In no case did we obtain a product melting as low as −20°. The solutions for infrared work were obtained by dissolving the freshly prepared crystalline α-hydroxyethyl peracetate in cold chloroform.

Infrared spectra. A Baird-Atomic infrared spectrophotometer Model 4-55 was used in this work. The chloroform solution of peroxide was introduced immediately after preparation into the previously cooled low-temperature cell[10] at 0°. A variable-path length cell was used in the reference beam to compensate for the chloroform absorption. A Teflon spacer cut from 0.020 mm. sheet was used in the cell since the normal lead spacer rapidly decomposed the peroxide.

The decomposition of α-hydroxyethyl peracetate at 0° to acetic acid was followed by allowing the solution to remain in the cell and scanning the carbonyl region periodically. Spectra of several reference compounds were obtained at ambient temperature except for acetaldehyde which was obtained at 0°. The compounds and the position (in microns) of their carbonyl bands are: peracetic acid (5.68); acetic acid (5.82); *t*-butyl peracetate (5.64); *t*-butyl acetate (5.79); and acetaldehyde (5.80).

Acknowledgment. We wish to thank Professor H. H. Wasserman of Yale University for helpful discussions and criticism, and to acknowledge the technical assistance of Mr. C. M. Lovell.

UNION CARBIDE CHEMICALS CO.
RESEARCH DEPARTMENT
SOUTH CHARLESTON, W. VA.

Acetals and Ketals of 1,3-Diols

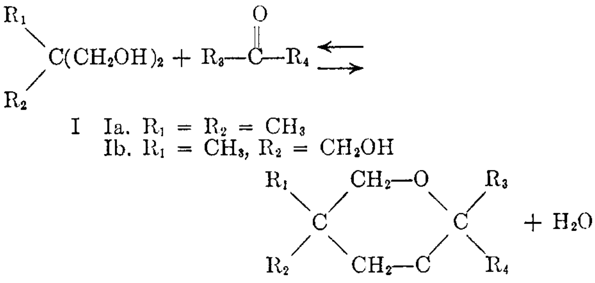
WALTER E. CONRAD, BRUCE D. GESNER, LEONARD A. LEVASSEUR, RAYMOND F. MURPHY, AND HELEN M. CONRAD

Received January 24, 1961

DISCUSSION

Many diacetals of pentaerythritol have been reported.[1] However, the monoacetals, monoketals, and diketals have been relatively neglected. We have investigated the synthesis of monoacetals and monoketals of pentaerythritol, and coadjutantly have prepared many diacetals and diketals of pentaerythritol and acetals and ketals of 2,2-dimethyl-propanediol-1,3 (Ia) and of 2-methyl-2-hydroxymethylpropanediol-1,3 (Ib) (Tables I, II, and III).

Acetals of 1,3-diols can be prepared by refluxing the diol with the aldehyde in the presence of an acid catalyst[1,2] even in the presence of some water.[3] With the exception of acetonals,[4] however, the corresponding ketals cannot be prepared in aqueous solution apparently because the equilibrium between I and II is unfavorable when both R_3 and R_4 are alkyl groups:



I Ia. $R_1 = R_2 = CH_3$
Ib. $R_1 = CH_3$, $R_2 = CH_2OH$

II

We have shown that most of the ketals are easily prepared, however, if the water is removed as it is formed during the reaction, by the use of an azeotropic head. Difficulty was experienced in the preparation of the ketals of benzophenone with Ia or Ib. The reactions were very slow, the yields were low, and much starting diol was recovered. Among carbonyl compounds whose ketals with Ia could not be isolated were fluorenone, benzoquinone, benzoin, benzalacetophenone, and mesityl oxide. Neither could the trisbutyral bis-Ib be formed by reaction of butyraldehyde with Ib in 3:2 molar ratio. Water evolved from all these reactions very slowly, and in part probably was formed by decomposition of the alcohol rather than by ketal formation.

