149–150°; n^{24}_D 1.4162; d^{24}_4 0.896; saponification equivalent, 127.0 (calcd. for a pentenol acetate, 128.0).

A portion of this material was saponified with aqueous sodium hydroxide and the pentenol was removed as an azeotrope by distillation. The water-insoluble layer was dried and found to have the properties: b. p. 139–140°, n^{15}_D 1.4307 (n^{25}_D 1.4270); d^{25}_4 0.8395; α-naphthylurethan derivative, m. p. 61.5–62°; analysis for N, 5.35% (calcd. for pentenol derivative, 5.48%).

The properties of pentene-4-ol-1 are described in the literature as follows: b. p. 140–142°; n^{15}_D 1.4305; d^{15}_4 0.848.

Summary

1. The preparation of pure 1,3- and 1,4-pentadienes by pyrolysis of the diacetates of 1,2- and 1,5-pentanediols is described. Since these diols are obtained as hydrogenation products from furfural, this method provides a means of converting furfural to pentadienes.

2. It has been shown that the pyrolysis of these pentanediol diacetates proceeds via the intermediate pentene-ol acetates.

3. A new compound, pentene-1-ol-1 acetate, has been isolated and characterized.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY,[1] PHILADELPHIA, PENNSYLVANIA]

Preparation and Pyrolysis of Alkyl Alpha-Acetoxypropionates. Effect of Structure on Yield of Acrylic Ester

BY C. E. REHBERG AND C. H. FISHER

Decomposition occurs at both ester groups when the acetyl derivatives of alkyl lactates (excluding methyl lactate,[2,3] benzyl lactate,[2] and certain other lactic esters[4,5]) are pyrolyzed at 500 to 575°. The purpose of the present work was to determine the feasibility of preparing various alkyl acrylates by pyrolyzing the corresponding α-acetoxypropionates and to obtain information on the relation between acetoxypropionate structure and yield of acrylic ester.

The acetoxypropionates were pyrolyzed as before[3,4,5] by passing their vapors through a hot Pyrex-glass tube. Uniform conditions (approximately 500° and 9 seconds of contact) were used in one series of experiments to afford a comparison of the behavior of the different esters. Studies made at these conditions (Table I) with 2-chloroethyl, isobutyl, 2-ethylbutyl, *n*-butyl, 2-ethylhexyl, and isopropyl acetoxypropionates gave rise to the corresponding acrylates in these diminishing yields: 51, 40, 31, 27, 20, and 0.3%. The extent of decomposition revealed somewhat the reverse order: 46, 31, 57, 61, 38, and 99%. At 525° and five seconds, *n*-propyl α-acetoxypropionate changed to *n*-propyl acrylate in 37% yield. Results with the corresponding ethyl ester were interesting in view of the high reported yield of ethyl acrylate by Burns, Jones and Ritchie.[2] At 4 to 26 seconds (500°) our yields of ethyl acrylate were but 19 to 15% although extent of pyrolysis nearly doubled with the longer period of contact.

TABLE I

PYROLYSIS OF α-ACETOXYPROPIONIC ESTERS

Expt.	Acetoxy-propionate	Temp., °C.	Feed rate, ml./min.	Contact, time, sec.[a]	Ester decomposed, %	Yield, %[b] Acrylate	Yield, %[b] Olefin[c]
1	Ethyl	500	3.2	4.3	43	19	44
2	Ethyl	450	2.7	6	18.2	33	..
3	*n*-Propyl	500	1.5	11.8	27	25	76
4	*i*-Propyl	500	2.2	8.7	99	0.3	67[d]
5	*n*-Butyl	500	1.5	9.3	61	27	46[d]
6	*i*-Butyl	500	1.2	8.1	31	40	45
7	2-Ethylbutyl	500	1.8	9.6	57	31	55
8	2-Ethylhexyl	500	2.3	8.8	38	20	29
9	Cyclohexyl	500	1.9	7.1	96	0	91[d]
10	β-Chloroethyl	500	1.5	8.1	46	51	..
11	Ethyl[e]	475	5 g.	7.1	78.7	71[f]	4

[a] Based on the free space of the pyrolysis tube in the furnace. [b] Based on ester decomposed. [c] Assumed to be the olefin corresponding to the alkoxy group. [d] Includes only the olefin condensed and isolated in the liquid pyrolysis product. [e] Ethyl α-acetoxyisobutyrate. [f] Ethyl methacrylate.

