

A General Synthesis of β -Allenic Esters from Prop-2-ynyl Alcohols

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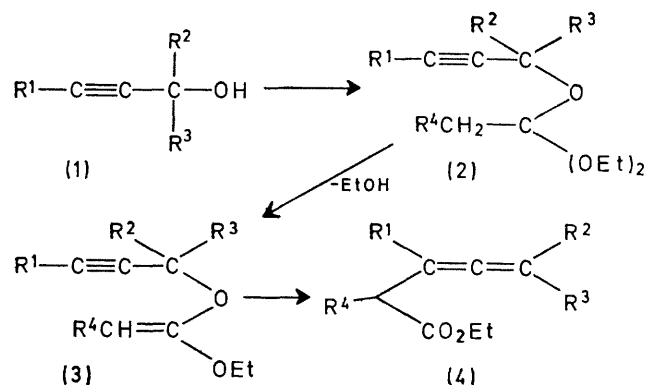
Summary β -Allenic esters are obtained by heating mixtures of prop-2-ynyl alcohols and orthoesters.

SEVERAL recent reports describe the synthetic adaptation of the aliphatic Claisen rearrangement of various vinyl prop-2-ynyl ethers (either pre-formed or generated *in situ*) which are thermally transformed into β -allenic ketones,¹ aldehydes,² and amides.³ These methods are limited in the sense that good yields of aldehydes and amides are obtained only for compounds with substitution in the α -position. We report here a related rearrangement which constitutes a good synthetic method for β -allenic ester derivatives with a full range of substitution.

The method is a modification of Johnson's stereoselective synthesis for trisubstituted olefins,⁴ which in the present instance involves heating a mixture of a prop-2-ynyl alcohol, 4–7 equiv. of triethyl orthoacetate, and a catalytic amount of propionic acid to *ca.* 140–150° for 1–5 h with removal of ethanol by distillation. The allenic esters were separated from the excess of orthoester and unreacted prop-2-ynyl alcohol by distillation. Yields were not optimized but were typically in the 50–60% range. Substitution of 2,4-dinitrophenol or toluene-*p*-sulphonic acid for propionic acid resulted in lower yields in the one case examined.

The results (Table) reveal that the reaction proceeds well

with a variety of prop-2-ynyl alcohols, giving good yields with substituents at either or both positions of the prop-2-ynyl alcohol and acceptable yields with the unsubstituted prop-2-ynyl alcohol (**1a**). Methyl substitution at the α -position was achieved in one instance by employing triethyl orthopropionate. The only alcohol studied which failed to undergo the indicated transformation was 2-phenylbut-3-yn-2-ol. It appears that β -allenic esters of almost any substitution pattern required can be synthesized by choosing the appropriate starting materials.



This reaction undoubtedly involves acid-catalysed transesterification and loss of ethanol from the resulting mixed orthoester (**2**) to generate (**3**), an appropriate substrate for Claisen rearrangement leading to allenic ester (**4**)

Conversion of prop-2-ynyl alcohols (**1**) into β -allenic esters (**4**)

	R ¹	R ²	R ³	R ⁴	h	Yield (%)
a	H	H	H	H	5 ^a	34
b	H	Me	H	H	1.5	63
c	H	Pr ⁿ	H	H	3	60
d	H	Me	Me	H	1.5	54
e	H	Me	Me	Me	5	59
f	Me	Me	Me	H	2	61
g	H	-[CH ₂] ₅ -		H	1	51

^a After removal of the excess of orthoester the reaction mixture was heated at 155° in diphenyl ether to complete the rearrangement.

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¹ G. Saucy and R. Marbet, *Helv. Chim. Acta*, 1967, **50**, 1158.

² E. R. H. Jones, J. O. Loder, and M. C. Whiting, *Proc. Chem. Soc.*, 1960, 180; D. K. Black and S. R. Landor, *ibid.*, 1963, 183; D. K. Black and S. R. Landor, *J. Chem. Soc.*, 1965, 6785; B. Thompson, U.S.P. 3,236,869/1966.

³ J. Ficini, N. Lumbroso-Bader, and J. Pouliquen, *Tetrahedron Letters*, 1968, 4139.

⁴ W. S. Johnson, L. Werthemann, W. R. Bartlett, T. J. Brocksom, T. L. Faulkner, and M. R. Peterson, *J. Amer. Chem. Soc.*, 1970, **92**, 741.