

Fig. 2.—Infrared absorption spectra: O, polyvinyl alcohol; Δ, its dinitrophenylhydrazone.

some residual acetyl groups which have not been removed by saponification. The peak at 6.05 μ which is shown by the polyvinyl alcohol is greatly reduced and shifted slightly to the higher wave lengths in the derivative. This may be due to terminal carbonyl in the untreated alcohol.

It was thought possible that acid methyl alcohol might react with polyvinyl alcohol to cause some ether formation. However, Zeisel determinations on polymers treated in this manner did not show the presence of any methoxyl groups.

Summary

During the hydrolysis of polyvinyl acetate and also during reesterification of polyvinyl alcohol, unexpected and irregular changes in the apparent molecular weight of the polymer have been noted. A possible explanation of this behavior is that polyvinyl alcohol may have one terminal aldehyde group which, under acid conditions, can undergo acetal formation with the hydroxyl groups of neighboring molecules. Under alkaline conditions an aldol or reverse aldol reaction may occur to cause changes in molecular size.

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RECEIVED MAY 20, 1943

[CONTRIBUTION FROM THE LABORATORIES OF CHEMISTRY AND PHYSICS, ILLINOIS INSTITUTE OF TECHNOLOGY]

The Aldol Condensation. II. The Reaction of Isobutyraldehyde with its Aldol¹

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Experimental work with the aldols is complicated by the fact that even such ordinary treatment as distillation may either eliminate water to produce the unsaturated compound or dealdolyze the material to the simple aldehyde. To obviate part of this difficulty the present work has been confined to 2,2,4-tetramethylaldol² (isobutyraldol) which, because of the two methyl groups in the alpha position, has practically no tendency to eliminate water during distillation. Experiments of others³⁻⁵ which have been confirmed in the present work have shown that this aldol can be distilled without excessive dealdolyzation at reasonable temperatures (below 120°).

2,2,4-Tetramethylaldol was first obtained by Urbain⁶ in 1895. Since that time a number of investigations have been undertaken to determine the nature of the condensation products formed when isobutyraldehyde is treated with

alkali.^{4,5,7} The results of these experiments are not in accord even for the condensation under mild conditions. According to the literature, the action of potassium hydroxide solutions at or below room temperature gives two main condensation products: a dimer that is 2,2,4-tetramethylaldol, and a trimer which has been identified as 2,2,4-trimethyl-3-hydroxypentyl isobutyrate. The structure of the aldol seems to have been fairly well established by means of a number of derivatives and by the ease of decomposition into isobutyraldehyde. The ester, on the other hand, has been identified by some investigators by the fact that it is converted to the salt of isobutyric acid and to 2,2,4-trimethyl-1,3-pentane-diol when refluxed with alcoholic alkali. Such treatment, of course, is standard procedure for identifying esters, but it will be shown in the following discussion that in the present case the conclusions drawn from this test were not justified. Actually this isobutyraldehyde trimer may not have been the ester at all, and failure to recognize this has been the cause of much confusion not only in the condensation of isobutyraldehyde but also in the condensation of other aldehydes as well.

(1) For the first article of this series see Saunders, Murray, Cleveland and Komarewsky, *THIS JOURNAL*, **65**, 1309 (1943).

(2) The aldols mentioned in this paper are systematically named as derivatives of aldol ($\text{CH}_3\text{CHOHCH}_2\text{CHO}$).

(3) Usherwood, *J. Chem. Soc.*, 1717 (1923).

(4) Grignard and Iliesco, *Compt. rend.*, **190**, 556 (1930).

(5) Kirchbaum, *Sitzb. Akad. Wiss. Wien*, **112**, 1069 (1903).

(6) Urbain, *Bull. soc. chim.*, **13**, 1048 (1895).

(7) Brauchbar, *Sitzb. Akad. Wiss. Wien*, **105**, 629 (1896).

Experimental

2,2,4,4-Tetramethylaldol.—A few drops of dibutylamine were added to a mixture of 100 ml. each of ether and isobutyraldehyde, and the mixture cooled to 0–5°. Ten per cent. potassium hydroxide was then added dropwise with vigorous stirring. The temperature of the reaction mixture was controlled from 5 to 10° by cooling and by the rate of adding the potassium hydroxide solution. The reaction was considered complete when the temperature no longer tended to rise on addition of more alkali. Approximately 70 ml. of potassium hydroxide solution was required. The organic layer was then washed three times with 5% sulfuric acid solution, dried with sodium sulfate, freed of ether in vacuum, and distilled. First a quantity of isobutyraldehyde is collected; then the aldol distills (b. p. 89–90° at 13 mm.). It is important that the organic layer be washed well with dilute acid.

