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(7) Preference of the methyl to the methylene adjacent to the sulfur may be presumably due to geometrical factors in the transition states.
(8) Hitachi-Perkin molecular weight measuring apparatus Model 115; in methanol.
(9) Quantum yield was determined in Pyrex tubes (10 mM) by potassium ferrioxalate actinometry using 313-nm light on a merry-go-round.
(10) The results suggest τ to be ~20 ns for diffusion control quenching, consistent with a triplet state largely quenched intramolecularly, or a singlet state. Thus the problem of the multiplicity involved remains uncertain.
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(13) Relative efficiencies of the formation of **2** were obtained in Pyrex tubes (acetone, 10 mM) using 313-nm light on a merry-go-round with **1e** as a standard.
(14) Y. Kanaoka and Y. Hatanaka, Abstracts, Symposium on Photochemistry, Tokyo, Oct 1975, p 151.
(15) No direct intramolecular interactions between the phthalimide and sulfide moieties of **1** as monitored by uv absorption, emission, or infrared spectra have been detected so far. However, a weak charge transfer band is observed in the uv spectrum of an ethanol solution of *N*-methylphthalimide (0.04 M) containing methyl butyl sulfide (0.4–1 M) to indicate existence of intermolecular interaction between the two moieties in the ground states.[18] Presumably intramolecular interaction of **1** in the ground or, much more likely, excited states could operate to freeze the degree of freedom as well as to facilitate proton transfer in the course of the reaction. Photoreactions and charge transfer of ketosulfides have been studied,[17] while the phthalimide ring is known to be a good π-acceptor.[18] Ample precedents of photoreactions by charge transfer mechanisms are found, for example, in photoreduction of ketones with amines.[19]
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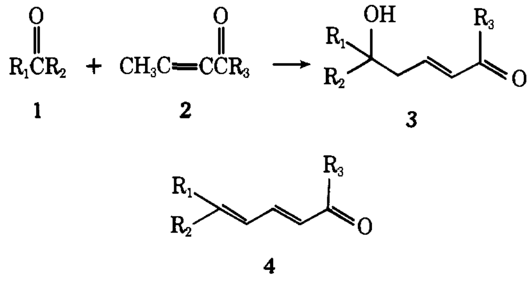
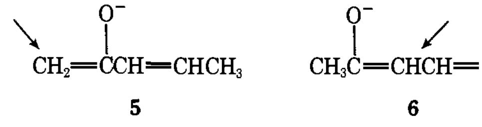
A New Synthesis of Vinylogous Aldols and Polyenones

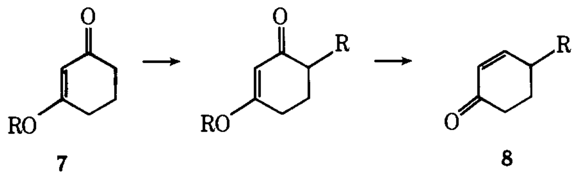
Sir:

We report here on a new and effective method for the simple introduction of an electrophile such as an aldehyde or ketone on the γ-carbon of an α,β-unsaturated ketone (**1** → **3**). The vinylogous aldols **3** are valuable per se, and also because their easy dehydration provides a convenient access to polyenic ketones **4**, especially since the aldehyde or ketone **1** could itself be unsaturated (vide infra). The difficulty in achieving this transformation stems, of course, from the fact that an α,β-unsaturated ketone such as ethylidene acetone (3-pentene-2-one, **2**, $R_3 = CH_3$) can be transformed either into a kinetic enolate **5**, leading to condensation at the methyl group, or into the (more difficultly obtainable) thermodynamic enolate **6**, which would normally lead to considerable condensation at the 3-position.[1]

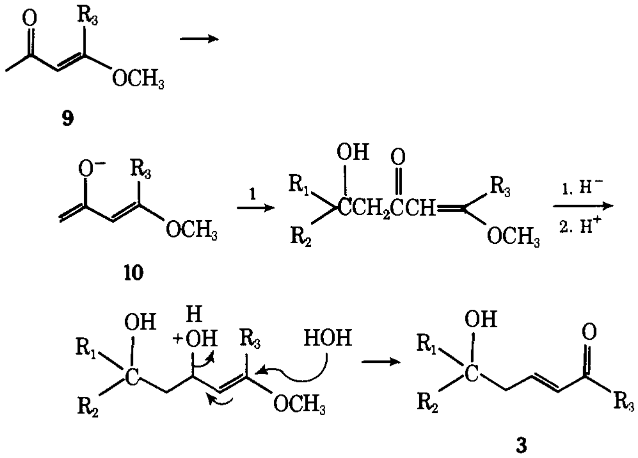




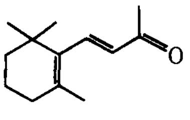
Our solution to the problem is based on the concept we introduced[2] for the construction of γ-substituted cyclic α,β-unsaturated ketones (**7** → **8**).



