

UNSATURATED BRIDGEHEAD SILICON INTERMEDIATES. DIPOLAR CHARACTER OF UNSATURATED SILICON–NITROGEN BONDS IN SUCH INTERMEDIATES *

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Summary

Photolysis of 1-azido-1-silabicyclo[2.2.1]heptane and 1-azido-1-silabicyclo[2.2.2.]octane give loss of nitrogen and rearrangement with ring enlargement yielding silimine reaction intermediates which were trapped by reaction with methyltrimethoxysilane and triethoxysilane. Evidence is presented which indicates that the unsaturated silicon–nitrogen bonds in the intermediates have considerable polar character and do not behave like triplet diradicals. The balance of the evidence favors, but does not completely prove, that the intermediates have significant π -bonding.

Introduction

Many unsaturated silicon–carbon [1] and silicon–nitrogen [2] intermediates have now been generated and trapped. Pyrolysis and photolysis methods lead to these interesting intermediates whose trapping behavior is considered to be in accord with approximate structural models A and B which picture the unsaturation as a combination of π -bonding and significant dipolar character.

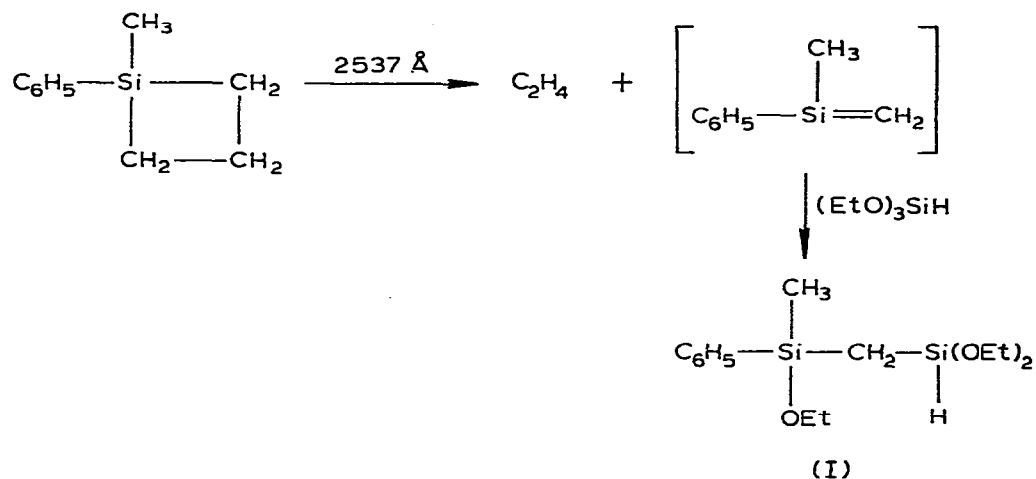


For silicon–carbon double bonds generated by photolysis, the following reac-

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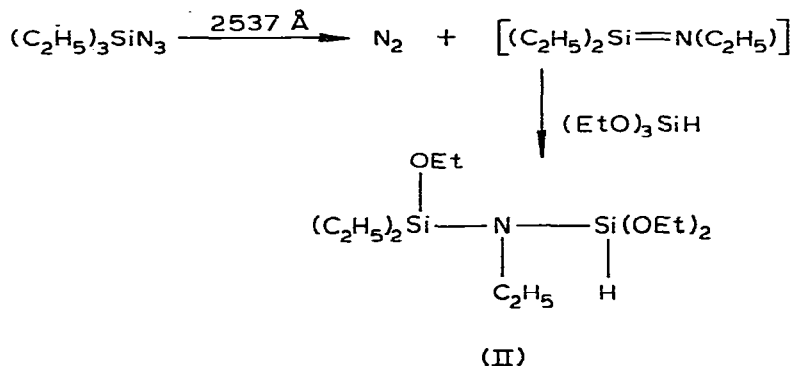
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tion sequence is particularly convincing evidence in favor of model A [3]:



Product I clearly results from addition of EtO to silicon and Si(H)(OEt)₂ to the carbon portion of a highly reactive unsaturated silicon-carbon linkage having considerable dipolar character; nucleophilic or electrophilic attack on an Si-O-C grouping is well known whereas radical attack under ordinary liquid-phase conditions is unknown for Si-O-C and well known for Si-H.

