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DEPARTMENT OF CHEMISTRY
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The Reaction of 1,3-Butadiene with Formaldehyde

BY O. C. DERMER, LEON KOHN AND WILLIAM J. NELSON

Whereas Gresham and Steadman[1] were unable to condense formaldehyde with 1,3-butadiene without a catalyst, the acid-catalyzed reaction has been reported to yield 4-vinyl-1,3-dioxane[2] (I), 5-vinyl-1,3-dioxane[3] (II), 5,6-dihydro-2H-pyran[2,3] (III) (predicted[4] as a product of the uncatalyzed reaction), 3-hydroxy-4-hydroxymethyltetrahydro-2H-pyran[2] (IV) or possibly the 3-hydroxymethyl-4-hydroxy isomer thereof, and the cyclic formal[2,3] (V) of the dihydroxy compound, presumably hexahydro-2H-pyrano[3,4]*m*-dioxin. However, II is an unexpected product for which no proof of structure was given; the only description of the III obtained "boiling point about 80°") does not agree well with the literature[4]; and analytical data were given only for IV. We are therefore recording work which was completed before the appearance of these patents and which confirms and extends their disclosures. I has been converted by catalytic hydrogenation into 4-ethyl-1,3-dioxane, by bromination into 4-(1,2-dibromoethyl)-1,3-dioxane, and by oxidation with hydrogen peroxide and formic acid[5] into 4-(1,2-dihydroxyethyl)-1,3-dioxane.

Experimental

4-Vinyl-1,3-dioxane (I).—The reaction of 1,3-butadiene and formaldehyde was effected at 0–30° and one atmosphere, with diethyl ether or glacial acetic acid as solvent and concentrated sulfuric acid (15–35% by volume) as catalyst. Anhydrous aluminum chloride proved ineffective as a catalyst. Paraformaldehyde suspended in a solution of the catalyst by stirring was treated with gaseous 1,3-butadiene until the desired gain in weight had occurred. After three to 16 hours the mixture was made basic with sodium hydroxide, refluxed therewith to destroy sulfuric esters, extracted with ether, and distilled. Yields of the formal (V) were inferior in all cases to those previously reported,[2,3] but 30% of the formaldehyde was found convertible to I by using 1.6 moles of diene per mole of aldehyde in ether.

The I obtained had the following constants: b.p. 144°, $n^{20}\text{D}$ 1.4439, d^{20}_4 1.00. An approximate determination of the heat of combustion[6] gave the value −844 ± 3 kcal./mole.

Anal. Calcd. for $C_6H_{10}O_2$: C, 63.1; H, 8.83; bromine number, 140; mol. wt., 114; *M*D, 30.3. Found: C, 63.3; H, 8.93; bromine number, 143; mol. wt. (in freezing benzene), 111; *M*D, 30.3.

We believe this product, evidently identical with that reported in the patents, is 4-vinyl-1,3-dioxane rather than the 5-vinyl isomer, not only because normal orientation in the Prins reaction calls for the former but because the compound is appreciably reactive at its boiling point toward sodium. This behavior is indicative of an allyl ether structure, present in I but not in II.

5,6-Dihydro-2H-pyran (III).—Treatment of 100 g. of paraformaldehyde in 200 ml. of anhydrous ether and 30 ml. of concentrated sulfuric acid with 60 g. of 1,3-butadiene during nine hours at 20–30° produced 36.6 g. of I (29% based on the diene), 20.8 g. of V (13%), and about 4 g. of a forerun material shown to be III by its properties. Found: b.p. 94–96°; $d^{28.5}_4$ 0.943; $n^{20}\text{D}$ 1.4451; bromine number, 184. Literature[4]: b.p. 93–94°; d^{19}_4 0.940; $n^{19}\text{D}$ 1.4477; bromine number (calcd.), 190.

3-Hydroxy-4-hydroxymethyltetrahydro-2H-pyran (IV).—A run in glacial acetic acid, including saponification of esters, gave not only IV, b.p. 128–133° at 2 mm., but an impure unsaturated alcohol, b.p. 93–102° at 2 mm., bromine number 140–146°, believed to be either 4-pentene-1,3-diol or 2-pentene-1,5-diol,[3] b.p. 85° at 5 mm., bromine number 157.