Ethyl butyl ketone reacted readily with Ia or Ib to form ketals, but with pentaerythritol the reaction was very slow. As pentaerythritol is quite insoluble in benzene and ethyl butyl ketone, the reaction was tried with diethylene glycol diethyl ether as a solvent. Although pentaerythritol is quite soluble in the latter at the boiling point, the reaction was still very slow, and a pure product was not isolated.

The preparation of the monoacetals of pentaerythritol and water-insoluble aldehydes presents special problems. Very few of these monoacetals have been reported.[1] The basis of the difficulty is that the pentaerythritol is insoluble in almost all organic solvents. Therefore, if the reaction is conducted with the pentaerythritol and the aldehyde in separate phases, when the monoacetal is formed, it dissolves in the aldehyde phase and quickly reacts further to form the diacetal. Only a few such monoacetals,[1,5] have been made by heterogeneous reaction. In this work it is found that these monoacetals are more conveniently prepared in a homogeneous solution in aqueous dioxane or diethylene glycol diethyl ether (Table III). For example, monobenzal pentaerythritol was prepared in 44% yield (Method B, Experimental).

Monoketals of pentaerythritol cannot be prepared by this method because they are unstable in the presence of water. It would seem that the

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[1] E. Berlow, R. H. Barth, and J. E. Snow, *The Pentaerythritols*, Reinhold Publishing Corp., New York, 1958.

[2] (a) A. Franke and E. Gigerl, *Monatsh.*, **49**, 8 (1928); (b) R. Dvorak and T. M. Lasch, *Monatsh.*, **51**, 59 (1929); (c) R. F. Fischer and C. W. Smith, *J. Org. Chem.*, **25**, 319 (1960); (d) R. I. Meltzer, A. D. Lewis, J. Volpe, and D. M. Lustgarten, *J. Org. Chem.*, **25**, 712 (1960).

[3] (a) H. Schulz and B. Tollens, *Ber.*, **27**, 1892 (1894); (b) A. Skrabal and S. Kalpasanoff, *Ber.*, **61B**, 55 (1928).

[4] A. Skrabal and M. Zlatewa, *Z. physik. Chem.*, **119**, 305 (1926).

[5] E. Bograchov, *J. Am. Chem. Soc.*, **72**, 2268 (1950).

TABLE I

CYCLIC ACETALS AND KETALS OF 2,2-DIMETHYLPROPANEDIOL-1,3[a]

Carbonyl Compound	M.P.	B.P.	Mm.	Yield, %	Method	Formula	Analyses, %
Acetaldehyde	—	58–60	52	28	B	$C_7H_{14}O_2$	Calcd. 64.58 C; 10.84 H
							Found 64.58 C; 10.83 H
Chloroacetaldehyde	—	96–99	34	72	B	$C_7H_{13}O_2Cl$	Calcd. 51.07 C; 7.92 H; 21.53 Cl
							Found 51.15 C; 8.03 H; 21.25 Cl
Propionaldehyde	—	76–78	54	54	B	$C_8H_{16}O_2$	Calcd. 66.61 C; 11.19 H
							Found 67.11 C; 11.48 H
Valeraldehyde	—	91–94	20	65	A	$C_{10}H_{20}O_2$	Calcd. 69.72 C; 11.71 H
							Found 68.19 C; 11.36 H
2-Ethylhexanal	—	57	0.4	16	A	$C_{13}H_{26}O_2$	Calcd. 72.84 C; 12.23 H
							Found 72.81 C; 12.46 H
p-Hydroxybenzaldehyde	135–138	—	—	65	A	$C_{12}H_{16}O_3$	Calcd. 69.20 C; 7.26 H
							Found 70.10 C; 7.77 H
Acetone	—	143	760	72	A	$C_8H_{16}O_2$	Calcd. 66.63 C; 11.18 H
							Found 66.36 C; 10.94 H
Methyl ethyl ketone	—	83–86	45	84	A	$C_9H_{18}O_2$	Calcd. 68.31 C; 11.47 H
							Found 68.42 C; 11.26 H
Ethyl *n*-butyl ketone	—	132	45	60	A	$C_{12}H_{24}O_2$	Calcd. 71.95 C; 12.08 H
							Found 71.92 C; 12.32 H
Benzophenone	84–85	—	—	18	A	$C_{18}H_{20}O_2$	Calcd. 80.56 C; 7.51 H
							Found 80.82 C; 7.83 H

[a] As far as we are aware, the only other acetals of pentaglycol reported in the literature are those of formaldehyde, isobutyraldehyde, heptaldehyde (Ref. 2b), and benzaldehyde (Ref. 2a), and the only ketals are those of cyclopentanone and cyclohexanone (Ref. 8).

