Phenyl *trans*-2-Chlorovinyl Sulphone, a Vinyl Cation Equivalent

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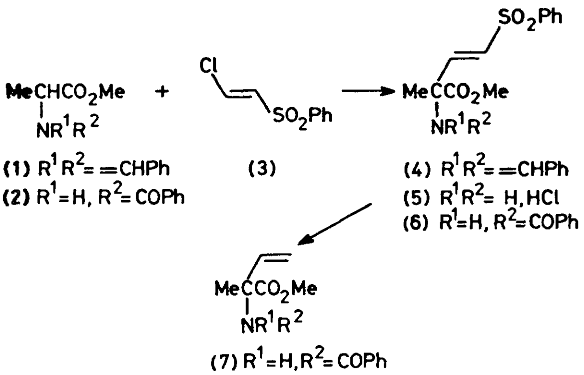
Summary Phenyl *trans*-2-chlorovinyl sulphone is a vinyl cation equivalent useful for the conversion of α-amino acids into α-vinyl α-amino acids.



It is known that phenyl *trans*-2-chlorovinyl sulphone (**3**) readily undergoes substitution with a variety of heteroatomic nucleophiles,[1] and that vinyl sulphones can be reduced to the corresponding olefins.[2] A sequential combination of these reactions, using a carbanionic nucleophile would appear, therefore, to offer a means for the electrophilic introduction of a vinyl unit at carbon. Our interest in α-vinyl α-amino acids as potential irreversible enzyme inhibitors[3] has led us to investigate, in a model sequence, the transformation of alanine to *N*-benzoyl-α-vinyl-alanine methyl ester, using phenyl *trans*-2-chlorovinyl sulphone (**3**) as a vinyl cation synthon.[4]

Thus the ester enolate derived from the ester (**1**)[5,6] adds, with concomitant elimination of chloride, to (**3**) at −78 °C to afford the phenyl *trans*-vinyl sulphone (**4**). Without purification compound (**4**) was treated with dilute hydrochloric acid, the resulting amine hydrochloride (**5**)† (m.p. 120 °C) being isolated in 83% overall yield. Compound (**5**) was converted into the benzamide (**6**)† (m.p. 143 °C) by routine methods, and (**6**) was readily desulphurized using aluminium amalgam,[2] to afford *N*-benzoyl-α-vinyl-alanine methyl ester (**7**)† (m.p. 109 °C) in 80% yield. Alternatively *N*-benzoylalanine methyl ester (**2**) can be directly converted, in 57% yield, into (**6**), *via* the reaction of its derived dianion[7] with (**3**).

Another α-vinyl α-amino acid in which the α carbon is also fully subsituted, α-vinyl-3,4-dihydroxyphenylalanine, has been made previously *via* reduction of acetylenic intermediates,[3,8] while Baldwin[9] has reported the synthesis of some βγ-unsaturated glycine analogues *via* reduction of the corresponding nitro derivatives. The use of a vinyl cation synthon offers a complementary strategy, as the α-vinyl α-amino acids may be prepared from the corresponding α-amino acids.

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† N.m.r. and i.r. spectra and elemental analyses are consistent with the proposed structure.

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