TABLE I

REDUCTIONS OF ACYCL FLUORIDES BY SILICON HYDRIDES

Silicon hydride (mmol)	Acyl fluoride (mmol)	Other additives (mmol)	Time, hr (temp, °C)	Acyl fluoride derivative, %	Silicon product, %
Et_3SiH (94)	n-C_4H_9COF (95)		24 (115)	n-$C_4H_9CO_2C_5H_{11}$-n, 71	Et_3SiF, 89
$(PhCH_2)_3SiH$ (83)	n-C_4H_9COF (87)		67 (125)	n-$C_4H_9CO_2C_5H_{11}$-n, 47	$(PhCH_2)_3SiF$, 95
Et_3SiH (140)	p-$C_6H_4(COF)_2$ (70)		6 (280)	Polymer,[a] 63	Et_3SiF, 65
Et_3SiH (160)	$(CH_3)_3CCOF$ (160)		8 (160)	$(CH_3)_3CCO_2CH_2C(CH_3)_3$, 74	Et_3SiF, 85
Ph_2SiH_2 (52)	n-C_4H_9COF (100)		10 (220)	Unidentified carbonyl compds	Ph_2SiF_2, 61
Et_3SiH (12)	n-C_4H_9COF (12)	n-$C_5H_{11}CHO$ (12)	27 (115)	n-$C_4H_9CO_2C_6H_{13}$-n[b]	Et_3SiF[b]
Et_3SiH (62)	n-C_4H_9COF (62)	C_6H_5CHO (62)	1 (125)	n-$C_4H_9CO_2CH_2C_6H_5$, 59	Et_3SiF, 87
Et_3SiH (16)	n-C_4H_9COF (16)	C_6H_5CN (15)	96 (125)	n-$C_4H_9CO_2C_5H_{11}$-n[c]	Et_3SiF[c]

[a] See text. [b] Identified by glpc and infrared spectrum. [c] By infrared spectrum; there was no evidence of the nitrile reacting.

occur under the reaction conditions, even in the presence of trace amounts of HF. Finally, if the mechanism of eq 3–6 is correct, the fact that no aldehyde is isolated, and that all added aldehyde reacts, indicates that reaction 5 is much faster than reaction 4.

Experimental Section

All of the silanes used were purchased from the Peninsular ChemResearch Corporation. Acyl fluorides were prepared from the corresponding chlorides by reaction with HF and had previously reported physical constants.[6] The physical constants of all products were identical with those in the literature, and the infrared spectra were in accord with their structures. Some typical procedures are given below.

Reaction of Pentanoyl Fluoride with Triethylsilane.—Into a 1.25-in.-i.d. Teflon tube equipped with a magnetic stirrer and under nitrogen was added 9.9 g of pentanoyl fluoride and 15.0 ml of triethylsilane. The solution was stirred and heated at 110–115° for 24 hr. After cooling, the material was distilled on a platinum spinning-band column to yield 12.8 g of Et_3SiF, bp 107–108.5°, and 5.8 g of pentyl pentanoate, bp 200–204.5°, $n^{23}D$ 1.4155.

Reaction of Terephthaloyl Fluoride with Triethylsilane.—An 80-ml bomb was loaded with 12 g of terephthaloyl fluoride and 22.7 ml of triethylsilane, evacuated, and then heated at 280° for 6 hr. The total recovery of a mixture of solid and liquid was 24 g. The material was subjected to a vacuum, and the volatile fraction was distilled to yield 12.4 g of Et_3SiF, bp 108–110.5°.

The solid was placed in a sublimator at 100° and 0.1 mm for 40 hr. The residue, 6.0 g, was, as indicated by pmr and infrared spectra, a polyester of terephthalic acid, 1,4-bis(hydroxymethyl)benzene and p-hydroxymethylbenzoic acid.

Anal. Calcd for $(C_8H_6O_2)_n$: C, 71.7; H, 4.5. Found: C, 71.3; H, 4.2.

Reaction of Pentanoyl Fluoride with Triethylsilane in the Presence of 2-Butenal.—Into a 50-ml round-bottom flask under nitrogen were charged 9.7 g of pentanoyl fluoride, 14.8 ml of triethylsilane, and 7.7 ml of 2-butenal. The liquid was heated slowly and stirred. When the oil bath reached *ca.* 70° a violent reaction took place; the mixture refluxed rapidly enough to fill the condenser tube with a solid column of liquid. After the reaction subsided, the flask was heated at 70–80° for an additional 10 min and then the contents were transferred to a spinning-band column and distilled. The distillate consisted of 12.7 g of Et_3SiF, bp 107–111°, and several fractions (9.7-g total) of a mixture of carbonyl compounds. Infrared and pmr spectra indicated these were mixtures of ester and a small amount of carboxylic acid. Some of the ester appeared to be one or more of the butenyl pentanoates.

