

The effect of branching on secondary alcohols such as 2-propanol was to retard the reaction. However, quite respectable yields were obtained on longer exposure times, *cf.* run 23 and 24.

There was an apparent discrepancy between the control run 1 with a 67% yield and run 7 with a 32% yield of water. We presume this was due to lack of attainment of equilibrium in the latter run. The yields as cited in Table I were determined with the use of an internal standard and must not be considered to be recovered yields. To obtain high recovery yields, the catalytic dehydrator washing procedure was of utmost importance.<sup>6</sup>

#### Experimental Section

The acid polymers used were sulfonated polystyrene copolymers with total exchange capacities on the dry basis of 4.5 mequiv/g (Rexyn 101 (H) R-231) and 4.8 mequiv/g (Rexyn 101 (H)-R-204) sold by Fisher Scientific Co., Fair Lawn, N. J. Anhydrous CaSO<sub>4</sub>, mesh size 40-80, was used. The acid polymer was dried in a 100° oven prior to use and the CaSO<sub>4</sub> dried at 180°. The glpc analyses were performed on a flame ionization Varian Model 1200-2 instrument equipped with a 6 ft × 1/8 in. 10% QF-1 column. Noteworthy were the facts that CaSO<sub>4</sub>·2H<sub>2</sub>O loses 1.5 mol of water at 128° and the remainder of the water at 163°.

**General Procedure.**—The acetic acid, acid polymer, CaSO<sub>4</sub>, internal standard, and alcohol were magnetically stirred in an erlenmeyer flask. At the designated time, the mixture was filtered and washed with a solvent. Benzene was used as the internal standard for all runs and the washing liquids were ether or bromobenzene for the methyl acetate runs, and ether or dioxane for 2-propyl acetate and 1-butyl acetate runs. The results reported in Table I were averages of several runs. There were no detectable differences noted on switching from one acid polymer to the other. All products were isolated and compared to authentic samples.

**Registry No.**—Methanol, 67-56-1; 1-butanol, 71-36-3; 2-propanol, 67-63-0.

**Acknowledgment.**—The authors are grateful to D. A. Kubik for helpful discussions and the drying agent data used in this paper. One of us (G. F. V.) acknowledges the partial support of a Faculty Research Grant from the University of North Dakota.

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### The Catalytic Dehydrator for Rapid Acetal and Ketal Synthesis

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Received November 17, 1970

The catalytic dehydrator,<sup>1</sup> composed of an acid polymer and a drying agent, has been employed for the synthesis of 1-butanol-ethylene glycol acetal, 2-propyl-1,3-dioxolane (I), and cyclohexanone-ethylene glycol ketal, 1,4-dioxaspiro[4.5]decane (II). The dehydrator accomplishes the synthesis by removal of the

water *via* the drying agent and the predried acid polymer, whereas the catalysis is accomplished by the strong acid polymer, a principle which conceivably can be applied to the corresponding base-catalyzed reactions as well.

Acid polymers alone have been employed for the synthesis of ketals.<sup>1-7</sup> The ketal II has been prepared in a 57% yield as the refluxing temperature using an acid polymer and a Barrett-type water separator.<sup>2</sup> With the same procedure I was prepared in a 92% yield.<sup>2</sup> As a comparison, an 85% yield of II was obtained using *p*-toluenesulfonic acid together with azeotropic distillation.<sup>8</sup>

A number of drying agents were tested for the present application. The order of decreasing effectiveness of those used with the synthesis of II is CaSO<sub>4</sub> > CaCl<sub>2</sub> > silica gel > molecular sieve 5A. Since CaSO<sub>4</sub> was found to be the most efficient dehydrator of the series, it was selected for the more comprehensive study.

Our efforts were directed toward using minimum practical quantities of both the acid polymer and the drying agent for the butanal reaction. In doing so, it was necessary to run a compromise balance between the minimum acid polymer necessary to obtain an adequate reaction rate and enough drying agent to put the equilibrium at or near completion without putting in an excess of either.

