

resolve the dimer isomers with 30% D.C. 710 Silicone Oil substrate were unsuccessful. Retention time ratios to cyclopentadiene dimer as standard, of the methylcyclopentadiene dimer isomers over D.C. 550 Silicone Oil at 107° are included in Table IV.

*Dimerization.* Methylcyclopentadiene monomer mixtures of desired composition were kept in a 60° waterbath. Dimerization was practically complete within 2-3 hr.

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[CONTRIBUTION FROM THE ORGANIC BASIC RESEARCH LABORATORY, THE DOW CHEMICAL COMPANY]

## Preparation of Ketals from 2,2-Dimethoxypropane<sup>1</sup>

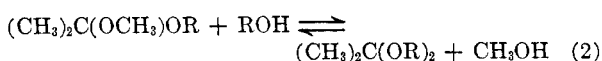
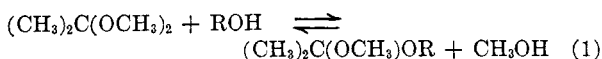
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Methods are given for preparing symmetrical and mixed ketals by alkoxy and ketone interchanges between 2,2-dimethoxypropane and alcohols, ketones, and other ketals. Properties of twenty-one ketals are given.

Acetone dimethyl acetal (2,2-dimethoxypropane) is now readily available<sup>2</sup> and transketalization methods have been developed by which it can be used to prepare a variety of other ketals. The methods comprise interchanging the alkoxy or ketone groups in a slightly acid medium, and both kinds of groups can, in effect, be interchanged simultaneously in the same mixture. Both symmetrical and mixed ketals, RR'C(OR'')<sub>2</sub> and RR'-C(OR'')OR''', can be obtained in good yields by proper choice of conditions. Occasional instances of the use of alkoxy interchange are found in the literature<sup>3</sup> but the reaction does not seem to have been studied extensively. The ketone interchanges are similar to the reactions with orthoesters studied by MacKenzie and Stocker.<sup>3a</sup> Mixed ketals have been obtained previously in isolated instances.<sup>4</sup> The use of 2,2-dimethoxypropane in preparing ketals avoids the necessity of obtaining the less accessible orthoesters or substituted acetylenes required by previous methods.<sup>3</sup>

Acidification of a mixture of 2,2-dimethoxypropane and an alcohol quickly establishes the equilibria (1), (2), and (3).



By distilling the methanol formed, the position of equilibrium can be shifted far in the direction of the new ketals. Methanol and 2,2-dimethoxypropane form a binary azeotrope (b.p. 61°, 56.5% dimethoxypropane by weight), but this is easily broken by using hexane or benzene as a solvent. With the methanol these hydrocarbons form lower-boiling azeotropes which are practically free of 2,2-dimethoxypropane. By their use the reactions can be brought nearly to completion at moderate temperatures without appreciable loss of 2,2-dimethoxypropane. These azeotrope relations also exist at reduced pressures so that low reaction temperatures can be maintained for preparing heat-sensitive ketals.

The mixed ketals are obtained from reaction (1) by using only one mole of alcohol per mole of 2,2-dimethoxypropane or other ketal. However, the simultaneous occurrence of reaction (3) limits the yield of the mixed ketal. If R is a lower primary alkyl radical, the methoxy and alkoxy groups will be distributed statistically as in the redistribution reaction of Calingaert and Beatty<sup>5</sup> and the theoretical yield of mixed ketal will be 50%. With the alkyl radical sterically or electronically considerably different from methyl, yields of the mixed ketals can exceed 50%. The higher symmetrical ketal is a usual by-product of the preparation of the mixed ketal. Two or more moles of alcohol per mole of 2,2-dimethoxypropane give predominantly the symmetrical ketal with small amounts of mixed ketal depending on the completeness of removal of the methanol.

The redistribution in reaction (3) has been demonstrated in both directions with acetone methyl and allyl ketals. The final ratio of mixed to symmetrical ketals was 2:1:1. In a simple mixture of ketals of the same ketone the redistri-

(1) Presented in part at the Gordon Research Conference on Organic Reactions and Processes, July 1958.

(2) The Dow Chemical Company, Midland, Mich.

