Initial β-Lactam Formation From 2-Cyclopropylpropene and Chlorosulphonyl Isocyanate

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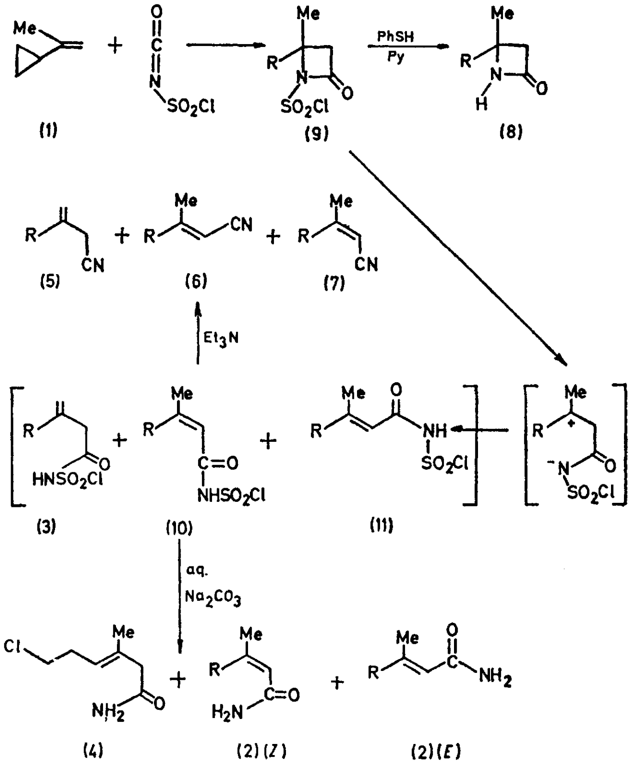
Summary Addition of chlorosulphonyl isocyanate to 2-cyclopropylpropene affords a β-lactam which rearranges through heterolytic cleavage and prototropic shift.

Recently three reports of the addition of chlorosulphonyl isocyanate (CSI) to bicyclic systems containing a vinylcyclopropane unit have appeared. The reaction with bicyclo[3,1,0]hex-2-ene yields solely a β-lactam[1] while bullvalene gives a β-lactam which undergoes subsequent rearrangement[2] and *cis*-bicyclo[6,1,0]-nonatriene systems yield *trans*-β-lactams presumably arising from the intermediacy of dipolar 1,3-bishomotropylium ions.[3] In each case it is implied that the addition takes place through initial formation of a dipolar adduct although no evidence is presented against initial ($\pi 2s + \pi 2a$) cycloaddition followed by heterolytic ring opening of the β-lactam.[4] We report here the results of the reaction of CSI and a nonbicyclic vinylcyclopropane, 2-cyclopropylpropene (1), a system which will clearly allow the nonbisecting geometry necessary for cyclopropyl stabilization.[5]

Equimolar amounts of CSI and (1) in ether at 0°, were stirred for 2 h at 25°; treatment with aqueous Na_2CO_3 afforded (2) (*E* and *Z*) and (4). Compound (4) presumably arises from attack of HCl on (3) which we have been unable to circumvent. Repeated fractional crystallization provided only a pure sample of (4), m.p. 113·0—114·5°.† If the reaction mixture (in $CHCl_3$) was treated with triethylamine, only the expected nitriles[6] (5), (6), (7) were formed; they could be separated by g.l.c.†

Although these products undoubtedly arise from dipolar intermediates, evidence for initial formation of β-lactams was obtained by admixture of CSI and (1) in ether at −60° followed by treatment with thiophenol-pyridine at −45°. Work-up and column chromatography (Florisil) afforded only the β-lactam (8) (53%), m.p. 39—41°.† Most conclusively, admixture of equimolar quantities of CSI and (1) in $CDCl_3$ at −78° warming to −60° and



R = Cyclopropyl throughout

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† Spectral (i.r., n.m.r., and mass) and analytical data supported the structural assignments proposed for all compounds.

recording of the n.m.r. spectrum showed complete disappearance of (1). The spectrum was consistent with the presence of compound (9). Upon warming to 0° (in the probe) the disappearance of the spectrum of (9) was observed with concurrent appearance of the combined spectra of (10) and (11) (*ca.* 3·5 to 1).

The addition of CSI to (1) appears to initially involve a concerted cycloaddition. Whether this is the case for previously reported bicyclic vinylcyclopropanes[1-3] is still not known but must certainly be considered. The ability of an *N*-chlorosulphonyl-β-lactam to undergo heterolytic ring-opening presumably can always be predicted on the basis of carbonium ion stabilities.

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