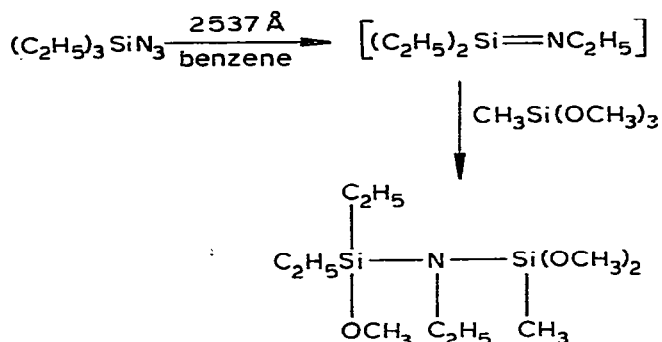
Similarly, the following photochemical reaction sequence which yields product II argues in favor of model B for the reaction intermediate [3].



Being convinced that the balance of the evidence favors approximate models A and B for reaction intermediates derived from simple systems, but realizing that the amounts of dipolar character as well as of $2p\pi-3p\pi$ bonding in such intermediates may be a sensitive function of structural detail in the precursor, we have synthesized and studied the photolysis of 1-azido-1-silabicyclo[2.2.1]-heptane and 1-azido-1-silabicyclo[2.2.2]octane. These studies were undertaken to determine the relative ease or difficulty posed by generation of a silicon-nitrogen double bond at bridgehead silicon in small bicyclic systems. Such intermediates, if formed, could possess a twisted $2p\pi-3p\pi$ component of the unsaturated linkage or, alternatively, be completely dipolar or triplet diradical without significant π -bonding.

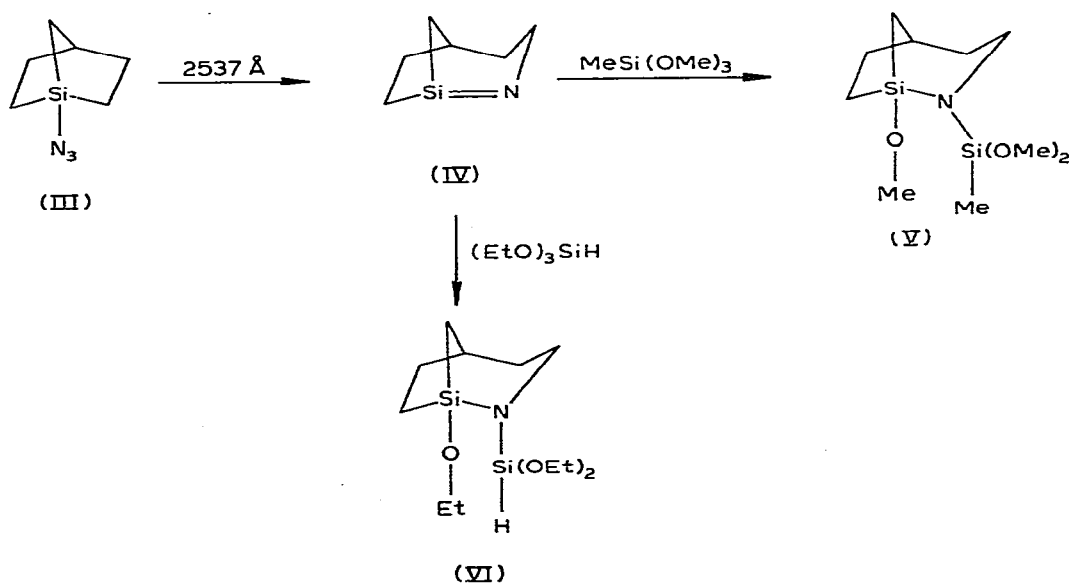
Results and discussion

In previous work [3] we found that $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ is an excellent trap for the silaimine derived from $(\text{C}_2\text{H}_5)_3\text{SiN}_3$ by photolysis giving 72% yield of isolated product. This reaction required ~ 12 h of irradiation in a quartz tube for completion.



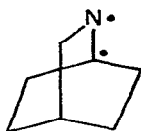
1-Azido-1-silabicyclo[2.2.1]heptane readily evolved nitrogen when irradiated neat, in cyclohexane solvent, or in benzene solvent, with 2537 Å light. A solution of III in cyclohexane plus a threefold excess of $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ was placed in a quartz tube and irradiated for 6–7 h with 2537 Å light. The sequence shown below in Scheme 1 resulted in an 80% yield of ring-expanded trapped silaimine, characterized as 1-methoxy-2-dimethoxymethylsilyl-1-sila-2-azabicyclo[3.2.1]octane (V). To elucidate, at least partially, the structure of the silaimine intermediate IV a similar experiment was done using a triethoxysilane trap and the same reaction time. Results of both studies are summarized in Scheme 1. Product VI was obtained in 79% yield.