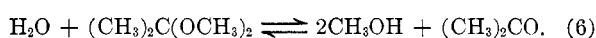
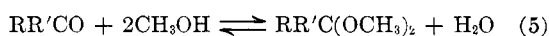
(3) Reviews are given in (a) C. A. MacKenzie and J. H. Stocker, *J. Org. Chem.*, **20**, 1695 (1955) and (b) R. B. Wagner and H. D. Zook, *Synthetic Organic Chemistry*, John Wiley and Sons, Inc., New York, 1953, Chap. 8.

(4) (a) C. D. Hurd and M. A. Pollack, *J. Am. Chem. Soc.*, **60**, 1905 (1938); (b) R. Alquier, *Bull. soc. chim.*, **10**, 197 (1943).

(5) G. Calingaert and H. A. Beatty, *Organic Chemistry, An Advanced Treatise*, Vol. II, 2nd ed., H. Gilman, Ed., John Wiley and Sons, Inc., New York, 1947, Chap. 24.

bution of alkoxy groups occurred rapidly in all of the examples studied. However, when a mixture of acetone dimethyl ketal and cyclohexanone dipropyl ketal was acidified and allowed to stand for thirty minutes before being made basic, distillation of the mixture resulted in almost quantitative recovery of the starting materials. But with methanol added to the mixture under the same conditions, six ketals and propyl alcohol were obtained in approximately the amounts required by the redistribution reaction. This behavior strongly suggests that a protonated alcohol molecule figures prominently in the mechanism of this reaction. The fact that the reaction evidently requires the presence of alcohol when the alkylidene groups are different but not when they are alike is still puzzling.<sup>5a</sup>

Methyl ketals of other ketones are obtained by acidifying a mixture of a ketone, methanol, and 2,2-dimethoxypropane and removing the acetone by distillation as it is formed. The reaction is very slow when care is taken to exclude alcohols or water, but it is fast when methanol is present. The rate increases with alcohol concentration. It therefore appears that the interchange proceeds by the coupled reactions



There is evidence that ketals decompose to some extent to alcohols and unsaturated ethers on acidification,<sup>6,7</sup> reaction (7)



and these traces of alcohol may account for the slow reaction observed when mixtures initially free of alcohol and water are acidified. In its requirement for alcohol this reaction resembles that of orthoesters and ketones.<sup>3a,8</sup> MacKenzie and Stocker propose an elaborate mechanism for the interaction of alcohols, ketones, and orthoesters,<sup>3a</sup> and it is quite possible that some ketal is formed in that way. A similar mechanism may also exist for the reaction of alcohols, ketones, and ketals. However, it is now known that ketals can be prepared in good yield and at least moderate (10–40%) conversion<sup>9</sup> directly from ketones and

(5a) The referee has pointed out that a possible explanation may lie in the relative ease of formation of unsaturated ethers from the ketals involved. Such ethers are possible intermediates in transketalizations of this type.

(6) D. B. Killian, G. F. Hennion, and J. A. Nieuwland, *J. Am. Chem. Soc.*, **57**, 544 (1935).

(7) H. P. Crocker and R. H. Hall, *J. Chem. Soc.*, **1955**, 2052.

(8) H. E. Carswell and H. Adkins, *J. Am. Chem. Soc.*, **50**, 235 (1928).

(9) (a) J. H. Brown, Jr., and N. B. Lorette, The Dow Chemical Company, U. S. Patent, **2,827,494**, March 18, 1958. (b) R. E. McCoy, A. W. Baker, and R. S. Gohlke, *J. Org. Chem.*, **22**, 1175 (1957). (c) N. B. Lorette, W. L. Howard, and J. H. Brown, Jr., in press, *J. Org. Chem.*

alcohols. The concept of coupled reactions of hydrolysis of one ketal (or orthoester) by the water resulting from direct formation of another ketal provides an alternate and possibly more likely mechanism for these reactions.

Ketals of ketones other than acetone and alcohols other than methanol can be made in a single reaction mixture by coupling their formation, reaction (8), with the hydrolysis of 2,2-dimethoxy-



propane, reaction (6). By conducting the reaction in benzene, both acetone and methanol can be simultaneously removed by distillation to shift the equilibrium, because of the proximity of the boiling points of acetone and the benzene-methanol azeotrope. Some mixed ketal,  $RR'C(OCH_3)OR''$ , may be obtained in this procedure, depending on the equilibrium constant of reaction (8) and the effectiveness of the distillation apparatus. Other interchanges such as reactions (1), (2) and (3) undoubtedly occur simultaneously in this procedure. This reaction closely resembles that of ketones, orthoesters, and alcohols studied by MacKenzie and Stocker.<sup>3a</sup>

Under acid conditions ketals can be decomposed according to reaction (7)<sup>3a,6,7</sup> and in some cases this reaction occurs at an appreciable rate at temperatures in the vicinity of 50°. Because they boil at low temperatures, the lower unsaturated ethers so produced will distill from the reaction zone and constitute a serious loss if they are formed in appreciable amounts. Both the lower and higher ethers will also polymerize in the presence of acid, especially if R is H. Therefore, the preparative reactions of this paper are best carried out under mild conditions, and the acid catalyst should be neutralized before isolation of the products.