Acetoxypropionates of secondary alcohols decompose more readily than esters of primary alcohols (Table I). Results obtained with the *n*-butyl and isobutyl esters suggest that the presence of only one β-hydrogen atom in the alkoxy group increases the stability. That the stability of the alkoxy group is related to the number of its β-hydrogen atoms (in the absence of other pronounced structural differences) is indicated also by the fact that the *n*-propyl and *n*-butyl acrylates were obtained in higher yields (under roughly comparable conditions) than ethyl acrylate. The pyrogenic behavior of methallyl[6] and tetrahydrofurfuryl[6] acetoxypropionates, however, shows that the number of β-hydrogen atoms is not always the determining factor. The β-chloroethyl group appears to be more resistant to decomposition than the ethyl, propyl, or butyl group, a 51%

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

(2) R. Burns, D. T. Jones and P. D. Ritchie, *J. Chem. Soc.*, 400, 1054 (1935); U. S. Patent 2,265,814, Dec. 9, 1941.

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yield of chloroethyl acrylate being obtained. Since a methoxy group[5] on the β-carbon atom also increases the thermostability of the ester, it appears that ortho, para-directing or electron-releasing groups stabilize the alkoxy groups in esters, but meta-directing or negative groups (compare the pyrogenic behavior of β-cyanoethyl acrylate[7]) in the β-position weaken them.

Pyrolysis of Ethyl α-Acetoxyisobutyrate.—To obtain a direct comparison of the thermal stability of acetoxypropionates and acetoxyisobutyrates, ethyl α-acetoxyisobutyrate was prepared and pyrolyzed. Even when the conditions were drastic enough to destroy most of the acetoxy ester, the principal product was ethyl methacrylate (Table I, Expt. 11). This suggests that acetoxyisobutyrates corresponding to the acetoxypropionates described in the present paper (excluding the esters of secondary alcohols) would give moderate or high yields of alkyl methacrylates on pyrolysis.

Experimental

Alkyl Lactates.—Commercial samples of ethyl, *n*-propyl, *i*-propyl, *n*-butyl, and *i*-butyl lactates were used. Cyclohexyl lactate was obtained from the Barrett Division of the Allied Chemical and Dye Corporation through the courtesy of Dr. W. O. Teeters.

2-Ethylbutyl, 2-ethylhexyl and β-chloroethyl lactates were prepared in yields of 74, 85, and 62%, respectively, by the alcoholysis of ethyl lactate. For the first two, aluminum alcoholate was used as the catalyst, and three times the theoretical amount of alcohol was added. For the chloroethyl ester, toluene-sulfonic acid catalyst and twice the theoretical amount of alcohol were used. In each case, the mixture was refluxed in a still while ethanol was removed as fast as formed. Finally, the higher lactate was distilled under reduced pressure. Boiling points of these three esters were, respectively: 112° (19 mm.), 132° (19 mm.), and 84° (4 mm.). Chloroethyl lactate had n^{20}_{D} 1.4510; d^{20}_{4} 1.2316; *MR* 33.34 (calcd., 33.34). The 2-ethylbutyl and 2-ethylhexyl lactates have been described previously.[8]

Chloroethyl lactate was also prepared by direct esterification; the reaction mixture consisted of 15 moles of ethylene chlorohydrin, 5 moles of lactic acid (80%, edible grade), 200 cc. of benzene, and 5 cc. of sulfuric acid. The mixture was refluxed with continuous removal of water until no more was produced. The sulfuric acid was neutralized with sodium acetate, and the mixture was distilled under reduced pressure; yield, 70%.

Alkyl α-Acetoxypropionates.—All the lactates were acetylated with acetic anhydride; 10% excess of anhydride was used, and a few drops of sulfuric acid was added as catalyst; yields usually were more than 90%. The boiling points of the acetoxypropionates were: *n*-propyl, 97° (23 mm.); isopropyl, 90° (25 mm.); *n*-butyl, 103° (15 mm.); isobutyl, 105° (23 mm.); 2-ethylbutyl, 97° (2 mm.); 2-ethylhexyl, 104° (1 mm.); cyclohexyl, 113° (5 mm.); and β-chloroethyl, 83° (1 mm.).