SCHEME 1



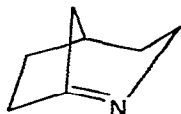
It is interesting that formation and trapping of IV, giving yields of 79–80%, proceeded at a somewhat faster rate than the corresponding formation of simple acyclic silaimine intermediates such as $[(C_2H_5)_2Si=NC_2H_5]$. This result indicates no great barrier toward formation of IV. Such a result lends itself to the speculation that, perhaps, in this special bridgehead case, geometry constrains the unsaturated linkage to have much decreased π -bonding.

However, the fact that our isolated 80% yield of trapped product derives from only one of two possible modes of rearrangement is, of itself, strong evidence for the presence of π -bonding in the silaimine intermediate (*vide infra*). Rearrangement with ring-expansion could also have proceeded via involvement of the 1 carbon bridge. But here, we are in agreement with the view of Reed and Lwowski [4] concerning the carbon analog of the intermediate which would be formed by such a rearrangement. They have stated that orthogonality of the planes of the p orbitals on C, and N in structure VII would constrain it to be a triplet diradical.



(VII)

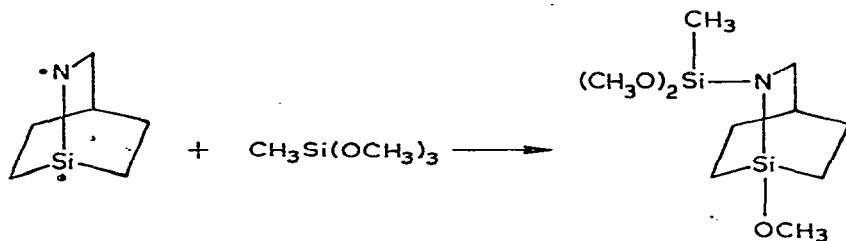
Whereas, structure VIII would seem to be acceptable for a short lived intermediate. Evidence in favor of generation of structure VIII by photolysis of 1-azidobicyclo[2.2.1]heptane was reported [4].



(VIII)

We believe this situation also obtains for our bridgehead silicon analogs, and that failure to obtain a trapped product having a bicyclo[2.2.2] system is strong evidence that a silaimine having substantial π -bonding was formed as the intermediate in the greatly favored mechanistic path to yield exclusively product V.

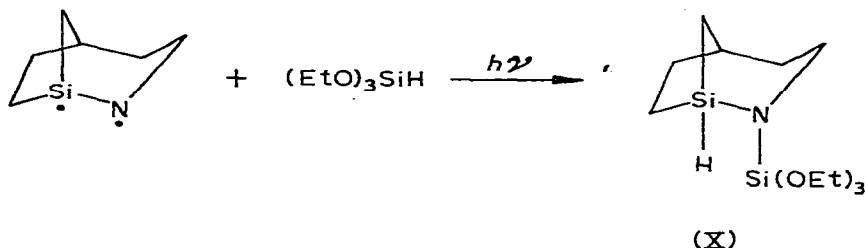
The mechanistic pathway not followed would lead to product IX.



(IX)