The vinylogous ester system present in the readily available enol ether of a 1,3-diketone (cf. **9**)[3] gives a kinetic enolate **10**[4] which reacts with aldehydes and ketones to give, after reduction and mild acid treatment, the vinylogous aldols **3**, the formal product of the condensation shown in **1** → **3** above.



The synthesis of vinylogous aldols is illustrated starting with β-ionone (**11**). A solution of 1 equiv of β-ionone in dry tetrahydrofuran was added slowly, at −78°, to a solution of the lithium enolate from 4-methoxy-3-pentene-2-one[5] (**12**), previously prepared by dropwise addition of 1 equiv of **12** in tetrahydrofuran to 1.1 equiv of a 0.5 M solution of lithium diisopropylamide in tetrahydrofuran at −78°, followed by stirring for 10 min. The solution was quenched after 20 min, while still at −78°, by addition 1.1 equiv of acetic acid. Unchanged starting material was removed after workup by bulb-to-bulb distillation under vacuum (85 °C, 0.5 mm), leaving the crude aldol **13**: λ 2.9, 6.3 μ; NMR δ 1.3 (s, $HOCCH_3$), 2.3 (s, $=C(COCH_3)CH_3$), 2.7 (d, J = 2 Hz, $CH_2C{=}O$), 3.65 (s, OCH_3), 5.5 (s, $HC{=}C(OCH_3)CH_3$),



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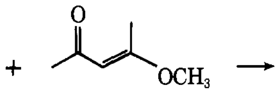

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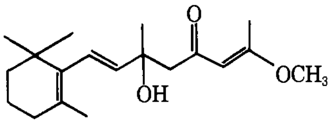

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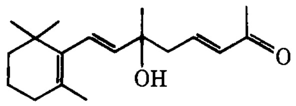

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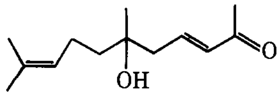

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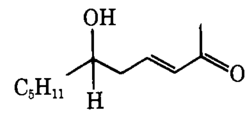
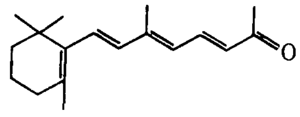


16

5.5 (d, J = 16 Hz), and 6.2 (br d, J = 16 Hz, $HC{=}CH$).[6] The crude aldol was reduced in benzene with 1.2 equiv of sodium bis-2-methoxyethoxyaluminum hydride (2 h, ~15°). Acidification to pH 2 with 1:7 sulfuric acid–ice water was followed by workup and purification by passing through silica gel (elution with methylene chloride). The vinylogous aldol **14** (40% from **11**) had R_f 0.15 on silica gel, λ 2.91, 5.98 μ; NMR δ 1.4 (s, $HOCCH_3$), 2.3 (s, $O{=}CCH_3$), 2.5 (br d, J = 7 Hz, $HOCCH_2C{=}C$), and 6.0–7.2 (m, $—HC{=}CHC({=}O)CH_3$). The vinylogous aldols **15** and **16** from 6-methyl-5-heptene-2-one and hexanal, respectively, were prepared similarly in ~50% overall yields. Dehydration of the vinylogous aldols to conjugated dienones is easily achieved, as we illustrate for the preparation of the C_{18} ketone **17**: methanesulfonyl chloride[7] (2 equiv in tetrahydrofuran) was added slowly to the vinylogous aldol **14** (0.5 M in tetrahydrofuran containing 7 equiv of triethylamine at 0°). Workup after 1 h (extraction with petroleum ether, filtration through silica gel) then gave the known **17** in 74% yield.[8,9] The known dienone **18**[10] (pseudoionone) was prepared similarly from **15**.



