Preparation and Decarboxylation of Allenyl Acetic Acids: a Route to Substituted Buta-1,3-dienes

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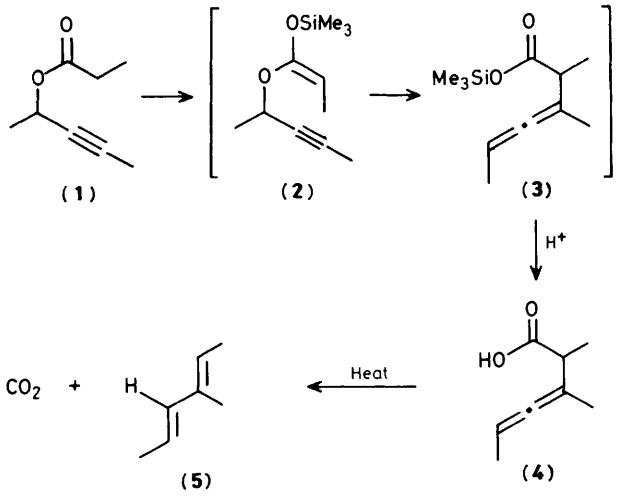
Propargylic esters undergo the Claisen ester rearrangement to give allenyl acetic acids which thermally decarboxylate to give substituted buta-1,3-dienes.

The enormous synthetic power of the Diels–Alder reaction, both in its intra- and inter-molecular forms, has stimulated interest in methods for 1,3-diene synthesis. We report here a convenient method for certain substitution patterns of such dienes which originate from prop-2-ynyl esters.

The strategy is outlined in Scheme 1, in which a prop-2-ynyl ester is converted, through the Claisen ester rearrangement,[1] into the allenyl acetic acid,[2] which is thermally decarboxylated to give the required diene. The prop-2-ynyl alcohols were prepared from the corresponding carbonyl compounds (by addition of the requisite acetylenic Grignard reagents) and acylated [acid chloride or anhydride, *N*,*N*-dimethylaminopyridine (DMAP), Et_3N] to give the starting esters (**1**). These esters were converted into the trimethylsilyl ketene acetals (**2**) [lithium hexamethyldisilazide (LHMDS) or lithium di-isopropylamide (LDA) in tetrahydrofuran (THF), −78 °C, followed by Me_3SiCl and warming to 40 °C] which spontaneously rearranged to give the allenyl acetic acid esters (**3**), isolated as the free acids (**4**).† These acids on heating in the absence of solvent underwent decarboxylation to give the dienes (**5**). In order to evaluate the scope and limitations of this transformation we have varied the substituents on the starting esters, with results shown in Table 1.

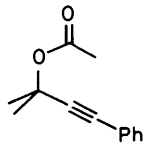
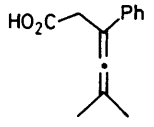
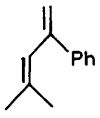
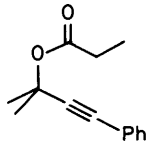
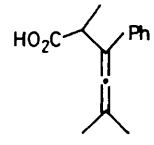
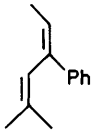
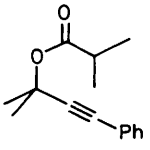
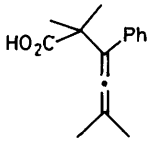
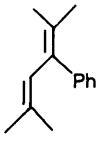
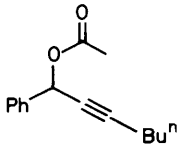
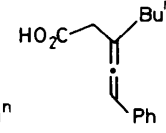
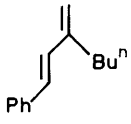
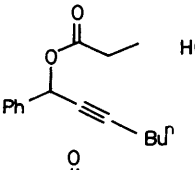
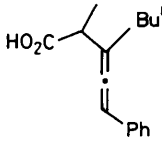
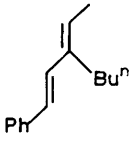
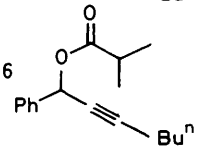
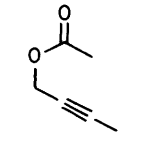
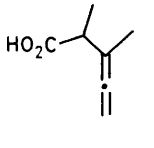
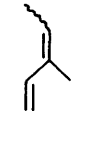
Several points emerge from this data. In those cases (entries 4—7) where competing deprotonation of the alkynyl group is possible then a large excess (3 equiv.) of base is required, presumably enabling the kinetically more labile ester hydrogens to be removed *before* base-catalysed acetylene–allene interconversion occurs. Indeed isobutyryl esters of potentially isomerising alcohols (entry 6) do not rearrange but give decomposition products from this alternative process. The formation of the ketene acetals from the tertiary alcohol derivatives (entries 1—3) is accompanied by some *C*-silyla-



