88% lauryl aldehyde based on the solid complex. The 2,4-dinitrophenylhydrazone was found to melt at 106° (uncor.). Oxidation with an acetone solution of potassium permanganate yields lauric acid, m. p. 44-45° (uncor.) in quantitative yield.

This investigation is being continued with the purpose of elucidating the mechanism of the reactions involved in order to arrive at an explanation as to why the reactions take a different course with variation in experimental technique.

Summary

Lauryl aldimine stannic chloride precipitate cannot be obtained by the Stephen reaction by adding lauryl nitrile to stannous chloride dissolved in ether with dry hydrogen chloride. By working up the ether solutions, di- and trimeric lauryl aldehyde polymers are isolated in approximately quantitative yield. The trimeric lauryl aldehyde, m. p. 101°, has not been reported previously.

By conducting the Stephen reaction in an inverse manner, i. e., addition of stannous chloride to an ether solution of lauryl nitrile saturated with hydrogen chloride, an ether soluble "liquid" type metallo complex of lauryl nitrile can be isolated in quantitative yield. It is quite resistant to hydrolysis, yielding monomeric lauryl aldehyde.

The ether insoluble "solid type" lauryl aldimine stannic chloride complex can be precipitated in high yield from a normal type of Stephen reaction by storing the clear solution at low temperatures. It has the composition postulated by Stephen of $[C_{11}H_{23}CH:NH\cdot HCl]_2SnCl_4$.


Ethyl Sorbate in the Diene Synthesis

BY M. WESLEY RIGG AND RUDOLPH ROSENTHAL

The recent literature contains numerous references to the polymerization reactions involving diene olefins and acrylic esters; however, very little work has been reported on the successful polymerization of sorbic acid and its esters. Thermal polymerization reactions[1,2,3,4a,b] have been reported; the results indicate that only dimeric and trimeric products were obtained. The principal reactions were Diels–Alder additions. Carpmaels and Ransford[5] report a mixed polymer of rubber-like properties obtained on emulsion polymerization of butadiene and ethyl sorbate. A mixed polymer was also obtained when butadiene or isoprene was polymerized with 3,5-heptadiene-2-one. Several Diels–Alder addition products of sorbic acid and its esters with maleic anhydride, acrylyl chloride, and vinyl phenyl ketone have been reported.[6,7,8,9] Houtz and Adkins[10] found that sorbic acid in dioxane was unaffected by the catalyst diisobutylene ozonide both at 23° and at 100°. It was also found that ethyl sorbate showed a 70% increase in viscosity using 3% pinene ozonide as catalyst, and 24% increase without catalyst in seventy-six days at 23°. In nine days at 100°, the viscosity increased six-fold without catalyst, and ten-fold with 3% ozonide as catalyst.

(1) Doebner, Ber., 35, 2129 (1902).

(2) Lennartz, Ber., 76B, 1006 (1943).

(3) Kuhn and Deutsch, Ber., 65B, 43 (1932).

(4) (a) Farmer and Morrison-Jones, J. Chem. Soc., 1339 (1940); (b) Wheeler, THIS JOURNAL, 70, 3467 (1948).

(5) Carpmaels and Ransford, British Patent 387,381, Feb. 6, 1933.

(6) Diels and Alder, Ann., 470, 91 (1929).

(7) Wicks, Daly and Lack, J. Org. Chem., 12, 713 (1947).

(8) Wagner-Jauregg and Helmert, Ber., 71B, 2535 (1938).

(9) Allen, Bell, Bell and Van Allan, THIS JOURNAL, 62, 656 (1940).

(10) Houtz and Adkins, ibid., 55, 1614 (1933).

