A New and Efficient Strategy for Non-stabilized Azomethine Ylide *via* Photoinduced Electron Transfer (PET) Initiated Sequential Double Desilylation

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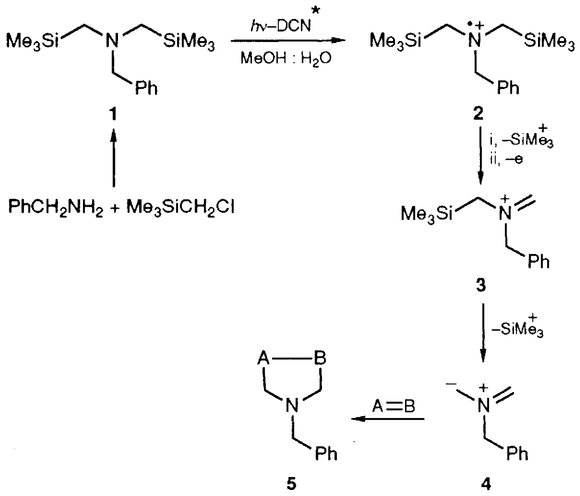
A practical approach for generating non-stabilized azomethine ylide by PET initiation is reported.

The study of synthetic and mechanistic problems related to the chemistry of PET generated amine radical cations has attracted considerable interest recently.[1,2] Our effort in this area has focused attention on the development of synthetically useful reactions from the photoreaction of amine-1,4-dicyanonaphthalene (DCN) pairs[3] and sequential electron–proton–electron transfer processes have been reported for generating reactive species such as nitrones[4] and iminium cations[5] in a 'true sensitized' manner. Based on an identical mechanistic paradigm, we report an unprecedented and practical approach for generating the non-stabilized azomethine ylide **4** from amine **1** by a sequential double desilylation strategy as shown in Scheme 1.

The desilylation phenomena of amine cation radicals in media favouring solvent separated ion-pairs (SSIP)[2,6] followed by sequential electron and super acid group (TMS$^+$) loss led us to consider this method for generating **4**.

The 1,3-dipolar cycloaddition of the azomethine ylide as a route to construct a stereospecific pyrrolidine ring system[7] represents a particularly attractive approach.[8] Owing to the importance of this ring system several classical methods for generating non-stabilized azomethine ylides have been reported.[9] Some of the most significant methodologies include fluoride ion initiated desilylation of trimethyl silyliminium salts[10] or cyano aminosilanes,[11] thermal opening of aziridines[12] and extrusion of CO_2 from amino acids[13] or dihydrooxazolidines.[14] A somewhat related photochemical route for vinyl azomethine ylide by sequential intramolecular electron transfer desilylation from trimethyl silyl allyl iminium salt has also been reported by Mariano and coworkers.[15] However, the present approach for generating **4** from amine **1** which is readily derivable in quantitative yield from the reactions of benzyl amine and trimethylsilyl methyl chloride,‡ represents a promising alternative to the existing methodologies. Notable aspects of this methodology are the use of aqueous solvent and the choice of wavelength. The reaction can occur by irradiating either with visible [>350 nm, DCA (9,10-dicyanoanthracene) as electron acceptor] or UV (>280 nm, DCN as electron acceptor) light.

In a typical reaction procedure, a methanol–water§ (9 : 1) solution of **1** (4.9 mmol) and DCN (1 mmol) containing the appropriate dipolarophile (8 mmol) was irradiated (450-W Hanovia medium pressure lamp, Pyrex filter, >280 nm, all light absorbed by DCN only)¶ for 3 h without prior removal of



Scheme 1 PET generation of azomethine ylide

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‡ Compound **1** could be synthesized quantitatively by heating primary amines and trimethylsilylmethyl chloride (TMS-CH_2Cl) in MeCN in the presence of K_2CO_3.

§ Among several solvents tried, MeOH : H_2O (9 : 1) gives the best results.

¶ Irradiation (>350 nm, Uranium yellow filter) using DCA as the electron acceptor gives an equally good result.

Table 1 Cycloadduct from PET generated non-stabilized azomethine ylide

Entry	Dipolarophile[a]	Yield of Cycloadduct (%)[b,c]
1	Benzophenone	80
2	Dimethyl fumarate	60
3	*trans*-Methyl cinnamate	78
4	*N*-Phenylmalimide	83
5	Ethyl acrylate	58
6	*trans*-1,2-Bis(phenylsulfonyl)ethylene	82
7	Phenyl vinyl sulfone	75
8	Dimethyl acetylenedicarboxylate	55[d]

[a] Reaction usually completed in 3 h. [b] Isolated yield, based on a single experiment. [c] Stereochemistry of corresponding pyrrolidines confirmed by ^{1}H NMR spectroscopy and comparision with authentic sample prepared by following the procedure given in ref. 11. [d] Ylides refer to pyrrole obtained by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone oxidation in benzene from crude irradiated mixture.

dissolved oxygen. Usual workup and chromatography purification (silica gel, finer than 200 mesh) gave the corresponding pyrrolidines.|| The DCN was recovered quantitatively (97%) after the reaction as mentioned earlier.[3] As indicated in Table 1, the azomethine ylide **4** derived from **1** can be trapped in moderate to high yields with a variety of dipolarophiles. The stereochemistry of the cycloadducts in entries 2, 3, 4 and 6 (Table 1) clearly indicates the stereospecific nature of cycloadditions.

As azomethine ylides generally prefer to react with electron defficient alkenes or alkynes, no attempt was made to study the cycloaddition with electron rich alkenes as such a pair of compounds possess a narrow dipole HOMO dipolarophile LUMO energy gap.[16]

In conclusion we have demonstrated a conceptually new and efficient method for generating azomethine ylide by PET initiation. Further study for generating chiral azomethine ylides using chiral amine precursors for **1** is in progress.

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|| No other product beside pyrrolidines were detected although some polymeric material is formed. All products gave satisfactory IR, mass and NMR spectral data.