mations. In the present work with mixtures which are slightly acid, it is apparent that the anions, particularly phosphate, have a significant effect.

In agreement with many previous workers, it was observed that there was little or no discoloration of the pure sugar on heating. The formation of small amounts of acid substances from the sugar lowered the *p*H to a greater degree than in the cases where buffers were present and the increase in acidity may be partly responsible for the increased stability to color change. In the low concentrations employed, neither the ammonium acetate nor glycine buffers showed much difference from phosphate of the same *p*H as regards the yellowing tendency.

Summary

Autoclaving of glucose solutions in the presence of a phosphate buffer at an initial *p*H of 6.4–6.6 gives a considerable conversion to ketoses. From polarimetric and chemical analytical data, D-fructose appears to be the major product, but small amounts of other ketoses may be formed. Two other buffers of similar *p*H are less effective. Increase in the amount of phosphate increases the conversion at the same *p*H. A small amount of bisulfite does not alter the extent of conversion. In the absence of sulfite the degree of discoloration is mainly a *p*H effect.

URBANA, ILL. RECEIVED SEPTEMBER 18, 1944

[CONTRIBUTION FROM NORTHERN REGIONAL RESEARCH LABORATORY,[1] PEORIA, ILL.]

The Preparation of 1,3- and 1,4-Pentadienes from Furfural

BY L. E. SCHNIEPP[2] AND H. H. GELLER[3]

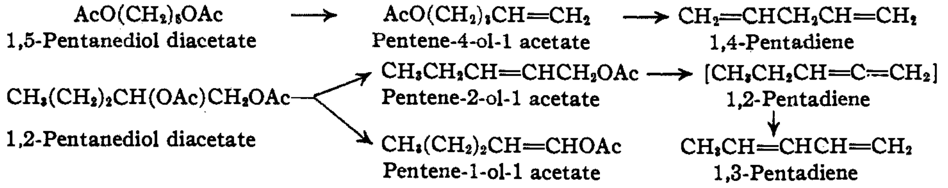
Catalytic conversion of 1,4- and 1,5-pentanediols to 1,3-pentadiene has been reported by Beati and Mattei.[4] The preparation of the pure 1,4-pentadiene has proven to be much more difficult because of its tendency to rearrange. The procedure of Shoemaker and Boord[5] is the best of the previously reported synthesis methods.

Pyrolytic decomposition of the diacetates of 1,2- and 1,5-pentanediols offers a new and convenient method of preparing the pure 1,3- and the 1,4-pentadienes from furfural hydrogenation products.

The formation and isolation of the 1,4-pentadiene as a pyrolysis product from the 1,5-diol diacetate is in general agreement with the findings of Van Pelt and Wibaut,[6] who found that double bond displacement did not normally occur when acetates of mono- and di-hydroxy compounds were converted to olefins by pyrolysis. This generalization does not apply, however, in the case of the 1,2-diol diacetate since only the 1,3-pentadiene was obtained as the pyrolysis product. The 1,2-diene, which is probably the initial reaction product, would be expected to rearrange to the 1,3-isomer under the influence of heat, as has been shown to be the case with 3-ethyl-1,2-pentadiene.[7]

The pyrolytic decomposition of the 1,5-pentanediol diacetate presents an attractive method of preparing 1,4-pentadiene. The pure diene was obtained in yields of 90–96% by pyrolyzing the diacetate at 575 ± 5°. Since the intermediate pyrolysis product, pentene-4-ol-1-acetate, which was isolated and identified, also yields 1,4-pentadiene on pyrolysis, nearly quantitative yields may be obtained by recycling the pyrolysis liquors until all of the acetates have been converted.

The conversion of 1,2-pentanediol diacetate to 1,3-pentadiene averaged 60–65% of the theoretical. The pentenol acetates remaining in the pyrolysis liquors did not yield any appreciable amount of diene on repyrolysis. The only intermediate isolated from these liquors was identified as the acetate of pentene-1-ol-1, since on hydrolysis it is converted to *n*-valeraldehyde and acetic acid. It appears, therefore, that the pyrolysis of 1,5- and 1,2-pentanediol diacetates proceeds by the routes



Experimental

1,2- and 1,5-Pentanediols.—Crude tailings from the commercial manufacture of tetrahydrofurfuryl alcohol were fractionally distilled under reduced pressure. The fraction boiling over the range of 90–150° (6 mm.) was collected and refractionated under atmospheric pressure. The fraction boiling at 205–211° was practically pure 1,2-pentanediol. The 1,5-pentanediol fraction was collected at 234–

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(4) Beati and Mattei, *Ann. Chim. Applicata*, **30**, 21 (1940).