The recovered yields reported in Table I were determined by glpc analysis. The internal standard was added subsequent to filtration and washing of the catalytic dehydrator. Since some of the I or II was retained by the catalytic dehydrator with simple filtration, the choice of solvent used to wash the catalytic dehydrator was extremely important. Unreproducible, low yields were obtained using ether as the washing solvent, whereas dioxane gave reproducible results, *cf.* runs 1 with 2 and 3 with 4.

The yields of both I and II could be made quantitative considering the experimental error. The task for the catalytic dehydrator was only a moderate one, however, since both reactions studied had equilibrium points near 60%, *cf.* runs 5 and 10 of Table I.  $D_{total}$ , defined as the total drying capacity of the dehydrator in relation to the water produced, only need be near 1 for near-quantitative formation of I and II.

Longer reaction times caused more erratic results although there seemed to be more product formed and less butanal present, *cf.* run 6 with 2. Suspecting retention of product in the inner regions of the solid catalytic dehydrator particles, I was placed in contact with various drying agents and the concentration monitored *vs.* time. It is evident from the data illustrated in Table II that the drying agents, CaSO<sub>4</sub>, CaCl<sub>2</sub>, and silica gel,

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TABLE I  
 YIELD DATA AND REACTION TIMES FOR THE ACETAL AND KETAL REACTIONS

Run	Compd	Acid polymer, g	Drying agent, g	Carbonyl reactant, mmol	Glycol, mmol	Time, min	$D_{total}^a$	$D_{CaSO_4}^b$	Yield, %
1	Butanal	0.10	1.50	11.3	5.39	30	0.7	0.4	50-65 <sup>c</sup>
2	Butanal	0.10	1.50	11.3	5.39	30	0.7	0.4	85 ± 2
3	Butanal	0.20	1.50	11.3	5.39	30	0.9	0.4	61-82 <sup>c</sup>
4	Butanal	0.20	1.50	11.3	5.39	30	0.9	0.4	99 ± 2
5	Butanal	<i>d</i>		11.3	5.39	2880			60 ± 2
6	Butanal	0.10	1.50	11.3	5.39	180	0.7	0.4	83-96
7	Butanal	0.10	0.00	11.3	5.39	30	0.3	0.0	77 ± 2
8	Butanal	0.20	0.00	11.3	5.39	30	0.5	0.0	93 ± 2
9	Butanal	0.10	0.00	11.3	5.39	180	0.3	0.0	88 ± 2
10	Cyclohexanone	<i>d</i>		9.7	5.39	30			57 ± 2
11	Cyclohexanone	0.10	1.50	9.7	5.39	30	0.8	0.5	91 ± 2
12	Cyclohexanone	1.02	0.00	9.7	5.39	30	2.9	0.0	78 ± 5
13	Cyclohexanone	1.02	0.97	9.7	5.39	30	3.3	0.4	97 ± 5
14	Cyclohexanone	1.01	1.77	9.7	5.39	30	3.7	0.6	92 ± 5
15	Cyclohexanone	0.50	1.73	9.7	5.39	30	3.5	0.6	94 ± 5

<sup>a</sup> Ratio of the drying capacity of the catalytic dehydrator to the water produced. <sup>b</sup> Ratio of the drying capacity of CaSO<sub>4</sub> to the water produced. <sup>c</sup> These samples had the catalytic dehydrator washed with ether rather than dioxane. <sup>d</sup> Catalyzed by *p*-toluene-sulfonic acid.

 TABLE II  
 RECOVERY OF 2-PROPYL-1,3-DIOXOLANE (I)

Drying agent	Time, hr	Recovery, %
CaSO <sub>4</sub>	0.5	99
	3	90
CaCl <sub>2</sub>	3	80
Silica gel, 6-16 mesh	1 <sup>a</sup>	71
	3 <sup>a</sup>	70
	6 <sup>a</sup>	66

<sup>a</sup> The drying agent was not washed in these cases. In all other runs, the drying agent was washed with dioxane.

all cause the end product to "disappear" with time. This was demonstrated to be an adsorption-inner diffusion process within the drying agent particles rather than a destructive chemical reaction because the missing starting material could be recovered from the drying agent by appropriate filtering and washing procedures. To further demonstrate this, a preparative scale reaction to make II was done using the proportions of run 11. A 92% recovered yield was attained despite the 6-hr reaction time. This was only possible when the washing portion of the work-up procedure was optimum.