Cyclohexyl and chloroethyl acetoxypropionates apparently are new compounds. The former had n^{20}_{D} 1.4450; d^{20}_{4} 1.0499; *MR* 54.31 (calcd., 54.11); *Anal.* Calcd. for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47; sapn. equiv., 107.5. Found: C, 61.54; H, 8.63; sapn. equiv., 107.1. The latter had n^{20}_{D} 1.4372; d^{20}_{4} 1.1937; and *MR* 42.73 (calcd. 42.70); *Anal.* Calcd. for $C_7H_{11}O_4Cl$: C, 43.20; H, 5.71; sapn. equiv., 65.7. Found: C, 43.58; H, 6.05; sapn. equiv., 64.9. The physical properties of the other esters agreed with those recorded in the literature.[8]

Reaction of Lactic Acid with Ethyl Acetate.—Attempts were made to prepare ethyl acetoxypropionate in high yields by the reaction of lactic acid with ethyl acetate.[9] Although ethyl acetoxypropionate was obtained in appreciable amounts, in most cases the principal product was ethyl lactate. After studying a number of the variables involved, the highest combined yield of ethyl lactate and ethyl acetoxypropionate (40.7% and 27.2%, respectively) was obtained by heating 1 mole of 100% lactic acid, 1 ml. of concentrated sulfuric acid, and 6 moles of ethyl acetate in a hydrogenation bomb at 180° for four hours. Yields of ethyl acetoxypropionate were approximately equal to those of methyl acetoxypropionate obtained in a previous study[10] by treating lactic acid with methyl acetate.

Pyrolysis Experiments.—In Experiment 6 (Table I) a Pyrex glass tube, 28 mm. o. d., filled with short lengths of small Pyrex-glass tubing, was used as a pyrolysis chamber. It had 113 ml. of free space, and the heated length was 32 cm. In all other experiments the tube was Pyrex glass, 26 mm. o. d.; the heated length was 32 cm. and unpacked; the free space was 87 ml. In Experiment 6 the acetoxypropionate was pumped into a preheater maintained at 250 to 260° so that the material was introduced into the pyrolysis unit as vapor. In all other experiments the liquid was pumped[11] directly into the pyrolysis unit. Usually 100 to 360 g. was pyrolyzed, the larger samples being used when conversion into acrylic ester was unusually low.

The contact times in Table I were based on the total free space of the 32-cm. length of the pyrolysis tube. The length of the tube within 15° of the specified temperature was determined for some experiments; the contact times based on the free space in this zone for experiments 1 to 6 were, respectively, 1.7, 2.8, 12.2, 1.3, 2.4, and 3 seconds.

Owing to the difficulty of separating the ethyl acrylate and acetic acid by distillation, the ethyl acrylate fraction was washed with water. Except where indicated, the yield of olefin includes both that condensed (solid carbon dioxide trap) and isolated by distillation and that not condensed but found in the gaseous products. Acetic acid and acetaldehyde were obtained in different amounts in all the experiments. Yields of carbon monoxide in Experiments 1 to 5 were 28, 37, 34, 39, and 46%, respectively.

Physical constants of the acrylic esters, which were readily polymerizable, were in agreement with those previously determined in this Laboratory.[12] Moreover, the molecular refractions calculated from the observed physical constants and the constants of Eisenlohr were in agreement.

Summary

The lactates of several primary, secondary, and branched-chain alcohols were acetylated, and the resulting α-acetoxypropionates were pyrolyzed. Alkyl acrylates were obtained in the following order of decreasing yields: β-chloroethyl, isobutyl, 2-ethylbutyl, *n*-butyl, *n*-propyl, 2-ethylhexyl, ethyl, isopropyl, and cyclohexyl. Virtually no acrylic ester was obtained from the secondary alkyl acetoxypropionates. Yields of acrylates from the primary alkyl esters ranged from about 20 to 50% of the theoretical.

PHILADELPHIA, PA.

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