Oxime of *keto*-L-Sorbose Pentaacetate.[28]—An amount of 5 g. of *keto*-L-sorbose pentaacetate[8,9] was dissolved in 250 cc. of boiling water. Hydroxylamine hydrochloride (2.5 g.) and potassium acetate (5 g.) were added to the hot solution which was then allowed to cool slowly to room temperature. Upon cooling to 0° and scratching the sides of the flask, the product crystallized; yield 1.3 g., m. p. 113–114°, spec. rot. −42° (23°, *c* 3, abs. $CHCl_3$, D line). An additional 0.4 g. was obtained by extraction of the mother liquor with chloroform. The constants were unaltered after recrystallization from solution in acetone-ether by the addition of petroleum ether.

Anal. Calcd. for $C_6H_8O_6N(CH_3CO)_5$: C, 47.41; H, 5.72; N, 3.46; CH_3CO, 12.3 cc. 0.1 *N* NaOH per 100 mg. Calcd. for $C_6H_9O_6N(CH_3CO)_4$: C, 46.28; H, 5.83; N, 3.86; CH_3CO, 11.0 cc. Found: C, 47.40; H, 5.88; N, 3.68; CH_3CO (O-acetyl[29]), 12.1 cc.

D-Sorbose (VI) from *keto*-D-Sorbose Pentaacetate.[28]—An amount of 2.43 g. of *keto*-D-sorbose pentaacetate was added to 100 cc. of 0.6 *N* barium hydroxide solution, previously cooled to *ca.* 5°. With occasional shaking, the crystals dissolved in about thirty minutes. The solution was kept for one hour longer at *ca.* 5° and then was saturated with carbon dioxide and the precipitated barium carbonate was removed by filtration. A slight excess of 2 *N* sulfuric acid was added slowly and the barium sulfate removed by filtration through a bed of Super-Cel (Johns-Manville). The excess sulfuric acid was then removed exactly with barium hydrate and the filtered solution was concentrated under reduced pressure at 40° to a sirup which crystallized spontaneously. The crystalline mass was stirred with 10 cc. of ethanol for filtration; yield 0.90 g. (80%), m. p. 158–160°, spec. rot. +40.5° (26°, *c* 3, H_2O, D line). Pure material was obtained on one recrystallization from water by the addition of absolute ethanol; m. p. 160–162°, spec. rot. +43 (24°, *c* 3, H_2O, D line, no significant mutarotation). For D-sorbose, Alberda van Ekenstein and Blanksma[15] reported the constants: m. p. 165°, spec. rot. +43° (*c* 1, H_2O, D line). For the enantiomorphic L-sorbose, Schlubach and Vorwerk[9] have recorded the constants: m. p. 159–161°, spec. rot. −43° (20°, *c* 2, H_2O, D line). Pigman and Isbell[30] record a small, complex mutarotation for L-sorbose.

Mucyldimethane Tetraacetate (VII).[24]—To a chloroform (40 cc.) solution of 1,8-bisdiazomucyldimethane tetraacetate[18] (2.00 g.), in a separatory funnel, was added 8 cc. of 47% hydriodic acid. The mixture was shaken until cessation of nitrogen evolution, diluted with water (40 cc.) and the chloroform layer removed and washed successively with water, aqueous sodium thiosulfate and water. A white crystalline solid was obtained on solvent removal from the dried chloroform solution; yield 1.60 g., m. p. 200–204°. Pure material was obtained on recrystallization from acetone by the addition of absolute ethanol; yield 1.35 g. (78%), m. p. 204–206°. The substance gave a positive iodoform test (iodoform identified by m. p. and mixed m. p.).

Anal. Calcd. for $C_{16}H_{22}O_{10}$: C, 51.21; H, 5.91. Found: C, 51.25; H, 5.85.

Summary

1. An improved demercaptalation procedure for *aldehydo*-D-xylose tetraacetate (I) is described.

2. The tetraacetates of D-xylonyl chloride (III) and of 1-desoxy-1-diazo-*keto*-D-sorbose (IV) have been synthesized. Reaction of the latter with acetic acid led to the synthesis of *keto*-D-sorbose pentaacetate (V), from which D-sorbose (VI) was obtained on saponification.

3. An oxime of *keto*-L-sorbose pentaacetate has been obtained.

4. *keto*-D,L-Sorbose pentaacetate is described.

5. Hydriodic acid reduction of 1,8-bisdiazomucyldimethane tetraacetate yielded mucyldimethane tetraacetate (VII).

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(28) Experimental work by Mr. Evan F. Evans.