Trimer of Isobutyraldehyde.—The organic layer from the above aldolization was washed thoroughly with water instead of dilute acid. On distillation no isobutyraldehyde is collected; the isobutyraldehyde trimer distills in at least 80% yield; b. p. 110–111° at 8 mm.; d_{25}^{25} 0.9670; n_D^{25} 1.4461.

Anal. Calcd. for $C_{12}H_{24}O_3$: C, 66.63; H, 11.19; mol. wt., 216. Found: C, 66.91; H, 11.00; mol. wt. (in benzene), 220, 221.

Reaction of Isobutyraldehyde with 2,2,4,4-Tetramethylaldol.—A mixture of 7.5 g. of 2,2,4,4-tetramethylaldol and 6.3 g. of isobutyraldehyde was placed in a tightly stoppered test-tube and allowed to remain at room temperature for four days. Distillation of the mixture produced 2.3 g. of the above isobutyraldehyde trimer.

Reaction of the Trimer with Alcoholic Alkali.—Twenty-one grams of isobutyraldehyde trimer was refluxed with 110 ml. of 15% alcoholic potassium hydroxide for two hours. Ten grams of 2,2,4-trimethyl-1,3-pentanediol (m. p. 51.8–52.2°) was obtained from the reaction mixture together with a quantity of isobutyric acid which was identified by its *p*-bromophenacyl ester (m. p. 76–77°).

The apparatus and experimental technique used in obtaining the Raman spectra are described elsewhere.⁸ Hg 4358 Å. was used for excitation. Exposures were about seven hours with a slit width of 0.08 mm.

In order to obtain the spectra of undistilled reaction mixtures it was necessary to distil all reactants, solvents, and reagents from a special all-glass distilling apparatus to eliminate fluorescent materials. All reaction vessels, stirrers, and other pieces of equipment which might come in contact with the reaction mixture were washed several times with ether that had been distilled in the all-glass apparatus. No cork, rubber, or stopcock grease was permitted to come in contact with any reactants, solvents, or reagents either during or after distillation.

Results and Discussion

In the absence of catalyst and at room temperature mixtures of 2,2,4,4-tetramethylaldol with isobutyraldehyde slowly become more viscous and after several days a quantity of iso-

butyraldehyde trimer can be isolated from the reaction mixture. An excellent method of showing the transition of the aldol-aldehyde mixture to the trimer was developed using Raman spectra. The reaction rate is low enough so that the spectrum of a freshly mixed aldol-aldehyde sample (1/1 molal ratio) shows simply the superposition of the spectra of the aldol and of the aldehyde (see Table I). In successive spectra, obtained at various times after mixing, marked changes could be observed. The strong lines at 770, 798 and 1722 cm.^{-1} which are characteristic of the mixture gradually faded out while the intense line at 787 cm.^{-1} , characteristic of the trimer appeared and became more intense as the reaction neared completion. At the end of three weeks the spectrum of the sample matched the spectrum of the trimer.

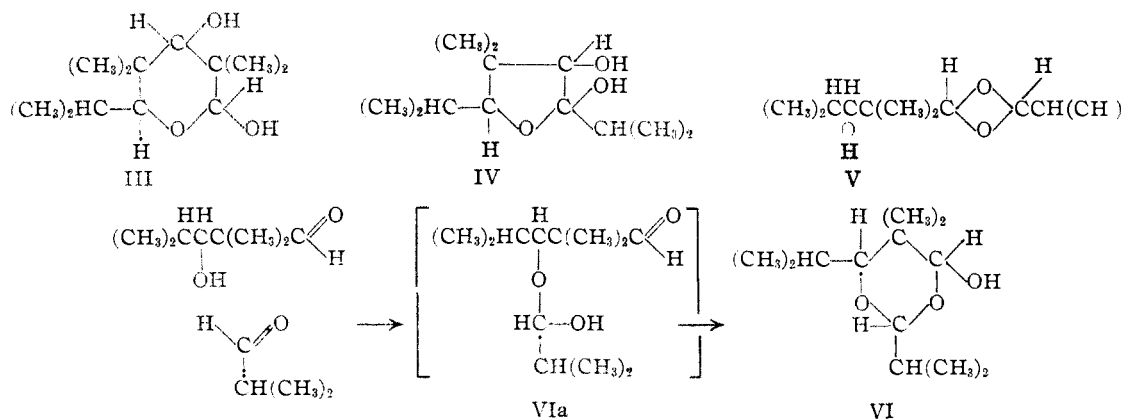
TABLE I
RAMAN SPECTRA OF ISOBUTYRALDEHYDE, 2,2,4,4-TETRAMETHYLALDOL, AND THE ALDOL-ALDEHYDE ADDITION COMPOUND