4-Ethyl-1,3-dioxane.—The hydrogenation of 11.4 g. of I in 150 ml. of ethanol at room temperature and 3 atmospheres pressure, with Raney nickel[7] catalyst, required about 45 minutes. Distillation gave a practically quantitative yield of 4-ethyl-1,3-dioxane, b.p. 140–142°, $n^{32}\text{D}$ 1.4176, d^{32}_4 0.949.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.1; H, 10.3; *M*D 31.0. Found: C, 62.4; H, 10.5; *M*D, 30.8.

4-(1,2-Dibromoethyl)-1,3-dioxane.—A solution of bromine in carbon tetrachloride was added to 10 g. of I until the color of bromine persisted. Fractional distillation gave a pale-colored liquid, b.p. 159–160° at 28 mm., $n^{30}\text{D}$ 1.5332, d^{30}_4 1.85.

Anal. Calcd. for $C_6H_{10}O_2Br_2$: C, 26.3; H, 3.65; Br, 58.4; *M*D, 46.5. Found: C, 26.1; H, 3.56; Br, 58.1; *M*D, 45.9.

4-(1,2-Dihydroxyethyl)-1,3-dioxane.—Twenty grams of I was added to 26 ml. of 30% hydrogen peroxide in 109 ml. of 90% formic acid and the mixture worked up by the method of Roebuck and Adkins.[5] Only 0.7 g. (2.7%) of 4-(1,2-dihydroxyethyl)-1,3-dioxane was obtained by repeated recrystallization from ethyl acetate and then isopropyl ether, m.p. 96–98°.

Anal. Calcd. for $C_6H_{12}O_4$: C, 48.6; H, 8.2. Found: C, 48.1; H, 8.2.

No 1,3-dioxane-4-carboxylic acid could be isolated from the reaction mixture of I and the theoretical amount of hot aqueous alkaline potassium permanganate. I showed no noticeable tendency to be polymerized by benzoyl peroxide or stannic chloride.

Hexahydro-2H-pyrano[3,4-*d*]*m*-dioxin (V).—This compound had m.p. 52° (from benzene or ligroin), b.p. 212–213° (distilled from sodium), $n^{26}\text{D}$ 1.4670 (supercooled), d^{26}_4 1.139 (supercooled).

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.3; H, 8.3; *M*D, 35.05. Found: C, 58.2; H, 8.4; *M*D, 35.1.

Reaction of V with excess 2,4-dinitrophenylhydrazine in 3 *N* hydrochloric acid unaccountably gave only 70–85% of the theoretical amount of formaldehyde 2,4-dinitrophenylhydrazone. Methanolysis[8] in boiling methanol failed, no methylal being produced. Hydrolysis with boiling 10% sulfuric acid and removal of formaldehyde as methylal gave an unpurified residual glycol that responded to the periodate test for hydroxyl groups on adjacent carbon atoms. This suggests (*via* opening of the pyran ring) that IV has the structure named and not that of the isomeric 3-hydroxymethyl-4-hydroxytetrahydro-2H-pyran.

Acetolysis of V by the method of Senkus[9] gave what appeared to be a pure compound, b.p. 196–197° at 30 mm., $n^{20}\text{D}$ 1.4535, d^{20}_4 1.16, but no reasonable structure has been devised for it.

Anal. Found: C, 50.6, 50.7; H, 6.9, 7.1; equiv. wt. by saponification, 123.

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DEPARTMENT OF CHEMISTRY
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Mixed Esters of Lactic and Fatty Acids[1]

BY M. L. FEIN

Earlier papers[2,3,4,5] described the preparation and properties of acylated derivatives of various lactic esters. This paper reports several additional members of this group of mixed esters of lactic acid. These esters are the pelargonates of some lactic esters and the laurates of ethyl and butyl lactyllactate corresponding to the general formulas $CH_3(CH_2)_7COOCH(CH_3)COOR$ and $CH_3(CH_2)_{10}COOCH(CH_3)COOCH(CH_3)COOR$. The latter may be considered as a derivative of lactyllactic acid.