(29) M. L. Wolfrom, M. Konigsberg and S. Soltzberg, THIS JOURNAL, **58**, 490 (1936).

(30) W. W. Pigman and H. S. Isbell, *J. Research Natl. Bur. Standards*, **19**, 443 (1937).

COLUMBUS, OHIO RECEIVED SEPTEMBER 29, 1943

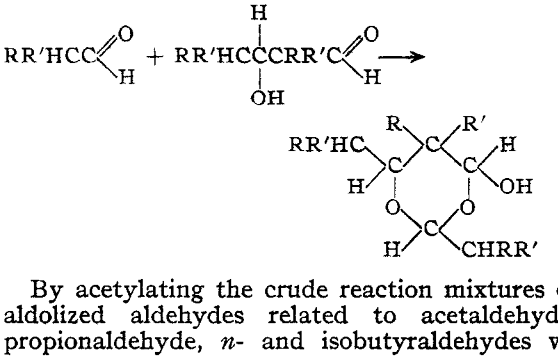
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Aldol Condensation. III. Aldol-aldehyde Addition Products and their Derivatives

BY ROBERT H. SAUNDERS AND M. J. MURRAY

Späth, Lorenz and Freund[1] and Hanschke[2] have recently independently reported the isolation of an addition product of acetaldehyde to aldol, together with the acetate and benzoate of this compound. While this work was still unknown to us, we reported an analogous compound formed by the reaction of isobutyraldehyde with its aldol.[3] Under the circumstances we are reporting the results of our research to date and are concluding our work on this phase of the problem.

The following equation shows the addition of aldehyde to its aldol to form a 1,3-dioxane derivative



I.

By acetylating the crude reaction mixtures of aldolized aldehydes related to acetaldehyde, propionaldehyde, *n*- and isobutyraldehydes we obtained the 6-acetoxy-1,3-dioxanes in about 70% yields. In one instance, namely, that from isobutyraldehyde, we also prepared the 6-methoxy-1,3-dioxane. Physical properties for

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(1) Späth, Lorenz and Freund, *Ber.*, **76B**, 57–68 (1943); *C. A.*, **37**, 4695 (1943).

(2) Hanschke, *Ber.*, **76B**, 180 (1943); *C. A.*, **37**, 5374 (1943).

(3) Saunders, Murray and Cleveland, THIS JOURNAL, **65**, 1714 (1943).

TABLE I

PROPERTIES OF SOME 1,3-DIOXANES

Notation	R	R′	X	B. p., °C.	Mm.	n^{25}_D	d^{25}_4	Mol. ref. Calcd.	Obs.	Mol. wt. Calcd.	Obs.[d]
A	H	H	H			1.4380	1.067	32.52	32.50		
B	Me	H	H	91.5	7	1.4408	1.001	46.38	46.21		
C	H[a]	H	Ac	85.5	10	1.4278	1.068	41.89	41.97	174	166
D	Me	H	Ac	100	7	1.4328	1.009	55.75	55.64		
E	Et	H	Ac	114	3	1.4378	0.9758	69.61	69.50	258	253
F	Me[b]	Me	Ac	93.5	2	1.4355	0.9726	69.61	69.44	258	255
G	Me[c]	Me	Me	110	20	1.4310	0.9220	64.98	64.70	230	225

[a] *Anal.* Calcd. for $C_8H_{14}O_4$: C, 55.2; H, 8.0. Found: C, 55.26; H, 7.83. [b] *Anal.* Calcd. for $C_{14}H_{26}O_4$: C, 65.1; H, 10.1. Found: C, 64.80; H, 9.76. [c] *Anal.* Calcd. for $C_{13}H_{26}O_3$: C, 67.7; H, 11.3. Found: C, 67.59; H, 11.04. Microanalyses performed by Dr. T. S. Ma, University of Chicago. [d] Cryoscopic in benzene.

seven of these compounds are listed in Table I. The R, R′ substituents refer to groups in formula I, and X refers to the group attached to oxygen on position 6.

It is interesting to observe the action of aldolizing conditions on the aldol from isobutyraldehyde: namely, 2,2,4,4-tetramethylaldol. This aldol, of course, is incapable of further aldol condensation and in the presence of cold, dilute alkali immediately begins to dissociate into the aldehyde-aldol equilibrium mixture. However, also catalyzed by base, the isobutyraldehyde formed in this dissociation rapidly reacts with the aldol to produce 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane (H) whose properties were described in a previous communication.[3] This reaction is accompanied by 1,3-dioxane formation between two molecules of the aldol, forming a white solid which is apparently the same material as the paraldol that deposits slowly from 2,2,4,4-tetramethylaldol samples.

