

A NOVEL SYNTHESIS OF ALLYL VINYL ETHERS¹

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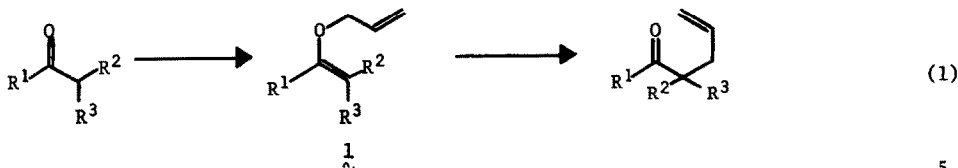
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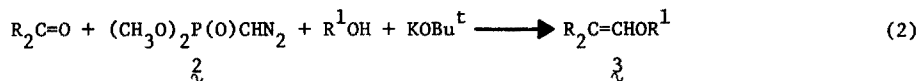
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Abstract: Base-promoted reaction of dimethyl diazomethylphosphonate (2) with aliphatic ketones in the presence of allylic alcohols affords aldehydic allyl vinyl ethers (3).

Allyl vinyl ethers, λ , are of interest because they undergo the Claisen rearrangement,² a sequence that accomplishes net α -allylation of carbonyl compounds (eq. 1). Modern methods for the preparation of aliphatic ethers have typically involved heating an excess of the carbonyl compound, as its ketal or as a simple enol ether, with the appropriate allylic alcohol and a catalytic amount of acid.^{3a} For those cases in which the alcohol is the more expendable reagent, it is used in large excess relative to the carbonyl component.^{3b} The ether λ that results is normally not isolable⁴ but undergoes rearrangement under the reaction conditions.^{3c}



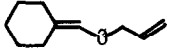


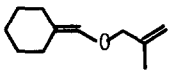


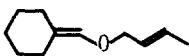
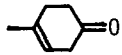

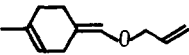


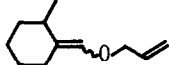


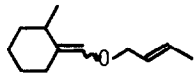

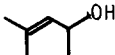
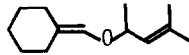

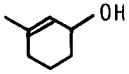
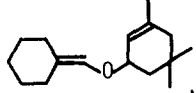

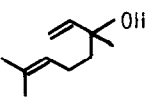
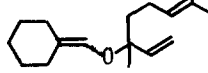
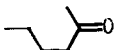

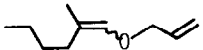


We have reported that the base-promoted reaction of dimethyl diazomethylphosphonate (2)⁵ with aliphatic ketones in alcoholic media affords aldehydic enol ethers, λ , in moderate to high yields (eq. 2).⁶ By analogy, use of an allylic alcohol in the reaction could give an allyl vinyl ether, λ ($R^1 = \text{Allyl}$). An alternate pathway, namely cyclopropanation of the pi bond of the alcohol, has precedent in the base-promoted reaction of aliphatic ketones and λ with alkenes;⁷ the potential importance of this reaction was difficult to predict with confidence.⁸



In the event, reaction of cyclohexanone with λ at room temperature in a solution of allyl alcohol and potassium *t*-butoxide gave λ [$R_2 = -(\text{CH}_2)_5-$, $R^1 = -\text{CH}_2\text{CH}=\text{CH}_2$]¹² in 60% yield, with

Table 1. Conversion of Ketones to Allyl Vinyl Ethers

| Entry ^a | Ketone | Alcohol | Ether ^b | Yield (%) ^c |
|--------------------|---|---|---|------------------------|
| 1 |  |  |  | 60 |
| 2 |  |  |  | 60 |
| 3 ^d |  |  |  | 50 |
| 4 ^d |  |  |  | 56 |
| 5 |  |  |  | 50 ^e |
| 6 |  |  |  | 51 |
| 7 |  |  |  | 43 |
| 8 |  |  |  | 46 |
| 9 |  |  |  | 20 |
| 10 |  |  |  | 13 (20) ^f |

^aAll reactions performed at room temperature with 1 mmol of ketone and 1.5 mmol each of dimethyl diazomethylphosphonate (**2**) and potassium *t*-butoxide unless noted otherwise. About 60 mmol of alcohol was used as reactant and solvent. For other details, see "Typical Procedure" section of this paper.

^bAll new compounds have mass, ir, and pmr spectra consistent with their assigned structures. As an example, see footnote 12.

^cBased on ketone and determined by pmr integration against benzene as an internal standard.

^dReaction performed at 0°.

^e*E:Z* ratio of 3.0:1.0 (see text).

^fYield obtained when 2.5 mmol of diazomethylphosphonate **2** was used.

no more than 5% of the cyclopropanation product being formed (pmr analysis of the crude reaction mixture). This represents the first reported example of generation of an allyl vinyl ether by way of the Wittig reaction. A previous attempt, that of Corey and Shulman, resulted in recovery only of starting materials upon reaction of cyclohexanone with allylidetriphenylphosphorane.¹³

This general methodology has thus far been extended to several types of allylic alcohols and four other ketones, and the results are collected in Table 1. It is clear that the method is successful with various cyclohexanones (entries 1, 4, and 5), although it gave a disappointingly low yield with single acyclic example examined (entry 10). The mildness of our technique is nicely illustrated by entry 4, in which an α,β -unsaturated cyclohexenone is converted to the corresponding allyl vinyl ether without prior base-catalyzed isomerization of the double bond.¹⁴ Entries 5 and 6 show that the sterically favored Z-isomer is formed preferentially,¹⁵ the result expected on the basis of the proposed mechanism of the reaction.⁶ Finally, 1° allylic alcohols generally give higher yields of ethers than do 2° or 3° examples (compare entries 1 and 2 with 7 through 9).

