

## INTRAMOLECULAR [3+2] CYCLOADDITION VERSUS 1,4-HYDROGEN SHIFT IN INDOLIUM-N-METHYLIDES

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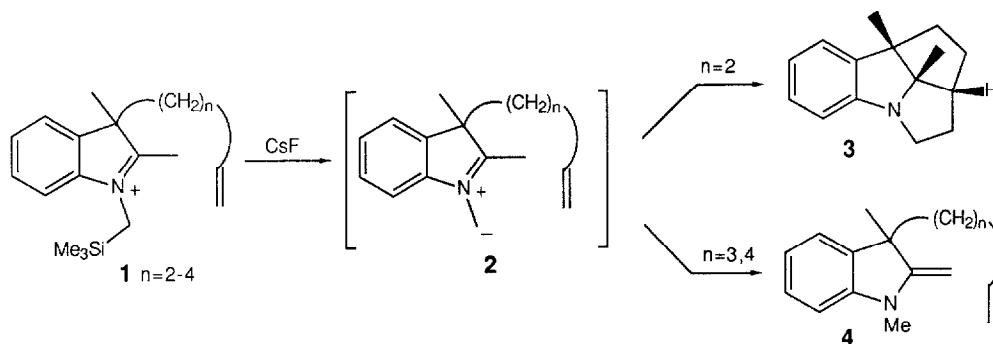
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*Summary* : 2,3-Dimethyl-3-(but-3-enyl)-indolium-N-methylide undergoes facile stereospecific intramolecular [3+2] cycloaddition to yield a novel tetracyclic indoline ring system. The analogous -(pent-4-enyl) and -(hex-5-enyl) systems fail to undergo cycloaddition but yield the corresponding N-methyl-2-methylene derivatives in moderate yield.

Indolium-N-methylides, which are a novel class of reactive azomethine ylide have been shown to undergo facile intermolecular 1,3-dipolar cycloaddition to electron deficient dipolarophiles to yield adducts possessing the pyrrolo [1,2-a] indoline skeleton<sup>1-3</sup>. As part of a study of the chemistry and synthetic applications of these species<sup>1</sup>, we wished to see if such systems were capable of undergoing intramolecular cycloaddition.

We now report that 2,3-dimethyl-3-alkenyl-indolium-N-methylides **2**, generated via fluoride-induced desilylation of the corresponding indolium salts **1** can undergo stereospecific intramolecular 1,3-dipolar cycloaddition to yield tetracyclic adduct **3** or a formal 1,4-hydrogen shift to give N-methyl-2-methylene indolines **4**.



The indolium salts **1** were prepared by N-alkylation of the corresponding indolenines with trimethylsilylmethyl triflate, themselves prepared by the alkylation of 2,3-dimethyl indole with the corresponding bromide or iodide. Treatment of salt **1** with caesium fluoride in acetonitrile at 60°C for the times indicated yielded either cycloadduct **3** or 2-methylene indoline **4**. The results of these experiments are summarised below.

<u>entry</u>	<u>salt 1</u>	<u>time (min)</u>	<u>product<sup>4</sup></u>	<u>isolated yield (%)</u>
1	n=2	15	3	51
2	n=3	20	4	64
3	n=4	10	4	73

Clearly only intramolecular cycloaddition involving formation of a pendant 5-membered ring system is successful (entry 1). It is noteworthy that in this case the reaction is essentially complete after 15 mins, even though this process involves cycloaddition to a non-activated double bond. In addition, cycloadduct **3** was formed stereospecifically and contained an all-cis ring fusion geometry<sup>5</sup>. For the attempted cycloadditions to yield six and seven membered rings (entries 2&3), inspection of molecular models of the transition states indicates the presence of severe steric interactions involving the 2-methyl substituent and methylene units on the alkenyl chain, clearly disavouring intramolecular cycloaddition and promoting the formation of exocyclic enamines **4** presumably via 1,4-hydrogen shift in ylides **2**<sup>6</sup>. The intermediacy of azomethine ylides **2** (n=3,4) was supported by the successful intermolecular cycloaddition with DMAD.

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#### References and notes

1. C.W.G. Fishwick, A.D. Jones, M.B. Mitchell and Cs. Szantay Jr., *Tetrahedron Lett.*, 1988, **29**, 5325.
2. D. Döpp, G. Rehmer and H. Brüggeman, *Chem. Ber.*, 1988, **121**, 1651.
3. A. Padwa, G.E. Fryxell, J.R. Gasdaska, M.K. Venkatramanan and G.S.K. Wong, *J. Org. Chem.*, 1989, **54**, 644.
4. All new compounds gave spectroscopic data consistent with the proposed structures.
5. The stereochemistry of the cycloadduct was determined from n.o.e. data.
6. The 1,4-hydrogen shift involving the 2-methyl substituent has been reported in similar systems, see ref. 2.

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