Other ketals than those of acetone or methanol can enter these exchange reactions. Ketals of aliphatic, alicyclic, and aromatic ketones and a variety of alcohols have been used. Other functional groups which are stable to the mild conditions of acidity and temperature used can be present and ketals containing these groups can be produced. Cyclohexanone dimethyl ketal can be obtained in good yield from methanol and cyclohexanone,<sup>9b</sup> and in high yield when the reaction is coupled with the hydrolysis of 2,2-dimethoxypropane. It enters the alcohol interchange reactions readily and is a good starting material for other ketals of cyclohexanone. Dimethyl ketals of acetophenone, butanone, and the pentanones have been prepared and react similarly. Combinations of these ketone and alcohol interchanges thus provide a general method for the preparation of many ketals. The properties and method of preparation of a number of ketals obtained in this way are given in Table I.

TABLE I  
PREPARATION AND PROPERTIES OF KETALS RR'(OR)''OR'''

Ketone	Ketal		R'''	Method	Yield, %	B.P. <sup>o</sup>	mm.	n <sub>D</sub> (T)	Density g./ml. (T)	$\Delta H_p^a$ kcal./g.- mole	Analyses			
	R''	R'''									Calcd.		Found <sup>b</sup>	
											C	H	C	H
Acetone	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>		A <sup>m</sup>	37	54	160	1.3811 (25)	0.834 (25)	8.4	61.0	11.9	61.1	11.8
	C <sub>2</sub> H <sub>5</sub>	C <sub>2</sub> H <sub>5</sub>		A	82	45	60	1.3861 (25) <sup>e</sup>		9.4				
	CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>		B	34	58	82	1.3902 (25)	0.835 (25)	10.8	63.6	12.2	63.8	12.1
	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>		A (B) <sup>m</sup>	78 (20)	78	54	1.3995 (25) <sup>d</sup>	0.828 (25)	11.7				
	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>		B	34	59	33	1.3980 (25)	0.836 (25)	10.9	65.7	12.4	65.6	12.5
	C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub>		A	82	89	20	1.4105 (25) <sup>e</sup>	0.831 (25)	13.6	70.2	12.9	70.2	13.0
	CH <sub>3</sub>	Allyl		B (C)	66 (48)	49	50	1.4040 (24)	0.859 (22)	9.8	64.6	10.8	64.8	10.8
	Allyl	Allyl		A	75	59	20	1.4228 (25)	0.866 (25) <sup>f</sup>	11.7	69.2	10.3	69.5	10.5
	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> Cl		A <sup>m</sup>	37	61	20	1.4219 (25)	1.022 (25)		47.2	8.6	47.0	8.6 <sup>g</sup>
	CH <sub>2</sub> CH <sub>2</sub> Cl	CH <sub>2</sub> CH <sub>2</sub> Cl		A	70	75	2	1.4513 (24)	1.132 (24)		41.8	7.0	42.1	7.1 <sup>h</sup>
Butanone	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>		A	55	40	8	1.4025 (24)	0.915 (24)		56.7	10.9	56.5	10.5
	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>		A <sup>m</sup>	27	82	7	1.4123 (24)	0.959 (25)		56.2	10.5	56.2	10.7
	CH <sub>3</sub>	Allyl		B (E) <sup>m</sup>	41 (14)	68	50	1.4146 (24)	0.867 (24)	10.9	66.6	11.2	66.7	11.2
	Allyl	Allyl		E	39	94	50	1.4300 (24)	0.872 (24)	11.8	70.6	10.7	70.8	10.9
	Allyl	Allyl		E	57	87	20	1.4343 (25)	0.877 (25)	12.1	71.7	10.9	71.8	10.9
	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>		E	63	62	1 <sup>i</sup>	1.4752 (25)	0.937 (25)		75.6	10.0	75.7	10.0
	Allyl	Allyl		E	53	98	20	1.4535 (24)	0.930 (24)	13.5	72.5	10.0	72.5	10.2
	CH <sub>3</sub>	CH <sub>3</sub>		D	95	63	20	1.4370 (25)	0.947 (25) <sup>j</sup>	11.2				
	CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>		C	50	87.5	19	1.4388 (22)	0.922 (25)		69.7	11.7	70.1	12.2 <sup>k</sup>
	C <sub>3</sub> H <sub>7</sub>	C <sub>3</sub> H <sub>7</sub>		A	86	103	12	1.4393 (24)	0.900 (25)	13.6	71.9	12.1	72.2	12.2
Cyclohexanone	Allyl	Allyl		E	74	98	10	1.4603 (24)	0.936 (24) <sup>l</sup>	13.6				

