Table I
Conversion of Ketones into α-Allyl Aldehydes

Ketone 3	Enamine 4[a]	Yield of 5, %[b]
4-Heptanone (**3a**)	+	61
3-Methyl-2-butanone (**3b**)	+	38
Cyclohexanone (**3c**)	+	39
2-Methylcyclohexanone (**3d**)	+	57[c]
Norbornanone (**3e**)	+	54
Acetophenone (**3f**)	+	*d*
Cyclooctanone (**3g**)	–	
Fenchone (**3h**)	Trace	

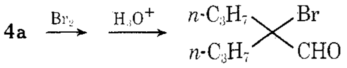
[a] +, enamine formation; –, no enamine formation. [b] No attempt was made to fully optimize yields. [c] A mixture of diastereomers (*ca.* 4:1) was obtained. [d] A mixture of alkylated and unalkylated aldehydes (*ca.* 1:1) was obtained.

Table II
α-Allyl Aldehydes 5

Compd	Bp, °C[a] (mm)	Mp, °C,[b] of 2,4-DNPH[c]
5a	83–85 (10)	164–165
5b	90–92 (50)	125–126
5c	109–111 (40)[d]	156–157[e]
5d	90–92 (10)	114–115
5e	112–114 (25)[f]	148–149[g]

[a] Uncorrected. [b] The melting points were determined using a Reichert hot stage apparatus and are uncorrected. [c] Satisfactory elemental analysis was obtained for all new aldehydes as their 2,4-dinitrophenylhydrazones. *Anal.* Calcd for $C_{17}H_{24}N_4O_4$ (**5a**): C, 58.61; H, 6.94; N, 16.08. Found: C, 58.87: H, 6.76; N, 16.18. Calcd for $C_{15}H_{20}N_4O_4$ (**5b**): C, 56.24; H, 6.29; N, 17.49. Found: C, 56.46; H, 6.48; N, 17.34. Calcd for $C_{17}H_{22}N_4O_4$ (**5d**): C, 58.95; H, 6.40; N, 16.17. Found: C, 59.10; H, 6.40; N, 16.19. [d] Lit.[14] bp 105–107° (32 mm). [e] Lit.[14] mp 156–157°. [f] Lit.[14] bp 120° (26 mm). [g] Lit.[14] mp 146–148°.

ment the enamine **4a** was brominated to give, after careful hydrolysis, the α-bromo aldehyde **6** in 33% yield (eq 2).



$$\mathbf{4a} \xrightarrow{Br_2} \xrightarrow{H_3O^+} (n\text{-}C_3H_7)_2C(Br)CHO \qquad (2)$$

6

Since these α-bromo aldehydes may be readily converted α,β-unsaturated aldehydes, the direct bromination of the *in situ* generated enamines constitutes a useful modification of this method.

Further investigations to extend the scope and utility of this new synthetic method are in progress.

Experimental Section

α-Allyl Dialkylaldehydes 5a–e. General Procedure. A well-stirred solution of diethyl pyrrolidinomethylphosphonate[12] (1, 3.65 g, 16.5 mmol) in 75 ml of anhydrous tetrahydrofuran was treated with *n*-butyllithium (8.7 ml of a 1.9 *N* hexane solution, 16.5 mmol) at −78° under dry nitrogen. After 1 hr, a solution of the appropriate ketone **3a–e** (15.0 mmol) in 10 ml of anhydrous tetrahydrofuran was added dropwise over a 10-min period, and the stirring was continued for 4 hr at −78° and then overnight at room temperature to give a solution of the enamine **4a–e.** Allyl bromide (13.0 ml) was added, the mixture was refluxed for 24 hr, 30 ml of 1 *N* hydrochloric acid was added, and the refluxing was continued for an additional 3 hr. After cooling, the reaction mixture was poured into water and the aqueous layer was extracted with ether. The combined organic layers were washed successively with 2 *N* hydrochloric acid and 10% sodium bicarbonate, and the aqueous washings were backwashed once with ether. The combined organic layers were dried ($MgSO_4$), the excess solvent was removed under reduced pressure, and the residue was distilled to afford the α-allyl dialkylaldehydes **5a–e.** See Table II for physical constants.

