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Wittig Olefination : An Efficient Route for the Preparation of Allyl Vinyl Ethers - Precursors for the Claisen Rearrangement

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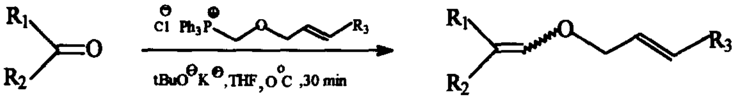
Abstract : A convenient procedure has been described for the preparation of allyl vinyl ethers-the precursors for the Claisen rearrangement

Over the years the Claisen rearrangement has emerged as a powerful synthetic tool.[1] Consequently, considerable efforts have been devoted to the preparation of allyl vinyl ethers, precursors for the Claisen rearrangement. Several methods [2-12] have been developed for the preparation or *insitu* generation of the allyl vinyl ethers. These include, the enol ether exchange with allyl alcohols catalyzed by mercuric acetate[5] or acids.[1,6] Preparation of these ethers via ketalisation of aldehydes[7] and ketones[8] with allylic alcohols has also been reported. Furthermore, Ireland-Claisen rearrangement,[9] involving allyl ester enolates and its modifications by Johnson[10] and Eschenmoser[11] is another useful procedure for the generation of allyl vinyl ethers. In spite of such an array of methods available for the generation of allyl vinyl ethers, there is a need for newer and efficient general methods to generate the allyl vinyl ethers.[12]

Our interest in this area has led us to explore alternative methods for the preparation of allyl vinyl ethers. In particular, a possible route based on Wittig olefination of ketones and aldehydes to furnish respective allyl vinyl ethers attracted our attention. Only a brief mention of this method exists.[13] It is reported that the method works with aryl ketones and aldehydes only. Further, no efforts to expand the scope of this method to aliphatic enolizable ketones and aldehydes have been reported so far. Moreover, no report exists in the literature regarding the preparation and reactions of the phosphoranes derived from substituted allyl alcohols. Similarly, application of this method in natural product synthesis has also not been reported. We report, herein, our efforts in these areas. Reaction of allyl chloromethyl ether[14] with triphenylphosphine in benzene gave allyloxymethylenetriphenylphosphonium chloride[15] **1** in near quantitative yield. Treating an equimolar mixture of the phosphonium salt **1** and a ketone in dry THF with 1.5 equivalents of potassium tertiary butoxide in tertiary butanol at ice bath temperature afforded the corresponding allyl vinyl ether [16,17] in good yield. Under these reaction conditions a variety of ketones and aldehydes furnished the corresponding allyl vinyl ethers in good yields (Tables I and II).

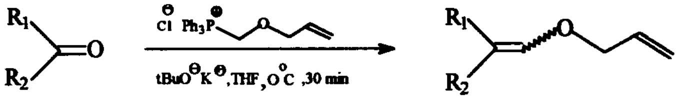
Table I : Reaction of allyloxy- and crotyloxy- methylene triphenylphosphonium chloride with aryl aldehydes and ketones

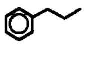
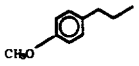
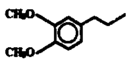
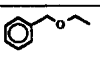
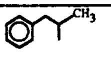
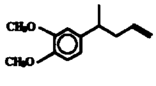
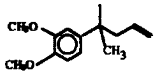


Sr.No.	R_1	R_2	R_3	%Yield[18]
1	p-Tolyl	Methyl	H	78
2	Phenyl	Methyl	H	76
3	Phenyl	n-Butyl	H	71
4	3,4-dimethyoxyphenyl	H	H	86
5	4-nitrophenyl	H	H	82
6	2-MOMphenyl	H	H	91
7	2-MOM,3-methoxyphenyl	H	H	89
8	2-MOM,4-methoxyphenyl	H	H	87
9	2-MOM,3,4-dimethoxyphenyl	H	H	83
10	2-MOM,4,6-dimethoxyphenyl	H	H	80
11	2-MOM,3-nitrophenyl	H	H	90
12	2-Hydroxyphenyl	H	H	10
13	p-Tolyl	Methyl	Methyl	74
14	3,4-dimethoxyphenyl	H	Methyl	83