Isobutyraldehyde ^a $\Delta\nu$ cm.^{-1} I	2,2,4,4-Tetramethylaldol, $\Delta\nu$ cm.^{-1} I	Aldol-aldehyde addition compound $\Delta\nu$ cm.^{-1} I
281 (1)		267 (1)
343 (2b)	321 (3)	314 (1)
399 (1)	360 (2)	
451 (1)	487 (2)	466 (1)
546 (1)	522 (2)	507 (2)
		561 (1)
630 (1)	618 (1)	630 (1)
798 (8)	770 (9)	787 (6)
	812 (1)	830 (1)
	834 (1)	849 (1)
841 (2)	882 (2)	882 (2)
	907 (3)	
917 (4b)	956 (4)	956 (3)
971 (1)	996 (1)	
	1095 (2)	
1111 (1/2)	1119 (1)	1105 (1b)
1141 (1/2)	1174 (4)	1179 (2)
1176 (1/2)	1204 (1)	1210 (1)
	1306 (1)	1306 (3)
1279 (3)	1450 (7)	1458 (7b)
1392 (1b)	1467 (7)	
1455 (6b)	1716 (5)	
1728 (4)	2715 (2b)	2788 (1)
2716 (4)		
2811 (2)		
2872 (10)	2869 (10)	2870 (10)
2911 (3)	2912 (10b)	2915 (10b)
2934 (8)		
2976 (8)	2978 (10b)	2968 (10)
		2982 (10b)

The spectrum reported here agrees closely with that obtained by Kohlrausch and Koppl, *Z. physik. Chem.*, **24B**, 370 (1934).

(8) Cleveland, Murray, Haney and Shackelford, *J. Chem. Phys.*, **8**, 153 (1940); Cleveland and Murray, *ibid.*, **7**, 396 (1939).

The absence of lines in the 1600 to 1800 cm^{-1} region in the Raman spectrum of the trimer is significant since it precludes the postulation of carbonyl groupings of any type in the structure of the aldol-aldehyde compound. The reaction of two molecules of aldehyde resulting in the destruction of the carbonyl function of both necessitates ring formation, and several cyclic forms can be written, III, IV, V and VI.



Compound III results from an aldol condensation between 2,2,4,4-tetramethylaldol and isobutyraldehyde followed by cyclization. The five-membered ring structure, IV, is simply a benzoin type condensation followed by internal hemiacetal formation. Such condensations, however, could not be expected to take place, particularly in the absence of catalyst. Compounds of type V are not well known, and if isobutyraldehyde and 2,2,4,4-tetramethylaldol react in this manner at room temperature when a catalyst is not present, this should be a general reaction for almost any two aldehyde groups, and certainly such is not the case. The formation of VI is brought about by the addition of isobutyraldehyde to the aldol to give the hemiacetal VIa which immediately cyclizes by another hemiacetal reaction to form VI. We believe that structure VI correctly represents the above aldol-aldehyde addition compound.

Either 2,2,4,4-tetramethylaldol or VI may be obtained from aldolized isobutyraldehyde, depending on whether traces of catalysts are present during the distillation of the crude product. Distillation in the presence of small amounts of acids or bases gives approximately equal molal quantities of the aldol and isobutyraldehyde, while distillation in the absence of such catalysts gives VI in yields of 80% or higher. In the presence of larger amounts of acids or bases

distillation produces complete dealdolization.

The undistilled product of the aldolization of isobutyraldehyde, whether or not traces of acids or bases are present has a spectrum which is identical with that of VI. Hence the crude product of the action of alkaline solutions on isobutyraldehyde under mild conditions contains no aldol as such, but exists in the form of the isobutyraldehyde trimer VI.