TABLE II

CYCLIC ACETALS AND KETALS OF 2-HYDROXYMETHYL-2-METHYLPROPANEDIOL-1,3

Carbonyl Compound	M.P.	B.P.	Mm.	Yield, %	Method	Formula	Analyses, %
Acetaldehyde	—	119–121	19	70	B	$C_7H_{14}O_3$	Calcd. 57.45 C; 9.65 H
							Found 56.18 C; 9.87 H
Chloroacetaldehyde	—	156–161	18	65	B	$C_7H_{13}O_3Cl$	Calcd. 46.54 C; 7.25 H; 19.63 Cl
							Found 46.56 C; 7.62 H; 20.18 Cl
n-Butyraldehyde	—	138–139	19	72	A	$C_9H_{18}O_3$	Calcd. 62.04 C; 10.41 H
							Found 62.46 C; 10.41 H
n-Valeraldehyde	—	156–166	19	46	A	$C_{10}H_{20}O_3$	Calcd. 63.79 C; 10.71 H
							Found 64.44 C; 10.65 H
Hexanal	—	171	23	64	A	$C_{11}H_{22}O_3$	Calcd. 65.31 C; 10.96 H
							Found 65.65 C; 10.83 H
2-Ethylhexanal	—	175–176	22	70	A	$C_{13}H_{26}O_3$	Calcd. 67.78 C; 11.38 H
							Found 67.86 C; 10.98 H
Benzaldehyde	87–89	—	—	66	A	$C_{12}H_{16}O_3$	Calcd. 69.22 C; 7.76 H
							Found 68.80 C; 7.42 H
Acetone	—	135	30	71	A	$C_8H_{16}O_3$	Calcd. 59.97 C; 10.07 H
							Found 59.89 C; 10.60 H
Methyl ethyl ketone	—	99–106	3	35	A	$C_9H_{18}O_3$	Calcd. 62.04 C; 10.41 H
							Found 61.51 C; 10.48 H
Cyclopentanone	—	155–157	17	77	A	$C_{10}H_{18}O_3$	Calcd. 64.48 C; 9.73 H
							Found 64.06 C; 10.23 H
Cyclohexanone	60–61	—	—	53	A	$C_{11}H_{20}O_3$	Calcd. 65.97 C; 10.07 H
							Found 66.08 C; 10.10 H
Benzophenone	103–104	—	—	3	A	$C_{18}H_{20}O_3$	Calcd. 76.03 C; 7.09 H
							Found 76.05 C; 7.29 H
Ethyl *n*-butyl ketone	—	165–166	35	71	A	$C_{12}H_{24}O_3$	Calcd. 66.67 C; 11.13 H
							Found 66.84 C; 11.18 H

monoketals could be prepared from the diketals of pentaerythritol by partial hydrolysis. Indeed the monoketal of pentaerythritol and cyclohexanone was isolated in 12% yield by hydrolysis in a solution of diethylene glycol diethyl ether containing one equivalent of water. The preparation by this method of the monoketal of methyl ethyl ketone failed, apparently because the monoketal was more easily hydrolyzed under these conditions than the diketal.