<sup>a</sup> Heat of vaporization calculated from Cox charts. <sup>b</sup> Average of duplicates which agreed within 0.3%. <sup>c</sup> Lit.<sup>7</sup> b.p. 113°,  $n_D^{20}$  1.3886, <sup>d</sup> Lit.<sup>7</sup> b.p. 91°,  $n_D^{20}$  1.4026. <sup>e</sup> Lit.<sup>10</sup> b.p. 64° (3),  $n_D^{20}$  1.4120. <sup>f</sup> Lit.<sup>14</sup> b.p. 61° (26),  $n_D^{20}$  1.4254,  $d_4^{20}$  0.870. <sup>g</sup> Cl: Calcd. 23.2; found 23.1. <sup>h</sup> Cl: Calcd. 35.3; found 35.1. <sup>i</sup> Lit.<sup>13</sup> b.p. 112–115° (10). <sup>j</sup> Lit.<sup>11</sup> b.p. 54–56° (13),  $n_D^{19.2}$  1.4416,  $d_4^{19.2}$  0.9528. <sup>k</sup> Analyzed 95% pure by vapor chromatography; mass and infrared spectra consistent with assigned structure. <sup>l</sup> Lit.<sup>11</sup> b.p. 106–108° (13),  $n_D^{17.5}$  1.4632,  $d_4^{17.5}$  0.9410. <sup>m</sup> Signifies that ketal was obtained as by-product of indicated method.

## EXPERIMENTAL

**Materials.** Acetone dimethyl acetal (2,2-dimethoxypropane) supplied by The Dow Chemical Company was used as received. The other materials were commercial products. The acid catalyst usually was *p*-toluenesulfonic acid monohydrate (Eastman Kodak Co.). The materials were used without being dried, except that where indicated the *p*-toluenesulfonic acid was dried by recrystallization from a toluene solution. Yields could possibly be improved in some cases by careful drying of the reactants.

**Alcohol interchange with 2,2-dimethoxypropane. Method A. Acetone dibutyl ketal.** Butyl alcohol (489 g., 6.60 moles), 2,2-dimethoxypropane (312 g., 3.00 moles), benzene (1.0 l.), and *p*-toluenesulfonic acid (0.2 g.) were combined and the mixture was distilled with fractionation, giving 570 ml. of distillate boiling from 57° to 59°. Addition of a l. of water to the distillate left 340 ml. of benzene phase, indicating the initial presence of 230 ml. of water-soluble material (theoretical for methanol, 243 ml.). The reaction mixture was cooled and a solution of 0.5 g. of sodium methoxide in 25 ml. of methanol was added rapidly with stirring in order to achieve nearly instantaneous neutralization. Distillation was resumed and the pressure was reduced as necessary so that the temperature in the flask did not exceed 130°. The following fractions were collected for examination: I, b. 36–45° (18 mm.),  $n_D^{25}$  1.3992, 62 g.; II, b. 45–88° (18 mm.), 9 g.; III, b. 88° (18 mm.) to 90° (19.5 mm.),  $n_D^{25}$  1.4105, 460 g.; residue, 31 g. Fraction I was recovered butyl alcohol and fraction III was acetone dibutyl ketal, 82% yield (lit.: b.p. 64.0° (2.3 mm.),  $n_D^{20}$  1.4128;<sup>3a</sup> and b.p. 64–64.5 (3 mm.),  $n_D^{20}$  1.4120<sup>10</sup>).