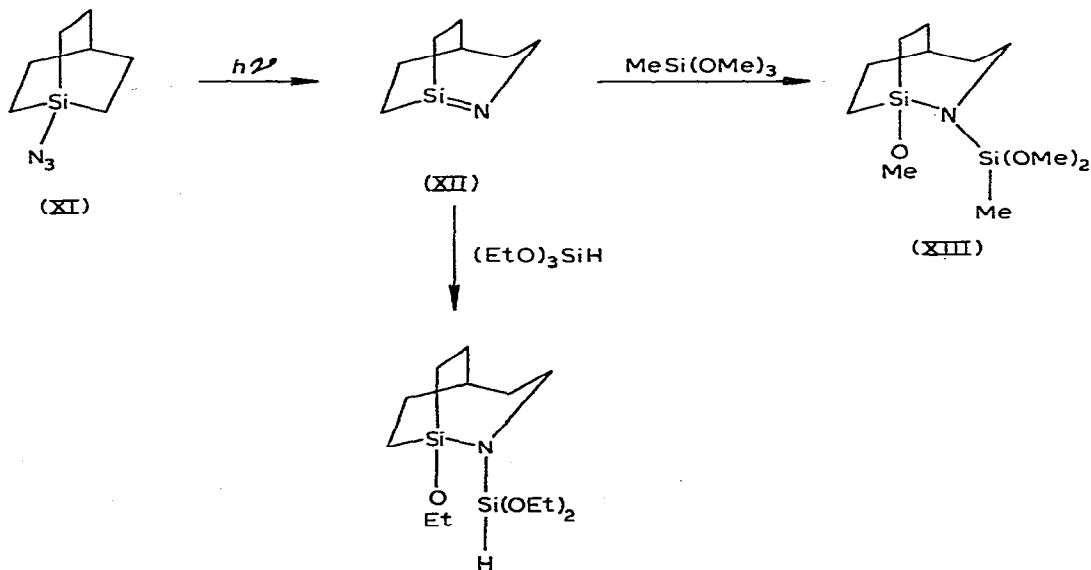
That product IX is not formed, is shown by the formation of only one product which has a clean triplet at δ 3.2 ppm in the NMR spectrum, characteristic for protons on carbon attached to N. Product IX would have a doublet due to the presence of an $\text{>N-CH}_2\text{-CH<}$ grouping.

Trapping of IV with $(\text{EtO})_3\text{SiH}$ was carried out essentially according to the procedure given above for the $\text{MeSi}(\text{OMe})_3$ trap. The result, addition of $\equiv\text{Si-OEt}$ across the unsaturated linkage in IV, rather than addition of $\equiv\text{Si-H}$ across that linkage is, by the arguments and data presented above and previously [3], very strong evidence that the unsaturated linkage in IV is not a triplet diradical. The latter radical structure would have given addition of $\equiv\text{Si-H}$ and yielded product X.



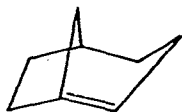
The actual product was shown unequivocally to have structure VI by NMR, mass and IR spectroscopy. The chemical shift for the singlet Si-H in product is at δ 4.25 ppm, which is close to δ 4.16 ppm for Si-H in $(\text{EtO})_3\text{SiH}$. For the clean singlet $\equiv\text{Si-H}$ in $(t\text{-Bu})_3\text{SiH}$ we observed δ 3.3 ppm. Furthermore, clear evidence in the NMR spectrum showed different OEt groups in structure VI. They should be equivalent in X, and Si-H in X should be a quintet instead of the actually observed singlet.

In the present work our studies were extended to the study and trapping of the silimine intermediate derived from 1-azido-1-silabicyclo[2.2.2]octane. The intermediate formed rapidly and was trapped in excellent yield by both $\text{MeSi}(\text{OMe})_3$ and $(\text{EtO})_3\text{SiH}$, as shown below to give products XIII and XIV, respectively.

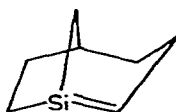


The fact that the mode of reaction for bicyclic intermediates IV and XII with $\text{CH}_3\text{Si}(\text{OCH}_3)_3$ and $(\text{EtO})_3\text{SiH}$ is the same as that for the simple silimine $\text{Et}_2\text{Si}=\text{NEt}$, would appear to be additional evidence in favor of formulation of IV and XII as having highly polarized twisted π -bonds.

We believe the balance of the present evidence favors significant π -bonding in the bridgehead silimine intermediates, but would not claim that it is completely established that such is the case. Further work is in progress to try to resolve our remaining doubts and, being stimulated by the excellent work of J.R. Wiseman who has reported generation and trapping of intermediate XV, we are undertaking the task of generation and trapping of the silicon analog XVI [5,6].



(XV)



(XVI)

An excellent study of the molecular structure of 1-methyl-1-silabicyclo-[2.2.1]heptane has been reported and the conclusion is reached that this compound has increased strain compared to norbornane due to replacement of a C—C bond by the substantially longer Si—C bond [7].

Experimental

Spectra

NMR spectra were taken on a Varian A-60 or Varian EM-360 instrument. IR spectra were taken on a Beckman IR-8 instrument. Low resolution mass spectra were taken on a Finnigan (3200) and high resolution mass spectra on a DuPont (21-942-B) instrument.