Certain interesting qualitative observations were made on the uncatalyzed hydrolysis of certain acetals and ketals (Table IV). It has usually been assumed in the past that acetals require an acid

TABLE III

CYCLIC ACETALS AND KETALS OF PENTAERYTHRITOL

Carbonyl Compound	M.P.	B.P.	Mm.	Yield, %	Method	Formula	Analysis, %	
Chloroacetaldehyde (mono)	114–116	—	—	74	B	$C_7H_{13}O_4Cl$	Calcd.	42.76 C; 6.66 H; 18.03 Cl
							Found	42.93 C; 6.53 H; 18.05 Cl
n-Butyraldehyde[a] (mono)	70–71[a]	—	—	41	B	$C_9H_{18}O_4$	Calcd.	56.84 C; 9.47 H
							Found	57.35 C; 9.79 H
n-Valderaldehyde (mono)	80–82	—	—	49	B	$C_{10}H_{20}O_4$	Calcd.	58.82 C; 9.80 H
							Found	58.86 C; 9.82 H
n-Valeraldehyde (bis)	57–58	—	—	31	A	$C_{15}H_{28}O_4$	Calcd.	66.17 C; 10.29 H
							Found	66.25 C; 9.93 H
Hexanal (mono)	80–82	—	—	48	B	$C_{11}H_{22}O_4$	Calcd.	60.55 C; 10.09 H
							Found	60.41 C; 10.30 H
2-Ethylhexanal (bis)	—	157–160	0.4	80	A	$C_{21}H_{40}O_4$	Calcd.	70.72 C; 11.31 H
							Found	71.14 C; 11.21 H
Methyl ethyl ketone (bis)	47–48	95–96	0.5	96	A	$C_{13}H_{24}O_4$	Calcd.	63.90 C; 9.90 H
							Found	63.47 C; 9.62 H
Pentanone-2 (bis)	42–44	115	0.5	96	A	$C_{15}H_{28}O_4$	Calcd.	66.17 C; 10.36 H
							Found	65.59 C; 9.66 H
Pentanone-3 (bis)	38–40	124	0.8	82	A	$C_{15}H_{28}O_4$	Calcd.	66.17 C; 10.36 H
							Found	66.24 C; 9.81 H
Cyclohexanone (mono)	122–124	—	—	12	C	$C_{11}H_{20}O_4$	Calcd.	61.11 C; 9.25 H
							Found	61.24 C; 9.49 H

[a] Ref. 9 reported a m.p. of 116° for this compound.

catalyst for hydrolysis. This is certainly the case for the formals of pentaerythritol,[4,6] and was found to be the case for the monoacetal and monobutyral. However, it was found that the monovaleral and monohexanal of pentaerythritol and the acetals of Ia and Ib are quite easily hydrolyzed by boiling water. As for the ketals, it has previously been reported[4] that the acetonals of pentaerythritol are hydrolyzed by boiling water. This behavior was found to hold for the acetonal of Ia and for the acetonal and cyclpentanone ketal of Ib.

EXPERIMENTAL[7]

Preparation of acetals and ketals. Method A. A mixture of 34.0 g. of pentaerythritol (0.25 mole) and 43.0 g. (0.55 mole) of methyl ethyl ketone with 1 g. of *p*-toluenesulfonic acid and 50 ml. of benzene was refluxed 5 hr., using an azeotropic head to remove water as it was formed. During this time, 9.0 ml. of water was collected. Triethylamine (0.54 g.) was added. The benzene was distilled at 20 mm. and 58.7 g. (96%) of bismethyl ethyl ketal of pentaerythritol was collected at 95–96° at 0.8 mm.

This procedure was successful, interestingly, even for acetone, as long as the material entering the azeotropic head was a one-plate distillate. If the experiment was done with a Vigreux column ahead of the azeotropic head, only one phase was obtained in the distillate, consisting of relatively pure acetone.

Amberlite IR-120 anion exchange resin (H form) was less reliable as a catalyst than the toluene sulfonic acid.

Those ketals for which both melting points and boiling points are reported were recrystallized from ligroin after distillation. The other solid compounds were isolated by recrystallization from benzene or benzene plus ligroin, except for the ketal of benzophenone and Ia, for which ethanol plus water was used.

The previously reported[8] ketal of Ia and cyclohexanone was found to have a b.p. 223–225° at 760 mm.

