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AN INTRAMOLECULAR CYCLOADDITION

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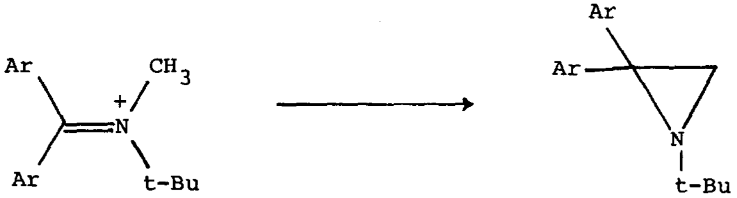
In a recent article, we observed that ketiminium (1) and aldiminium (2) salts reacted with sodium bis(trimethylsilylamide) to yield products which contained aziridine rings.[1] In each case we speculated that aziridine formation occurred via cyclization of a 1,3-dipolar azomethine ylid. Attempts to intermolecularly intercept or otherwise confirm this postulate were not successful. We now would like to report the intramolecular interception of one of these 1,3-dipoles.



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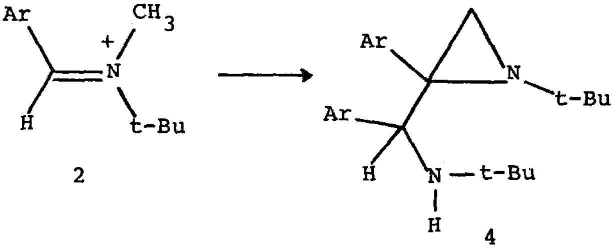

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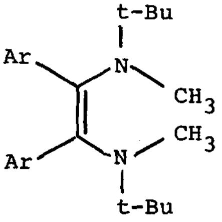

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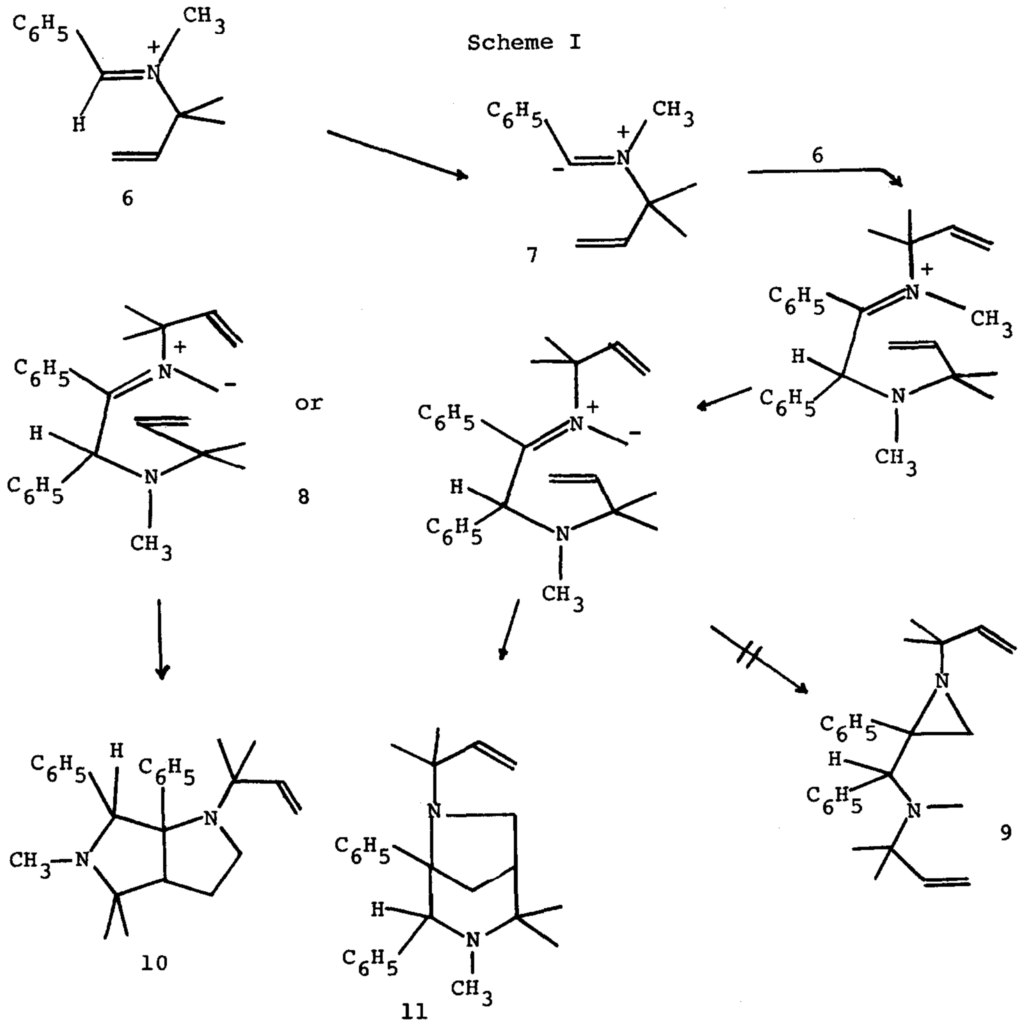
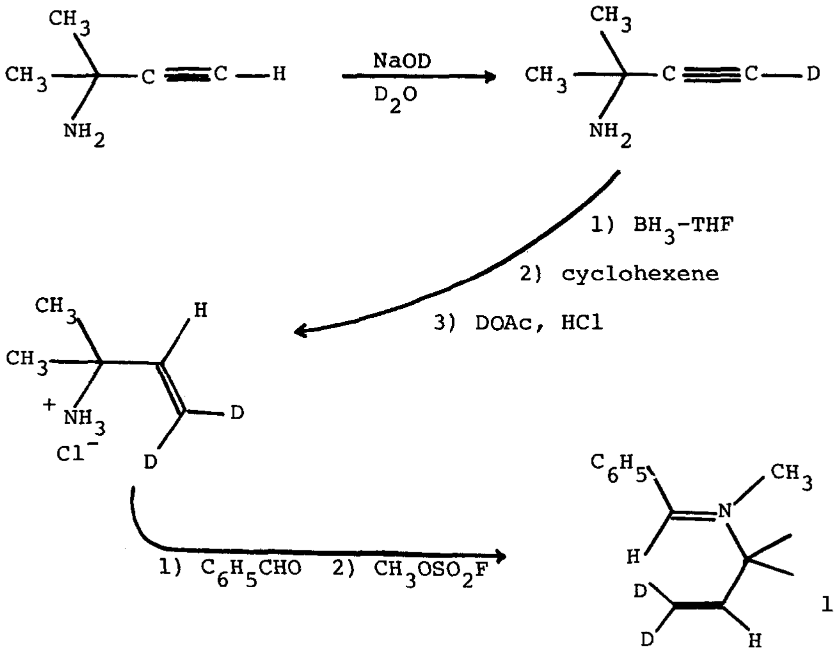
Reaction of aldiminium salt (6)[2] with sodium bis(trimethylsilylamide) yielded a single dimeric product (m.p. 63.5-64^{o}) in 35% yield.[4] The nmr spectrum of this product revealed that only one each of the original two vinyl and two methyl groups were still intact. Structures compatible with these requirements could be written by modification of our proposed mechanism for the formation of 4 and 5 from 2. Thus, (Scheme I) instead of ring closure of 1,3-dipole 8 to yield 9, internal cycloaddition could yield the novel structures 10 or 11.[5]