Analysis and separation of reaction mixtures

In most cases reactions were monitored by using a HP-7620A (F10) research chromatograph fitted with a 12 ft \times 1/8 in stainless steel column packed with 5% UC-W-98, 50/100 mesh. Separations were carried out by preparative GLC using a Varian 920 having a 10 ft \times 3/8 in column packed with 10% QFI on 45/60 chromosorb G or 5% SE30 on 45/60 chromosorb W.

Photolysis apparatus and procedure

The silyl azide, trapping agent and solvent were weighed into a two dram, screw cap vial and shaken until homogeneous. Most of the solution was then transferred by syringe into a 0.5 cm \times 15 cm nitrogen filled quartz tube sealed with a rubber serum cap. The tube was then clamped inside a Rayonet Photochemical Reactor equipped with 16 RPR-2537 lamps for photolysis at 254 nm. All photolyses were carried out in an atmosphere of dry nitrogen.

Even though some of the azide may remain when the photolysis is stopped, yields are based on the amount of material actually collected using preparative

GLC and assuming that all of the limiting reagent (silyl azide) has been consumed.

Preparation of bridgehead silyl chlorides

These were prepared according to published methods [6] *.

Preparation of 1-azido-1-silabicyclo[2.2.1]heptane and 1-azido-1-silabicyclo[2.2.2]octane.

1-Chloro-1-silabicyclo[2.2.1]heptane (4.0 g, 0.027 mol) was added by syringe to a suspension of 2 g (0.03 mol) of sodium azide in 15 ml of freshly distilled acetonitrile. During mixing of the reagents and an 18 h period of refluxing an atmosphere of dry nitrogen was maintained. Subsequent to filtration of the product under dry nitrogen, solvent was removed under vacuum and 3 g of product (71% yield) was isolated by preparative GLC. The product had: IR (CCl_4) 2150 cm^{-1} (SiN_3); NMR benzene- d_6 δ 0.3 (6H, m, $\text{Si}(\text{CH}_2)_3$), 1.35 (4H, m, $(\text{CH}_2)_2$), 1.85 ppm (1H (bridgehead), m); mass spectrum shows m/e 153 (72, M^+) and 125 (100, $M^+ - 28$). The fact that the highest peak in the mass spectrum corresponds to the loss of molecular nitrogen parallels the behavior observed for purely organic azides.

The 1-azido-1-silabicyclo[2.2.2]octane was prepared and isolated in exactly the same way. From 5 g (0.031 mol) of 1-chloro-1-silabicyclo[2.2.2]octane there was isolated by preparative GLC a yield of 2.2 g (0.013 mole, 42% yield) of 1-azido-1-silabicyclo[2.2.2]octane. The product had: IR (neat) 2150 cm^{-1} (SiN_3); NMR (CCl_4) δ 0.8 (6H, m, $\text{Si}(\text{CH}_2)_3$), 1.5 (1H, (bridgehead) m), 1.9 ppm (6H, m, $(\text{CH}_2)_3$); mass spectrum shows m/e 167 (85, M^+) and 139 (100, $M^+ - 28$).

Photolysis of 1-azido-1-silabicyclo[2.2.2]octane in the presence of triethoxysilane

Triethoxysilane (0.1 g, 0.65 mmol) was mixed with 0.03 g (0.18 mmol) of the silyl azide in 0.5 ml of dry cyclohexane as solvent. The photolysis was monitored by IR following the disappearance of the SiN_3 band at 2180 cm^{-1} and by analytical GLC. After approximately 9 h the product was separated by preparative GLC and had: NMR (CDCl_3), δ 0.8 (4H, m, $\text{Si}(\text{CH}_2)_2$), 1.75 (7H, m, $(\text{CH}_2)_3$ and bridgehead proton), 2.95 (2H, m, $\text{N}-\text{CH}_2$), 3.65 (2H, quartet, $\text{O}(\text{CH}_2)\text{CH}_3$, J 7 Hz), 3.7 (4H, $(\text{OCH}_2\text{CH}_3)_2$, J 7 Hz), 4.41 ppm (1H, s, Si-H). IR (CCl_4), 2150 (Si-H), 1100 cm^{-1} (SiOC). High resolution mass spectrum, m/e 303.1687 (21, calcd. for $\text{C}_{13}\text{H}_{29}\text{NO}_3\text{Si}_2$, M^+ 303.1685) 274.1295 (49, calcd. for $\text{C}_{11}\text{H}_{24}\text{NO}_3\text{Si}_2$, $M^+ - \text{C}_2\text{H}_5$ is 274.1297). The product XIV was 1-ethoxy-2-diethoxysilyl-1-sila-2-azabicyclo[3.2.2]nonane, 0.15 g. (75% yield).

