REACTION OF TRIMETHYLSILYL AZIDE WITH BRIDGED BICYCLIC OLEFINS

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Summary

Bridged bicyclic olefins were found to undergo facile 1,3-cycloaddition reaction with trimethylsilyl azide. Norbornene produced *cis,exo*-1-trimethylsilyl-4,7-methano-3a,4,5,6,7,7a-hexahydrobenzotriazole, while norbornadiene formed a diadduct with *cis,exo*-stereochemistry, together with 2-trimethylsilyl-1,2,3-triazole produced by a retro-Diels—Alder reaction of an intermediate mono-adduct. Dicyclopentadiene reacted only at the norbornene position while α-pinene did not react with trimethylsilyl azide. In contrast to aryl- and sulfonyl-azide adducts of norbornene derivatives, which decompose upon heating, the present adducts were recovered unchanged after prolonged treatment at 205°C.
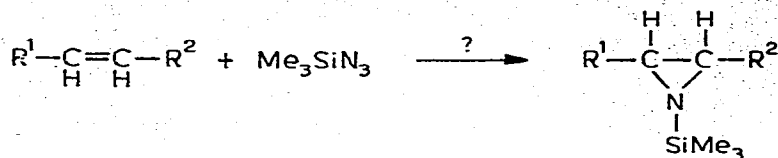
Introduction

The 1931 report by Alder and Stein of the addition of phenyl azide to bicyclopentadiene and other bicycloheptenes [1], yielding triazolines, sparked prodigious study of 1,3-cycloaddition reactions, creating a corpus of well-documented work on the reaction of olefins with azides [2]. For a series of olefins, rate of reaction with phenyl [3] or tosyl [4] azide correlated well with heats of hydrogenation; greater enthalpy of hydrogenation implied greater ring strain [5] and faster reaction with azide. The synthetic details of this triazoline preparation have been known for some time [2,6].

Less well-studied has been the interaction of silyl azides with olefins. Ettenhuber and Rühlmann [7] reported that long heating (up to 10 days) of trimethylsilyl azide with cyclohexene or vinyltriethylsilane afforded a modest yield of

the corresponding aziridine:

$$R^1-\underset{H}{\underset{|}{C}}=\underset{H}{\underset{|}{C}}-R^2 \; + \; Me_3SiN_3 \quad \xrightarrow{\;?\;} \quad R^1-\underset{\underset{N}{\diagdown\;/}}{\overset{H}{\overset{|}{C}}}-\overset{H}{\overset{|}{C}}-R^2$$

$$\underset{SiMe_3}{\underset{|}{N}}$$

This report was surprising to us in view of the sluggishness of trimethylsilyl azide as a 1,3-dipole toward nitriles [8] and maleimides [9] and the well-known correlations of dipolarophile reactivity with structure [4]. In our laboratory when carefully purified trimethylsilyl azide and cyclohexene were heated at reflux for two weeks, gas chromatographic analysis indicated no comsumption of olefin, implying that the uncatalysed reaction of unstrained olefin with silyl azide is exceedingly sluggish [10].

Results

   When equimolar quantities of norbornene or 1-methylnorbornene and tri-methylsilyl azide (TMSA) were heated at reflux for 16 h, 1-trimethylsilyl-1,2,3-triazoline adduct (I) was produced in excellent yield. The enhanced reactivity of norbornene relative to cyclohexene towards TMSA is well-explained by olefin activation produced by ring strain. This reactivity is further exemplified by the reaction of TMSA with dicyclopentadiene, which produced adduct II, where addition occurred exclusively at the strained (norbornyl type) olefin; prolonged refluxing in the presence of excess TMSA failed to produce any trace of diadduct III. Similar results were reported for the reaction of phenyl azide with dicyclopentadiene [1a]. For these three olefins, distilled yields of adduct were greater than 85%.
   Contrariwise, reaction of norbornadiene with varying molar ratios of TMSA gave only meager amounts of diadduct IV and no mono-adduct VI. The major product was 2-trimethylsilyl-1,2,3-triazole V, and small quantities of the adduct II (derived from dicyclopentadiene) were also isolated. In contrast to the straight-forward cycloadditions of norbornene and dicyclopentadiene, the products from norbornadiene can only be rationalized by postulating a scheme in which mono-adduct VI is initially produced and then partitioned between two compet-ing reactions (see Scheme 1).
   That VI possessed but limited thermal stability is suggested by the observation that the mono-adduct of norbornadiene and phenyl azide decomposes at 90—100°C to 1-phenyl-1,2,3-triazole [3]. In the present case, decomposition of VI would produce 1-silylated triazole (VII), which could isomerize via 1,5-sigmatropic rearrangement to V, such rearrangement being well-known in the silyltriazole series [11].
   A bridged bicyclic system with moderate strain, d,l-α-pinene, failed to react after 20 h at reflux, implying that the double bond in a bicyclo[3.1.1]heptyl system is less strained than that of a bicyclo[2.2.1]heptyl system and hence insufficiently activated to react with TMSA.
   All the trimethylsilyltriazolines isolated (Ia, Ib, II and IV) exhibited surpris-ing thermal stability. In contrast with aryl- and sulfonyl-azide adducts of bi-

