extinction of 362 at 220 mμ, indicating a normal structure. It was also found that the acid formed by aqueous hydrolysis of the anhydride group has an even lower value of ϵ = 192, probably because of better purification. However, alkaline saponification produced an isomeric tribasic acid with the high value of ϵ, 6,350 at 220 mμ, indicating that the double bond had shifted to a position α-β to a carboxyl group, by the action of alkali.

Wicks, *et al.*, observed that the normal addition product changed into a conjugated form with simultaneous decarboxylation when it was heated to 190°. They commented on the fact that this adduct must have the normal structure in contrast to the conjugated structure suggested by Farmer and Warren,[5] who suggested the conjugated structure on the basis of the formation of strongly enolic compounds at an early stage of oxidation, and stated that "The structure of the sorbic acid derivative is not easily demonstrated. The oxidation products are liquids, difficult to isolate in a pure state. . . ." Since they used alkaline permanganate for oxidation, it is possible that their results were due to rearrangement caused by the alkali in their oxidation medium.

It thus appears that the thermal polymerization of methyl sorbate at 180–230° produces about equal amounts of two mixtures of dimeric esters—A, having the normal position of the ring double bond, and B, in which a double bond exists in the α-β position with respect to a carbomethoxy group.

Experimental

Preparation and Fractionation of Methyl Sorbate Dimer.—Methyl sorbate was prepared from sorbic acid (Carbide and Carbon Chemicals Corp.) by direct esterification using *p*-toluenesulfonic acid catalyst. The ester was distilled through a Podbielniak Hyper-Cal column to afford a main fraction of constant boiling point 60° at 12 mm.; (found sap. eq. 125.6, theory 126.1); $\epsilon_{258 m\mu}$ 27,500; $n^{30}D$ 1.4984.

Methyl sorbate was polymerized by heating approximately a kilogram of it for four hours at 190° (initial reflux) to 230° under nitrogen. The crude polymer was fractionated through the Podbielniak column at 3 mm. head pressure and at reflux settings from 10–1 to 40–1. The following fractions were obtained:

1. Monomer, 4.4%, b.p. to 43°, $n^{30}D$ 1.4976
2. Intermediate, 0.8%, b.p. 43–119°, $n^{30}D$ 1.4730
3. Dimeric ester A, 43.0%, b.p. 119–123°, $n^{30}D$ 1.4730, d^{30} 1.0495 (M_r = 67.39, E = +0.36), sp. $\alpha^{1 cm.}_{220 m\mu}$ = 2.7 (ϵ = 680)
4. Intermediate, 6.7%, b.p. 123–135°, $n^{30}D$ 1.4795
5. Dimeric ester B, 32.5%, b.p. 135–40°, $n^{30}D$ 1.4860, d^{30} 1.0636 (M_r = 68.05 E = 1.02), sp. $\alpha^{1 cm.}_{220 m\mu}$ = 49.9 (ϵ = 12,600)
6. "Push over," 2.6%, b.p. 124° at 1.4 mm., $n^{30}D$ 1.4873
7. Residue, 7.6%, $n^{30}D$ 1.4993

Refractionation of Fraction 3 at 3 mm. afforded the following fractions:

1. Forerun, 6%, b.p. 84–120°, $n^{30}D$ 1.4740 to 1.4714
2. Dimeric ester A-1, 46.9%, b.p. 120–121°, $n^{30}D$ 1.4715, d^{30} 1.0466 (M_r = 67.39, E = +0.36), sp. $\alpha^{1 cm.}_{220 m\mu}$ = 3.1 (ϵ = 782)
3. Intermediate, 15.1%, b.p. 121–122°, $n^{30}D$ 1.4728 to 1.4736
4. Dimeric ester A-2, 27.1%, b.p. 122°, $n^{30}D$ 1.4740 to

---

[3] Bruylants and Castle, *Bull. soc. chim. Belg.*, **34**, 261 (1925).

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

[5] Farmer and Warren, *J. Chem. Soc.*, 897–909 (1929).

1.4750 (av. 1.4746), d^{30} 1.0534 (M_r = 67.32, E = +0.29), sp. $\alpha^{1\text{ cm.}}_{220\text{ m}\mu}$ = 2.0 (ϵ = 504).