Some preliminary results are available from experiments designed to assess the effect on the yield of decreasing the excess of alcohol used in the reaction. Such experiments anticipate synthetic projects in which the allylic alcohol would be a more difficultly obtainable material as compared to those reported in Table 1. These results are recorded in Table 2. Although yields clearly are decreased by lowering the amount of alcohol used, the decrease is

TABLE 2. Yield of Allyl Vinyl Ether as Function of Alcohol Concentration and Reaction Mode.

| Entry ^a | Alcohol ^b | T (°C) | Mode ^c | Yield (%) ^d | Entry ^a | Alcohol ^b | T (°C) | Mode ^c | Yield (%) ^d |
|--------------------|----------------------|--------|-------------------|------------------------|--------------------|----------------------|--------|-------------------|------------------------|
| 1 | 73 | 25 | A | 60 | 5 | 5 | 0 | B | 26 |
| 2 | 10 | 25 | A | 33 | 6 | 5 | 0 | C | 43 |
| 3 | 10 | 0 | A | 44 | 7 | 5 | 0 | D | 39 |
| 4 | 5 | 0 | A | 40 | | | | | |

^aMolar ratio of cyclohexanone:2:KOBu^t of 1.0:1.5:1.5 was used; one mmol of ketone was used.

^bMolar ratio of allyl alcohol that was used.

^cMode A: A solution of ketone and 2 was added during 15 min to a solution of the alkoxide and the alcohol. The resulting mixture was stirred for 1-1.5 h prior to workup; mode B: Same procedure as A except that 2 was added to a solution of the other reagents; mode C: Same procedure as A except that the alkoxide was added to a solution of the other reagents; mode D: A solution of alcohol and alkoxide in 3 mL of pentane was added to the mixture of ketone and 2.

^dDetermined by pmr integration against benzene as an internal standard.

not unacceptable. Consequently, our technique holds promise for the synthesis of more complex allyl vinyl ethers. Such studies are currently in progress.

~~Typical Procedure:~~ A solution of dimethyl diazomethylphosphonate (2, 0.23 g, 1.5 mmol) and cyclohexanone (0.10 g, 1.0 mmol) in 2 mL of allyl alcohol was cooled to 0° under an atmosphere of dry nitrogen. To this magnetically stirred mixture was added a solution of potassium t-butoxide (0.17 g, 1.5 mmol) in 3 mL of allyl alcohol over a period of 1-2 min. Gas evolution was immediately evident. The reaction mixture was stirred at 0° for 1.5 h, after which 25 mL of pentane was added. The resulting solution was washed sequentially with water (2 x 25 mL) and brine (2 x 25 mL) and then dried (Na₂SO₄). Solvents were removed under vacuum, and the residue was subjected to spectroscopic analysis. Analytical samples were obtained by chromatography over silica gel.

References and Notes

1. The partial support of this work by the Robert A. Welch Foundation and the University Research Institute is gratefully acknowledged.
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6. Gilbert, J.C.; Weerasooriya, U. Tetrahedron Lett., 1980, 2041.
7. Gilbert, J.C.; Weerasooriya, U.; Giamalva, D. Tetrahedron Lett. 1979, 4619.
8. Cyclic allylic alcohols, with the exception of 2-cyclopenten-1-ol, react with dichlorocarbene to give dichlorocyclopropanes. Reaction of allyl alcohol itself with this carbene apparently involves the OH group exclusively,¹⁰ whereas the more nucleophilic pi-bond is the site of reaction in 1,3,3-trimethylallyl alcohol.^{9a} Newman reports reaction at the OH function of 2-methylallyl alcohol by the species (diazonium ion? carbene?) derived by base-promoted decomposition of N-nitrosooxazolidones.¹¹
9. a) Seyferth, D.; Mai, V.A. J. Am. Chem. Soc. 1970, 92, 7412; b) Ellison, R.H. J. Org. Chem. 1980, 45, 2509.
10. Seyferth, D.; Mai, V.A.; Mui, J.Y.-P.; Darragh, K.V. J. Org. Chem. 1966, 31, 4079.
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12. HRMS: 152.1208 (found); 152.1201 (calc. for C₁₀H₁₆O); IR (neat): 1680 cm⁻¹ (s), 1650 cm⁻¹ (w); PMR (CCl₄): δ 1.30-1.75 (m, 6H), 1.75-2.40 (m, 4H), 4.05-4.20 (d x m, 2H), 4.95-5.40 (m, 2H), 5.60-6.20 (m, 2H).
13. Corey, E.J.; Shulman, J.E. J. Am. Chem. Soc. 1970, 92, 5522.
14. At equilibrium, the ratio of α,β:β,γ-unsaturated ketones is 70:30; Lewis, K.G.; Williams, G.J. Tetrahedron Lett. 1965, 4573.
15. The stereochemical assignment was made on the basis of analysis of the pmr spectrum with the aid of lanthanide-induced shift reagents.

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