Novel Preparation of a βγ-Unsaturated Methyl Ester from an Allylic Alcohol

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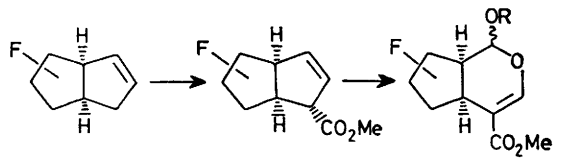
Summary The ester enolate Claisen rearrangement of the α-methoxyacetate of the allylic alcohol (**2**) followed by oxidative decarboxylation of the dianion derived from the resulting α-methoxycarboxylate provides an efficient

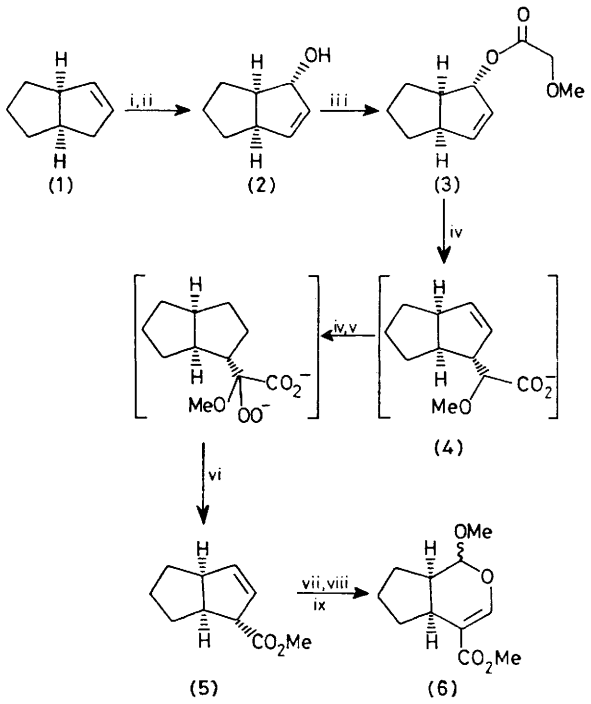
preparation of the β,γ-unsaturated ester (**5**), and hence leads to (**6**), the functionality of which is common to many mono- and sesqui-terpenes.

OUR studies[1] on the total synthesis of terpenes from readily available bicyclo[3.3.0]octane systems have led to the need for effecting the overall transformation in Scheme 1. We detail here an efficient sequence for the regiospecific introduction of an allylic methoxycarbonyl group.† Transformation of the alkene (**1**) to the allylic alcohol (**2**) *via* the epoxide and then formation of the α-methoxyacetate (**3**), followed by the ester enolate Claisen rearrangement of Ireland[2] and then the oxidative decarboxylation sequence of Wasserman,[3] results in the methyl ester (**5**).



SCHEME 1

Thus, the α-methoxyacetate (**3**),‡ when converted into the enolate[2] with lithium di-isopropylamide (LDA) at −78 °C in tetrahydrofuran (THF) followed by warming at 60 °C for 30 min was smoothly and cleanly transformed to a 2:1 mixture of the diastereomeric α-methoxycarboxylates (**4**), characterized as the methyl esters.‡ Without isolation, these carboxylates were converted into the dianions by further addition of LDA at −5 °C, which were then oxidized with dry oxygen at −78 °C.[3] After addition of camphorsulphonic acid, the reaction mixture was warmed to and then left at room temperature for 2 h. Aqueous work-up afforded an 82% yield of the unsaturated ester (**5**),‡ with spectra essentially identical with an analytically pure sample. Completion of the sequence by ozonolytic cleavage, reduction, and acid-catalysed methanolysis afforded, in 50% yield, a 9:1 mixture of the anomers (**6**) identical with that previously obtained by Tietze.[4]



SCHEME 2. Reagents: i, *m*-chloroperbenzoic acid–CH_2Cl_2; ii, $LiNEt_2$–Et_2O; iii, $MeOCH_2COCl$–pyridine; iv, $LiNPr^i_2$–THF; v, O_2–THF, −78 °C; vi, camphorsulphonic acid; vii, O_3, CH_2Cl_2; viii, Zn–HOAc; ix, MeOH–H^+.

Initial investigations with other allylic alcohols suggest that the high yield and purity here described may be unique to the cyclopentenyl system.

We are currently implementing this sequence in the synthesis of sarracenin[5] and xylomollin[6].

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† The procedure described by Büchi (G. Büchi, M. Cushman, and H. Wüest, *J. Amer. Chem. Soc.*, 1974, **96**, 5563) for the introduction of an allylic dimethylamido group works very poorly here. For a recent transformation of an allylsilane to this functional group see B.-W. Au-Yeung and I. Fleming, *J.C.S. Chem. Comm.*, 1977, 81.

‡ Satisfactory spectral and either high resolution mass or elemental microanalytical data were obtained for all new compounds.

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