

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 acid² 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 .[†]

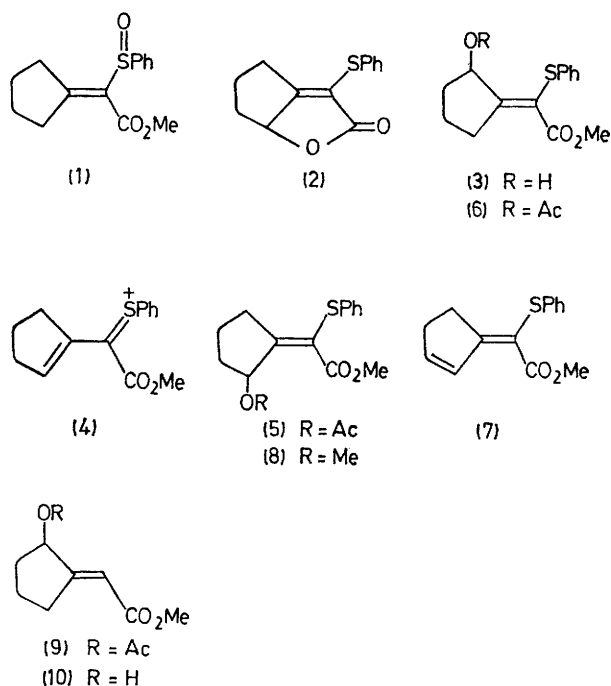
Treatment of (**1**) with refluxing dioxan-dil. H_2SO_4 (6*N*; 1:4 v/v) for 3 h gave a 53% yield of the α -phenylthio-

[†] 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 inertness⁴ 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 Ac₂O-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



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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² K. Iwai, M. Kawai, H. Kosugi, and H. Uda, *Chemistry Letters*, 1974, 385.

³ R. Pummerer, *Ber.*, 1909, **42**, 2282; 1910, **43**, 1401; L. Horner and P. Kaiser, *Annalen*, 1959, **626**, 19; C. R. Johnson and W. G. Phillips, *J. Amer. Chem. Soc.*, 1969, **91**, 682; T. Durst, in 'Advances in Organic Chemistry,' eds. E. C. Taylor and H. Wynberg, vol. 6, Interscience, New York, 1966, p. 356.

⁴ W. E. Parham and L. D. Edwards, *J. Org. Chem.*, 1968, **33**, 4150.

⁵ D. A. Evans and G. C. Andrews, *Accounts Chem. Res.*, 1974, **7**, 147.