In order to determine whether B was formed by thermal rearrangement of A during the polymerization a sample of A was heated at 220° for four hours in an evacuated sealed glass tube. The product then had a Sp. $\alpha^{1\text{ cm.}}_{220\text{ m}\mu}$ = 4.83 or ϵ = 1,200. This is only about one-tenth the ϵ of B, and indicates that very little of B arises from thermal isomerization of A.

Crystalline Dimer of Methyl Sorbate.—Fraction A-2 (20 g.), crystallized from 300 cc. of Skelly F at −60°, gave a gummy precipitate which, when recrystallized twice from the same volume of the same solvent at −40°, gave a 29% yield of crystals, m.p. 62–65°. Two more recrystallizations from the same solvent (37 cc./g.) at −40° afforded crystals (A-2-p) melting at 64.5–65.5° in a yield of 24.7% based on fraction A-2, 6.4% based on A, or 2.7% on original methyl sorbate.

Anal. Calcd. for $C_{14}H_{20}O_4$; C, 66.6; H, 7.99. Found: C, 66.4; H, 7.90; n^{70}_{D} 1.4585, d^{70} 1.0174, (M_r = 67.68, E = +0.65), sp. $\alpha^{1\text{ cm.}}_{220\text{ m}\mu}$ = 1.37 (ϵ = 346). The filtrate material was recovered: d^{30} 1.0532, n^{30}_{D} 1.4748 (M_r = 67.38, E = +0.35), d^{70} 1.0177, n^{70}_{D} 1.4586 (M_r = 67.67, E = +0.64). No crystalline methyl ester melting above room temperature could be isolated from A-1 or B by a similar procedure.

The crystalline dimer of sorbic acid, m.p. 216°, was prepared by refluxing A-2-p with 100% excess of 1.5 *N* potassium hydroxide in 77% methanol for two hours, at which time 98.5% of the theoretical amount of alkali had been consumed. Acidification of the alkaline mixture and removal of alcohol under vacuum yielded the dimer of sorbic acid, m.p. 216.7° (cor.), in 72.3% yield.

Anal. Calcd. for $C_{12}H_{16}O_4$; C, 64.3; H, 7.19; neut. equiv., 112.1. Found: C, 64.0; H, 7.35; neut. equiv., 113.3, sp. $\alpha^{1\text{ cm.}}_{220\text{ m}\mu}$ = 30.7 (ϵ = 6,900).

The anhydride, prepared according to Farmer and Morrison-Jones[5] melted at 83.5–85° (cor.) (m.p. 84° according to them). The acid absorbed one mole of hydrogen rapidly (1.04 moles in thirty minutes, palladium-on-charcoal) and a second mole so slowly that quantitative measurement was impractical. After hydrogenation for four days, the product was isolated, m.p. 186–189° (m.p. 188° according to Farmer and Morrison-Jones[5] for the tetrahydro dimeric acid).

The methyl ester of the disorbic acid, m.p. 216°, was prepared in quantitative yield by action of diazomethane in ether. It was distilled through a small Vigreux column and boiled at 130–135° at 2.8 mm., n^{30}_{D} 1.4860. Found: sapn. eq., 123; theory, 126; d^{30} 1.070, n^{30}_{D} 1.4860 (M_r = 67.65, E = +0.62), sp. $\alpha^{1\text{ cm.}}_{220\text{ m}\mu}$ = 34.6 (ϵ = 8,720). It was a viscous liquid which did not crystallize, even on cooling and seeding with A-2-p ester. Saponification afforded the dimeric acid, m.p. 216–217° (cor.).

The iodine values of the various dimeric acids and esters were in accord with the structure indicated by the spectral data. It is known that a double bond α-β to the carboxyl group does not respond to the usual methods for determining iodine number.[6] Thus, the conjugated acid, m.p. 216°, and the methyl ester prepared from it had iodine numbers of 112.6 and 110.3, respectively (theory 113 and 100.8, respectively, for one double bond, 226 and 201.6, respectively, for two double bonds), and Fraction B had an iodine number of 110.4.