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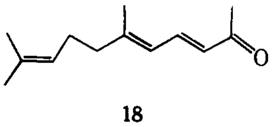

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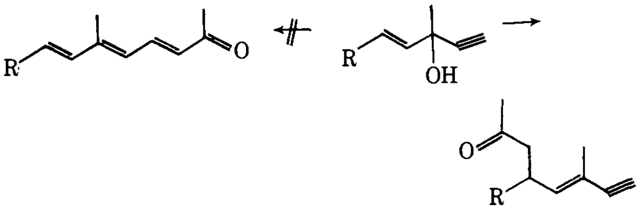
Although the overall yields of vinylogous aldols are only moderate (40–50%), the simplicity of the sequence and its compatibility with the existence of sensitive functionality (e.g., polyenes) should make it generally useful.[11] It is also worth emphasizing that the present method is of some importance in the construction of polyenones in general. There are at least two excellent methods[12] for the construction of conjugated *di*enones. They are, however, not suitable for the construction of more highly conjugated systems, such as **17**, because in such a situation the intermediates would undergo chain extension by rearrangement toward the double rather than the triple bond.



Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

References and Notes

(1) Cf. H. O. House, "Modern Synthetic Reactions," 2d ed., W. A. Benjamin, Menlo Park, Calif., 1972.
(2) G. Stork and R. Danheiser, *J. Org. Chem*, **38**, 1775 (1973).
(3) These are readily available by either of two methods: enol ether formation starting with symmetrical 1,3-diketones (cf. ref 5) or, in general, by alkoxide addition to conjugated ethynyl ketones.
(4) G. Stork, G. A. Kraus, and G. Garcia, *J. Org. Chem.*, **39**, 3459 (1974).
(5) Prepared from trimethyl orthoformate, acetyl acetone, and a small amount of *p*-toluenesulfonic acid in benzene–methanol at room temperature for 2 days, followed by distillation, according to unpublished results by R. Borch in this laboratory. For another, less convenient, method, cf. D. V. C. Aurang, *Can. J. Chem.*, **49**, 2672 (1971).
(6) NMR spectra are in deuteriochloroform and ir spectra are taken neat.
(7) In some related cases, superior results were obtained by the use of *p*-toluene sulfonylisocyanate as the dehydrating agent. (cf. L. C. Roach and W. H. Daly, *Chem. Commun.*, 606 (1970)).
(8) We thank Professor K. Nakanishi for the authentic sample which had been prepared according to J. F. Arens and D. A. Van Dorp, *Recl. Trav. Chim. Pays-Bas*, **65**, 338 (1946).
(9) The C_{18} ketone **17** thus obtained is an 85:15 *E*:*Z* mixture around the 9–10 double bond.
(10) Identified by comparison with an authentic sample.
(11) We have, for instance, used the vinylogous aldol **16** as the starting material for an "ene synthesis" of prostaglandins: G. Stork and G. A. Kraus, in preparation.
(12) W. Kimel, N. W. Sax, S. Kaiser, G. C. Eichmann, G. O. Chase, and A. Ofner, *J. Org. Chem.*, **23**, 153 (1958), and especially, G. Saucy and R. Marbet, *Helv. Chim. Acta*, **50**, 1158 (1967).

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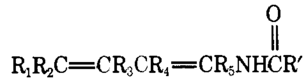
Synthesis of Trichloroacetamido-1,3-dienes. Useful Aminobutadiene Equivalents for the Diels–Alder Reaction

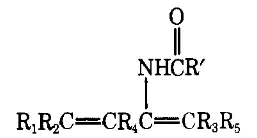
Sir:

Nitrogen substituted 1,3-dienes have received little study.[1,2] The most common examples are the sensitive N,N-disubstituted dieneamines, which are available by condensation of an unsaturated carbonyl compound with a secondary amine.[2,3] Acyclic dieneamides such as **1** and **2** are virtually unexplored.[2] For example, in the parent butadiene system only a single report exists of the synthesis of the 2-acetamido- and 2-benzamido derivatives,[4] while the corresponding 1-isomers are apparently unknown.[5] In this communication we report that thermolysis of propargylic trichloroacetimidates affords a general, one-step route to a variety of trichloroacetamido-substituted 1,3-dienes (**1** and **2**, $R'{=}CCl_3$, $R_4{=}H$). The thermal rearrangement of propargylic imidates has not to our knowledge been previously reported.[10] Since the trichloroacetyl group can be removed by treatment with dilute base,[11] dienes such as **1** and **2** ($R'{=}CCl_3$) hold particular synthetic interest as amino-1,3-diene equivalents for the Diels–Alder reaction. Few ni-



$$R_1R_2C{=}CR_3CR_4{=}CR_5NH\overset{\overset{O}{\|}}{C}R'$$

1



$$R_1R_2C{=}CR_4\overset{\overset{NH\overset{\overset{O}{\|}}{C}R'}{|}}{C}{=}CR_3R_5$$

2