According to the charge distribution on the double bonds assigned by Price,[11] the carbon atoms should have charges as indicated in the formula
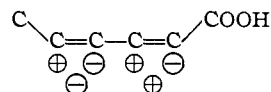
Heinanen[12] also predicted the same charge distribution on the ethyl sorbate molecule but did not discuss the question of olefin addition. Farmer and Morrison-Jones,[4] as a result of their work on the thermal polymerization of methyl sorbate in which dimeric esters were obtained, pointed out that either both polarized forms must exist at the same time or that the addition is a free radical reaction.
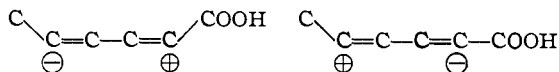
Their decision was based upon the isolation of two dimeric forms and a residue which they predicted might contain the remaining two isomeric forms which would be expected from a free radical mechanism.

Since little information is available concerning the successful polymerization of ethyl sorbate or sorbic acid, it was considered of interest to determine the activity of ethyl sorbate under the influence of various catalysts which are known to cause polymerization: namely, heat, peroxide in bulk, peroxide in solvent, persulfate in emulsion, and low temperature polymerization by

(11) C. C. Price, "Reactions of the C–C Double Bond," Interscience Pub. Co., New York, N. Y., 1946, pp. 33, 49.

(12) P. Heinanen, Ann. Acad. Sci. Fennicae, A49, No. 4, 112 pp. (1938).

TABLE I
EMULSION POLYMERIZATION

No.	Ethyl sorbate Taken	Ethyl sorbate Recd.	Dienophile	Taken	Recd.	Diene addition	Polymerization
1	30	20	....			3	Small amount
2	22.5	12	Methyl acrylate	7.5	..	10	Small amount
3	17.5	5.5	Ethyl acrylate	12.5	..	18.5	Trace
4	9.5	..	Ethyl fumarate	20.5	9	16	Trace
5	19	14	Vinyl acetate	11	2	2	Trace
6	17.5	13.5	Methyl crotonate	12.5	2	3	Trace
7	17.5	8	Styrene	12.5	8	10	Rubber-like polymer
8	20	..	Isoprene	10	..	15	15 g. viscous polymer

TABLE II
SOLVENT POLYMERIZATION

No.	Ethyl sorbate Taken	Ethyl sorbate Recd.	Dienophile		Diene addition	Polymerization
9	30	25	....		3	None
10	17.5	5	Ethyl acrylate	12.5	17.5	Trace
11	13.5	4	Ethyl fumarate	16.5	23.0	Trace
12	19.0	14	Vinyl acetate	11.0	2	Trace
13	17.5	15	Methyl crotonate	12.5	3	Trace
14	17.5	7.5	Styrene	12.5	9, b. p. 158–161° (4 mm.)	2.5 polymer
					3, above 160° (4 mm.)	
15	20.0	13.0	Isoprene	10.0	3, b. p. 105° (4 mm.)	Trace
					2, b. p. 110–130° (4 mm.)	
					5, b. p. 130–200° (4 mm.)	

acidic catalysts such as aluminum chloride or boron trifluoride. It was also deemed of interest to determine whether ethyl sorbate would form a copolymer with various monomeric olefins and olefinic esters, e. g., methyl and ethyl acrylate, ethyl fumarate, methyl crotonate, styrene, vinyl acetate, allyl formate, allyl succinate and isoprene.

Experimental

Sorbic acid, obtained from Union Carbide and Carbon Co., was stated to have the properties: m. p. 134.5°; b. p. 228° (with decomposition); 99% by weight sorbic acid on a dry basis, with a maximum of 10% water added for shipping purposes.

Methyl acrylate and **ethyl acrylate,** from Rohm and Haas Co., contained 0.25% inhibitor which was removed by distillation.

Methyl crotonate, from Shawinigan Chemical Corp., was used after one distillation.

Ethyl fumarate, furnished by the Pfizer Chemical Co., was used without distillation.

Vinyl acetate, from the Niacet Co., was purified by distillation.

Allyl formate, from the Hooker Electro-chemical Co., was used without distillation.

Styrene, furnished by the Dow Chemical Co., was used after distillation.

Isoprene, obtained from Phillips Petroleum Co., was used after distillation.