Registry No.—n-$C_4H_9CO_2C_5H_{11}$-n, 2173-56-0; $(CH_3)_3CCO_2CH_2C(CH_3)_3$, 5340-26-1; n-$C_4H_9CO_2C_6H_{13}$-n, 1117-59-5; n-$C_4H_9CO_2CH_2C_6H_5$, 10361-39-4; Et_3SiF, 358-43-0; $(PhCH_2)_3SiF$, 429-76-5; Ph_2SiF_2, 312-40-3; polyester of terephthalic acid, 1,4-bis(hydroxymethyl)benzene, and p-hydroxymethyl benzoic acid, 30135-79-6.

Acknowledgment.—The author wishes to thank Messrs. Lawrence Whyte, William Whisler, and Robert Hamilton for technical assistance.

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[6] G. Olah and J. Kuhn, *Org. Syn.*, **45**, 3 (1965).

The Catalytic Dehydrator for Rapid Ester Synthesis

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We wish to report a potentially important modification in the use of ion exchange resins (acid polymers) as catalysts, *i.e.*, the combination of an acid polymer with a drying agent, the catalytic dehydrator, for the purpose of promoting acid-catalyzed, equilibrium reactions which have water as one of the products.

The advantages of the catalytic dehydrator over conventional esterification techniques are (1) the reaction can be done at room temperature or lower, a factor which may prove valuable for heat sensitive compounds; (2) the reaction apparatus is simple; (3) theoretically the catalytic dehydrator can be reused;[1] (4) it can be made quantitative in many cases; (5) it is a one-step reaction from the acid and the alcohol; and (6) the reaction work-up is simple since both of the components of the catalytic dehydrator are insoluble in the reaction media.

The catalytic dehydrator was used in two ways, first, in a column with the acid and alcohol flowing through it and, second, as a component in a stirred mixture of the alcohol and acid. The latter proved more valuable for this study because the exposure time could be more carefully controlled although both were successful. The data in Table I were obtained by the second procedure.

The two reactions studied in detail were chosen on the basis of their equilibrium points and adaptability to glpc analysis. As a control, the extent of esterification at a given time using p-toluenesulfonic acid as the catalyst was given in entries 1–4 and 12 on Table I. Although rate studies using the acid polymer were not undertaken, it was quite apparent from the data of Table I that the esterification rate of 1-butanol was much slower than that of methanol which was in ac-

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[1] N. G. Polyanskii, *Russ. Chem. Rev.*, **39**, 244 (1970).

TABLE I
YIELD DATA FOR ESTERIFICATIONS

Run	Alcohol	Solvent	Reaction ratio, acid:alcohol (v/v)	Time	Acid polymer: dehydrator (g/g)	D_{total}	Acid polymer	Yield, ±5%
1	Methanol		1:10	10 min	[a]			67
2	Methanol		1:10	14 hr	[a]			82
3	Methanol	Ether, 10 ml	2:0.6	10 min	[a]			21
4	Methanol	Ether, 10 ml	2:0.6	17 hr	[a]			59
5	Methanol		1:10	10 min	10:0	16.1	R204	87
6	Methanol		1:10	10 min	3:7	6.3	R204	94
7	Methanol		1:10	10 min	3:0	4.7	R231	32
8	Methanol		1:10	20 min	3:7	6.3	R204	93
9	Methanol	Ether, 10 ml	1:2	20 min	3:7	6.3	R231	52
10	Methanol		10:0.6	120 min	3:7	7.5	R204	73
11	Methanol	Ether, 10 ml	2:0.6	20 min	3:7	7.5	R231	33
12	1-Butanol		1:10	60 min	[a]			58
13	1-Butanol		1:10	60 min	3:7	6.3	R231	84
14	1-Butanol		1:10	60 min	3:0	4.7	R231	26
15	1-Butanol		1:10	10 min	3:7	6.3	R204	22
16	1-Butanol		1:10	160 min	3:0	4.7	R231	58
17	1-Butanol		1:10	17 hr	3:7	6.3	R231	100
18	1-Butanol		1:10	190 min	3:0	4.7	R231	68
19	1-Butanol		1:10	14 hr	3:0	4.7	R231	100
20	1-Butanol		1:10	60 min	3:7[b]		R231	52
21	1-Butanol		1:10	90 min	3:7[b]		R231	65
22	1-Butanol		1:10	17 hr	3:7[b]		R231	93
23	2-Propanol		1:10	17 hr	3:7	6.3	R231	91
24	2-Propanol		1:10	17 hr	3:7[b]		R231	73

[a] No catalytic dehydrator used in these runs. The reactions were catalyzed by *p*-toluenesulfonic acid. [b] Anhydrous silica gel used as the drying agent.

cordance with the results of Karpov and Brystrova[2] using the acid polymer alone. As a consequence, the 1-butanol reaction provided the better test of the capabilities of the catalytic dehydrator.

Calcium sulfate was selected as the drying agent. Although it was shown not to dry polar media to the same extent as the others,[3] it had a more desirable feature of being able to dry solutions more rapidly than others tested. Anhydrous silica was also tried but found to be slower than $CaSO_4$.

An obvious problem with commercially available acid polymers was that they contain 40–50% water by weight as supplied which first had to be removed if the drying agent was to affect the esterification equilibrium. This was done by air drying the acid polymer in a 100–110° oven for 24 hr.