Both CaSO<sub>4</sub> and the dried acid polymer effectively accomplished the yield enhancement in contrast to the ester studies where it was found that the CaSO<sub>4</sub> was more efficient than the acid polymer.<sup>1</sup> The addition of CaSO<sub>4</sub> for the formation of II increased the yield 19%, *cf.* run 12 with 13. For the preparation of I, CaSO<sub>4</sub> enhanced the yield by 8%, *cf.* run 2 with 7, and 6%, *cf.* run 4 with 8, depending upon the amount of acid polymer present. Noteworthy is the comparison of run 8 with that of 7. Doubling the amount of the acid polymer increased the yield by 16% which effectively demonstrates the good drying ability of the acid polymer.<sup>1</sup> It is significant that small amounts of the acid polymer induced high conversions.

The 30-min reaction time was determined to be a minimum for quantitative conversions with these amounts of the catalytic dehydrator. At this time,

the absorption-inner diffusion processes are also at a minimum.

#### Experimental Section

The acid polymers used were sulfonated polystyrene copolymers with total exchange capacities on the dry basis of 4.5 mequiv/g (Rexyn 101 (H) R-231) and 4.8 mequiv/g (Rexyn 101 (H) R-204) sold by Fisher Scientific Co., Fair Lawn, N. J. Finely ground, anhydrous CaSO<sub>4</sub> was used. The acid polymer was dried in a 100° oven prior to use and the CaSO<sub>4</sub> dried at 200°. The glpc analyses were performed on a flame ionization Beckman GC-5 equipped with a 20 ft × 1/8 in. 20% Carbowax 20M (Chromosorb W) column.

**General Procedure for Ketal Formation.**—The carbonyl compound was stirred at room temperature with ethylene glycol and the catalytic dehydrator. To terminate the reaction, it was filtered, and the solid washed with a solvent. For the structure proofs, the products were isolated by distillation and identified by comparison of physical properties to literature values<sup>2,9</sup> and nmr analysis. For obtaining the results in Table I, an internal standard was added to the filtrate and the filtrate analyzed by glpc. The internal standards were inert materials of noninterfering retention times. The acid polymer used was Rexyn 101CH, R-204, a sulfonated polystyrene copolymer, and the drying agent was anhydrous CaSO<sub>4</sub>. Each item of data reported in Table I is the average of several runs.

**Preparative Scale Ketalization of Cyclohexanone.**—Reagent cyclohexanone, 30 ml (28.4 g, 0.290 mol), 90 ml (100.4 g, 1.620 mol) of ethylene glycol, 3.0 g of cation exchange resin, and 46.5 g (0.392 mol) of anhydrous calcium sulfate were added to a dry 500-ml erlenmeyer flask. The mixture was stirred for 6 hr. Diethyl ether (75 ml) was then added and the mixture was allowed to stir for an additional 10 min. Next the mixture was filtered with suction and the filtered material washed alternately with 50-ml portions of water and diethyl ether until most of the ketal odor disappears from the filtered catalytic dehydrator. Sodium chloride (30 g/100 ml of wash water) was added to the filtrate, the layers were separated, and the organic layer was dried over anhydrous potassium carbonate. The dry organic layer was distilled through a 15-in. Vigreux column. The column was washed with ether and the washing liquid distilled in a semimicro Vigreux column. The two appropriate fractions were combined to give 37-38 g (90-92%) of 1,4-dioxaspiro[4.5]decane, a colorless liquid: bp 65-67° (10 mm);  $n_D^{25}$  1.4572 [lit.<sup>9</sup> bp 65-67° (13 mm);  $n_D^{25}$  1.4575-1.4565].

**Registry No.**—I, 3390-13-4; II, 177-10-6.

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