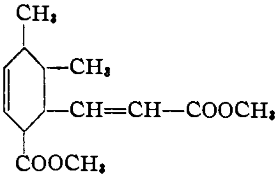
The non-conjugated methyl ester fractions A, A-1, A-2 and the crystalline methyl ester A-2-p had iodine numbers of 154.2, 156.7, 148.6 and 134.7, respectively, showing the greater absorption of halogen by the β-γ double bond. Iodine numbers were determined by the rapid Wijs method of Hoffman and Green.[7]

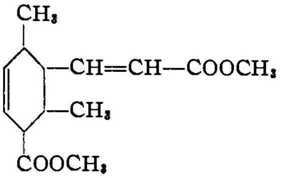
The values of the molecular refractions did not show as much exaltation as would be expected for the conjugated forms, and the nonconjugated forms showed a slight exaltation. Dimer esters A, A-1 and A-2 showed exaltations of +0.36, +0.36 and +0.29, respectively, at 30°. The crystalline dimer ester had an exaltation of +0.65 at 70°, while the filtrate material from it had a value of +0.35 at 30° but +0.64 at 70°. Dimer ester B had an exaltation of +1.02 at 30° while the ester obtained by the action of diazomethane on the dimer acid, m.p. 216°, had a value of +0.62 at 30°. The slight exaltation shown by the nonconjugated esters and the only slightly greater exaltation shown by the conjugated esters is an anomaly which cannot be explained at present.

Discussion

The data presented prove the exact structure of only the non-conjugated crystalline dimeric ester, A-2-p, which must correspond to structure III. This is the only reasonable nonconjugated structure which would be expected to isomerize by the action of alkali to I, the structure previously proven for the dimeric acid of m. p. 216°. The data do indicate that the dimeric ester, mixture A, has essentially the normal, non-conjugated structures shown in III and IV, with the possibility of a number of *cis–trans* isomers.

The fact that B has a strong absorption at 220 mμ (ϵ = 12,600) while A develops only a slightly increased absorption (ϵ = 1,200) when heated under conditions comparable to those of the polymerization indicates that very little of B arises from thermal isomerization of A. Structures with α-β unsaturation other than by shift of the ring double bond in III or IV could arise if the γ-δ double bond of the original sorbic ester acted as the dieneophile. The possible structures for B on this basis would be


V


VI

with the possibilities of a number of *cis–trans* isomers. These proposed structures for B would also account for the fact that Farmer and Morrison-Jones obtained from B by alkaline saponification no appreciable amounts of the dimer acids obtained from A by alkaline saponification.

Acknowledgments.—The author is indebted to the Office of Naval Research for a grant which made this investigation possible. The assistance of Mr. H. Boyd in making the spectral readings is gratefully acknowledged.

Summary

1. Confirming Farmer and Morrison-Jones, methyl sorbate was found to polymerize to a mixture which is mostly dimeric, and which was separated into Fractions A of low and B of high refractive indices. Efficient fractional distillation resulted in much higher yields of A and B than reported by them.

---

[6] Caldwell and Piontkowski, THIS JOURNAL, **56**, 2086–2089 (1934).

[7] Hoffman and Green, *Oil and Soap*, **16**, 236–8 (1939).

2. Dimeric ester mixture A apparently has the normal non-conjugated structure expected as a result of dimerization by way of a Diels–Alder reaction, with α-β double bond acting as dieneophile, resulting in structures III and IV.

A crystalline dimeric methyl ester has been isolated from A by refractionation and crystallization. It is nonconjugated, but gives the conjugated acid, m. p. 216°, of Farmer upon alkaline saponification. The probable structure of this ester is discussed and is believed to be III.

3. Dimer ester B apparently has a double bond α-β or conjugated to a carbomethoxy group. To a large extent this is apparently due to the γ-δ double bond in the sorbic ester acting as the dieneophile, resulting in structures V and VI, with various *cis–trans* isomers possible.

MINNEAPOLIS, MINNESOTA RECEIVED MARCH 29, 1948

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, GENERAL MILLS, INC.]

1,4-Addition Reactions. II. Addition of Ethyl Malonate to Acrolein[1]

BY DONALD T. WARNER AND OWEN A. MOE

In a previous publication,[2] the 1,4-addition of ethyl acetamidomalonate and other closely related compounds to acrolein was reported. This is the first instance of a successful 1,4-addition between a malonate system and an α,β-unsaturated aldehyde. The present report is concerned with the extension of this reaction to other mono-substituted malonic esters. However, this type of reaction is not limited to mono-substituted malonates possessing only one α-hydrogen atom. Either ethyl malonate or ethyl cyanoacetate readily yields a 1,4-addition product with acrolein.