The total capacity of both the acid polymer and $CaSO_4$ for absorbing water under practical conditions was determined in order to evaluate the total drying capacity of the dehydrator in relation to the water produced (D). The predried acid polymer was capable of increasing its weight by 50% when exposed to wet ether for 30 min followed by a 15-min vacuum filtration and air drying for 24 hr. Anhydrous $CaSO_4$ gained 6.3% in weight when exposed to the wet ether treatment.

A 10-g quantity of catalytic dehydrator was chosen arbitrarily and a 3:7 ratio of acid polymer:$CaSO_4$ was found to be an optimum balance of catalytic and drying activity. Presumably, the excess drying capacity required for short reaction times was not necessary for reactions whose equilibria lie close to the products, but it was advisable for others.

Since the dried acid polymer had a drying capacity of its own, its effect on the equilibrium alone was determined. By comparing reaction 1 with that of 5 in Table I, it was obvious that the reaction was shifted by 20% toward products, *i.e.*, from 67 to 87%, due to the effect of the dry acid polymer alone. Presumably the methyl acetate equilibrium could be shifted to completion if enough acid polymer were added or the reaction time increased, *cf.* run 5 with 7. However, the acid polymer was a slow drying agent. If the amount of acid polymer was kept constant, then the effect of $CaSO_4$ could be measured. By doing this, the 10-min reaction yield of methyl acetate was reduced by 62%, *cf.* run 6 with 7, and the 1-butyl acetate yield by 58%, *cf.* 13 with 14. This difference was a dramatic demonstration of the rapid drying action of $CaSO_4$. The effect of ether as a solvent was to retard the reaction rate, *cf.* run 8 with 9. The reaction rate was slower when the acid was in excess than when the alcohol was in excess, *cf.* run 8 with 10, as was found with acid polymer alone.[4] The reaction mixtures tended to turn yellow if the optimum reaction time were exceeded; however, the yields were not significantly changed by this discoloration.

The slower esterification reaction employing 1-butanol was made to go to the extent of 84% in 1 hr and quantitatively overnight. Significantly, the reaction was quantitative using the acid polymer alone with long reaction times; however, the reaction rate was faster in the presence of the drying agent, *cf.* 13 with 14. A practical yield of 65–75% using conventional techniques has been reported for this reaction.[5]

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(2) Cited in ref 1.

(3) B. D. Pearson and J. E. Ollerenshaw, *Chem. Ind.* (*London*), **9**, 370 (1966).

(4) Cited in ref 1.

(5) R. Adams, J. R. Johnson, and C. F. Wilcox, Jr., "Laboratory Experiments in Organic Chemistry," 6th ed, Macmillan, New York, N. Y., 1970, p 223.

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.[6]

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 $CaSO_4$, mesh size 40–80, was used. The acid polymer was dried in a 100° oven prior to use and the $CaSO_4$ 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 $CaSO_4 \cdot 2H_2O$ loses 1.5 mol of water at 128° and the remainder of the water at 163°.

General Procedure.—The acetic acid, acid polymer, $CaSO_4$, 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.

[6] V. I. Stenberg, G. F. Vesley, and D. A. Kubik, *J. Org. Chem.*, **36**, 2550 (1971).

The Catalytic Dehydrator for Rapid Acetal and Ketal Synthesis

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The catalytic dehydrator,[1] 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.[1–7] The ketal II has been prepared in a 57% yield as the refluxing temperature using an acid polymer and a Barrett-type water separator.[2] With the same procedure I was prepared in a 92% yield.[2] As a comparison, an 85% yield of II was obtained using *p*-toluenesulfonic acid together with azeotropic distillation.[8]

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 $CaSO_4 > CaCl_2 >$ silica gel > molecular sieve 5A. Since $CaSO_4$ 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, $CaSO_4$, $CaCl_2$, and silica gel,

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[1] G. F. Vesley and V. I. Stenberg, *J. Org. Chem.*, **36**, 2548 (1971).

[2] M. J. Astle, J. A. Zaslowsky, and P. G. Lafyatis, *Ind. Eng. Chem.*, **46**, 787 (1954).

[3] P. Mastagli, Z. Zafiriadis, and G. Lagrange, *C. R. Acad. Sci.*, **237**, 187 (1953); *Chem. Abstr.*, **48**, 11385*e* (1954).

[4] Olin Mathieson Chemical Corp., British Patent, 739,022 (1955); *Chem. Abstr.*, **50**, 15592*e* (1956).

[5] T. R. E. Kressman, *Ind. Chem.*, **36**, 3 (1960); *Chem. Abstr.*, **54**, 7004*e* (1960).

[6] Farbenfabriken Bayer A.-G., German Patent, 882,091 (1953); *Chem. Abstr.*, **52**, 11121*a* (1958).

[7] Celanese Corp. of America, U. S. Patent, 2,840,615 (1958); *Chem. Abstr.*, **52**, 17109*g* (1958).

[8] M. Sulzbacher, E. Bergmann, and E. R. Pariser, *J. Amer. Chem. Soc.*, **70**, 2827 (1948).