

Synthesis of (\pm)-Versimide

By P. R. ATKINS and I. T. KAY*

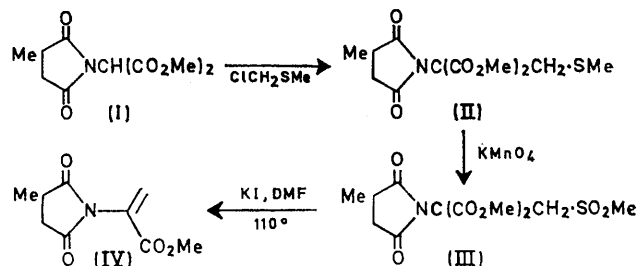
(Imperial Chemical Industries, Plant Protection Limited, Jealott's Hill Research Station, Bracknell, Berkshire)

Summary Following a mild decarbomethoxylyative β -elimination reaction, dimethyl 2-(methylsuccinimido)-2-(methylsulphonylmethyl) malonate gives (\pm)-versimide in high yield.

A RECENT Patent¹ claiming the insecticidal properties of versimide, methyl (+)-(*R*)- α -(methylsuccinimido)acrylate,² a mould metabolite from *Aspergillus versicolor*, prompted our investigation of routes to this compound. The instability of versimide at elevated temperatures or in the presence of base¹ imposes restrictions on possible routes to it, and we report here a mild decarbomethoxylyative β -elimination reaction which gives (\pm)-versimide in high yield.

The reaction of methylsuccinimide as its sodium salt in methanol with dimethyl bromomalonate gave the succinimidomalonnate (I) as a colourless waxy solid, m.p. 86°. An attempt to use this intermediate in an approach to versimide based upon the β -elimination reported recently³ to give α -methylene- γ -butyrolactones, was frustrated by its failure to undergo the Mannich reaction. As an alternative therefore, a C(1)-substituent, destined to become the methylene group of versimide, was introduced by the reaction of the anion derived from the malonnate (I) with chloromethyl methyl sulphide which gave the oily sulphide (II). The derived sulphone (III), m.p. 140°, with an

excess of potassium iodide in dimethylformamide (DMF) (110°; 30 min) gave, following the loss of CO₂, a mixture of dimethylsulphone and (\pm)-versimide as the sole detectable



products. After chromatography (silica-ether) the racemic natural product was obtained (81%) as a colourless oil, the physical properties (i.r., n.m.r., ref. index) of which were as reported² for versimide. The work was extended to the preparation of the succinimido-(oil; n_D^{20} 1.4980) and phthalimido-(m.p. 107°) analogues of versimide, and in all cases the elimination reaction proceeded smoothly to give the anticipated products in high yields.

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¹ B.P. 1,187,070/1970.

² A. G. Brown, *J. Chem. Soc. (C)*, 1970, 2572.

³ E. S. Behare and R. B. Miller, *Chem. Comm.*, 1970, 402.