**Mixed ketals by alcohol interchange. Method B. Butanone allyl methyl ketal.** Allyl alcohol (58 g., 1.0 mole), butanone dimethyl ketal (118 g., 1.00 mole), 200 ml. of benzene, and 0.2 g. of *p*-toluenesulfonic acid were combined and distilled at atmospheric pressure with fractionation until the head temperature was 61° at which time 110 ml. of distillate had been obtained. The distillation was interrupted and the reaction solution was made basic by the addition of 0.3 g. of sodium methoxide dissolved in 10 ml. of methanol. Distillation was continued at atmospheric pressure until the temperature in the flask reached 122°, at which time the pressure was reduced to 100 mm. The following three fractions were obtained (principal component, boiling range at 100 mm., mid-range boiling point, number of moles): butanone dimethyl ketal, 42–68°, 51°, 0.17; butanone allyl methyl ketal, 68–102°, 84°, 0.41; butanone diallyl ketal, above 102°, 111° (third plateau on boiling point curve, distillation stopped), 0.30 (distillate plus residue; the refractive index of the residue at 24° was 1.4310, compared to  $n_D^{25}$  1.4300 for butanone diallyl ketal). The losses comprised 0.12 mole of butanone moiety and 0.25 mole of methoxyl indicating a loss of 0.12 mole of the lower symmetrical ketal, probably by pyrolysis to unsaturated ether. The yield of mixed ketal was 41%, or 82% of the theoretical 0.50 mole predicted by the redistribution reaction.

**Mixed ketals from symmetrical ketals. The redistribution reaction with ketals. Method C. a. Acetone allyl methyl ketal.** Acetone dimethyl ketal (208 g., 2.00 moles) and acetone diallyl ketal (312 g., 2.00 moles) were mixed and acidified with 0.1 g. of *p*-toluenesulfonic acid. After 15 min. at 24° the solution was made basic by the addition of 0.3 g. of sodium methoxide dissolved in 10 ml. of methanol. Fractional distillation on a 1000 × 25 mm. column packed with 1/8-in. glass helices gave 99 g. (0.95 mole) of acetone dimethyl ketal boiling at 43° (200 mm.), 250 g. (1.92 moles) of acetone allyl methyl ketal boiling at 81° (200 mm.), and 148 g. (0.95 mole) of acetone diallyl ketal boiling at 77° (50 mm.). The redistribution reaction requires a mole ratio of 1:2:1. The yield of mixed ketal was thus 96%.

**b. Disproportionation of mixed ketals.** Acetone allyl methyl ketal (520 g., 4.00 moles) was acidified with 0.2 g. of *p*-toluenesulfonic acid and allowed to stand for 15 min. at 24°. It was then made basic by adding 0.3 g. of sodium methoxide in 10 ml. of methanol and distilled at 200 mm., giving 103 g. (0.99 mole) of acetone dimethyl ketal boiling at 43° and 262 g. (2.02 moles) of acetone allyl methyl ketal at 81°. The distillation residue ( $n_D^{24}$  1.4233, 161 g.) was shown by infrared spectroscopy to be essentially pure acetone diallyl ketal (1.03 moles).

In a similar manner 4.00 moles of acetone butyl methyl ketal gave 0.98, 1.95, and 0.97 moles of the three ketals. During the acid phase of the reaction a sample withdrawn after 8 min. and made basic had the same infrared spectrum as the final reaction solution which was made basic after 1 hr. The reaction is evidently completed in 8 min. or less.