Scheme I



Unfortunately, neither chemical degradation nor detailed spectral analysis allowed an unambiguous distinction between structures 10 and 11. For this reason the dideutero analog (12) of 6 was synthesized according to the procedure of Scheme II.

Scheme II



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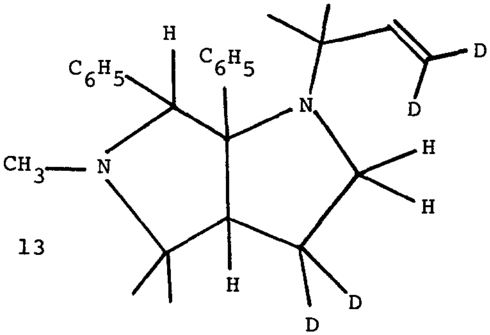
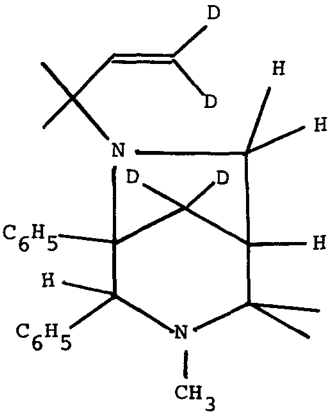
Deprotonation of 12 yielded a tetradeutro dimer. The complex two proton multiplet present in 10 at 1.4-2.2δ was absent in the nmr spectrum of this dimer. In addition, the three proton multiplet between 2.3 and 3.3δ had been resolved into an AB quartet (J=10Hz) superimposed upon a singlet. This result is consistent with structure 13 and not 14. We, therefore, assign structure 10 to the dimer.[6]



13



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The regioselectivity of the intramolecular cycloaddition is analogous to that demonstrated by Padwa in his nitrile ylid studies.[7] Intramolecular cycloadditions of 1,3-dipoles constitute a recent extension of heterocyclic syntheses with 1,3-dipoles. The reaction described here is apparently the first example of an azomethine ylid participation in such an intramolecular cycloaddition.

References and Footnotes

1. James A. Deyrup and William A. Szabo, J. Org. Chem., 40, 2048 (1975).

2. This unstable salt was prepared by alkylation of the corresponding imine via the previously described procedure. The imine was prepared from benzaldehyle and 3-amino-3-methyl-1-butene[3] and alkylated without prior purification.

3. cf G.F. Hennion and K.W. Nelson, J. Am. Chem. Soc., 75, 2142 (1957).

4. Satisfactory elemental analyses, mass spectra and pmr spectra were obtained for all new compounds unless otherwise noted.

5. The rest of the nmr spectrum of the dimer was consistent with either structure. A singlet at 4.38δ was assigned to the benzylic hydrogen. The relative integrated ratios of the respective peaks were in agreement with the predicted values.

6. Inspection of models reveals that there are no compelling reasons for stereochemical assignment based either on the lowest energy transition state or on spectral analysis.

7. A. Padwa and N. Kamigate, J. Am. Chem. Soc., 99, 1871 (1977).

8. A. Padwa, Angew. Chem. Int. Ed. Engl., 15, 123 (1976).