(5) Shoemaker and Boord, THIS JOURNAL, **53**, 1505 (1931).

(6) Van Pelt and Wibaut, *Rec. trav. chim.*, **60**, 55 (1941).

(7) Mereschkovski, *J. Russ. Phys.-Chem. Soc.*, **45**, 1940 (1913).

240°. Refractionation of both cuts gave the pure diols having the properties

1,2-Pentanediol: b. p. 210–211°, $n^{24}\mathrm{D}$ 1.4390, d^{24}_4 0.9691
1,5-Pentanediol: b. p. 239–240°, $n^{26}\mathrm{D}$ 1.4480, d^{26}_4 0.989

Additional quantities of these diols were prepared by the high-pressure hydrogenation of furfuryl alcohol over copper chromite catalyst by the method of Connor and Adkins.[8] The reaction mixture was fractionally distilled. The combined yield of 1,2- and 1,5-pentanediols was 70% of the theoretical.

1,2- and 1,5-Pentanediol Diacetates.—Both the 1,2- and the 1,5-diols were acetylated by the following procedure: Six hundred and thirty-two grams (6.07 moles) of the diol was heated to 150° in a three-necked flask equipped with a dropping funnel, reflux condenser, and thermometer. Acetic anhydride, 1365 g. (13.3 moles), was added through the funnel over a period of one hour. The reaction mixture then was refluxed for two hours, after which it was fractionally distilled under reduced pressure. The purified diol diacetates had the following properties:

1,2-Pentanediol diacetate: b. p. 216–217°, $n^{28}\mathrm{D}$ 1.4167; d^{28}_4 1.048; saponification equivalent, 94.0 (calcd. 94.0).
1,5-Pentanediol diacetate: b. p. 244°, $n^{26}\mathrm{D}$ 1.4250; d^{26}_4 1.020; saponification equivalent, 94.9 (calcd. 94.0).

Pyrolysis of 1,2- and 1,5-Pentanediol Diacetates

Apparatus.—The pyrolysis apparatus consisted of a constant-feed pump, an electrically heated preheating section, and a stainless steel pyrolysis tube made of a 4-m. length of $^1/_8$-inch (I. P. S.) stainless steel (18-8-Cb) pipe coiled to fit into a 20 × 25 cm. gas-heated lead bath. The outlet end of this coil was welded into the side of an 18-inch length of $^3/_4$-inch stainless steel pipe which functioned as an air-cooled condenser. The top of this pipe was connected to a water-cooled condenser. A vapor line connected the top of this condenser to a Dry Ice-cooled trap which was vented to a wet-test meter. The base of the stainless steel air-cooled condenser was connected to a liquid trap which drained to a receiving flask. A thermocouple well was inserted into the middle of the lead bath and all temperatures were measured by an iron–constantan thermocouple.

Procedure.—The diol diacetates were charged into graduates from which they were pumped, at constant rates, to the preheater from which the vapors entered the pyrolysis coil. The lead bath surrounding the pyrolysis coil was maintained at as nearly a constant temperature as possible throughout the run. The vapors from the pyrolysis coil entered the steel pipe and condenser system where the higher boiling products were condensed and drained into the receiving flask. The less readily condensable gaseous products escaped from the top of the water-cooled condenser and were condensed in the Dry Ice-cooled trap. Any gases not condensable at Dry Ice temperatures passed on to the wet-test meter where their volumes were measured. Part of the dienes were dissolved by the condensing liquids in the condenser system and were collected in the liquid receiving flask. These were recovered from the pyrolysis liquors by fractional distillation. The diene-free liquors were either recycled through the pyrolysis system until all diene-producing intermediates were expended, or worked up for purposes of by-product or intermediate identification.

1,3-Pentadiene.—It was found that a temperature of 590 ± 5° was necessary to effect the thermal decomposition of the 1,2-pentanediol diacetate within a reasonable length of time. After establishing this fact, several runs were made at different feed rates to determine the optimum operating rate. The following table illustrates the yield data at various diacetate feed rates:

Feed rate, g./min.	Temp., °C.	1,3-Pentadiene, % yield	Non-condensable gas production, liters/mole
3.25	590 ± 5	63.2	4.9
4.07	590 ± 5	64.8	2.9
4.13	590 ± 5	65.3	5.3
6.24	590 ± 5	61.1	3.5

These data show that a diacetate feed rate of 4.13 g./min. gives the best yield. Recycling of the pyrolysis liquors did not give any material improvement, although analysis of these liquors showed the presence of acetates.

