Additions of Isocyanides to Aziridines

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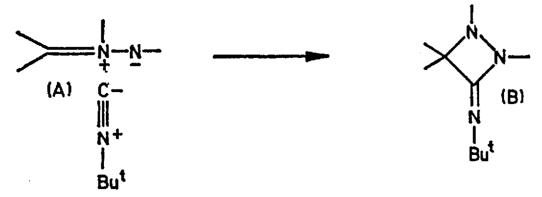
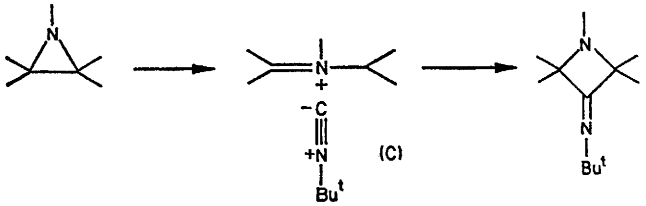
Summary Certain aziridines react with t-butyl isocyanide to give aminoketenimines rather than the products of 3 + 1 cycloaddition to the intermediate azomethine ylides.

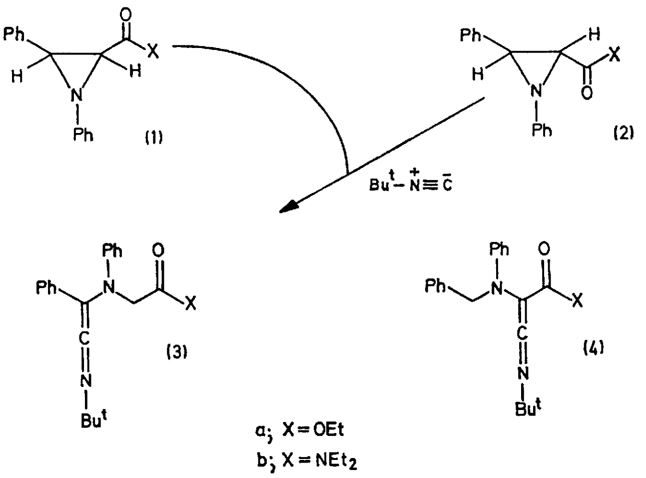
We reported previously that azomethine imines (A) could be induced to form 3 + 1 cycloadducts (B) with Bu^{t}NC.[1] Because such 3 + 1 cycloadditions are still rare and remain mechanistically ambiguous, we sought other 3 + 1 cycloadditions which might be more amenable to study. We report the attempted addition of Bu^{t}NC to the azomethine ylides of type (C).



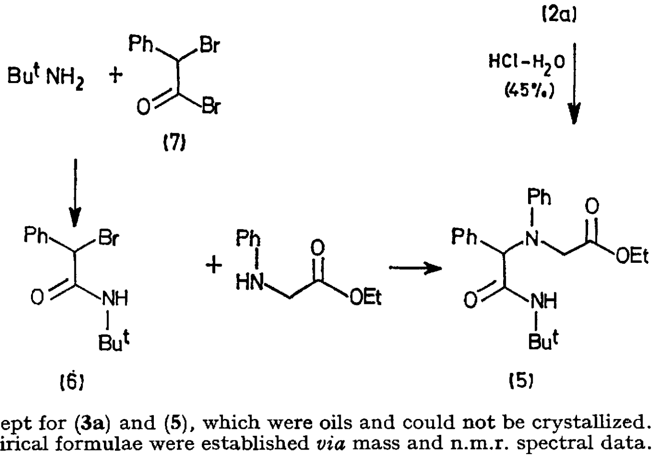


Reaction of the aziridines (**1b**) and (**2a**)[2] with a two-fold excess of Bu^{t}NC in CCl_4 for 80 h yielded 1 : 1 adducts in 66 and 92% yields respectively. Both products had, in addition to the appropriate carbonyl peak, i.r. spectral peaks at 2000 cm^{-1} instead of the expected peaks around 1730 cm^{-1}.[3] The n.m.r. spectra of both products showed the expected number and kinds of protons attributable to the aromatic rings and the X substituent. In addition, the product from (**1b**) had a 2H singlet at δ 4·16 and that from (**2a**) had a corresponding singlet at δ 4·20. We attributed the i.r. peak to a ketenimine unit and thus assigned structure (**3**) to this product.†

Since these spectral data do not unambiguously rule out the alternative structure (**4**), the product from (**2a**) was hydrolysed to the amide (**5**). This amide was in turn synthesized in two steps from (**7**) *via* (**6**).



When (**2a**) was heated for extended periods in a large excess of Bu^{t}NC without solvent, an equilibrium mixture of (**1a**) and (**2a**) was produced. Compound (**3**) or other



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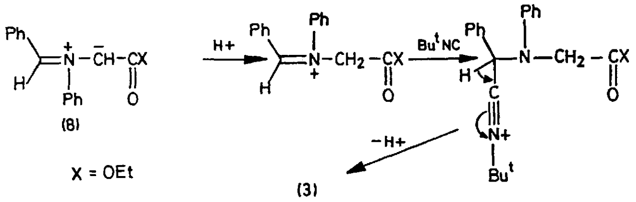
† Satisfactory analyses were obtained for all new compounds except for (**3a**) and (**5**), which were oils and could not be crystallized. For these compounds purity was assessed *via* t.l.c. analyses. Empirical formulae were established *via* mass and n.m.r. spectral data.

products were not detected. Since the azomethine ylide (**8**) is an intermediate in the isomerization process, this demonstrates that the dipole does not react with Bu^tNC.



We have previously observed that traces of acid impurities in nonbasic solvents such as CCl_4 result in efficient acid-catalysed additions.[2] We propose, therefore, that (**3**) is formed as in the Scheme, which is analogous to other reported additions initiated by electrophilic attack on azomethyne ylides.[2,4] The failure of (**8**) to undergo cycloaddition with Bu^tNC is surprising in view of the successful cycloadditions of analogous azomethine imines. The origin of this difference is not obvious but our observations illustrate the subtlety of factors which govern cycloadditions. Formation of (**3**) is thus another example of the novel synthetic utility implicit in these two-step non-concerted additions.

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[1] J. A. Deyrup, *Tetrahedron Letters*, 1971, 2191.

[2] J. A. Deyrup, *J. Org. Chem.*, 1969, **34**, 2724.

[3] *Cf.* J. A. Deyrup, M. M. Vestling, W. V. Hagan, and H. Y. Yun, *Tetrahedron*, 1969, **25**, 1467.

[4] M. Vaultier, R. Danion-Bougot, D. Danion, J. Hamelin, and R. Carrie, *Tetrahedron Letters*, 1973, 1923, 2881; F. Texier and R. Carrie, *ibid.*, 1971, **4163**; P. B. Woller and N. H. Cromwell, *J. Heterocyclic Chem.*, 1968, **5**, 579.