Vinylogous Pummerer Rearrangement of Methyl Cyclopentylidene(phenylsulphinyl)acetate

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Summary Methyl cyclopentylidene(phenylsulphinyl)acetate undergoes a vinylogous Pummerer rearrangement to give allylic oxygen-functionalised phenylthio-derivatives.

RECENTLY, several examples of the rearrangement of vinyl sulphoxides have been reported.[1] We now describe a new type of rearrangement, the vinylogous Pummerer rearrangement, of the acetate (**1**).

Compound (**1**) was prepared (60% overall) by sequential treatment of cyclopentanone with the dilithio-derivative of (phenylthio)acetic acid[2] at −60 °C to give a hydroxy-carboxylic acid, esterification with diazomethane, dehydration with $SOCl_2$–pyridine at 22 °C (1 h) and 70 °C (3 h) to methyl cyclopentylidene(phenylthio)acetate, and oxidation with *m*-chloroperbenzoic acid at 0 °C.†

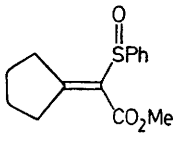
Treatment of (**1**) with refluxing dioxan–dil. H_2SO_4 (6N; 1:4 v/v) for 3 h gave a 53% yield of the α-phenylthio-

† All compounds were characterized by combustion analysis as well as by i.r. and n.m.r. spectroscopy.

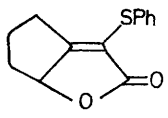
butenolide (**2**) accompanied by a trace of the hydroxy-ester (**3**). The transformation of (**1**) into the allylic hydroxylated products (**2**) and (**3**) could be accounted for by a mechanism including a vinylogous Pummerer type rearrangement-type intermediate (**4**),[3,4] with concomitant lactonisation in the case of (**2**).

The same rearrangement was also induced, in contrast to the inertness[4] of simple vinyl sulphoxides by hot acetic anhydride. The reaction of (**1**) with acetic anhydride at 75 °C for 3 h afforded two regioisomeric acetoxy-esters, (**5**) (50%) and (**6**) (15%), and the conjugated dienoic ester (**7**) (19%), respectively. At reflux temperature compound (**7**) was the sole product. Although definite evidence has not been obtained, the positions of the acetoxy-group in (**5**) or (**6**) and the endocyclic double bond in (**7**) were tentatively assigned from the following evidence. (i) The acetoxy-function may be preferentially introduced at the allylic carbon atom *cis* to the ester group analogous to the predominant formation of the lactone (**2**). (ii) The major isomer (**5**) was easily converted into (**2**) (44%), (**7**) (8%), and the methoxy-ester (**8**) (19%) by treating with perchloric acid in ether at room temperature.‡

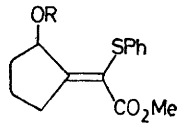
Furthermore, addition of pyridine affects markedly not only the reaction rate but also the rearrangement pathway. Thus, treatment of (**1**) with Ac_2O–pyridine (2:1) at room temperature overnight afforded the sulphur-free acetoxy-ester (**9**) in 83% yield [in the absence of pyridine (**1**) remained unchanged]. The geometry of the substituents in (**9**) was confirmed by saponification with NaOMe in MeOH to the hydroxy-ester (**10**) (91%). The formation of (**9**) may be explained by assuming pyridine-catalysed migration of the double bond in (**1**) to the endocyclic position, followed by the allylic sulphoxide-sulphenate rearrangement recently reported by Evans and Andrews.[5]



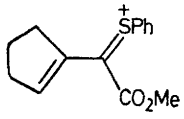
(1)



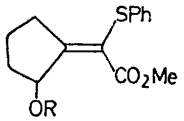
(2)



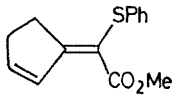
(3) R = H
(6) R = Ac



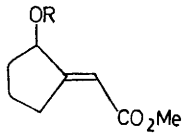
(4)



(5) R = Ac
(8) R = Me



(7)



(9) R = Ac
(10) R = H

The present reaction should be useful for introduction of an allylic hydroxy- or acetoxy- group to an acrylic ester unit.

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‡ All attempts at alkaline hydrolysis and desulphurisation of (**5**) and (**6**) for correlation with (**2**), (**3**), or (**9**) were unsuccessful.

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