Stereospecific *cis* Radical Addition. Convincing Evidence for a 1,3-Radical Transfer Reaction

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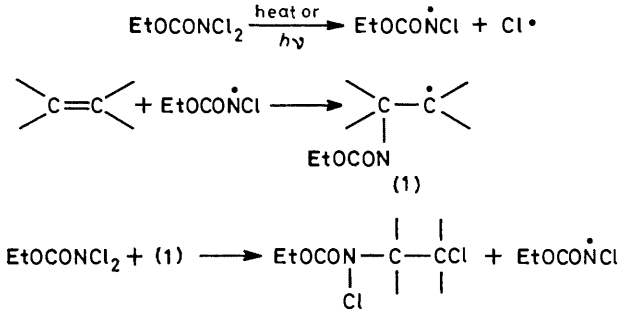
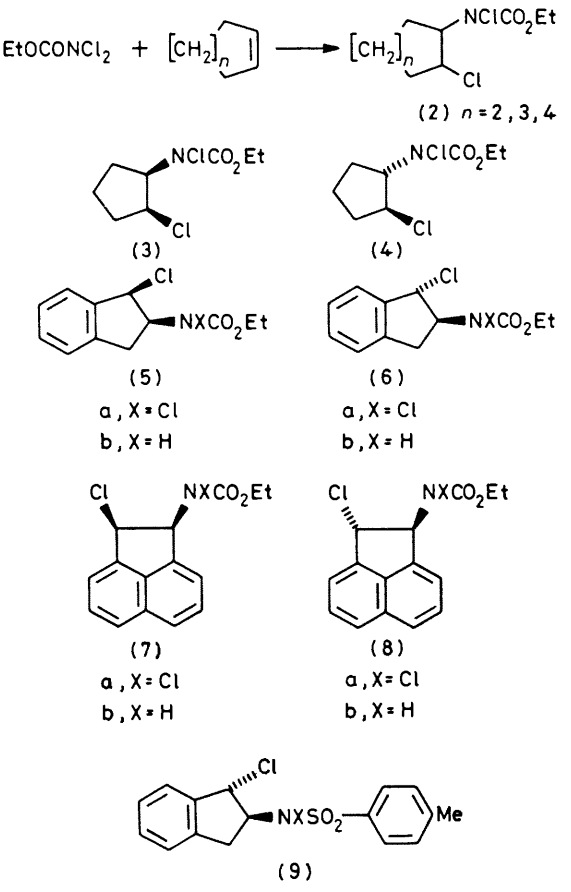
Summary The addition of ethyl *NN*-dichlorocarbamate or *NN*-dichlorophosphoramidates to five-membered cyclic alkenes at 0 °C is stereospecific and *cis*; these results are conveniently explained by a 1,3-atom shift mechanism.

THE addition of ethyl *NN*-dichlorocarbamate (DCC)[1] and *NN*-dichlorophosphoramidates (DCPA)[2] (WARNING)† to carbon–carbon double bonds is a well established reaction of considerable synthetic use.[3,4] Evidence for the radical nature of both of the reactions is available[1,2] and Foglia and Swern[1] have suggested the mechanism shown in the Scheme for the addition of DCC. The stereochemistry of these reactions has not been studied in any detail, however, *cis*, *trans*,[1,6] and cyclic[1] alkenes are all reported to give mixtures of isomers.



SCHEME

We have investigated the reactions of both DCC and DCPA with cyclic alkenes and found that in certain cases the addition is stereospecific and *cis*. DCC reacts on stirring at room temperature in benzene with cyclohexene, cycloheptene, and cyclo-octene to give the corresponding 2-chloro-*N*-chlorocarbamate (**2**) as a mixture of isomers (t.l.c.).‡ A similar reaction with cyclopentene at 0 °C gave a single product (**3**), while reaction at room temperature gave an isomeric product (**4**) and no detectable amount of (**3**) (n.m.r.). The isomer (**3**) could be readily converted into (**4**) by gentle heating. Under similar conditions, indene gave (**5a**) at 0 °C and (**6a**) at room temperature and acenaphthylene gave (**7a**) at 0 °C and (**8a**) at room temperature. In each case the isomer obtained at 0 °C could be converted into that obtained at room temperature by gently heating in benzene solution. In all cases the *N*-chloro group could be reduced to N–H, by treatment with sodium metabisulphite solution below 10 °C, without affecting the stereochemistry (n.m.r.). Analogous isomeric addition products were obtained from reactions of cyclopentene and indene with DCPA.‡