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Registry No.—1, 51868-96-3; **3a,** 123-19-3; **3b,** 563-80-4; **3c,** 108-94-1; **3d,** 583-60-8; **3e,** 497-38-1; **3f,** 98-86-2; **5a,** 51868-97-4; **5a** 2,4-DNPH, 51868-98-5; **5b,** 51868-99-6; **5b** 2,4-DNPH, 51911-65-0; **5c,** 29517-58-6; **5c** 2,4-DNPH, 51869-00-2; *cis*-**5d,** 51869-01-3; *cis*-**5d** 2,4-DNPH, 51869-02-4; *trans*-**5d,** 51869-03-5; *trans*-**5d** 2,4-DNPH, 51869-04-6; **5e,** 29517-67-7; **5e** 2,4-DNPH, 51869-05-7.

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Catalytic Dehydrator. A Simplified Isolation Procedure for Acetals and Ketals

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The catalytic dehydrator is defined as a combination of an ion exchange resin (a sulfonated polymer) and a drying agent, and it promotes acid-catalyzed, equilibrium reactions in which water is one of the products. At the present time, it has been applied to the synthesis of esters,[1] ketals, and acetals.[2] We now wish to present additional data on the use of the catalytic dehydrator for the synthesis of acetals and ketals together with a simplified preparative isolation procedure.

In regard to structural effects, aldehydes produce higher yields of acetals than comparable ketones form ketals. As the data of Table I indicate, the 1,2-ethanediol–acetal yield from phenylacetaldehyde is greater than the 1,2-ethanediol–ketal yield from phenylacetone. Similarly the acetal yield from diphenylacetaldehyde is higher than the ketal yield from 1,1-diphenylacetone. Similar results have been observed using a cation-exchange resin and a water separator.[3] For example, Astle, *et al.*, obtained a 92% yield of 2-propyl-1,3-dioxolane from butanal and 1,2-ethanediol but

Table I
Substituent Effect on Acetal and Ketal Formation Using the Catalytic Dehydrator

Compd	Registry no.	Carbonyl, mmol	1,2-Ethanediol, mmol[b,c]	Resin, g	$CaSO_4$, g	Yield,[a] %	Registry no.	Lit. yield, %	D_{total}
Cyclohexanone	108-94-1	9.7	53.9	0.5–1.0	0.97–1.77	74–89	177-10-6	75–85[d]	1.8–3.6
Acetophenone	98-86-2	8.6	53.9	0.5	1.5	22–24	3674-77-9	80–85[e,f]	2.3
Benzaldehyde	100-52-7	11.0	53.9	0.5	1.5	67–70	936-51-6	83[e]	1.8
Phenylacetone	100-79-7	9.0	53.9	0.5	1.5	62–68	4362-18-9	90[f]	2.2
Phenylacetaldehyde	122-78-1	9.4	53.9	0.5	1.5	81–83	101-49-5	58[g]	2.1
1,1-Diphenylacetone	781-35-1	9.0	53.9	0.5	1.5	48–51	52002-91-2	45[h]	2.2
Diphenylacetaldehyde	947-91-1	9.6	53.9	0.5	1.5	70–74	4359-35-7	70[i]	2.1

[a] These yields were determined by glpc analysis of the ether extract solution. [b] There was an error committed in our previous report.[2] The amount of 1,2-ethanediol used in that data was 53.9 mmol rather than 5.39 mmol as reported. [c] Registry no., 107-21-1. [d] R. A. Daignault and E. L. Eliel, *Org. Syn.*, **47,** 37 (1967). [e] M. Sulzbacher, E. Bergmann, and E. R. Pariser, *J. Amer. Chem. Soc.*, **70,** 2827 (1948). [f] F. Alderweireldt and M. Anteunis, *Bull. Soc. Chim. Belg.*, **74,** 488 (1965). [g] Prepared by a base process on a dichloride: V. M. Naidan, N. V. Dzumedzei, and A. V. Dombrovskii, *Zh. Org. Khim.*, **1,** 1377 (1965); *Chem. Abstr.*, **64,** 721c (1966). [h] Prepared in our laboratory using *p*-toluenesulfonic acid and the benzene azeotrope. [i] R. Soulier and J. Soulier, *Bull. Soc. Chim. Fr.*, 2048 (1969).