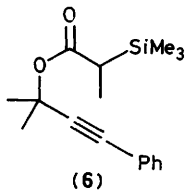
Scheme 1

† All new compounds have given satisfactory spectral and analytical data.

Table 1.

Entry	Ester	Allenyl acetic acid	% Yield	Diene	% Yield
1			50[a]		80[d]
2			54[b]		86[d]
3			86[a]		86[e]
4			80[c]		70[f]
5			60[c]		64[f]
6		— [g]		— [g]	
7			70[c]		100[f]

[a] Using 1 equiv. of LHMDS or LDA and Me_3SiCl. [b] Using 2 equiv. of LHMDS and Me_3SiCl. [c] Using 3 equiv. of LHMDS and Me_3SiCl. [d] Decarboxylation temp. 140 °C. [e] Decarboxylation temp. 180 °C. [f] Decarboxylation temp. 250 °C. [g] No rearrangement (using 3 equiv. of base) but decomposition products obtained.



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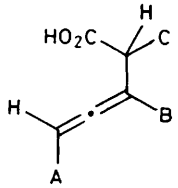

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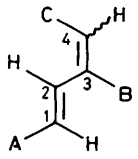

(8)

tion, which in one case led to the isolation of the unrearranged α-silyl ester (**6**) (entry 2).[3]‡

Finally alkyl substituents at the allene terminus (entries 1—3), definitely increase the ease of decarboxylation (140—180 °C) *vs.* the phenyl and hydrogen substituents (entries 5—7) (250 °C) presumably as a result of the increased electron density in these alkyl substituted allenes.

At present our knowledge of the stereochemistry of this new diene synthesis is limited but for the cases in Table 1 we conclude for the decarboxylation (**7**) to (**8**) that the 1,2-double bond is preferentially formed in the (*E*)-configuration (entries 4 and 5) whereas the 3,4-double bond in one case (entry 2) is entirely (*E*) while in another (entry 7) it is a mixture of (*E*) and (*Z*) forms. The factors controlling these effects are currently under investigation.

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‡ In the absence of silylating agent, only decomposition products were obtained, proving that the ketene acetals, (**2**), were indeed the reactive intermediates.

References

1 R. E. Ireland, R. H. Mueller, and A. K. Willard, *J. Am. Chem. Soc.*, 1976, **98**, 2868.

2 A report of the Claisen ester rearrangement of a propargyl ester has recently appeared, although the diene synthesis reported herein has not been described, *cf.* T. Hudlicky, L. D. Kwart, M. H. Tiedje, B. C. Ranu, R. P. Short, J. O. Frazier, and H. L. Rigby, *Synthesis*, 1986, 716.

3 The tendency towards *C*-silylation of enolates derived from the esters of hindered alcohols by Me_3SiCl has been previously observed. *cf.* M. W. Rathke and D. F. Sullivan, *Synth. Commun.*, 1973, **3**, 67.