## The Coupled Ionic Addition of NN-Dichlorourethane and Acetonitrile with Styrene and Indene

By B. CROOKES, T. P. SEDEN, and R. W. TURNER\*

(Imperial Chemical Industries Limited, Pharmaceuticals Division, Alderley Park, Macclesfield, Cheshire)

THE free-radical addition of NN-dichlorourethane (D.C.U.) to olefins was recently described,<sup>1</sup> and the coupled ionic addition<sup>2</sup> of NN-dichloro-sulphonamides and acetonitrile to olefins has been demonstrated.<sup>3</sup> We report the analogous coupled addition of NN-dichlorourethane and acetonitrile with styrene and indene.



Treatment of styrene with NN-dichlorourethane in acetonitrile solution gave, after washing with sodium hydrogen sulphite solution, the free-radical addition product (I) in 85% yield. However, when the reaction was carried out in the presence of one mole of aluminium chloride at 0°, followed by stirring for several hours at room temperature, 1-ethoxycarbonyl-2-methyl-4-phenyl-2-imidazoline (II) (purified by preparative v.p.c. using 10% S.E.E.-301 on 60-85 Phase Sep. N., oven temperature 240°,  $M^+$  232) was obtained in 42%

yield. The 100 Mc./sec. n.m.r. spectrum (CDCl<sub>3</sub>) showed a multiplet (five protons) centred at  $\tau 2.78$ (C<sub>6</sub>H<sub>5</sub> protons), a multiplet (one proton) at  $\tau$  5.02 (X proton of the ABX system, also exhibiting long-range coupling with the ring methyl group protons), a multiplet (3 protons) at  $\tau$  5.87 (CH<sub>2</sub> protons of the ethyl group and the A proton of the ABX system), a quartet (one proton) at  $\tau 6.4$ (B proton of ABX system), a doublet (3 protons) at  $\tau$  7.63 (ring CH<sub>3</sub> protons coupled to the X proton of the ABX system, J 1.0 c./sec.), and a triplet (3 protons) at  $\tau$  8.76 (CH<sub>3</sub> protons). The structure of the 2-imidazoline was verified by synthesis from the urethane (I). Treatment of (I) with acetonitrile in concentrated sulphuric acid gave (II) in 70% yield, a Ritter reaction taking place followed by cyclisation. The 2-imidazoline was hydrolysed by boiling water to give the acetate (III), m.p. 140°, in good yield, whilst more vigorous hydrolysis with concentrated hydrochloric acid gave phenylethylenediamine in 32% yield.

A similar coupled ionic addition reaction was also observed with indene, the cis-fused imidazoline (V) (purified by v.p.c., oven temperature 260°,  $M^+$  244) was obtained in 25% yield. The 100 Mc./ sec. n.m.r. spectrum (CDCl<sub>3</sub>) showed the single benzylic proton as a quartet centred at  $\tau 4.60$ . The coupling constant for the bridgehead protons was 9.0 c./sec. indicative of a *cis*-fusion,<sup>4</sup> further coupling with the ring methyl protons  $(I \cdot 4 c)$ sec.) explained the occurrence of the quartet.

The formation of the 2-imidazoline (II) from styrene is thought to involve the initial formation of the coupled ionic addition product (IV), presumably complexed with aluminium chloride. Subsequent treatment with hydrogen sulphite solution causes breakdown of this complex and cyclisation to give (II). In the case of indene the intermediate complex, arising from a stereospecific trans-addition, undergoes a similar decomposition and cyclisation, which incorporates an inversion, to give the observed *cis*-fused imidazoline (V).

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