Ethyl sorbate was prepared by refluxing sorbic acid with ethyl alcohol in the presence of concentrated sulfuric acid as catalyst, and benzene. The water formed in the reaction was removed by azeotropic distillation. The excess alcohol and benzene was removed under reduced pressure, and the ethyl sorbate recovered and purified by vacuum distillation. The refractive index of our ethyl sorbate was n^{20}D 1.4951, compared to the value n^{20}D 1.50227 reported by Auwers.[18] The refractive index of a sample of ethyl sorbate obtained from Union Carbide and Carbon Co. agreed with our value.

(18) Auwers, J. prakt. Chem., [2] 168, 375 (1911).

Emulsion Polymerization

The method proposed by C. F. Fryling,[14] involving the use of small Pyrex reaction tubes, was employed for the emulsion polymerization tests. Fifty-four grams of water, 2 g. of sodium oleate, 30 g. of monomers and 0.2 g. of ammonium persulfate in a sealed reaction tube were placed in an air oven at 110°, and revolved at a speed of approximately 4 r.p.m. for twenty-four hours. The reaction tubes were flushed with nitrogen before and after being filled since oxygen was found to inhibit the reactions. The oil layer (no emulsion was present) was separated from the aqueous layer, dried over anhydrous sodium sulfate, and distilled under reduced pressure to recover the products of the reaction. The results of these experiments will be found in Table I.

Solvent Polymerization

Fifty-two grams (60 ml.) of xylene, 30 g. of monomer, and 0.1 g. of benzoyl peroxide were placed in a reaction tube, flushed with nitrogen, sealed, and heated for seventy-two hours at 100°. The resulting mixture was separated by vacuum distillation. The results of these experiments will be found in Table II.

Bulk and Heat Polymerization Reactions

Ten grams of monomer and 0.1 g. of benzoyl peroxide were placed in a reaction tube, and heated for twenty-four hours at 95°. The resulting mixture was separated by vacuum distillation. The results are shown in Table III.

Discussion of Experimental Results

Dimeric Material Obtained from Ethyl Sorbate.—The boiling point and refractive index of the high boiling compound, b. p. 110–165° (6 mm.), n^{20}D 1.4780–1.4806 are similar to the values obtained by Farmer and Morrison-Jones[4] on the products obtained by heat-polymerization of methyl sorbate. They found that the heterogeneous material could be separated into two

(14) C. F. Fryling, Ind. Eng. Chem., 16, 1 (1944).

No. benzoyl	Ethyl per- oxide taken	Sorbate catalyst recov- ered	Dienophile		Temp., °C.	Time, hr.	Diene addition polymerization
16	10	8		95		24	Trace
17	8		Methyl acrylate (5)	Reflux		11	9
18[a]	0			200		8	4
19[a]	16	1	Methyl acrylate (10)	Reflux		8	17
20[a]	7	2	Ethyl acrylate (5)	Reflux		1.5	7
21[a]	16	3	Ethyl fumarate (20)	Reflux		2	31
22[a]	7		Vinyl acetate (43)	Reflux, sealed tube 105			Monomers only recovered
23[a]	7		Allyl formate (43)	Reflux, sealed tube 105			Monomers only recovered
24[a]	15		Maleic anhydride (105)	Reflux		2	19
25[a]	5		Maleic anhydride (2.5)	Reflux		1.5 min.	Crystal. m. p. 118–119
26[a]	16		Allyl succinate (20)	Reflux		2.5	
27[b]	15	14		76		0.5	No reaction
28[c]	15	135		76		0.5	No reaction

[a] No catalyst.   [b] Low temperature, boron trifluoride etherate.   [c] Low temperature, anhydrous aluminum chloride.

constant-boiling mixtures, n^{18}D 1.47806 and n^{17}D 1.49063. The boiling point of their original di-. meric material was 110-150° (3 mm.).

Addition Product Formed from Ethyl Sorbate and Methyl Acrylate.—The following ratios of ethyl sorbate to methyl acrylate were used: 75-25, 50-50, 25-75, by weight, and equimolar ratios. The same compound was isolated in each case, b. p. 107° (1 mm.), n^{20}D 1.4626. The yield varied directly with the length of time heated, with no recoverable amount being formed unless the materials were heated for at least two hours at 95°. The best yields were obtained when equimolar ratios of monomers were used.

