

## PREPARATION OF ALLYL VINYL ETHERS BY WITTIG REACTION OF ALLYL FORMATES

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*Substituted allyl vinyl ethers are obtainable by the reaction of allyl formates with Wittig reagents. Reactivity of some of the produced allyl vinyl ethers was also examined.*

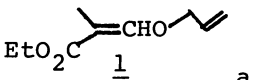
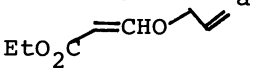
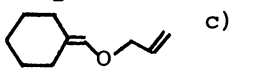
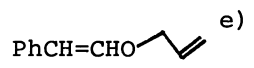
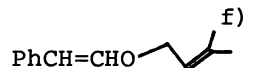
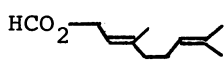
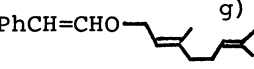
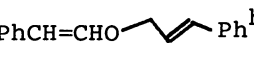
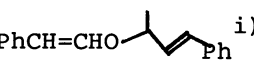
In recent years, Claisen rearrangement of appropriately functionalized allyl vinyl ethers has been used extensively as a useful synthetic method to construct  $\gamma,\delta$ -unsaturated carbonyl compounds.<sup>1)</sup> Allyl vinyl ethers are usually produced by vinylation of allyl alcohols using vinyllating agents such as orthoacetates. Besides them, two unique reactions to produce the ethers have been reported,<sup>2)</sup> in which ketones were converted to allyl vinyl ethers by the action of appropriate Wittig-Horner reagents. In this communication, we would like to report a new approach for the synthesis of allyl vinyl ethers.

Although some reports on Wittig reaction of esters have appeared,<sup>3)</sup> to the best of our knowledge, Wittig reaction of esters has never been applied to the synthesis of allyl vinyl ethers. We have already reported<sup>4)</sup> that dichloromethylenetriphenylphosphorane does react with esters to afford dichlorovinyl ethers and that formates are more reactive than other esters. As an extension of this reaction, we examined the reactivity of allyl formate toward various kinds of phosphoranes, and found that allyl vinyl ethers are actually produced in fair yields (equation 1).



Thus, a solution of (carbethoxyethylidene)triphenylphosphorane (13.8mmol) and allyl formate (40mmol) in toluene (30ml) was heated to 90°C for 14hrs. Hexane and ether were added to the reaction mixture, and precipitate was filtered off. The filtrate was concentrated and distillation afforded allyl 2-carbethoxy-1-propenyl ether 1 [bp 48-50°C/0.07 Torr; NMR(CDC1<sub>3</sub>)  $\delta$  1.27(3H), 1.75(3H,d,J=1Hz), 4.14(2H), 4.43(2H,m), 5.1-5.5(2H,m), 5.7-6.2(1H,m), 7.32(1H,bs); correct elemental analysis] in 60% yield. We prepared several substituted allyl vinyl ethers in a similar way, and the results are summarized in Table.<sup>5)</sup> Stabilized phosphonium ylids as well as di-substituted methylene ylids produced the expected