**Methyl ketals from ketones and 2,2-dimethoxypropane. Method D. a. Cyclohexanone dimethyl ketal.** Cyclohexanone (196 g., 2.00 moles), 2,2-dimethoxypropane (250 g., 2.40 moles), 200 ml. of methanol (156 g., 4.87 moles), and 0.05 g. of *p*-toluenesulfonic acid were mixed and distillate was removed as fast as possible through a 1200 × 19 mm. column packed with 1/8-in. glass helices while the head temperature was kept below 58°. The reflux ratio at first was 3:2, but was raised to 19:1 as the distillation progressed. After 268 ml. of distillate had been collected, the head temperature could not be kept below 58° so it was allowed to rise to 63° at which time a total of 298 ml. (236 g.) of distillate (A) had been obtained. The odor of 2,2-dimethoxypropane was very strong in the distillate boiling at 61° (the boiling point of its azeotrope with methanol) indicating its presence in excess at the end of the period of acetone production. The distillation was interrupted and the reaction solution was made basic by the addition of 0.1 g. of sodium methoxide dissolved in 10 ml. of methanol. Distillation was resumed at reduced pressure giving an additional 62 g. of methanol in the receiver and 22 g. in the cold trap. The remaining solution was distilled at about 45 mm. giving the following fractions: I, 27 g., b.p. 68–80° (44 mm.),  $n_D^{25}$  1.4420, [37% cyclohexanone and 63% cyclohexanone dimethyl ketal (by infrared analysis)]; II, 230 g.,  $n_D^{25}$  1.4380, b.p. 80° (44 mm.) to 82° (47 mm.), [pure cyclohexanone dimethyl ketal (lit.,<sup>11</sup> b.p. 54–56° (13 mm.),  $n_D^{19.2}$  1.4416)]; III, 25 g.,  $n_D^{25}$  1.4390, (distillation residue and column holdup, slightly impure ketal). The distillation was taken to dryness, leaving only the trace residue of salts; fraction III was obtained by allowing the fractionating column to drain back into the flask, adding ether to wash the column, and evaporating the ether on the steam bath. There was a loss of 8 g. The total yield of the ketal was 95%, and 5% of the cyclohexanone was recovered.

The 236 g. of distillate A from the acid solution was redistilled, giving 134 g. boiling from 54–56.5°, 77 g. boiling from 56.5–63.5° (methanol-ketal azeotrope, b.p. 61°), and a residue of 10 g. ( $n_D^{25}$  1.3307, methanol). The azeotrope<sup>12</sup> of acetone and methanol boiling at 55.5° is 88% acetone by weight, indicating 118 g. of acetone in the 134 g. fraction (theor. acetone 116 g.).

**b. The effect of alcohol concentration.** Three moles each of cyclohexanone and 2,2-dimethoxypropane were mixed, acidified with dried *p*-toluenesulfonic acid and allowed to stand for 41 hr. at room temperature. The solution was made basic and distilled on the 1200 × 19 mm. fractionating column. After only 33 ml. had distilled, the material distilling was mainly 2,2-dimethoxypropane, indicating practically no production of acetone. A similar solution, but containing in addition 2 moles of methanol per mole of cyclohexanone, was acidified as before and made basic after 4 hr. Distillation gave a 70% yield of pure cyclohexanone dimethyl ketal and an additional 8% in forerun and residue. Attempts to shift the equilibrium by distilling ace-

(11) B. Helferich and J. Hausen, *Ber.*, **57B**, 795 (1924).

(12) L. H. Horsley and co-workers, *Azeotropic Data*, American Chemical Society, Washington, D. C., 1952, p. 29.

(10) H. B. Dykstra, *J. Am. Chem. Soc.*, **57**, 2255 (1935).

tone from acidified mixtures of cyclohexanone and 2,2-dimethoxypropane, even at reduced pressure and with acid concentrations of the order of 0.001*M*, resulted in the formation of unsaturated ethers and methanol, and thus made it impossible to keep the reaction mixture free of the alcohol. Yields of 20–50% of the ketal were obtained in these cases, depending on the treatment.

The first 100 ml. of distillate from a mixture of 1.0 mole of acetophenone, 1.5 moles of 2,2-dimethoxypropane, 410 ml. of hexane, and 0.2 g. of *p*-toluenesulfonic acid contained 28% (vol.) of isopropenyl methyl ether and 1.0% acetone, while in a second experiment with the same amounts of ketone and ketal but with 2.0 moles of methanol and only 330 ml. of hexane (to make equal dilutions in both cases) the first 100 ml. of distillate contained 20% acetone and less than 1% isopropenyl methyl ether.

*c. Redistribution with acetone dimethyl ketal and cyclohexanone dipropyl ketal.* An equimolecular mixture of acetone dimethyl ketal (52 g., 0.50 mole) and cyclohexanone dipropyl ketal (100 g.) was acidified with 10 mg. of *p*-toluenesulfonic acid and allowed to stand at 24° for 30 min. It was then made basic by the addition of 100 mg. of sodium methoxide in 5 ml. of methanol. Fractional distillation gave first the azeotrope of methanol and acetone dimethyl ketal, then the remainder of the acetone dimethyl ketal, and finally the cyclohexanone dipropyl ketal. Total recoveries of the two ketals were 96% and 99% respectively. No more than traces of the other possible ketals were shown by either the distillation curves or refractive index measurements.