The Raman spectra of the 1,3-dioxanes which we have prepared are shown in Table II. The dioxane from *n*-butyraldehyde was the only one encountered that could not be distilled without dissociation. Its spectrum is rather incomplete since the fluorescent material present, most of which was removed with charcoal, did not permit the long exposures needed to obtain good spectrograms of this compound. For the Raman spectrum of H see reference 3. The spectra of A and B will be found listed under the headings "acetaldol" and "propionaldol" in a previous communication.[4]

There are several interesting features of these spectra which it will be well to point out, the first of which concerns the symmetrical breathing frequency of a flexible ring structure such as is found in 1,3-dioxane. This frequency in 1,3-dioxane itself lies at 834 cm.$^{-1}$ and is very intense, certainly the strongest line in the spectrum.[5] As the symmetry of the ring is destroyed by the substitution of different groups, the intensity of this line decreases and finally in highly unsymmetrical compounds ceases to be significant for identification purposes. In the present group of compounds the ring frequency produces a fairly strong line only for the 1,3-dioxane from acetaldehyde and for its acetate.

TABLE II[a]

RAMAN SPECTRA OF SOME SUBSTITUTED 1,3-DIOXANES

G	F	K[b]	E	D	C
Δν I	Δν I	Δν I	Δν I	Δν I	Δν I
132(1b)					
	223(1b)		226(0)		227(1)
	263(1b)				255(1)
303(1vb)		287(2)	291(3)	298(1)	
				337(1b)	
				374(1)	380(1b)
				434(1)	450(2)
476(2)	481(1)			474(3)	481(3)
				512(1)	
	536(1)			542(1)	539(4)
591(1)					
623(1)	643(½)		620(0)	629(1)	627(2)
791(4)	791(3)				
					815(5)
832(1)	838(1)		826(0)	825(1)	834(1)
871(2)	869(2)				
				895(2)	
923(1)	925(3)	906(2)	900(5)	914(3)	
953(3)	962(3)	956(1)	956(1)	947(3)	938(1)
		1019(2)			983(0)
1035(1)		1043(2)	1033(3)	1030(1)	
				1064(3)	
1122(1vb)	1118(0)			1119(1)	1105(1)
1176(3)	1185(2)	1152(2)	1161(3)	1176(3)	1161(3b)
1219(1b)	1208(0)				1220(1)
1248(2)	1248(1)				
			1273(0)		
1300(2)	1308(2)	1303(2)	1300(2)	1290(1b)	1327(1)
					1344(2)
1354(3)	1350(2b)		1382(2)	1368(3b)	1377(2)
		1436(3)	1438(4)	1441(6)	
1453(6)	1460(6)	1455(6)	1457(6)	1464(6)	1450(5)
	1761(2)		1751(2)	1752(2)	1754(2)
2712(1)	2724(1)	2726(1)	2735(1)	2741(1)	
2832(3)					2813(1)
2872(9)	2876(7)	2876(10)	2876(9)	2880(7)	2876(3)
2911(10)			2917(8)		
2958(8)	2939(9)	2928(9b)	2941(10)	2939(10)	2937(10)
2986(7)	2978(9)	2961(5)	2969(6)	2978(6)	2987(6b)

[a] Δν = Raman displacement in cm.$^{-1}$, I = estimated intensity, b and vb = broad and very broad, respectively. [b] 2,4-Dipropyl-5-ethyl-6-hydroxy-1,3-dioxane.

The compounds which were made from isobutyraldehyde contain neopentyl skeletons. A neopentyl group will produce a highly symmetrical vibration, somewhat similar to the breathing frequency of a ring structure, which gives rise to an intense Raman line in the region from 750 to 800 cm.$^{-1}$. The neopentyl vibration in H, F and G produces a strong line at about 790 cm.$^{-1}$ in

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(4) Saunders, Murray, Cleveland and Komarewsky, THIS JOURNAL, **65**, 1309 (1943).

(5) Unpublished results from this Laboratory.

each case; while this vibration for 2,2,4,4-tetramethylaldol, where the neopentyl group is not part of a ring system, drops to 770 cm.$^{-1}$. These two neopentyl lines were extremely useful in following the formation of H in the mixtures of isobutyraldehyde and 2,2,4,4-tetramethylaldol.[3]

The Raman lines in the 1750 cm.$^{-1}$ region for the acetates are due, of course, to the vibrations of the ester carbonyl group. It is interesting to note the similarity of the spectra of these acetates to the spectra of the parent 6-hydroxy-1,3-dioxanes.