The 1,3-pentadiene remaining dissolved in the pyrolysis liquors was removed by fractional distillation. The fraction boiling at 38–42° was combined with the diene collected in the Dry Ice-cooled trap and the composite was redistilled. The pentadiene so obtained had the following properties: b. p. 42.9–43.9°, $n^{20}\mathrm{D}$ 1.4314; d^{20}_4 0.6822; tetrabromo derivative m. p. 114° (literature 114°).

1,4-Pentadiene.—The pyrolysis of 1,5-pentanediol diacetate was conducted at 575 ± 5°. It was found that the conversion rate was very slow at 550° and that excessive decomposition occurred at 600°.

In a typical run, 185 g. (0.983 mole) of the diacetate was fed to the preheater and pyrolysis-coil system at a rate of 3.3 g./min. The pyrolysis liquor collected in the receiving flask was fractionally distilled, and the distillate boiling at 26–28° was combined with the diene collected in the Dry Ice-cooled trap. The combined diene fractions were redistilled. Sixty-one grams of 1,4-pentadiene, 91% of the theoretical, was obtained. This product had the properties: b. p. 26.8–27.4°; $n^{26}\mathrm{D}$ 1.3865; d^{26}_4 0.657; tetrabromo derivative m. p. 85.5–86° (literature 85.5–86°).

The yield of 1,4-pentadiene was improved by operating at faster feed rates and recycling the pyrolysis liquors several times. It was found that three passes sufficed to convert all of the residual acetates to the diene. By feeding the initial diacetate at a rate of 6.9 g./min. a 64% yield was obtained. The pyrolysis liquors were recycled at a rate of 6.0 g./min. and the cumulative yield increased to 84%. The liquors from the second pass were recycled at 3.1 g./min. and the pentadiene collected raised the overall yield to 96% of the theoretical. At this point the pyrolysis liquor was essentially acetic acid.

Isolation and Identification of Pyrolysis Intermediates

Pentene-1-ol-1 Acetate.—The pyrolysis liquor produced during the pyrolysis of 1,2-pentanediol diacetate was drowned in four parts of ice water. The water-insoluble layer was separated, washed acid-free with cold water, dried, and distilled. The main fraction of the distillate had the following properties: b. p. 148–149°; $n^{26}\mathrm{D}$ 1.4213; d^{26}_4 0.896; saponification equivalent, 129.0 (calcd. for a pentenol acetate, 128.0).

A portion of this material was hydrolyzed by boiling in a hydrochloric acid–diethylene glycol solution. On distillation of the hydrolysis mixture an azeotrope distilling at 82° was collected. This fraction separated into two layers. The upper, water-insoluble layer was separated, dried, and redistilled. It was characterized as an aldehyde and had the following properties, corresponding to *n*-valeraldehyde: b. p. 102–103°; $n^{25}\mathrm{D}$ 1.3948; d^{25}_4 0.8167; 2,4-dinitrophenyl hydrazone derivative, m. p. 107°; dimethone derivative, m. p. 104–105°.

The properties of *n*-valeraldehyde and its derivatives are reported in the literature[9] as follows: b. p. 103.7°; $n^{20}\mathrm{D}$ 1.3944; d^{20}_4 0.8095; 2,4-dinitrophenylhydrazone derivative, m. p. 98° and 106.5–107°; dimethone derivative, m. p. 104.5–105°.

Pentene-4-ol-1 Acetate.—The pyrolysis liquor produced from a one-pass pyrolysis of 1,5-pentanediol diacetate, which gave a 72% yield of 1,4-pentadiene, was drowned in four volumes of ice water. The water-insoluble layer was separated, washed acid-free with cold water, dried, and distilled. The distilled material had the properties: b. p.

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(8) Connor and Adkins, This Journal, **53**, 1091 (1931).

(9) Huntress and Mulliken, "Identification of Pure Organic Compounds," J. Wiley and Sons, Inc., New York, N. Y., 1941, p. 51.

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	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[5] 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.

[3] Lee T. Smith, C. H. Fisher, W. P. Ratchford and M. L. Fein, *Ind. Eng. Chem.*, **34**, 473 (1942).

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[6] C. H. Fisher, C. E. Rehberg and Lee T. Smith, *ibid.*, **65**, 763, 1003 (1943).