Experimental Procedure : *The aldehyde/ketone(10 mmol) and allyloxymethylenetriphenylphosphonium chloride(12 mmol) are suspended in freshly dried and distilled THF(25 ml) under the inert atmosphere of argon. After stirring this suspension at icebath temperature for 15 min, a solution of potassium tertiary butoxide(15 mmol, freshly prepared from clean potassium metal and dry tertiary butanol) in tertiary butanol(20 ml) was added, dropwise, over a period of 30 min. On completion of the reaction (TLC check, typical time 30 min), it was subjected to normal aqueous workup followed by stripping off the solvent by normal distillation on water bath. The crude product*[19] *so obtained was purified by gravity column chromatography on silica gel column to get pure product.*

Table II : Reaction of allyloxymethylenetriphenylphosphonium chloride with acyclic enolizable aldehydes and ketones



Sr No	R1	R2	R3	Yield(%)[18]
1		H	H	85
2		Me	H	79
3		Me	H	81
4		Me	H	77
5		Me	H	62
6		H	H	83
7		H	H	81

Aryl aldehydes and ketones afforded the respective allyl vinyl ethers in good to excellent yields (Table I). In general, electron donating or withdrawing groups are tolerated under these conditions and have virtually no effect on the course and yield of the reaction. However, a free phenolic hydroxyl drastically reduces the yield of the allyl vinyl ether (entry No.12, Table I).

Under these new reaction conditions, the reaction of the enolizable acyclic aliphatic ketones and aldehydes furnished the corresponding allyl vinyl ethers in good to excellent yields (Table II). These results are in contrast to the reported failure of the enolizable ketones to furnish the allyl vinyl ethers under the published reaction conditions.[13] However cyclic aliphatic ketones like cyclohexanone or alpha tetralone failed to react under these new reaction conditions as well. Surprisingly, it was further observed that the degree of steric congestion around an enolisable acyclic aliphatic aldehyde or ketone has practically no effect on the yield of the reaction (entry Nos. 5,6,7 Table II).

With the intention to further expand the scope of this method, we prepared another Wittig salt analogous to allyloxymethylenetriphenylphosphonium chloride 1. Starting from crotyl alcohol and paraformaldehyde and adopting the reported conditions,[14] chloromethyl crotyl ether was prepared. Treatment of this ether with triphenylphosphine in benzene gave the crotyloxymethylenetriphenylphosphonium chloride[20] **2** in near quantitative yield. Reaction of this salt **2**, under the same conditions as above, furnished the corresponding crotyl vinyl ethers in good yields(entry No. 13,14, Table I).

Thus, unlike most other methods, the present method allows the isolation, purification and characterization of allyl vinyl ethers. Further we have shown that under these new reaction conditions one can prepare allyl vinyl ethers not only from aryl aldehydes and ketones but even from acyclic enolizable aliphatic aldehydes and ketones in good yields. Moreover under these conditions, steric congestion around aldehydes and ketones poses no problem in generating allyl vinyl ethers in good yields. Preparation of crotyloxymethylenephosphonium chloride **2** and its reaction with ketones and aldehydes has demonstrated that phosphoranes derived from substituted allyl alcohols react with same efficiency as that of the parent one. This should expand the scope of this method, in organic synthesis in general and natural product synthesis in particular, to a great extent. Currently efforts in this direction are in progress. Further investigations to bring the cyclic enolizable ketones under the ambit of the present method are in progress as well.

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15. m.p. 140- 142 °C (lit.13 136- 138°C) ; IR(cm^{-1}) : 1632, 1600, 1450, 1225, 1120, 940.
    ^{1}HNMR (CDCl3) : δ 4.39 (d, 2H, J= 5.1 Hz); 5.24 (m,2H); 5.70 (m, 1H); 5.83 (d, 2H, J=4.6Hz); 7.8 (m, 15H)
16. All new compounds gave satisfactory spectral data and elemental analysis.
17. Allyl vinyl ethers were obtained as E:Z (1:1) mixtures which were inseparable by column chromatography on silica gel.
18. The product yields represent the yields by weighing the products after isolation and purification on silica gel column.
19. The crude product was always contaminated by small amount of triphenylphosphine apparently generated during the reaction Such generation has been documented .[21]
20. m.p. : 145-147°O; IR (cm^{-1}) : 1622, 1590, 1441, 1220, 1110, 912; ^{1}HNMR($CDCl_3$) δ 1.53 (d, 3H, 5.39Hz, =C-CH3), 4.18 (d, 5.65, Hz, 2H, O-CH2), 5.34(m. 2H,), 5.62 (d, 4.12Hz, 2H, P-CH2-O), 7.66 (m, 15H)
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