Table. Preparation of allyl vinyl ethers

Phosphorane	Allyl formate	Solvent	Reaction temp. (°C)	Product	Yield (%)
$\text{Ph}_3\text{P}=\text{C}(\text{CH}_3)\text{CO}_2\text{Et}$	$\text{HCO}_2\text{CH}_2\text{CH}=\text{CH}_2$	toluene	90		60
$\text{Ph}_3\text{P}=\text{CHCO}_2\text{Et}$	$\text{HCO}_2\text{CH}_2\text{CH}=\text{CH}_2$	toluene	90		29
$\text{Ph}_3\text{P}=\text{C}(\text{cyclohexyl})$ <sup>b)</sup>	$\text{HCO}_2\text{CH}_2\text{CH}=\text{CH}_2$	THF	50		54
$\text{Ph}_3\text{P}=\text{CHPh}$ <sup>b)</sup>	$\text{HCO}_2\text{CH}_2\text{CH}=\text{CH}_2$	THF	66 <sup>d)</sup>		82
$\text{Ph}_3\text{P}=\text{CHPh}$ <sup>b)</sup>	$\text{HCO}_2\text{CH}_2\text{CH}=\text{CMe}_2$	THF	66 <sup>d)</sup>		33
$\text{Ph}_3\text{P}=\text{CHPh}$ <sup>b)</sup>		THF	66 <sup>d)</sup>		83
$\text{Ph}_3\text{P}=\text{CHPh}$ <sup>b)</sup>	$\text{HCO}_2\text{CH}=\text{CHPh}$	THF	66 <sup>d)</sup>		60
$\text{Ph}_3\text{P}=\text{CHPh}$ <sup>b)</sup>	$\text{HCO}_2\text{CH}(\text{CH}_3)\text{CH}=\text{CHPh}$	THF	66 <sup>d)</sup>		61
$\text{Ph}_3\text{P}=\text{CHCH}_3$ <sup>b)</sup>	$\text{HCO}_2\text{CH}_2\text{CH}=\text{CHPh}$	THF	r. t.	—	—

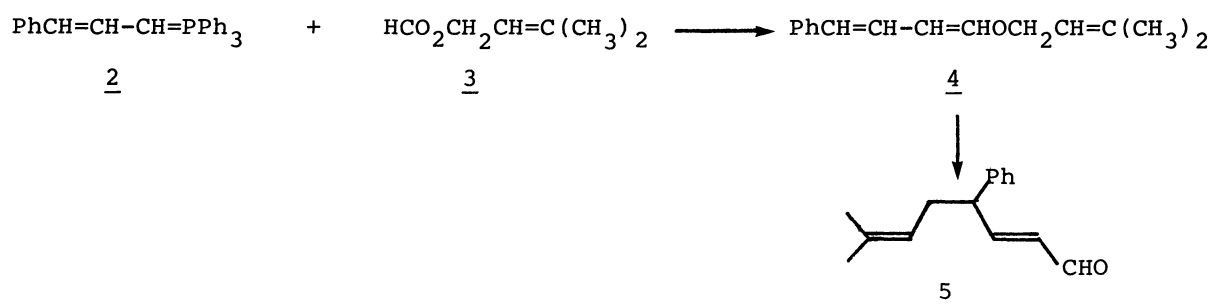
a) Bp 55°C/0.1 Torr; NMR  $\delta$  1.27(3H), 4.13(2H), 4.35(2H,m), 5.2-5.5(3H,m), 5.7-6.2(1H,m), 7.57(d,J=12.5Hz). b) Phosphoranes were prepared in situ from the corresponding phosphonium salts and butyllithium. c) Ref. 2b. d) THF refluxing temperature. e) NMR  $\delta$  4.30(2H,m), 5.1-5.4(2H,m), 5.7-6.2(2H,m), 6.97(1H,d,J=13Hz), 7.24(5H). f) NMR  $\delta$  1.71(3H,s), 1.77(3H,s), 4.33(2H,d,J=7Hz), 5.43(1H,t,J=7Hz), 5.87(1H,d,J=13Hz), 7.00(1H,d,J=13Hz), 7.23(5H). g) NMR  $\delta$  1.60(3H,s), 1.67(3H,s), 1.70(3H,s), 2.07(4H,bs), 4.33(2H,d,J=7Hz), 5.07(1H,m), 5.42(1H,t,J=7Hz), 5.85(1H,d,J=13Hz), 7.02(1H,d,J=13Hz), 7.22(5H). h) Mp 88-89°C; NMR  $\delta$  4.53(2H,d,J=6Hz), 5.97(1H,d,J=13Hz), 6.33(1H,dt, J=16,6Hz), 6.72(1H,d,J=16Hz), 7.05(1H,d,J=13Hz), 7.1-7.5(10H). i) NMR  $\delta$  1.45(3H,d,J=7Hz), 4.55(1H,m), 6.06(1H,d,J=13Hz), 6.25(1H,dd,J=16,6Hz), 6.60(1H,d,J=16Hz), 6.97(1H,d,J=13Hz), 7.2-7.5(10H).

ethers in fair yields, while non-stabilized mono-substituted methylene ylid gave no ether product.

