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

Acetal of	Recovered Compounds, Mole %		
	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

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cis- and *trans*-Methyl Propenyl Ethers

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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)	250(20)
	620(40)	535(40)
	754(45)	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)	0.7754(25)
	0.7724(20)	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.

TABLE II

Analytical Distillation of Mixed Ethers

		Composition, ml.[a]					
Fraction	B.P.	*cis*-Ether	*trans*-Ether	Methanol	Carbonyl Compounds[b]	Other Impurities	Total
1	37-45	21.4	0.8	2.0	0.2	0.1	24.5
2	45	39.8	3.4	0.1	0.2	0.0	43.5
3	45-48	1.8	3.7	0.0	0.0	0.0	5.5
4	49	0.1	16.8	0.1	0.0	0.0	17.0
Residue		0.0	0.8	0.0	0.5	4.7	6.0

[a] Composition determined by infrared analysis. [b] Calculated as acetone.

The reaction mixture was then neutralized with 0.3 g. of sodium methoxide and distilled with fractionation. The following fractions were collected: I, b.p. 50-89°, 1580 g.; II, b.p. 89°, 1490 g.; residue, 95 g. Analysis of fraction I by vapor phase chromatography showed that it consisted of 50 g. of propionaldehyde (0.9 mole), 1095 g. of acetone (19.0 moles), 170 g. of methanol (5.3 moles), 50 g. of acetone dimethyl ketal (0.5 moles), and 215 g. of propionaldehyde dimethyl acetal (2.1 moles). Analysis of the residue showed that it contained 5 g. of the acetal, and higher boiling materials. Fraction II was propionaldehyde dimethyl acetal (1490 g., 14.4 moles, 73% yield). Total yield of the acetal was 84%.

Pyrolysis of acetal to methyl propenyl ethers. The pyrolysis column was a 65-cm. glass tube (28 mm. I.D.) wrapped with a nichrome heating wire and equipped with five equally spaced thermocouple wells. The first 5 cm. was packed with glass wool to serve as a preheater. The remainder of the column was packed with berl saddles which had been washed with a 1% aqueous solution of phosphoric acid and dried. Propionaldehyde dimethyl acetal (420 g., 4.0 moles) was passed through the column at 300-325° at a rate of 65-75 ml./hr. The pyrolyzate was collected in a stirred receiver containing 1.0 g. of sodium methoxide in 50 ml. of methanol. Chromatographic analysis showed 81% conversion to methyl propenyl ethers. The pyrolyzate was combined with an equal volume of toluene and washed three times with a total of 400 ml. of dilute aqueous sodium hydroxide. The toluene layer was separated, dried over potassium carbonate, and distilled. The fraction boiling up to 60° (235 g.) was collected by distillation and found by chromatographic analysis to consist almost entirely of methyl propenyl ethers with a ratio of *cis* to *trans* isomers of approximately 5:2. Yield based on unrecovered acetal was nearly quantitative.

Separation of cis and trans isomers. The mixed ethers were distilled on a 1200 × 19 mm. column packed with $^1/_{16}$ in. glass helices with a reflux ratio of 50:1. End fractions containing 80% or more of one isomer were collected, and middle fractions were re-distilled. These 80% fractions were combined and redistilled to give fractions 95% pure or better which were combined and redistilled. When sufficient amounts of each isomer were obtained for characterization, chromatographically better than 99% pure, distillation was discontinued. The physical properties were determined on these products and are summarized in Table I.

A 96.5-ml. batch of the mixed isomers was analytically distilled on a concentric tube column having 145 theoretical plates at total reflux. The column was operated at a reflux ratio of 100:1 during the day and total reflux overnight for approximately 30 days. Results of the distillation are summarized in Table II.

Anal. Calcd. for C_4H_8O: C, 66.63; H, 11.18. Found for *cis*: C, 66.43; H, 10.99. Found for *trans*: C, 66.68; H, 11.21.

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Preparation and Reactions of 2,4-Tolylene Diisothiocyanate

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The patent literature refers to the formation of polythiourethanes from diisothiocyanates and various difunctional compounds possessing active hydrogen. The objective of this work was to prepare 2,4-tolylene diisothiocyanate and to investigate its reactions with diols, polyols and diamines in a preliminary way. A method similar to that of Connolly and Dyson[5] was chosen for the preparation.

2,4-Tolylene diisothiocyanate[1,2] has been prepared by heating 2,4-tolylene-ω-diphenyldithiourea with concentrated hydrochloric acid and from 2,4-tolylenediamine and thiophosgene.[3]

Lellmann[4] heated 2,4-tolylenediamine with ammonium thiocyanate at 120-130° to obtain this product. In all of these preparations the yields were low.

Phenyl isothiocyanate[5] has been made by treating aniline dissolved in hydrochloric acid with stannous chloride and perchloromethyl mercaptan.

Yields of 2,4-tolylene diisothiocyanate obtained by the method described herein using perchloromethyl mercaptan were low. The product consisted of yellow needles. Much unidentified dark colored

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(1) O. Billeter and A. Steiner, *Ber.*, **18**, 3294 (1885).

(2) R. Lussy, *Ber.*, **8**, 669 (1875).

(3) A. Steiner, *Ber.*, **20**, 230 (1887).

(4) E. Lellman, *Ann.* 221, 10 (1883).

(5) J. M. Connolly and G Malcom Dyson, Jr., *Chem. Soc.*, 679 (1935).