Photolysis of 1-azido-1-silabicyclo[2.2.1]heptane in the presence of triethoxysilane

After photolysis for 9 h using a 1/3 ratio of silyl azide to triethoxysilane in cyclohexane solvent, preparative GLC yielded one major product in ~79%

* For references to the preparation and properties of the bridgehead chlorides and for a summary, see ref. 6.

yield identified as 1-ethoxy-2-diethoxysilyl-1-sila-2-azabicyclo[3.2.1]octane. NMR (CCl_4) 0.45 (4H, m, $\text{Si}(\text{CH}_2)_2$), 1.26 (9H, t, $\text{Si}(\text{OCH}_2\text{CH}_3)$ plus $\text{Si}(\text{OCH}_2\text{CH}_3)_2$, J 7 Hz) (these comprise two overlapping triplets), 1.74 (6H, m, $(\text{CH}_2)_3$) 2.15 (1H, m, bridgehead proton), 3.82 (2H, quartet, $\text{Si}(\text{OCH}_2\text{CH}_3)$, J 7 Hz), 3.8 (4H, quartet, $\text{Si}(\text{OCH}_2\text{CH}_3)_2$, J 7 Hz), 4.28 ppm (1H, s, Si-H) IR (CCl_4), 1100 (SiOC), 2210 cm^{-1} (SiH). High resolution mass spectrum, m/e 289.1531 (13.4, calcd. for $\text{C}_{12}\text{H}_{27}\text{O}_3\text{NSi}_2$, M^+ 289.1529).

Photolysis of 1-azido-1-silabicyclo[2.2.1]heptane in the presence of methyltrimethoxysilane

This photolysis was carried out by our typical procedure as described above. The silyl azide (0.1 g, 0.65 mmol) was mixed with 0.26 g (2 mmol) of methyltrimethoxysilane. After 9 h of irradiation GLC analysis followed by preparative GLC gave one major product in ~85% yield identified as 1-methoxy-2-dimethoxysilyl-1-sila-2-azabicyclo[3.2.1]octane: NMR (CDCl_3) δ 0.08 (3H, s, SiCH_3), 0.55 (4H, m, $\text{Si}(\text{CH}_2)_2$), 1.62 (5H, m, $(\text{CH}_2)_2$ and bridgehead H), 3.2 (2H, t, N- CH_2 , J 9 Hz), 3.4 (3H, s, SiOCH_3), 3.5 (3H, s, SiOCH_3) and 3.62 (3H, s, SiOCH_3); IR (CCl_4), 1100 (SiOC), 1250 (SiCH_3), 920 cm^{-1} (SiNSi); high resolution mass spectrum m/e 261.12187 (58.29 calcd. for $\text{C}_{10}\text{H}_{23}\text{NO}_3\text{Si}_2$, M^+ 261.1217), 246.1013 (100, calcd. for $\text{C}_9\text{H}_{20}\text{NO}_2\text{Si}_2$, M^+ -15, 246.09817).

Photolysis of 1-azido-1-silabicyclo[2.2.2]octane in the presence of methyltrimethoxysilane.

Photolysis was carried out as described above, using a 1/3 ratio of silyl azide to methyltrimethoxysilane. The product, XIII, was obtained in ~80% yield and identified as 1-methoxy-2-dimethoxymethylsilyl-1-sila-2-azabicyclo[3.2.2]nonane: NMR (CDCl_3) δ 0.1 (3H, s, SiCH_3), 0.75 (4H, m, $\text{Si}(\text{CH}_2)_2$), 1.76 (7H, m, $(\text{CH}_2)_3$ and bridgehead H), 3.0 (2H, m, N(CH_2)) 3.35 (3H, s, $\text{Si}(\text{OCH}_3)$) 3.47 ppm (6H, s, $\text{Si}(\text{OCH}_3)_2$); IR (CCl_4), 1260 (Si- CH_3), 1090 cm^{-1} (SiOCH_3). High resolution mass spectrum m/e 275.1467 (63.5, calcd. for $\text{C}_{11}\text{H}_{25}\text{NO}_3\text{Si}_2$ 275.1499), 260.1092 (100, calcd. for $\text{C}_{10}\text{H}_{22}\text{NO}_3\text{Si}_2$ 260.1132, M^+ -15).

Acknowledgement

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