only a 21% yield of 2-propyl-2-methyl-1,3-dioxolane from 2-pentanone and 1,2-ethanediol. At higher temperatures, the cation-exchange resin alone produces similar results, *i.e.*, a 79% yield of the 1,2-ethanediol–acetal from 2-methylpropanal and a 42% yield of corresponding ketal from 3-methyl-2-butanone.[4]

When the carbonyl group is conjugated with an aromatic ring, the yields are also reduced. Using 1,2-ethanediol, benzaldehyde produces 67–70% of the corresponding acetal (Table I) whereas phenylacetaldehyde gives its acetal in 81–83% yield under comparable conditions. Further, phenylacetone is converted to its ketal in 62–68% yield by the catalytic dehydrator whereas acetophenone gives only 22–24% of its ketal. Thus it appears that the additional conjugation of the carbonyl with its concomitant reduction in the carbonyl reactivity serves to inhibit the formation of ketals and acetals. This preferential phenomenon is of potential advantage when preparing monoacetals in compounds where several competing carbonyl groups are present.

The yields of acetals and ketals are sensitive to changes in substituents on the α carbon atom of the aldehyde or ketone. Phenylacetaldehyde yields 81–83% of 2-benzyl-1,3-dioxolane with the catalytic dehydrator whereas diphenylacetaldehyde produces 70–74% of 2-diphenyl-1,3-dioxolane. Similarly phenylacetone yields 62–68% of 2-benzyl-2-methyl-1,3-dioxolane while 1,1-diphenylacetone gives 48–51% of 2-diphenylmethyl-1,3-dioxolane.

Though optimum particle size for the calcium sulfate in the catalytic dehydrator has not been systematically studied, we have observed that the smaller the particle size, the higher the yield of products for a given reaction time. Presumably this is due to the increased surface area per gram on the smaller sized particles. If the work-up involves filtration as previously recommended for preparative work, then there is a point of diminishing returns on particle size because powder greatly retards filtration by clogging filter pores. The problem of slow filtration combined with the adsorption–inner diffusion process whereby the product is partially lost to the inner regions of the calcium sulfate[2] is now solved by a modified work-up procedure. At the termination of the reaction, the calcium sulfate particles are partially dissolved in a water solution and extracted with ether. Emulsions result if the quantity of water added is too small.

Preferably, the solvents should be dry before use. Minor amounts of water in the solvents and reactants can be tolerated; however, more catalytic dehydrator is required when the water content of the initial reaction mixture is significant.

Experimental Section

The ion exchange resins 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. The ion exchange resins were dried at 100° for 24 hr and stored in a desiccator prior to use, and the $CaSO_4$ (Drierite) was dried and stored at 200°. The glpc analyses were performed on a flame ionization Varian Model 1200-2 instrument equipped with columns containing 20% Carbowax 20–5% KOH on Chromosorb W.

General Procedure Illustrated for Cyclohexanone. A dry 500-ml erlenmeyer flask was fitted with an efficient mechanical stirrer. To the flask were added 28.4 g (30.0 ml, 0.29 mol) of cyclohexanone, 100.4 g (90 ml, 1.62 mol) of 1,2-ethanediol, 3.0 g of an anhydrous ion-exchange resin, and 46.5 g (0.342 mol) of finely ground anhydrous calcium sulfate. The viscous 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. Water (150 ml) was added, and the mixture was stirred again for 10 min. The layers were separated using a separatory funnel and the water layer was washed with 75 ml of diethyl ether. The combined ether layers were dried with anhydrous calcium sulfate and filtered and the solvent was removed by distillation. The product was obtained by distillation through a 90-cm spinning band column. After distillation, 1,4-dioxaspiro[4.5]decane was obtained as a colorless liquid, bp 51–52° (3 mm), $n^{22}D$ 1.4572. The yield was 31.9 g (79%).

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