

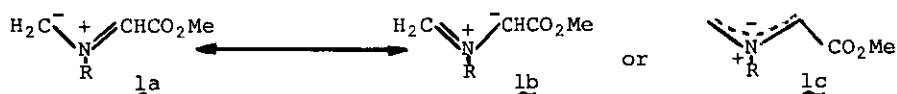
A DEFINITE EVIDENCE ON THE AMBIVALENT AZOMETHINE YLIDE INTERMEDIATES
RESULTED BY THE SILICON-CARBON BOND CLEAVAGE

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The two 1,3-dipolar cycloadditions [A, B] indicate that the azomethine ylide intermediates resulted by the silicon-carbon bond cleavage are the ambivalent ones. Regio- and stereoselectivity of products in 1,3-dipolar cycloadditions via the silicon-carbon bond cleavage are explained by the frontier molecular orbital theory.

[A] Methyl N-(trimethylsilylmethyl)iminoacetate as a synthon 1a reacted with dipolarophiles in the presence of benzyl bromide or a catalytic amount of trifluoroacetic acid to give N-benzyl or N-unsubstituted pyrrolidines, the latter of which were purified after N-acylation because of their instability. This reaction and the base-promoted 1,3-dipolar cycloaddition of N-(phenylthiomethyl)amino acid esters as a synthon 1b have been found to proceed via the common ambivalent azomethine ylide intermediates (1a $\longleftrightarrow$ 1b or 1c).



[B] Deuterated N-benzyl-N-(methoxymethyl)trimethylsilylmethylamine (2) and N-benzyl-N-(phenylthiomethyl)trimethylsilylmethylamine (3) reacted with dimethyl benzylidenemalonate in the presence of a catalytic amount of trifluoroacetic acid or fluoride anion to give a 1 : 1 mixture of pyrrolidines 5a and 5b.