Experimental

Preparation of the 6-Acetoxy-1,3-dioxanes.—The parent aldehyde was aldolized as described previously,[3] and the ether separated from the dried reaction product at the water pump. Equal volumes of this crude 1,3-dioxane, anhydrous pyridine, and acetic anhydride were mixed, and the reaction mixture allowed to stand overnight at room temperature. The acetic acid, pyridine, and excess acetic anhydride were then distilled off and the product fractionated under reduced pressure.

Preparation of G.—To 300 g. of 1% anhydrous methyl alcoholic hydrochloric acid was added 60 g. of H. This reaction mixture was sealed up in a 500-cc. flask for eighteen days. At the end of this time the reaction mixture was neutralized, diluted with water, and the organic layer fractionated under reduced pressure. Nineteen grams of the methyl ether was obtained; for physical properties see Table I.

The Aldolization of 2,2,4,4-Tetramethylaldol.—The aldolization of 14.4 g. of 2,2,4,4-tetramethylaldol was performed by the method previously described.[3] The crude product was washed well with water, dried, and freed of ether at the water pump. Distillation of this material produced 8.7 g. of H, and 3.5 g. of a white solid remained in the distilling flask. This white solid after two recrystallizations from petroleum ether melted at 105–107° which is the melting point found for the paraldol of 2,2,4,4-tetramethylaldol after recrystallization from the same solvent. This paraldol does not melt sharply and has a different melting point (within a range of 15°) when recrystallized from different solvents. This is probably due to the presence of several isomeric forms.

The apparatus and experimental technique for obtaining the Raman spectra are the same as were used in previous work.[3] The compounds studied gave very weak spectra so that long exposures were necessary.

Summary

1. The acetates of 2,4-diethyl-5-methyl-6-hydroxy-1,3-dioxane and 2,4-dipropyl-5-ethyl-6-hydroxy-1,3-dioxane, and the acetate and methyl ether of 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane have been prepared and characterized.

2. The Raman spectra of the above compounds, of 2,4-dipropyl-5-ethyl-6-hydroxy-1,3-dioxane, and of 2,4-dimethyl-6-acetoxy-1,3-dioxane are reported.

3. It has been shown that the main product from the aldolization of 2,2,4,4-tetramethylaldol is 2,4-diisopropyl-5,5-dimethyl-6-hydroxy-1,3-dioxane.

CHICAGO, ILL. RECEIVED OCTOBER 8, 1943

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

A Study of the Haloform Reaction

BY RICHARD T. ARNOLD, ROBERT BUCKLES[1] AND JANET STOLTENBERG

Except for halogen-containing intermediates,[2,3] no neutral compounds have been isolated as products from the haloform reaction. In order to establish the structure of the methyl ketone (I) obtained from 5-methoxytetralin by means of the Friedel–Crafts reaction, the substance was treated with an aqueous methanol hypochlorite solution. To our surprise there was obtained, in addition to the small amount of expected carboxylic acid (II), a considerable quantity of a neutral, halogen-free solid whose analysis and molecular weight indicated the formula $C_{13}H_{16}O_3$. An 83% yield of this same compound was obtained if hypobromite solutions were employed. The method of preparation and the constitution of the starting materials permit only two reaonable structures for this formula, namely, III and IV.

It was at first supposed that the neutral substance was the ketol (IV) formed by hydrolysis of the phenacyl chloride which is presumably the first intermediate in the haloform reaction.[2] That this supposition was incorrect was indicated by the stability of the substance toward potassium permanganate, lead tetraacetate and periodic acid. Furthermore, no methane was liberated in the Zerewitinoff test.

Proof of the ester structure III was established by saponification to the acid II and the reconversion of II into III by treatment with diazomethane.

It seems surprising that methyl esters have not been reported previously as products of the haloform reaction since the procedure employed above is a typical one. We now believe that in aqueous methanol solution methyl esters are always formed but are so readily hydrolyzed that their isolation is difficult. In the experiment reported here, the temperature of the reaction mixture was not permitted to rise and the insoluble methyl ester crystallized from the solution as it was formed.

When the haloform reaction was carried out in aqueous dioxane solution (to prevent ester formation), a chlorine-containing acid (V) was formed as the sole product. That this substance was not formed during the haloform reaction but in-

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(1) du Pont Postdoctorate Fellow, 1942–1943.

(2) Fuson and Bull, *Chem. Rev.*, **15**, 275 (1934).

(3) Aston, Newkirk, Dorsky and Jenkins, THIS JOURNAL, **64**, 1413 (1942).