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THE REACTION OF VINYL AZIDES WITH SULFOXONIUM YLIDS.[1] SYNTHESIS OF N-VINYL TRIAZOLINES AND VINYL AZIRIDINES.

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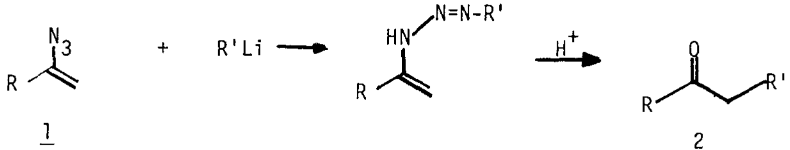
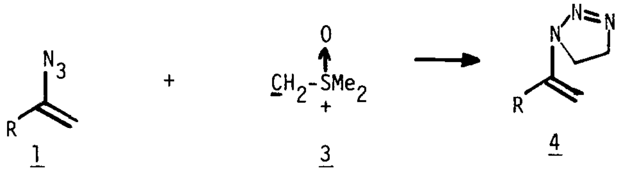
Summary: Vinyl azides 1 react with dimethylsulfoxonium ylid 3 at the azide function to produce in high yield 1-vinyl-4,5-unsubstituted-Δ^2-1,2,3-triazolines 4. Vacuum flash pyrolysis of 4 furnished N-vinylaziridines 7 without formation of pyrrolines.

Vinyl azides are versatile synthons capable of reacting at the terminal nitrogen, the internal nitrogen or the olefinic double bond with electrophiles or nucleophiles.[2] The olefinic function in such molecules may alter the reactivity of the azide by providing increased stabilization of the negative charge on nitrogen, thus increasing their reactivity toward nucleophilic reagents. Although simple azides react with ylids,[3] the reaction of vinyl azides with sulfur ylid 3 has not been investigated. Recently we reported that vinyl azides 1 are attacked by carbanions (alkyllithium reagents) and undergo an interesting alkyl transfer to the vinyl function that involves triazenes as intermediates[4] (see Scheme I).



Scheme I

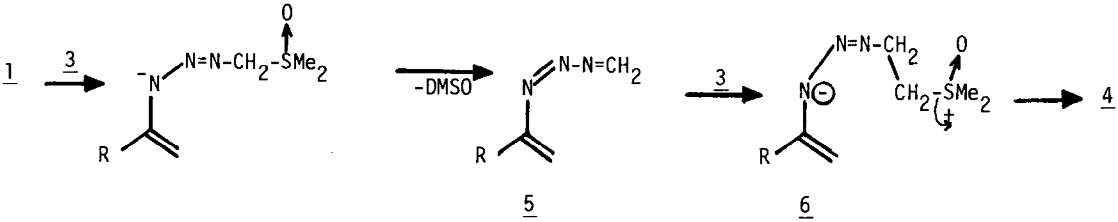
It was therefore interesting to establish whether stabilized carbanions such as ylids 3, will undergo similar transformations and lead to alkylated ketones 2. When dimethylsulfoxonium ylid 3 was reacted with vinyl azides 1, the reaction took a different course and lead to formation of N-vinyl-Δ^2-triazolines 4 cleanly and in high yield (see Table I), without involvement of the vinyl function (Scheme II).



Scheme II

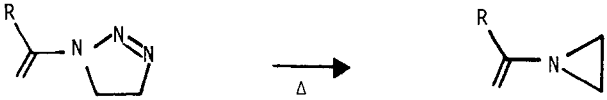
Ring substituted Δ^2-triazolines are readily available from cycloaddition of azides with substituted olefins[5] but the only reported route to 4,5-unsubstituted triazolines involves either the addition of sulfoxonium ylids[3] or via ring expansion of sometimes explosive aziridine derivatives.[6] Our route represents the first reported synthesis of N-vinyl-triazolines of type 4.

A possible pathway in the formation of 4 is shown in Scheme III and involves intermediate triene 5 which would react with another mole of 3 in conjugate addition to produce 6. Ring closure to a 5- rather than to a 7-membered ring affords N-vinyltriazoline 4. In the instance where R:Ph, polymeric product rather than triazoline 4 was obtained, together with small amounts of a crude product that appears to indicate by nmr the presence of 5.



Scheme III

Pyrolysis of the Δ^2-triazolines 4 proceeds smoothly to give N-vinylaziridines 7 in good yield (see Table I). Both pyrolysis and photolysis have been used to convert Δ^2-triazolines into aziridines,[4] but vinylaziridines, especially if they possess an electron withdrawing group on the olefinic function lead to 5-membered ring pyrrolines.[7] The absence of such olefinic substituents in our substrates 4 probably accounts for the fact that pyrrolines were not observed during the pyrolysis of 4 to 7.



4 7

We found the best conditions for clean conversion of 4 to 7 to be flash vacuum pyrolysis at *ca*. 250°.

The triazolines were prepared by the addition of 20 mmol of vinyl azide to 2 equivalents of dimethylsulfoxonium ylid in dimethylsulfoxide. After stirring for 12 hr at room temperature, 100 ml of diethyl ether was added to the reaction mixture which was then washed with 500 ml of water in five portions. The ether was dried and removed under vacuum to afford the pure triazoline in high (89-95%) yield (see Table I).

Pyrolysis of the triazolines in refluxing toluene (3 hr) gave 7 in 65-85% isolated yield, while flash vacuum pyrolysis led to higher yields (93-97%) of the neat vinyl aziridines 7 (Table I). For example, 3,3-dimethyl-1-azido-1-butene 1c was converted to the corresponding triazoline 4c. The nmr spectrum (CCl_4) showed peaks at δ6.8 (one proton doublet, J=15 Hz), δ4.28 (one proton doublet, J=15 Hz), δ3.82 (two proton triplet, J=10 Hz), δ2.82 (two proton triplet, J=10 Hz), and δ0.8 (nine proton singlet). Upon heating, 4c was converted to 7c. The nmr spectrum (CCl_4) showed peaks at δ5.9 (one proton doublet, J=14 Hz), δ4.96 (one proton doublet, J=14 Hz), δ1.62 (four proton singlet) and δ1.02 (nine proton singlet).

Since vinyl azides are easily accessible from olefins, the scope of this reactions is widely expanded. Further work on the synthetic utility and mechanism of the reactions and on the novel class of compounds is currently under way.

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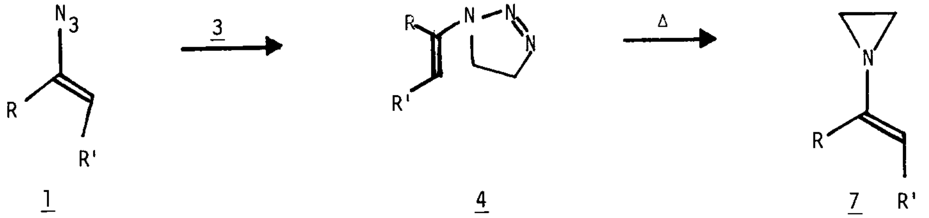
TABLE I

Conversion of Vinyl Azides (1) to Δ^2-1,2,3-Triazolines (4) and N-Vinylaziridines (7).



	R	R'		Yield (%)		Yield (%)
1a	Ph	CH_3	4a	95	7a	93
1b	nBu	H	4b	91	7b	93
1c	H	tBu	4c	93	7c	94
1d	—$(CH_2)_6$—		4d	89	7d	91

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