

INTRAMOLECULAR 1,3-DIPOLAR CYCLOADDITIONS
OF VINYL AZIDES

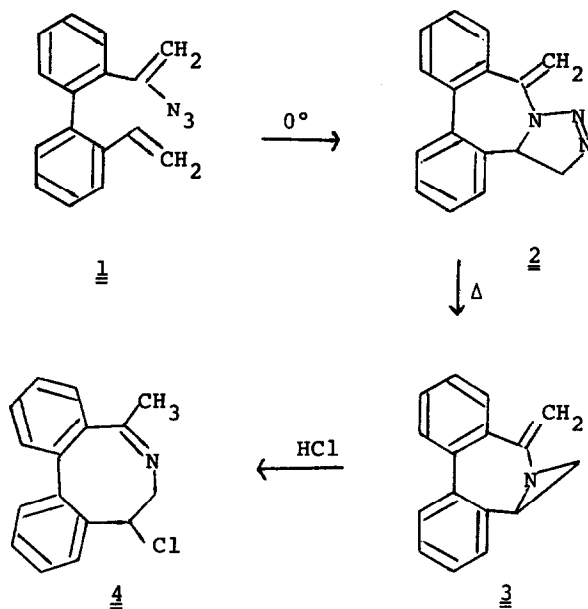
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Intramolecular 1,3-dipolar cycloaddition is an extremely versatile and important reaction. The range of synthetic possibilities which it opens for the construction of fused heterocycles is extremely large.¹ With azides, intramolecular cycloadditions have been occasionally reported²⁻⁵ but systematic data are available only for a series of azidoalkenes.⁴ Although bimolecular 1,3-dipolar cycloadditions of vinyl azides have appeared in the literature,⁶⁻⁸ intramolecular cycloadditions of this 1,3-dipole have not been described. The present communication reports the first example of such a process.

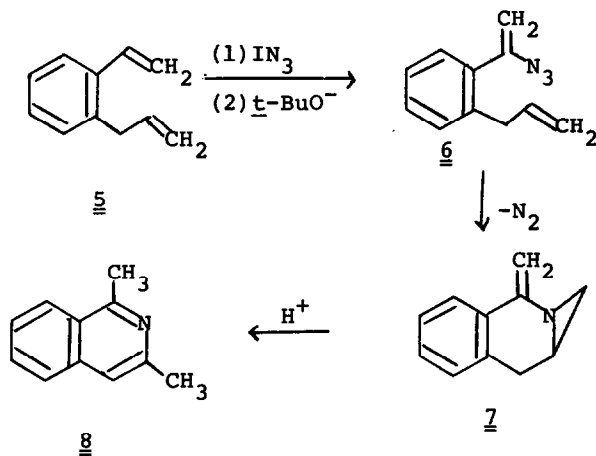
Reaction of iodine azide with 2,2'-divinylbiphenyl⁹ followed by treatment of the initially formed iodine azide adduct with potassium *t*-butoxide gave mono-vinyl azide 1. When 1 was allowed to stand at 0° for 3 days, it quantitatively cyclized to give Δ^2 -1,2,3-triazoline 2, mp 140-142°, nmr (CDCl₃, 100 MHz) τ 6.00 (dd, 1H, J = 17.0 and 10.0 Hz), 5.62 (s, 1H), 5.31 (dd, 1H, J = 10.0 and 3.0 Hz), 4.90 (dd, 1H, J = 17.0 and 3.0 Hz), 4.73 (s, 1H), and 2.32-2.92 (m, 8H). Further heating of this material resulted in the loss of nitrogen and formation of 3,11b-dihydro-3-methylene-1H-azirino[1,2-a]dibenz[c,e]azepine (3), nmr (CDCl₃, 100 MHz) τ 8.01 (d, 1H, J = 3.0 Hz), 7.49 (d, 1H, J = 6.0 Hz), 6.67 (dd, 1H, J = 6.0 and 3.0 Hz), 5.57 (s, 1H), 5.43 (s, 1H), and 2.37-2.88 (m, 8H). Treatment of 3 with hydrochloric acid afforded chloride 4 in high yield.



Although the isolation of 2 from 1 is not surprising, it is noteworthy as the first example of intramolecular cycloaddition of a vinyl azide. Thermolysis of vinyl azides generally produce 2H-azirines by a process involving ring closure simultaneous with loss of nitrogen.¹⁰ The facile formation of 2 is also unusual in light of the earlier work of Logothetis⁴ who found that azidoalkenes require heating at 50° for 18 hr before intramolecular cycloaddition will occur. The high reactivity of vinyl azide 1 toward dipolar cycloaddition can be nicely rationalized by the frontier molecular orbital method. 1,3-Dipolar cycloadditions of azides with olefins may be classified as a set which involves dipole LUMO-dipolarophile HOMO control.^{11,12} Attachment of a phenyl group to the π -system will raise the HOMO and lower the LUMO energy levels of the olefin and thus bring about an acceleration of the rate of 1,3-dipolar cycloaddition with azides. Another factor which undoubtedly plays an important role in the intramolecular cycloaddition reaction of vinyl azide 1 is the high degree of order present in the transition state. Bimolecular cycloadditions exhibit large negative entropies of activation¹³ since the reactants must be

precisely aligned with respect to each other. The interplay of favorable entropy and enthalpy factors in the above system undoubtedly facilitates the rate of cycloaddition.

We also attempted to study the intramolecular 1,3-dipolar cycloaddition reaction of the closely related vinyl azide 6 in order to assess the generality of this cycloaddition. Treatment of *o*-allylstyrene (5) with iodine azide followed by reaction with potassium *t*-butoxide afforded vinyl aziridine 7 as the major product; nmr (CDCl₃, 100 MHz) τ 7.24-7.40 (m, 2H), 6.1-6.4 (m, 1H), 5.90 (dd, 1H, $J = 17.0$ and 8.0 Hz), 5.58 (dd, 1H, $J = 17.0$ and 11.0 Hz), 2.4-3.0 (m, 4H). Thick layer chromatography of 7 resulted in the opening of the three-membered



ring and gave 1,3-dimethylisoquinoline (8)¹⁴ in quantitative yield. The formation of 7 from 5 can reasonably be interpreted in terms of a rapid intramolecular 1,3-dipolar cycloaddition of an initially formed vinyl azide (6) followed by loss of nitrogen.

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