

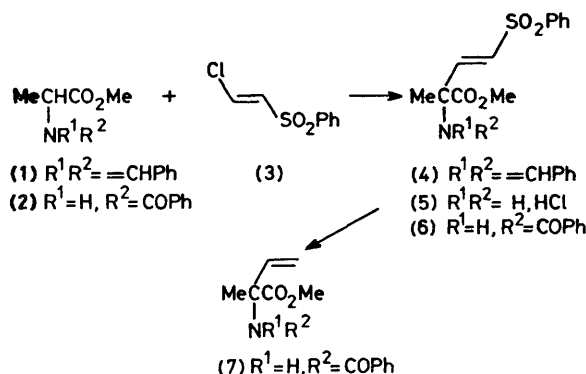
## Phenyl *trans*-2-Chlorovinyl Sulphone, a Vinyl Cation Equivalent

By BRIAN W. METCALF\* and EDITH BONILAVRI

(Centre de Recherche Merrell International, 16, rue d'Ankara, 67084 Strasbourg Cedex, France)

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

It is known that phenyl *trans*-2-chlorovinyl sulphone (3) readily undergoes substitution with a variety of heteroatomic nucleophiles,<sup>1</sup> and that vinyl sulphones can be reduced to the corresponding olefins.<sup>2</sup> 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  $\alpha$ -vinyl  $\alpha$ -amino acids as potential irreversible enzyme inhibitors<sup>3</sup> has led us to investigate, in a model sequence, the transformation of alanine to *N*-benzoyl- $\alpha$ -vinyl-alanine



methyl ester, using phenyl *trans*-2-chlorovinyl sulphone (3) as a vinyl cation synthon.<sup>4</sup>

Thus the ester enolate derived from the ester (1)<sup>5,6</sup> adds, with concomitant elimination of chloride, to (3) at  $-78^{\circ}\text{C}$  to afford the phenyl *trans*-vinyl sulphone (4). Without purification compound (4) was treated with dilute hydrochloric acid, the resulting amine hydrochloride (5)<sup>†</sup> (m.p.  $120^{\circ}\text{C}$ ) being isolated in 83% overall yield. Compound (5) was converted into the benzamide (6)<sup>†</sup> (m.p.  $143^{\circ}\text{C}$ ) by routine methods, and (6) was readily desulphurized using aluminium amalgam,<sup>2</sup> to afford *N*-benzoyl- $\alpha$ -vinyl-alanine methyl ester (7)<sup>†</sup> (m.p.  $109^{\circ}\text{C}$ ) 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<sup>7</sup> with (3).

Another  $\alpha$ -vinyl  $\alpha$ -amino acid in which the  $\alpha$  carbon is also fully substituted,  $\alpha$ -vinyl-3,4-dihydroxyphenylalanine, has been made previously *via* reduction of acetylenic intermediates,<sup>3,8</sup> while Baldwin<sup>9</sup> has reported the synthesis of some  $\beta\gamma$ -unsaturated glycine analogues *via* reduction of the corresponding nitro derivatives. The use of a vinyl cation synthon offers a complementary strategy, as the  $\alpha$ -vinyl  $\alpha$ -amino acids may be prepared from the corresponding  $\alpha$ -amino acids.

(Received, 3rd July 1978; Com. 698.)

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

<sup>1</sup> F. Montanari, *Gazzetta*, 1956, **86**, 415.

<sup>2</sup> V. Pascali and A. Umani-Ronchi, *J.C.S. Chem. Comm.*, 1973, 351.

<sup>3</sup> B. W. Metcalf and K. Jund, *Tetrahedron Letters*, 1977, 3689.

<sup>4</sup> Two other vinyl cation synthons have been reported: T. Oishi, H. Takechi, and Y. Ban, *Tetrahedron Letters*, 1974, 3757; G. A. Koppel and M. D. Kinnick, *J.C.S. Chem. Comm.*, 1975, 473.

<sup>5</sup> G. Stork, A. Y. W. Leong, and A. Touzin, *J. Org. Chem.*, 1976, **41**, 3491.

<sup>6</sup> P. Bey and J. P. Vever, *Tetrahedron Letters*, 1977, 1455.

<sup>7</sup> A. P. Krapcho and E. A. Dundulis, *Tetrahedron Letters*, 1976, 2205.

<sup>8</sup> D. Taub and A. A. Patchett, *Tetrahedron Letters*, 1977, 2745.

<sup>9</sup> J. E. Baldwin, S. B. Haber, C. Hoskins, and L. I. Kruse, *J. Org. Chem.*, 1977, **42**, 1239.