Phenyl Vinyl Sulphoxide, a Vinyl Carbonium Ion Synthetic Equivalent

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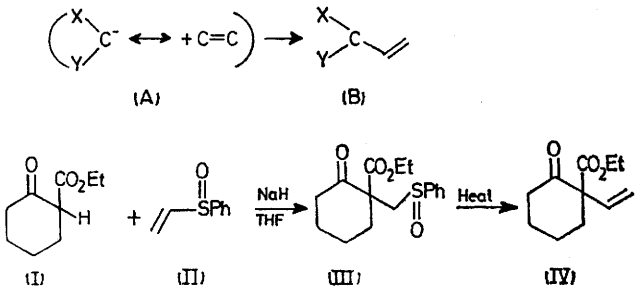
Summary Reaction of ethyl 2-oxocyclohexanecarboxylate (I) with phenyl vinyl sulphoxide (II) and sodium hydride followed by pyrolysis of the resulting phenylsulphonylethyl compound (III) gives the 1-vinyl compound (IV).

IN view of the isolation and structural proof of the antitumour sesquiterpene vernolepin,[1] which has an angular vinyl substituent, we have investigated methods of introducing a terminal vinyl group.[2] The early introduction of such a group as a protected equivalent was considered to be a crucial step in our syntheses. We thought that the work of Tsuchihashi and his co-workers[3] demonstrating that *p*-tolyl vinyl sulphoxides undergo Michael reactions and that of Trost and Saltzmann[4] using the pyrolysis of sulphoxides in generating olefins could be combined, providing the synthetic equivalent of the vinyl carbonium ion, (A) → (B). A method for vinyl group synthesis has been reported recently,[5] and we report here the reaction of compound (I) with phenyl vinyl sulphoxide (II), which was prepared by treatment of phenyl disulphide with vinyllithium and subsequent oxidation with peroxy-acid.

Treatment of (I) (2 equiv.) with NaH (1 equiv.) and phenyl vinyl sulphoxide (1 equiv.) in tetrahydrofuran at reflux afforded after workup and preparative thick-layer chromatography a 50% yield of (III) as a mixture of diastereoisomers; τ ($CDCl_3$) 2·5 (m, Ph), 5·8 (q, CO_2Et), 6·8—8·8 (side-chain and ring H); *m/e* 223 ($M^+ + 1$) and 125 (100%). Subsequent pyrolysis of (III) in refluxing toluene for 72 h afforded the previously reported[5] compound (IV) (60%).



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[1] S. M. Kupchan, R. J. Hemingway, D. Werner, A. Karim, A. T. McPhail, and G. A. Sim, *J. Amer. Chem. Soc.*, 1968, **90**, 3596.
[2] Two syntheses of the bicyclic vernolepin skeleton have been reported, see P. A. Grieco and K. Hiroi, *Tetrahedron Letters*, 1973, 1831; R. D. Clark and C. H. Heathcock, *ibid.*, 1974, 2027.
[3] G. Tsuchihashi, S. Mitamura, S. Inoue, and K. Ogura, *Tetrahedron Letters*, 1973, 323.
[4] B. M. Trost and T. N. Salzmann, *J. Amer. Chem. Soc.*, 1973, **95**, 6840.
[5] T. Oishi, H. Takechi, and Y. Ban, *Tetrahedron Letters*, 1974, 3757.