

A NEW SYNTHESIS OF α,β -UNSATURATED KETONES

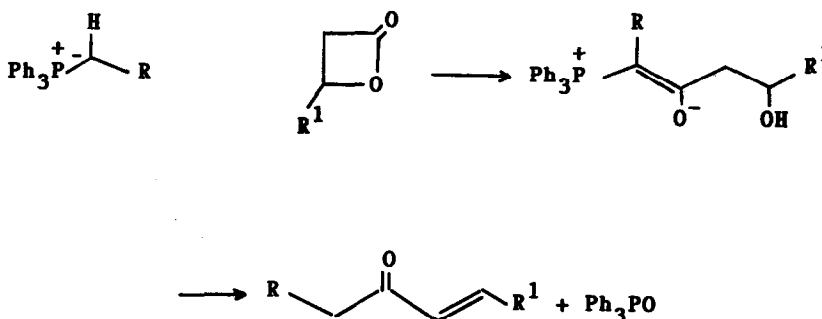
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Summary : α,β -unsaturated ketones have been obtained by thermolysis of δ -hydroxy β -keto triphenylphosphoranes prepared from the corresponding β -keto phosphoranes.

In a preceding paper (1), we have described a new extrusion reaction of triphenylphosphine oxide by thermolysis of the condensation product of a β -propiolactone and an ylide. (Scheme I)

SCHEME I



The scope of this practical synthesis of α,β -unsaturated ketones appears to be limited because of the relative inaccessibility of β -propiolactones.

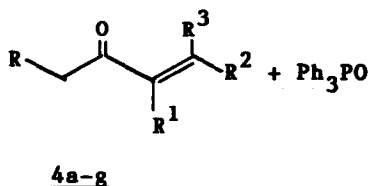
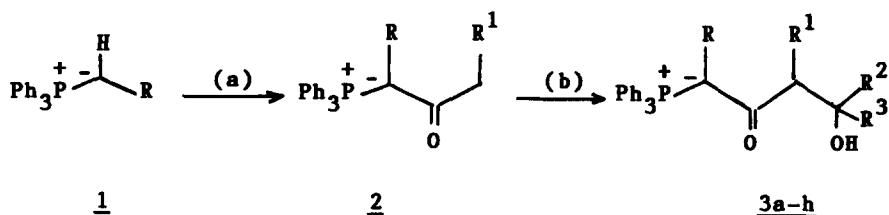
In this communication, we show that the extrusion described above may be the key step in a new general method for the synthesis of α,β -unsaturated ketones. (Scheme II)

The first step, (a), is a well known reaction : the acylation can be performed by the reaction of the ylide 1 with an acyl chloride (2), an acid anhydride (3), a thiol ester (4) or an aryl ester (5). The two latter reagents provide the keto-ylide 2 without the necessity of a transylidation.

The second step (b) has been previously described (6) with acetylmethylenetriphenylphosphorane (2, R = R¹ = H). We have found that this reaction is a general one and affords the compounds 3 in good yield whatever R, R¹, R² and R³.

The pyrolysis is accomplished by heating at 150-170°C under reduced pressure for 20-30 minutes. The ketone is condensed on a cooled trap. Examination of the ¹H-NMR spectra shows that the synthesis is stereoselective and affords only the α,β -unsaturated ketones possessing the E-configuration (95 %).

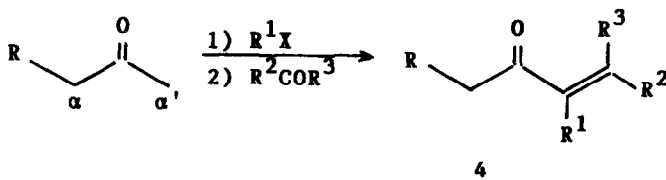
SCHEME II

(a) R¹COX(b) nBuLi, R²COR³

	R	R ¹	R ²	R ³
a	H	H	H	H
b	H	H	C ₃ H ₇	H
c	H	H	p-CH ₃ O-C ₆ H ₄	H
d	H	H	-(CH ₂) ₄ -	H
e	H	CH ₃	CH(CH ₃)C ₂ H ₅	H
f	CH ₃	CH ₃	H	H
g	C ₆ H ₅	H	C ₃ H ₇	H
h	CH ₃	CH ₃	CH(CH ₃)C ₂ H ₅	H

In principle, this synthesis could be envisioned to take place through alkylation of the enolate anion followed by an alkydenation reaction. (Scheme III)

SCHEME III



Unfortunately, in this last scheme, when starting from di-symmetric ketones, a mixture of different ethylenic ketones is obtained. In contrast, our method appears to be efficient because it permits a differentiation between α and α' sites. (7)

The table below shows the possibilities offered by this new synthesis.

Table α,β -unsaturated ketones 4

	Yield (%)	Eb ($^{\circ}\text{C}/\text{mmHg}$)	Lit. data
<u>4a</u>	40	48-52/350	33-4/130 (9)
<u>4b</u>	65	83-5/15	91-5/25 (10)
<u>4c</u>	72	80/5	-
<u>4d</u>	45	70/6	68/9 (11)
<u>4e</u>	62	80/15	-
<u>4f</u>	66	115-8/760	117-9/760 (12)
<u>4g</u>	61	76-9/2	-

yields represent pure isolated products

As shown in the table, a range of substitutions are possible using this method. However, we observe that the pyrolysis of bulky alcohols 3 is sometimes difficult. Thus, the alcohol 3h fails to give the corresponding α -ethylenic ketone 4h.

References :

- (1) J. Le Roux and M. Le Corre, J. Chem. Soc., Chem. Commun., 19, 1464 (1989),
- (2) H. J. Bestmann, Tetrahedron Lett., 7 (1960),
- (3) P. A. Chopard, R. J. G. Searle and F. H. Devitt, J. Org. Chem., 30, 1015 (1965),
- (4) H. J. Bestmann and B. Arnason, Tetrahedron Lett., 455 (1961); Chem. Ber., 95, 1513 (1962),
- (5) S. Tripett and D. M. Walker, J. Chem. Soc., 1266 (1961),
- (6) J. P. Taylor and J. F. Wolf, J. Chem. Soc., Chem. Commun., 876 (1972),
- (7) For a review of the syntheses of α,β -unsaturated ketones see reference (8),
- (8) D. A. Oare, M. A. Henderson, M. A. Sanner and C. H. Heathcock, J. Org. Chem., 55, 132 (1990),
- (9) A. Whol and A. Prill, Ann., 440, 142 (1924),
- (10) E. R. Alexander and G. R. Coroar, J. Am. Chem. Soc., 73, 2721 (1951),
- (11) D. Plouin, R. Glenat and R. Heilman, Ann. Chim., 191 (1967),
- (12) J. Colonge, Bull. Soc. Chim. Fr., 2116 (1936).

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