Isomerisation of Prop-2-ynylic Esters into 1,2- and 1,3-Dienyl Esters†

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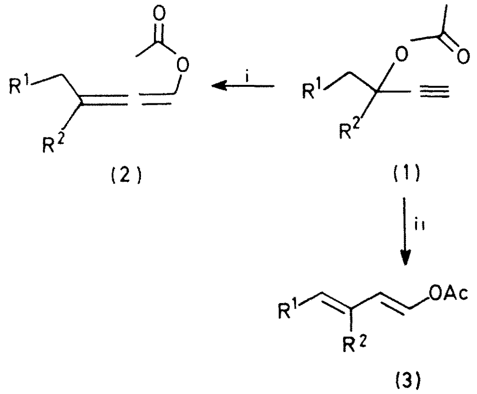
Summary While the prop-2-ynyl acetates (**1**) rearrange to the allenyl acetates (**2**) in boiling benzene containing copper(I) chloride, in the presence of silver trifluoroacetate the butadienyl acetates (**3**), useful in Diels–Alder reactions, are formed in high yield.

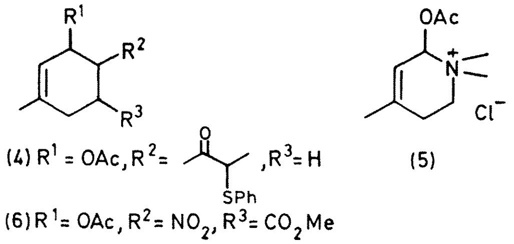
Allenyl (**2**), and particularly 1,3-dienyl (**3**), acetates are valuable synthetic intermediates. We report improved and specific ways of making them from prop-2-ynyl acetates (**1**).[1,2]

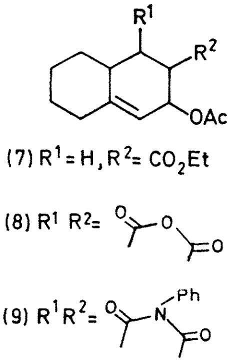


a; $R^1 = H$, $R^2 = Me$
b; $R^1R^2 = [CH_2]_4$
c; $R^1R^2 = [CH_2]_3$
d; $R^1 = H$, $R^2 = $ 4-methylcyclohex-3-enyl

Reagents: i, Cu_2Cl_2, boiling benzene; ii, $AgOCOCF_3$, in boiling benzene.

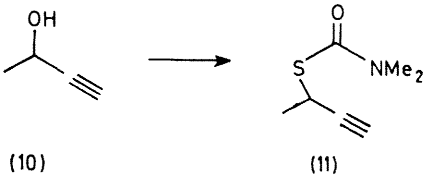
When the acetate (**1a**) was heated in benzene containing a catalytic quantity of silver tetrafluoroborate, the isomer (**2a**) was formed in 60% yield, as reported.[2] A better procedure, however, was to boil (**1a**) in benzene in the presence of Cu_2Cl_2, which gave (**2a**) quantitatively. Heating (**1a**) in benzene (or toluene) with silver trifluoroacetate surprisingly produced the diene (**3a**) as the sole product (7 : 1 *trans* : *cis*). These conditions also transformed the presumed intermediate (**2a**) into (**3a**). The same result was obtained when platinum chloride was used as catalyst in place of silver trifluoroacetate.





The dienes (**3**) underwent Diels–Alder reactions with suitable electron-poor olefins (Table).

Thus (**1a**) (3·4 g) in benzene (60 ml) containing silver trifluoroacetate (0·3 g) was heated under reflux for 6 h, cooled, and poured into water, and the organic layer was washed with aqueous $NaHCO_3$. Evaporation of the solvent gave (**3a**) (3·1 g, 91%), b.p. 62 °C at 15 mmHg (lit.,[3] 66—68 °C at 29 mmHg).



Table

Diene	Dienophile	Solvent	Product[a]	Yield[b]/%
(**3a**)	$CH_2{=}CHC(:O)CH(SPh)Me$	Boiling THF[c]	(**4**)	52
(**3a**)	$Me_2N^+{=}CH_2Cl^-$	MeCN[d]	(**5**)	64
(**3a**)	$O_2NCH{=}CHCO_2Me$[e]	Benzene[d]	(**6**)	63
(**3b**)	Ethyl acrylate	Boiling THF	(**7**)	64
(**3b**)	Maleic anhydride	Boiling THF	(**8**)	72
(**3b**)	*N*-Phenylmaleimide	Boiling benzene	(**9**)	91

[a] Assumed *endo*-addition, partly confirmed by n.m.r. spectroscopy. [b] Pure isolated product. [c] THF = tetrahydrofuran. [d] At room temperature. [e] *trans*.

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† No reprints available.

In contrast, treatment of the prop-**2**-ynyl alcohol (**10**) with sodium hydride in dimethylformamide at 5 °C, followed by dimethylthiocarbamoyl chloride gave the product (**11**) and none of the allene

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[3] J F W Keana, J S Bland, P E Eckler, and V Nelson, *J Org Chem* , 1976, **41**, 2124