A Triaziridine

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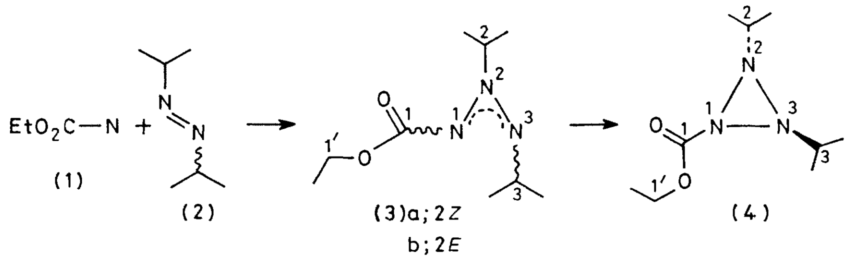
Summary The three-nitrogen chain of an azimine has been cyclized photochemically to a triaziridine, the structure of which has been deduced by an interpretation of its spectral properties.

Triaziridines have been postulated,[1] but no authentic example has been isolated.[2] We have prepared 1-ethoxycarbonyl-*trans*-2,3-di-isopropyltriaziridine (**4**) (20%) by u.v. photolysis of the azimine (**3a**). Compound (**3a**) or its stereoisomer (**3b**) (each 30%), were obtained from the addition of ethoxycarbonylnitrene (**1**)[3] to an excess of (*E*)- or (*Z*)-azoisopropane (**2**), respectively.

The adducts (**3**) are the first examples of open-chain acylazimines. In addition to the fact that two (and only two) readily interconvertible stereoisomers of (**3**) were obtained, the following spectroscopically deduced structural aspects (see the Scheme) of both stereoisomers are similar to those of other open-chain azimines.[4] The π-system of the azimine function causes the u.v. absorption and the ^{1}H n.m.r. deshielding of the isopropyl methine protons (2-H and 3-H). The coplanarity thus implied is confirmed by the ^{1}H n.m.r. equivalence of the geminal (enantiotopic[5]) substituents on all three prochiral centres [C(2), C(3) and C(1′)]. As expected for structure (**3**), the two (hetero-



Scheme.

	(**3a**)	(**3b**)	(**4**)
λ (cyclohexane)/nm (ϵ)	285 (7300)	289 (7400)	283(300)
ν (neat)/cm^{-1}	1673	1677	1750
δ (room temp., CDCl$_3$)/p.p.m. (J/Hz)			
2-H	5·52/sept (6), 1H	4·87/sept (6), 1H	2·12/sept (6), 2H
3-H	4·30/sept (6), 1H	4·10/sept (6), 1H	
1′-H$_2$	4·12/q (7), 2H	4·20/q (7), 2H	4·30 4·24 AB-part of ABX$_3$
1′-CH$_3$	1·31/t (7), 3H	1·5—1·1/m, 3H	1·31/t (7), 3H
2-CH$_3$	1·45/d (6), 6H	1·56/d (6), 6H	1·3—1·2/coalescence signal, 12H[a]
3-CH$_3$	1·21/d (6), 6H	1·36/d (6), 6H	

[a] The methyl ester corresponding to (**4**) showed two doublets (J 6 Hz) at 50 °C and four doublets (J 6 Hz) below -20 °C in the same range.

topic[5]) isopropyl groups are ^{1}H n m r non-equivalent The i r carbonyl band at lower frequency than that of the urethanes implies conjugation between the carbonyl and the azimine function

In clear contrast with the above are the properties of the triaziridine (**4**) (see the Scheme) The u v absorption has practically disappeared and the i r carbonyl band has moved to higher frequency Only one stereoisomer of (**4**) was observed The two (now homotopic[5]) isopropyl groups have become ^{1}H n m r equivalent, as seen in the single ^{1}H n m r signal for the two isopropyl methine protons (2-H and 3-H) This signal, furthermore, occurs at remarkably high field, an effect which has been observed with other 3-membered heteroring systems [6,7]

Of stereochemical interest is the ^{1}H n m r -visible diastereotopicity[5] of the geminal substituents of all three prochiral centres of (**4**) [C(2), C(3) and C(1′)] The chiral induction on C(1′) is due to the *trans*-arrangement of the two isopropyl groups on the triaziridine ring Evidently, N(2) and N(3) exhibit considerable pyramidal stability, as is consistent with the trend shown in the comparison of aziridines and diaziridines [6] The homotopicity[5] of the two isopropyl groups signifies dynamic conical symmetry of the ethoxycarbonyl group around a line which bisects the outer angle of the 3-membered ring at N(1) The high frequency of the i r carbonyl absorption suggests that the effect of electron localization (pyramidalization), due to the fully nitrogenous 3-membered ring, is stronger than that of the amide-type electron delocalization (planarization) at N(1) The localization facilitates the rotation around the amide bond, the delocalization on the other hand, lowers the activation energy of the pyramidal inversion at N(1) A 63 kJ/mol barrier was estimated for this dynamic process from the low temperature doubling of the isopropyl methine ^{1}H n m r signal

On standing at room temperature, the triaziridine (**4**) is reconverted into the azimines (**3a**) and (**3b**) with a half-life of 3 5 days

The substances (**3a**), (**3b**), and (**4**) are oils, their elemental analyses and mass spectra are consistent with the structures given Details and other examples will be published elsewhere

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