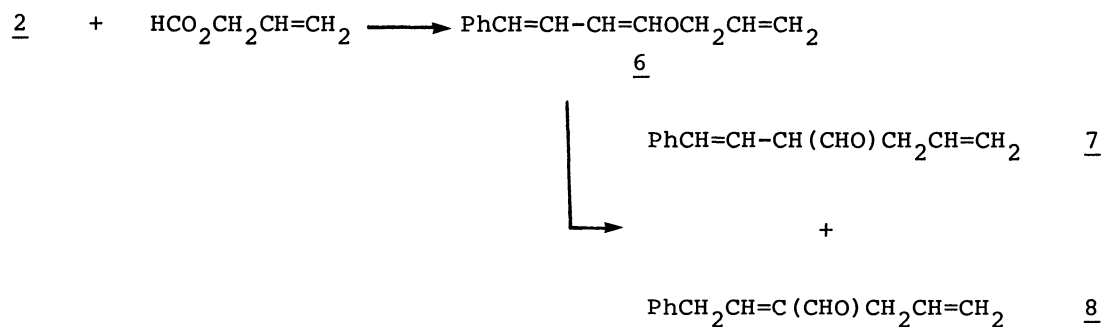
Rearrangement of produced allyl vinyl ethers was briefly examined. When 3,3-dimethylallyl 2-phenylvinyl ether was placed neat in an NMR tube and heated to 120°C for 2 hrs, the NMR spectrum showed only a new set of absorptions attributable to 3,3-dimethyl-2-phenyl-4-pentenal [NMR  $\delta$  1.03(3H,s), 1.10(3H,s), 3.33(1H,d,J=3Hz), 4.93(1H,d,J=18Hz), 5.03(1H,d,J=11Hz), 5.97(1H,dd,J=18,11Hz), 7.27(5H,bs), 9.97(1H,d,J=3Hz)]. Rearrangement of 1 proceeded more slowly than the above case (19hrs in refluxing xylene), and ethyl 2-formyl-2-methyl-4-pentenoate [NMR  $\delta$  1.27(3H), 1.30(3H,s), 2.53(2H,m), 4.20(2H), 5.0-5.3(2H,m),

5.5-6.0(1H,m), 9.73(1H,s)] was obtained in 67% yield after chromatographic purification.

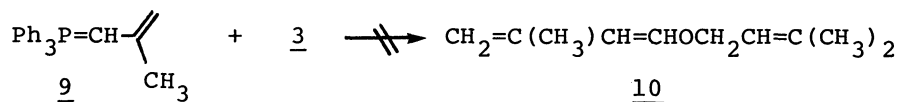
With a hope to extend this reaction to Claisen-Cope type rearrangement, we treated (3-phenyl-2-propenylidene)triphenylphosphorane 2 with 3,3-dimethylallyl formate 3 in THF, and the expected ether 4 could be isolated. Claisen-Cope type rearrangement proceeded by refluxing a xylene solution of 4 for 3 hrs, and 7-methyl-4-phenyl-2,6-octadienal 5 [NMR  $\delta$  1.54(3H,s), 1.64(3H,s), 2.48(2H,t, J=8Hz), 3.50(1H,bq, J=7.5Hz), 5.01(1H,bt, J=7.5Hz), 6.04(1H,ddd, J=16,8,1Hz), 6.88(1H,dd, J=16,7.5Hz), 7.1-7.5(5H,m), 9.49(1H,d, J=8Hz)] was obtained in 50% yield (from 2).



When 2 was similarly allowed to react with allyl formate in THF, vinyl ether 6 was obtained. In this case, however, the products of thermolysis (refluxing in xylene for 2 hrs) were Claisen rearrangement product 7 and its double bond isomer 8.<sup>6)</sup>



We then examined the reaction of formate 3 with phosphorane 9 in THF. Disappointingly, however, expected allyl vinyl ether 10, which would produce citral after rearrangement, could not be obtained at all.



## REFERENCES AND NOTES

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