Another equimolecular mixture of these ketals was made as before and 10 g. of methanol and 10 mg. of *p*-toluenesulfonic acid were added. After 30 min. at 24° the solution was made basic in the same manner. Distillation of the solution gave the following fractions (boiling range, mid-range boiling point, and composition of fraction given): I, 36–40.5° (303 mm.), 39° (303 mm.), azeotrope of methanol and 2,2-dimethoxypropane; II, 40.5–65° (303 mm.), 47° (303 mm.), azeotropes of methanol and propyl alcohol with 2,2-dimethoxypropane; III, 65° (303 mm.) to 50° (81 mm.), 45° (81 mm.), azeotrope of propyl alcohol and acetone methyl propyl ketal; IV, 50–71° (81 mm.), 58° (81 mm.), acetone methyl propyl ketal; V, 71–93° (81 mm.), 88.5° (81 mm.), acetone dipropyl ketal; VI, 93° (81 mm.) to 75° (19 mm.), 60.5° (19 mm.), cyclohexanone dimethyl ketal; VII, 75–87.5° (19 mm.), 87.5° (19 mm.), cyclohexanone

methyl propyl ketal; VIII, above 87.5° (19 mm.), —, residue and column holdup (isolated by washing the packed column with ether and evaporating the ether, and identified as a mixture of the methyl propyl and dipropyl ketals of cyclohexanone by infrared spectroscopy). The mid-range boiling points were taken from well defined plateaus on the distillation curve, except for fraction II which gave no plateau. From the known composition of the azeotropes and by means of infrared spectrophotometric analyses the following recoveries were determined (given in gram-moles): methanol 0.24 (including 0.12 added when inactivating the catalyst), propyl alcohol 0.19, and the six ketals in order of increasing molecular weight 0.14, 0.25, 0.09, 0.15, 0.25, 0.10.

*Ketals from ketone, alcohol, and 2,2-dimethoxypropane. Method E. Acetophenone dipropyl ketal.* A solution of acetophenone (120 g., 1.00 mole), propyl alcohol (480 g., 8.00 moles), 2,2-dimethoxypropane (156 g., 1.5 moles), 300 ml. of hexane, and 0.2 g. of *p*-toluenesulfonic acid was distilled through a 1000 × 25 mm. column packed with 1/8-in. glass helices with the reflux ratio being adjusted so that the head temperature remained below 50°. After each 150–200 ml. of distillate was obtained, an equal volume of hexane was added to the boiling solution until 530 ml. of distillate had been collected. The still-head temperature then slowly rose to 64° at which time the total distillate volume was 770 ml. The reaction mixture was made basic by rapidly adding 0.2 g. of sodium methoxide in 10 ml. of methanol. Distillation was resumed and the pressure was reduced as necessary in order to keep the temperature in the flask below 100–110°. After a forerun which included some acetone dipropyl ketal, a residue of 190 ml. ( $n_D^{25}$  1.4820) remained. After two distillations through a 3-in. column packed with Berl saddles, this residue gave 141 g. of acetophenone dipropyl ketal, b.p. 61° (1 mm.),  $n_D^{25}$  1.4750, 63% yield (lit.<sup>13</sup> b.p. 112–115° (10 mm.)).

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[CONTRIBUTION FROM THE ORGANIC BASIC RESEARCH LABORATORY, THE DOW CHEMICAL COMPANY]

## Ketals of Monohydric Secondary Alcohols<sup>1</sup>

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Alkoxy interchange between secondary alcohols and simple ketals gives ketals containing secondary alkoxy groups in good yields. Such ketals can also be made by the addition of secondary alcohols to  $\alpha,\beta$ -unsaturated ethers and by disproportionation reactions. Ketals with secondary alkoxy groups can be prepared directly from ketones and secondary alcohols by coupling the reaction with the hydrolysis of another ketal. Mixed ketals in which the alkoxy groups may be either both secondary or only one secondary and one primary can also be made by these methods.

The preparation of ketals of primary alcohols by alcohol interchange reactions with dimethyl ketal has been discussed in a previous paper.<sup>2</sup> This reaction has now been extended to include

the preparation of ketals of monohydric secondary alcohols. There are two previous references in the literature to the successful preparation of ketals of this type. Stevens, McLean, and Weinheimer<sup>3</sup> obtained relatively unstable  $\alpha$ -hydroxyketals by

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