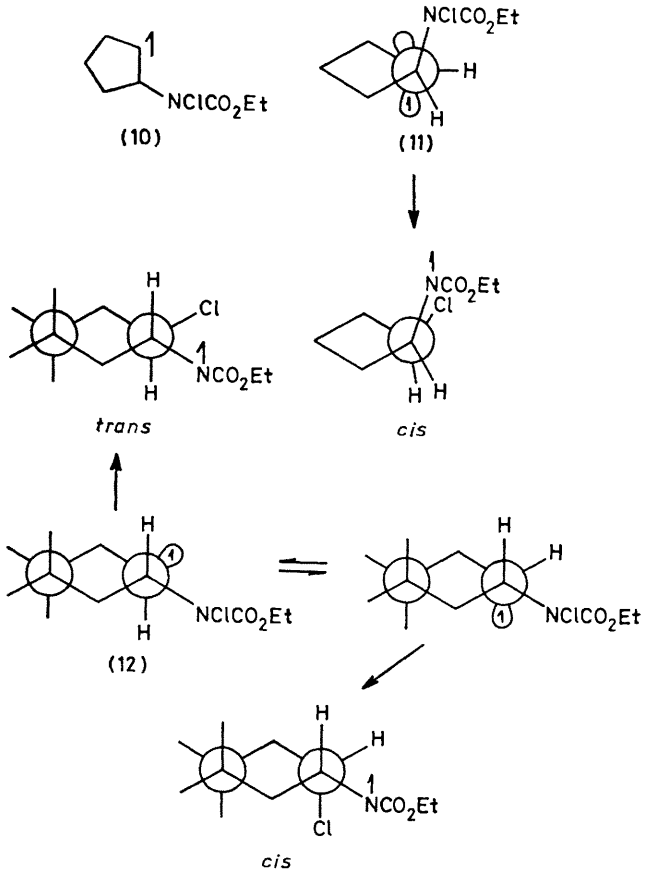


In all cases the mass spectrum gave a molecular ion at an *m/e* value equivalent to that of a simple adduct and analysis indicated only covalently bound chlorine; for the reduced adducts the i.r. spectra showed an absorption close to 3230 cm^{-1}. The obvious interpretation of these results is formation of a *cis*-chlorocarbamate at 0 °C, which could be isomerised to *trans* on heating, while reaction at room temperature involved isomerisation of the initially formed *cis* isomer or possibly direct formation of the *trans*. This was confirmed by the ^1H n.m.r. spectrum of the reduced indene adducts (**5b**), and (**6b**) and reduced acenaphthylene adducts (**7b**) and (**8b**).

The *cis* stereochemistry of (**5b**) is indicated by the broad doublet (δ 3·18) observed for the methylene group, suggesting that these protons have approached equivalence owing to the adjacent carbamate group being forced towards the plane of the ring by the *cis* chlorine atom.[7] Similarly, in the *cis* acenaphthylene isomer (**7b**) (J_{HH} 3 Hz) steric

† WARNING: A violent explosion occurred during one preparation of dimethyl *NN*-dichlorophosphoramidate by the method described in Reference 2, resulting in serious injury to one of us (B.J.W.). In view of this we have not attempted any further preparations of *NN*-dichlorophosphoramidates and advise those doing so to exercise the greatest caution.

‡ Satisfactory microanalytical data have been obtained for all new compounds described.



hindrance increases the dihedral angle and leads to a decrease in the *cis* coupling constant.[8] Seden and Turner have obtained one isomer (**9**) (which they designate *trans*) from the reaction of *NN*-dichloro-*p*-toluenesulphonamide with indene.[9] The n.m.r. spectrum of (**9**) is closely related to that of compound (**6**), which we designate *trans*.

The stereospecific *cis* addition observed for five-membered cyclic alkenes can be explained in terms of an intramolecular 1,3-chlorine atom transfer in the intially formed radical (**10**); this step controls the stereochemistry as can be seen from the Newmann projection (**11**). A similar reaction of the analogous intermediate (**12**), obtained from cyclohexene, should give a mixture of isomers.

Examples of 1,3-atom shifts are relatively rare; however, this can be explained by the restrictions imposed by bond dissociation energies, lone-pair availability, and unfavourable entropy factors. In view of the last of these it would be dangerous to extend the 1,3-atom shift mechanism to the large body of N–Cl additions to acyclic double bonds.

The above mechanism does not require a formal 1,3-bridged radical intermediate;[10] however, it is noteworthy that molecular orbital calculations[11] not only indicate that a relatively low energy pathway for 1,3-atom rearrangement exists, but also suggest that 1,3-atom bridging provides an intermediate of significantly lower energy than 1,2-atom bridging.

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