The molecular weight of this product, determined by the Beckmann freezing point method, was found to be 228 ± 2, which corresponds to a compound which would be formed by a Diels-Alder type of addition between the two monomers. The two possible structures of a Diels-Alder addition product are
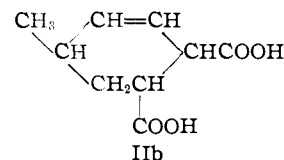
Ia

and

Ib
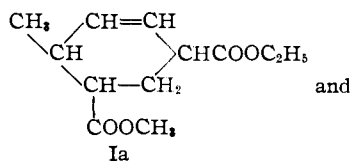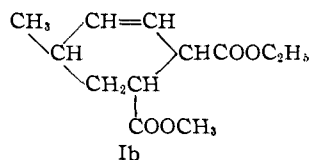
On saponification and acidification, a dicarboxylic acid which had one of the following structures was isolated

IIa

or

IIb
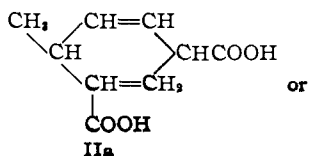
If the structure were that depicted by IIb, an anhydride should be formed on heating; however, all attempts to prepare an anhydride by heating failed. 4-Methylisophthalic acid was prepared from the compound. Wagner-Jauregg and Helmert[8] prepared a compound by refluxing sorbyl chloride and acrylyl chloride in xylene, and hydrolyzing the product. Upon dehydrogenating with bromine, they found that the two carboxyl groups were not on adjacent carbon atoms since the final product was 4-methylisophthalic acid. This supports the belief that IIa is the correct structure of compound II.

Product Formed from Ethyl Sorbate and Ethyl Fumarate.—There is only one possible structure for this addition product: b. p. 165° (3 mm.), n^{20}D 1.4630, mol. wt., 328.

Mol. wt. 312
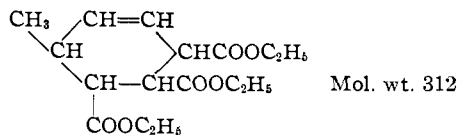
Product Formed from Ethyl Sorbate and Vinyl Acetate.—The monomers were the only products recovered on heat polymerization. However, a small yield, 6-13%, of an addition compound was formed in the emulsion and solvent techniques, b. p. 135-145° (4 mm.), n^{20}D 1.4830, mol. wt., 150.

Product Formed from Ethyl Sorbate and Methyl Crotonate.—In the emulsion and solvent polymerization attempts, approximately 10-20% of an addition compound was isolated, b. p. 125-135° (2 mm.), n^{20}D 1.4680, mol. wt. 230.

Products Formed from Ethyl Sorbate and Styrene.—The monomeric, dimeric and trimeric materials recovered from the solvent polymerization technique were partially separated by fractional distillation. The dimeric material was found to contain a small amount of monomer, and the trimeric material contained a small amount of dimer. A further fractionation could not be made because of the small amount of material recovered: b. p. 158-161° (4

mm.), n^{20}D 1.5060, mol. wt., 250; b. p. above 160° (4 mm.), n^{20}D 1.5180, mol. wt., 380.

A small yield of a rubber-like polymer was obtained from the emulsion polymerization technique, which contained approximately one acid group per 10 styrene molecules. The molecular weight of the polymer could not be determined by the freezing point method.

Products Formed from Ethyl Sorbate and Isoprene.— The monomeric, dimeric and trimeric materials obtained from solvent polymerization were partially fractionated by vacuum distillation: b. p. 105° (4 mm.), n^{20}D 1.4741, mol. wt., 200; b. p. 110–130° (4 mm.), n^{20}D 1.4820, mol. wt., 280; b. p. 130–200° (4 mm.), n^{20}D 1.4940, mol. wt., 500.

