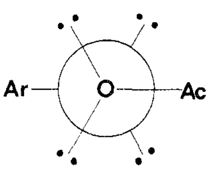
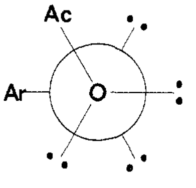


IIA



IIB

forms. Neither have such forms been revealed by the nmr spectra of several derivatives from Table I. Within the temperature interval −50 to 55°, which was limited by the solubility and stability of the compounds, no additional signals or shifts were observed. We conclude that the conformation IIa is the prevailing one, or even the only one present.

The result shows that the interaction of the two acyl groups is negligible as anticipated, but it is somewhat surprising with respect to the interactions about the I–O bonds. If we compare the two staggered conformations IIa and IIb in terms of Wolfe's theory[11] of gauche interaction, we would give IIb the preference. It has the bonds I–C and O–C in the gauche positions and in addition there is a double Edward–Lemieux effect[11] (a polar bond between two electron pairs) destabilizing the form IIa. We could conclude that Wolfe's concept is not applicable to dsp^3-hybridized atoms;[12] *e.g.*, the C$_1$–I–O angle of 90° could produce greater repulsion between phenyl and carbonyl groups, not fully compensated by the C–I and I–O bond lengths. Alternatively, the apparent exception could be caused by the presence of acyl groups. On the other hand, we do not find any clear reason why the repulsion between phenyl and carbonyl should exceed that between phenyl and, *e.g.*, alkyl. In addition, disagreement was found even with other compounds[13] where similar arguments do not apply. Hence, there is a more probable explanation that the whole theory,[11] although promising, is not valid without exceptions in its simplified form.

Experimental Section

Materials. *I,I*-Diacyloxyiodobenzenes were prepared by the known procedure[14] and found to be 99% pure by iodometry.

Physical Measurements. The same method was used as previously,[1-5,8] except that the concentration of benzene solutions was lowered to 10^{-3}–10^{-2} *M* owing to the low solubility.

Acknowledgment. Thanks are due to Mrs. M. Kuthanová for technical assistance in physical measurements and to Dr. V. Jehlička for the control.

Registry No.—Ia, 3240-34-4; Ib, 6973-73-5; Ic, 6597-18-8; Id, 51716-26-8; Ie, 38469-36-2; If, 38469-37-3.

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A Facile Method for the Transformation of Ketones into α-Substituted Aldehydes

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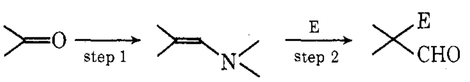
The introduction of dissimilar geminal substituents with concomitant creation of a quaternary carbon center remains a problem in the synthesis of natural products, where fully substituted carbon atoms commonly occur. Recent approaches to geminal alkylation involve the use of the thio-Claisen rearrangement,[2] the base-induced decomposition of methyl dialkylcyanodiazenecarboxylates,[3] the acid-catalyzed rearrangement of cyclopropyl ethers,[4] the [2,3] sigmatropic rearrangement of allylic sulfonium ylides[5] and allylic ammonium ylides,[6] the [2,3] sigmatropic rearrangement of sulfur-stabilized carbenoids,[7] the addition of organocopper or organolithium reagents to α, β-ethylenic sulfur compounds,[8] and the spiro annelation procedure based upon the rearrangements of oxaspiropentanes.[9] Unfortunately, these methods typically involve multistep procedures with the isolation of intermediates. We now wish to report an efficient, one-pot procedure for the one-carbon homologation of ketones to α-allyl aldehydes which may, in principle, be extended to the synthesis of other α-substituted aldehydes and ketones.

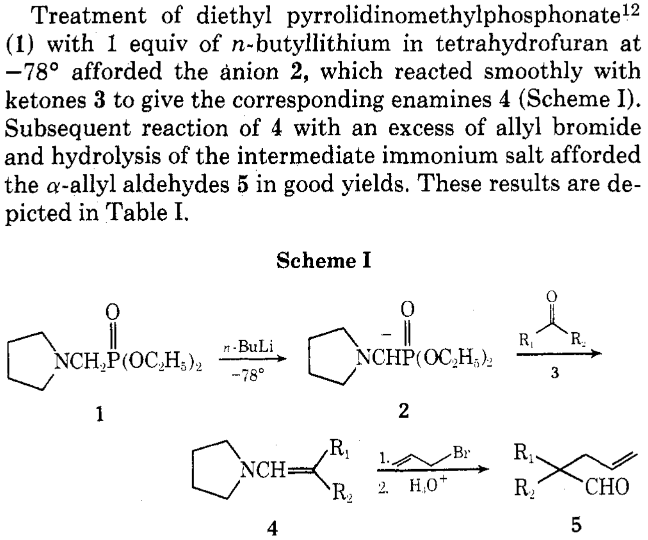
It is well known that enamines of aliphatic α-disubstituted aldehydes react readily with electrophilic reagents such as allyl bromide to afford, upon hydrolysis, α-allyl dialkylaldehydes.[10] It occurred to us that the conversion of a ketone with one-carbon homologation to the enamine of an α-disubstituted aldehyde, and the subsequent reaction of the thus formed enamine *in situ* with an appropriate electrophilic reagent (E), would provide an efficacious synthesis of a quaternary carbon atom possessing two substituents of differing functionality (eq 1). We envisioned that a modified Wittig reaction of a dialkylaminomethylphosphonic acid ester with a ketone would effect the conversion indicated in step 1.[11]



(1)

Treatment of diethyl pyrrolidinomethylphosphonate[12] (1) with 1 equiv of *n*-butyllithium in tetrahydrofuran at −78° afforded the anion 2, which reacted smoothly with ketones 3 to give the corresponding enamines 4 (Scheme I). Subsequent reaction of 4 with an excess of allyl bromide and hydrolysis of the intermediate immonium salt afforded the α-allyl aldehydes 5 in good yields. These results are depicted in Table I.

Scheme I



The enamines 4a–e which were generated are very useful synthetic intermediates which undergo a wide variety of transformations.[13] For example, in a preliminary experi-

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	

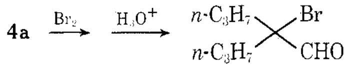
[a] +, enamine formation; −, no enamine formation. [b] No attempt was made to fully optimize yields. [c] A mixture of diastereomers (*ca.* 4:1) was obtained. [d] A mixture of alkylated and unalkylated aldehydes (*ca.* 1:1) was obtained.

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).



6 (2)

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.

Acknowledgment. We wish to thank the Alexander von Humboldt-Stiftung of West Germany for their generous financial support of this program.

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