With this in mind it is of interest to note the results of the experiments of Usherwood³ who has studied the kinetics of the 2,2,4,4-tetramethylaldol formation. In these experiments various mixtures of isobutyraldehyde and the aldol were permitted to come to equilibrium in the presence of potassium carbonate solution. At 60° equilibrium was reached in about ten hours, and by distillation of the mixtures thus formed it was decided that at equilibrium 33.2% of isobutyraldehyde and 66.8% of the aldol were present. These data are very close to the values 33 1/3% isobutyraldehyde and 66 2/3% aldol which would be obtained by distillation of VI in the presence of a trace of catalyst. Thus the formation of VI during the aldolization of isobutyraldehyde restricts the theoretical yields of the aldol to 66 2/3% based on the starting material; the highest yields of 2,2,4,4-tetramethylaldol reported in the literature are the 60-61% yields obtained by Grignard and Iliesco.⁴

The large amount of data which have been accumulated for the aldols indicates that the reaction between an aldol and an aldehyde group is a general one. As aldols age they become progressively more and more viscous finally depositing waxy, white crystals which are known as paralldols. These paralldols are dimers of the parent aldols and their formation has been reported for

almost every aldol investigated. Recent evidence⁹ indicates that the dimer contains a six-membered ring similar to the one which has been suggested in VI. In the Raman spectra of aldol (acetaldol), and 2,4-dimethylaldol (propionaldol) no carbonyl was detected even immediately after distillation.¹ Either distillation did not break down the initial aldol-aldehyde addition product, or the reaction of the aldol with itself was so rapid that no aldehyde groups remained by the time the spectrum could be obtained. 2,4-Diethylaldol (*n*-butyraldol) is the first aldol of the series in whose Raman spectrum a characteristic carbonyl line has been detected, but a few days after distillation dimerization becomes nearly complete and the carbonyl line disappears from the spectrum. For 2,2,4,4-tetramethylaldol the carbonyl line can be seen in the spectrum several weeks after distillation. Thus, it appears, the more hindered the hydroxyl and carbonyl groups of an aldol the slower is its dimerization.

Due to the difficulty in distilling the condensation products and due to the temporary nature of the lower monomeric aldols we have not yet determined with certainty whether compounds similar to VI appear during the syntheses of the lower aldols. Shilov¹⁰ has suggested that the formation of such a compound may be the limiting factor in the formation of aldol; and this may, in fact, be the reason that the condensation stops before high molecular weight resins are produced even under the mild conditions employed in aldolization.

The acetate of a cyclic compound of type VI has been reported by Marvel, Harmon and Riddle,¹¹ who condensed acetaldehyde with vinyl acetate.

The physical properties of the addition compound, VI, are similar to those which have been reported for the ester, 2,2,4-trimethyl-3-hydroxypentyl isobutyrate, obtained by action of alkaline

(9) Späth and Schmid, *Ber.*, **74B**, 859 (1941).

(10) Shilov, *J. Applied Chem., U. S. S. R.*, **8**, 93 (1935); *C. A.*, **29**, 6880 (1935).

(11) Marvel, Harmon and Riddle, *J. Org. Chem.*, **4**, 252 (1939).

solutions on isobutyraldehyde. When VI is refluxed with 15% alcoholic potassium hydroxide for two hours both isobutyric acid and 2,2,4-trimethyl-1,3-pentanediol can be isolated from the reaction mixture. The course of this reaction possibly is the dissociation of VI into isobutyraldehyde and the aldol, followed by a crossed Cannizzaro reaction. In this way, products are formed which would normally be expected from the hydrolysis of the above-mentioned ester. It is only natural, then, that some investigators have mistaken the addition compound VI for 2,2,4-trimethyl-3-hydroxypentyl isobutyrate. Investigations are now being carried on to determine whether this ester can be obtained from the condensation of isobutyraldehyde.

We wish to acknowledge helpful discussions with Dr. H. I. Bernstein.

Summary

1. It has been shown that isobutyraldehyde reacts with 2,2,4,4-tetramethylaldol (isobutyraldol), with or without a catalyst, to produce a compound which is identical with that formed by the action of potassium hydroxide solutions on isobutyraldehyde under mild conditions.

2. Since the above reaction takes one-third of the isobutyraldehyde out of action during an aldolization, the theoretical yield of 2,2,4,4-tetramethylaldol is limited to 66 $\frac{2}{3}$ % based on the starting material.

3. It is proposed that the structure of the trimer of isobutyraldehyde formed during aldolization is 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane.

4. It is suggested that this 2,2,4,4-tetramethylaldol-isobutyraldehyde addition product has been erroneously identified by others as 2,2,4-trimethyl-3-hydroxypentyl isobutyrate.

5. The Raman spectra of 2,2,4,4-tetramethylaldol and of the addition product of this aldol with isobutyraldehyde are reported for the first time.

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RECEIVED MAY 10, 1943