Method B. Synthesis of acetals in aqueous solution. To a mixture of 125 ml. of dioxane, 125 ml. of water, and 21.5 g. (0.25 mole) of *n*-valeraldehyde, 34.0 g. (0.25 mole) of pentaerythritol and 1 g. of Amberlite IR-120 were added. After 2 hr. refluxing, the Amberlite was filtered off, and 230 ml. of solvent distilled at 20 mm. The residue, on filtration and recrystallization from toluene, yielded 24.6 g. (52%) of monovaleral pentaerythritol, m.p. 79–83°, raised to 80–82° by recrystallization from benzene.

The monobutyral of pentaerythritol could not be separated from the dibutyral by simple recrystallization from an organic solvent. The separation was achieved by extracting the residue with water after removal of the dioxane, filtering off the dibutyral, evaporating the water, and then recrystallizing the relatively pure monobutyral from benzene. The melting point was 70–71°, compared to the 116° previously reported.[9]

With water soluble aldehydes, the dioxane was omitted. With acetaldehyde and propionaldehyde, the reaction was conducted at 70° in a pressure flask with shaking (Parr-Adams apparatus).

Method C. Hydrolysis of biscyclohexanone ketal of pentaerythritol to the monoketal. A solution of 29.6 g. (0.1 mole) of the biscyclohexanone ketal of pentaerythritol[10] in 150 ml. of diethylene glycol diethyl ether was refluxed in the presence of 1 g. of Amberlite IR-120 while water was being added dropwise to it. Simultaneously the water-cyclohexanone azeotrope was distilled off through a Vigreux column. When 9.8 g. (0.1 mole) of cyclohexanone had been collected in this manner, the reaction was stopped. The Amberlite and most of the unchanged pentaerythritol were removed by filtration, the solvent distilled *in vacuo*, and the residue recrystallized from benzene, yielding 2.5 g. (12%) of monocyclohexanone ketal of pentaerythritol (m.p. 122–124°). A total of 10.4 g. of impure pentaerythritol, m.p. 200–245°, was recovered.

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(6) L. Orthner and G. Freyss, *Ann.*, **484**, 131 (1930).

(7) Microanalyses were performed by Weiler and Strauss Laboratories, Oxford, England; melting points and boiling points were uncorrected.

(8) M. S. Newman and R. J. Harper, *J. Am. Chem. Soc.*, **80**, 6350 (1958).

(9) Deutsche Gold- und Silber Scheideanstalt, Ger Pat. **828,105** (Jan. 14, 1952); ref. 1, p 150.

(10) H. J. Backer and H. B. J. Schurink, *Rec. trav. chim.*, **50**, 1066 (1931); *Chem. Abstr.*, **26**, 964 (1932).

The monobutyral and the monovaleral of pentaerythritol were also prepared in good yield by this method.

Uncatalyzed hydrolyses of acetals and ketals. A solution of 0.054 mole of acetal or ketal in a mixture of 15 ml. of water and 15 ml. of dioxane was refluxed for 2 hr. If acetone was formed, it was distilled. The reaction mixture was then distilled. The carbonyl compound was isolated either as such, or as the dinitrophenylhydrazone in the first portion of the distillate. The dehydrated reaction mixture was either distilled or extracted with benzene to recover the unchanged acetal. The diols are insoluble in cold benzene. The acetonal of Ia and the acetonal and cyclopentanone ketal of Ib were hydrolyzed extensively or completely under these conditions. The results for some acetals are summarized in Table IV; only the 0 and 100% figures have quantitative significance.