Approximately 50% yield of a viscous, brown polymer was obtained from the emulsion technique.

Summary

Ethyl sorbate was found to form Diels–Alder addition products in good yield with methyl acrylate, ethyl acrylate, and diethyl fumarate, independent of the method of polymerization or the catalyst employed.

Ethyl sorbate was found to form addition products in poor yield with methyl crotonate and vinyl acetate.

Dimeric and trimeric materials were formed from ethyl sorbate with styrene and isoprene in solvent polymerization. Materials with rubber-like properties were formed by emulsion polymerization of ethyl sorbate and styrene. A very viscous liquid was formed by emulsion polymerization of ethyl sorbate and isoprene.

No polymeric materials were obtained by low temperature polymerization.

Similar dimeric materials were obtained from each of the various methods of polymerization, and it would appear that the catalyst had very little, if any, effect upon the product formed.

2,3-Benzylidene-1,4-anhydro-D-mannitol. A Case of Benzylidene Migration

BY RICHARD E. REEVES

Hockett and co-workers[2] have recently pointed out that the substance of m. p. 162° which was designated by Brigl and Grüner[3] as "1,6-dibenzoyl-2,4-anhydro-3,5-benzal-mannit" is actually a derivative of 1,4-anhydro-D-mannitol (1,4-mannitan). On the basis of a repetition and extension of their work, we have confirmed this ring structure, but we have also acquired new evidence which requires revision of the positions assigned to the substituent groups.[4]

Hockett, et al., removed the benzoyl groups from the compound mentioned above and obtained a crystalline monobenzylidene-mannitan melting at 143–144° to which they assigned the structure 5,6-benzylidene-1,4-mannitan by observing its behavior when subjected to lead tetraacetate oxidation. We have obtained the same substance, but have observed that it is unstable in glacial acetic acid, the medium used for the oxidation, and rearranges into an isomer of levo optical rotation melting at 94–96°. This rearrangement was missed by the workers cited and they were consequently led to several erroneous conclusions. From experimental observations summarized below, it is concluded that our new monobenzylidenemannitan is 2,3-benzylidene-1,4-mannitan. The exact structures

of Brigl and Grüner's dibenzoylmonobenzylidene-mannitan and of Hockett's monobenzylidene-mannitan remain uncertain at this point, but our observations impose conditions that are not met by the structures that have been proposed.[2,3]

The reactions under discussion are shown in the following chart where structural formulas are used for the substances for which definite assignments are possible.

The structure of V has been established by the observation that one mole of lead tetraacetate is consumed at the rate characteristic of aliphatic alpha glycols[5] and by its oxidative cleavage with buffered periodate to yield virtually an equimolecular quantity of formaldehyde.

The isomeric monobenzylidenemannitan (IV) is probably not itself actually oxidized by lead tetraacetate since its apparent rate of consumption of this oxidant parallels very closely its rate of conversion into V (Fig. 1, Curve B). Hockett considered it to be oxidized because his observations were made under such circumstances that an unobserved rearrangement had evidently occurred before addition of lead tetraacetate (Fig. 1, Curve A). The conversion of IV into V apparently represents a clear case of benzylidene migration. Since IV does not react rapidly with lead tetraacetate the 5,6-benzylidene-1,4-mannitan structure proposed for this substance[2] is undoubtedly incorrect.

By rebenzoylation of Hockett's monobenzylidenemannitan IV we have obtained Brigl and

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry. Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Hockett, Fletcher, Sheffield, Goepp and Soltzberg, THIS JOURNAL, 68, 930 (1946).

(3) P. Brigl and H. Grüner, Ber., 67, 1582–1589 (1934).

(4) Hockett and co-workers revised Brigl and Grüner's structure to 2,3-dibenzoyl-5,6-benzylidene-1,4-mannitan.

(5) Hockett, Conley, Yusem and Mason, THIS JOURNAL, 68, 922 (1946); cf. Criegee, Büchner and W. Walther, Ber., 73, 571 (1940).