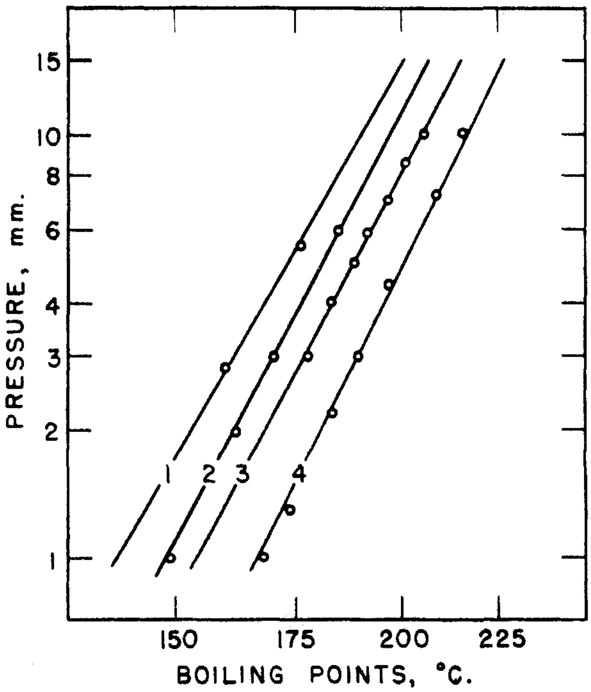

Fig. 1.—Boiling points of lactate pelargonates: 1. 2-butoxyethyl lactate pelargonate; 2. *n*-butyl phthalate; 3. 2-chloroethoxyethyl lactate pelargonate; 4. 2-(2-butoxyethoxy)-ethyl lactate pelargonate.

Experimental

Materials.—2-Butoxyethyl, 2-(2-butoxyethoxy)-ethyl and 2-chloroethoxyethyl lactates were prepared as described previously.[2,6] Ethyl lactyllactate was obtained by distillation of ethyl polylactate prepared by the self-alcoholysis of ethyl lactate.[7]

TABLE I

PROPERTIES OF PELARGONATES AND LAURATES OF LACTIC ESTERS

	Yield, %	B.p. °C.	B.p. Mm.	$n^{20}D$	d^{20}_4	Viscosity at 20°C., centipoises	Ester equivalent Found	Ester equivalent Calcd.	Carbon,[a] % Found	Carbon,[a] % Calcd.	Hydrogen, % Found	Hydrogen, % Calcd.
2-Butoxyethyl lactate pelargonate	64	160	2.8	1.4379	0.9564	...	165.2	165.2	65.32	65.42	9.98	10.37
2-(2-Butoxyethoxy)-ethyl lactate pelargonate	79	168	1.0	1.4402	0.9740	13.74	186.4	187.2	63.86	64.17	9.89	10.23
2-Chloroethoxyethyl lactate pelargonate	85	178	3.0	1.4496	1.0530	17.98	...[b]	...	56.23	57.05	8.39	8.68
Ethyl lactyllactate laurate	83	171	0.9	1.4392	0.9810	25.24	125.3	124.2	64.84	64.48	9.82	9.74
Butyl lactyllactate laurate	..	186–190	1.2	1.4415	0.9677	22.38	132.6	133.5	65.47	65.97	10.02	10.07

[a] The author is indebted to C. L. Ogg and Mary J. Welsh for analytical data. [b] % Cl 10.62 (found); 10.53 (calcd.).

Preparation of Esters.—The lactate pelargonates were prepared by acylating the appropriate lactate with redistilled pelargonyl chloride; ethyl lactyllactate laurate by acylation of ethyl lactyllactate with redistilled lauroyl chloride. The conventional acid chloride acylation method was employed.[3,4] Butyl lactyllactate laurate was obtained as a by-product in the esterification of butyl lactate with lauric acid in a modification of the method described in an earlier paper.[8]

The esters prepared and their properties are listed in Table I. These esters exhibited slight solubility (less than 0.03 g. per liter) in water at room temperature, and were found to be compatible with ethyl cellulose though incompatible with cellulose acetate.

Vapor pressures of the lactate pelargonates were determined by distillation in a tensimeter still.[9] The boiling points in the range of 1 to 10 mm. are shown in Fig. 1. The line for *n*-butyl phthalate is included for purposes of comparison.

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[1] Not copyrighted.

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[10] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture.

Structure of the Addition Product of *p*-Toluenesulfinic Acid and Formaldehyde

BY LAMAR FIELD AND PAUL H. SETTLAGE

The formation of an addition product from *p*-toluenesulfinic acid and formaldehyde has been reported by von Meyer,[1] who regarded it as having

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