TABLE IV

HYDROLYSIS OF ACETALS AND KETALS

	Recovered Compounds, Mole %		
Acetal of	Starting material	Carbonyl compound	Diol
2,2-Dimethylpropanediol-1,3 and			
Acetaldehyde	—	13	32
n-Valeraldehyde	—	—	40
2-Methyl-2-hydroxymethylpropanediol-1,3 and			
Acetaldehyde	—	—	25
n-Butyraldehyde	—	4	18
Pentaerythritol and			
Acetaldehyde	100	—	0
n-Butyraldehyde	90	—	0
n-Valeraldehyde	72	—	14
n-Hexanal	—	—	25

Acknowledgment. We gratefully acknowledge grants for the support of undergraduate research from the Research Corp., the National Science Foundation, and the Petroleum Research Fund administered by the American Chemical Society. A few of the acetals and ketals reported here were synthesized by Messrs. Ernest E. Bedard, Robert J. Bucko, and by Miss Nancy L. Hare.

DEPARTMENT OF CHEMISTRY
BRADFORD DURFEE COLLEGE OF TECHNOLOGY
FALL RIVER, MASS.

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cis- and *trans*-Methyl Propenyl Ethers

WILLIAM L. HOWARD, ELIZABETH C. JACOBSEN, AND ROBERT A. NEWTON

Received January 27, 1961

Methyl propenyl ether has been mentioned in the literature,[1] but isolation of the *cis* and *trans* isomers has not been reported. During some studies on derivatives of propylene oxide several years ago, two of us separated and identified these isomers by gas chromatography. Configurations were assigned to the components giving the two peaks on the basis of infrared spectra of partially separated mixtures obtained by fractional distillation. Interest was renewed in separation of the isomers by the appearance of a paper[2] on the preparation of crystalline polymers of alkyl propenyl ethers in which it was stated that the *cis* and *trans* methyl isomers could not be separated by distillation.

The mixture of isomers to be separated was obtained by vapor phase pyrolysis of propionaldehyde dimethyl acetal and contained the *cis* and *trans* forms in a ratio of about 5 : 2. The samples for characterization were obtained by successive fractional distillations in a packed column, and each isomer was over 99% pure by gas chromatography and infrared spectrophotometry. The behavior of the mixture in a single batch distillation was determined with a concentric tube column. Structures assigned on the basis of infrared spectra[3] confirmed the expectation that the lower boiling ether is the *cis* isomer, the higher *trans*, shown by their strong absorptions at 13.8 μ and 10.3 μ respectively.

The use of the commercially available ketal 2,2-dimethoxypropane[4] as a water scavenger and source of methoxyl groups provides a convenient laboratory method for the preparation of methyl acetals of aldehydes. Good yields can be obtained because of a favorable equilibrium constant, and the coupling of the endothermic hydrolysis of the ketal with the exothermic formation of the acetal results in a very mild but fast reaction.

EXPERIMENTAL

Propionaldehyde dimethyl acetal. Propionaldehyde (1160 g., 20.0 moles), acetone dimethyl ketal (2040 g., 19.6 moles), methanol (45 g., 1.5 moles), and *p*-toluenesulfonic acid (0.3 g.) were combined and allowed to stand overnight.

TABLE I

PHYSICAL PROPERTIES OF METHYL PROPENYL ETHERS

Property	*cis*	*trans*
Vapor pressure, mm. (T°)[a]	280(20) 620(40) 754(45)	250(20) 535(40) 745(49)
ΔH_v, kcal./g.-mole (25°)[b]	7.28	6.96
F.P.°	−114.41	−99.71
n_D^{25} [a]	1.3884	1.3870
Density, g./cc. (T°)	0.7663(25) 0.7724(20)	0.7754(25) 0.7813(20)
Viscosity, centistokes (20°)	3.45	3.48

[a] Lit.[1b] b.p. 45–47°, n_D^{25} 1.3850. [b] Heat of vaporization calculated from Cox charts.

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(1)(a) Ruhrchemie A.-G. (Walter Rottig and Otto Liethen, inventors), Ger. Patent **906,517**, March 15, 1954; (b) Roche Products Ltd., Brit. Patent **756,632**, Sept. 5, 1956.

(2) R. F. Heck and D. S. Breslow, *J. Polymer Sci.*, 41, 520 (1959).

(3) G. J. Dege, R. L. Harris, and J. S. MacKenzie, *J. Am. Chem. Soc.*, 81, 3374 (1959).

(4) The Dow Chemical Company.