The 1,4-addition involving ethyl malonate and acrolein proceeded smoothly in the presence of an alkaline catalyst. The product, γ,γ-dicarbethoxybutyraldehyde I, was obtained in 50% yield. When I was separated from the crude reaction product by distillation under reduced pressure, a considerable quantity of a nearly colorless, viscous residue remained. This residue, probably the di-substitution product, is now being investigated further.

The structure of compound I was proved by an unequivocal synthesis involving the alkylation of ethyl malonate with β-chloropropionaldehyde diethylacetal.

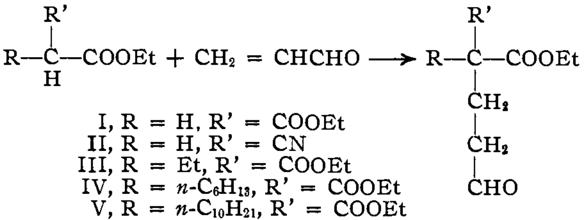
Reduction of the aldehydo compound I in the presence of Raney nickel catalyst yielded ethyl α-carbethoxy-δ-hydroxyvalerate which was characterized as the 3,5-dinitrobenzoate. The ethyl α-carbethoxy-δ-hydroxyvalerate was converted by the action of ammonia into α-carbamyl-δ-hydroxyvaleramide which in turn yielded a 3,5-dinitrobenzoate.

Addition of ethyl cyanoacetate to acrolein yielded the aldehydo compound II which was characterized as the 2,4-dinitrophenylhydrazone.

The 1,4-addition reactions of ethyl alkylmalonates gave the aldehydo compounds III, IV and V, where the alkyl groups were ethyl, hexyl and decyl, respectively. The aldehydo compound V was not purified by distillation under reduced pressure and the crude product yielded an oily 2,4-dinitrophenylhydrazone. However, this crude product V, when subjected to catalytic reduction in the presence of Raney nickel, yielded a carbinol which formed a crystalline 3,5-dinitrobenzoate. The aldehydo compounds III and IV yielded crystalline 2,4-dinitrophenylhydrazones.

γ-Acetoxy-γ,γ-dicarbethoxybutyraldehyde, VI, was prepared by the 1,4-addition of ethyl acetoxymalonate to acrolein. It was characterized as the 2,4-dinitrophenylhydrazone.

Certain features of the reaction between ethyl bromomalonate and acrolein are noteworthy. When the reaction was carried out in the presence of sodium ethoxide, difficulty was encountered in maintaining the alkalinity of the reaction mixture. In order to maintain alkalinity it was necessary to add a molar equivalent of the base. The product formed a 2,4-dinitrophenylhydrazone (m. p. 142–142.5°). However, this 2,4-dinitrophenylhydrazone did not contain bromine. Elementary analysis of the 2,4-dinitrophenylhydrazone indicated that the aldehydo compound was 4,4-dicarbethoxy-3-butenal which could arise from the dehydrohalogenation of the normal 1,4-addition product, VII. The occurrence of the dehydrobromination was not too surprising in view of the fact that a molar equivalent of the base had been employed. Supporting evidence for this structure was obtained by catalytic reduction of this product in the presence of 5% palladium-on-charcoal. The reduction product was γ,γ-dicarbethoxybutyraldehyde, I, identical with a specimen synthesized in another manner.



$$\mathrm{R-\overset{R'}{\underset{H}{C}}-COOEt + CH_2=CHCHO \longrightarrow R-\overset{R'}{\underset{\underset{\underset{CHO}{|}}{\underset{CH_2}{|}}}{\underset{CH_2}{|}}}{C}-COOEt}$$

I, R = H, R' = COOEt
II, R = H, R' = CN
III, R = Et, R' = COOEt
IV, R = n-C_6H_{13}, R' = COOEt
V, R = n-$C_{10}H_{21}$, R' = COOEt
VI, R = CH_3COO, R' = COOEt
VII, R = Br, R' = COOEt

---

[1] Paper No. 92, Journal Series, Research Laboratories, General Mills, Inc.

(2) Moe and Warner, THIS JOURNAL, **70**, 2763 (1948).