

Phenyl Vinyl Sulphoxide, a Vinyl Carbonium Ion Synthetic Equivalent

By G. A. KOPPEL* and M. D. KINNICK

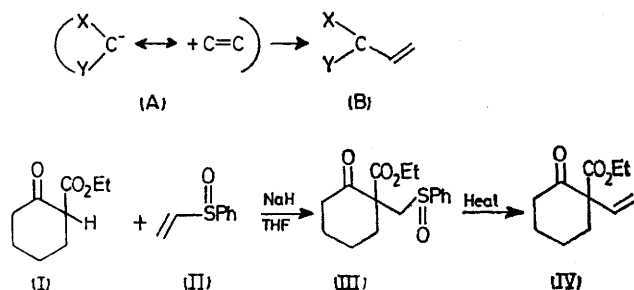
(The Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana 46206)

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

IN view of the isolation and structural proof of the anti-tumour 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-workers³ demonstrating that *p*-tolyl vinyl sulphoxides undergo Michael reactions and that of Trost and Salzmann⁴ 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 vinyl-lithium 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 (CDCl₃) 2.5 (m, Ph), 5.8 (q, CO₂Et),



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 reported⁶ compound (IV) (60%).

(Received, 6th March 1975; Com. 283.)

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.