SCHEME 1

(Ia) R = H
(Ib) R = CH₃

(II)

(III)

(VI)

Me₃Si—N—N
      N
(VII)

(IV)

II

N—N
 N
 SiMe₃
(V)
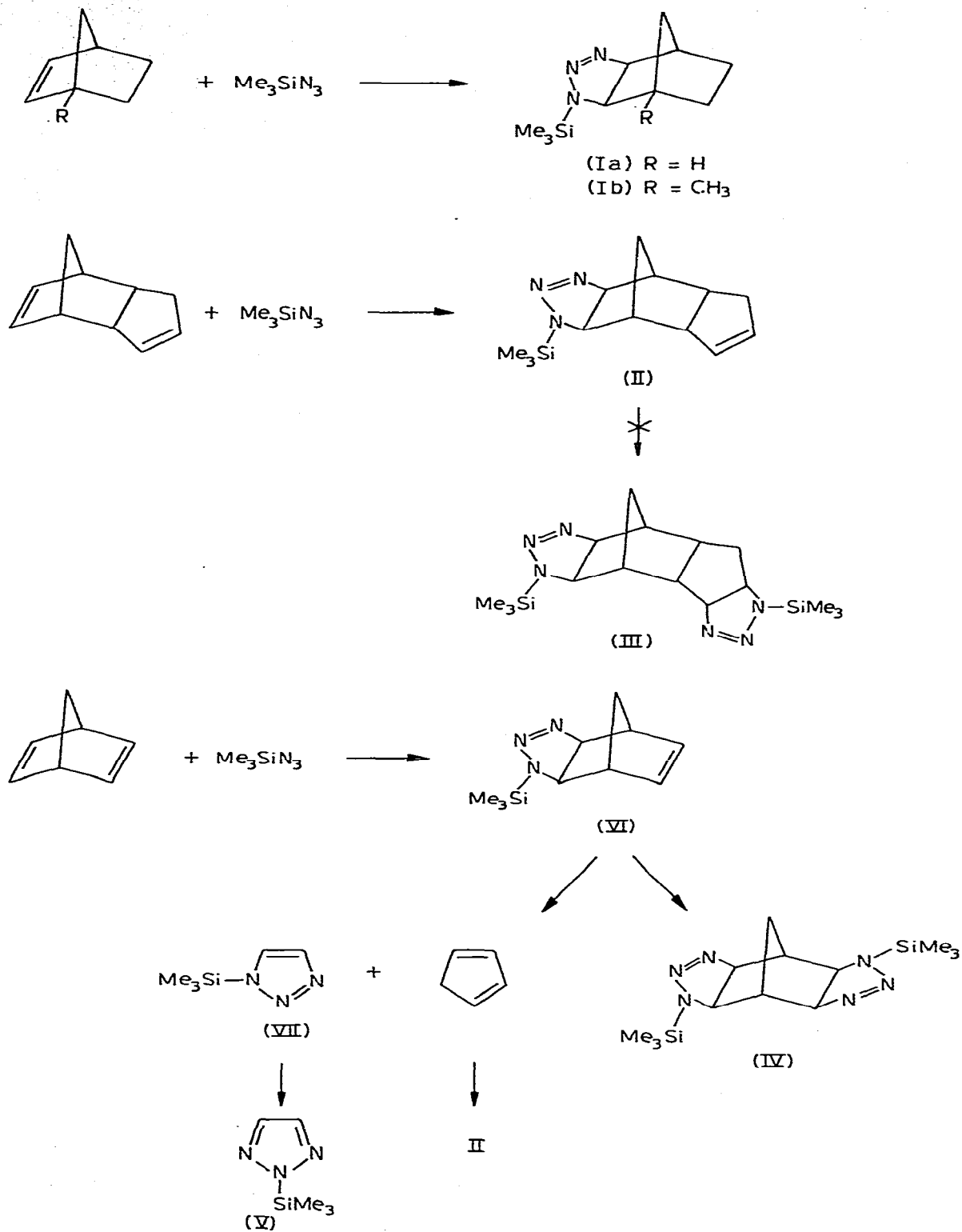
cyclic olefins, which lose nitrogen when heated above 90—100°C forming imines and aziridines [12], no thermal decomposition of the silylated adducts could be detected during gas chromatography at a column temperature of 200°C. No evolution of nitrogen from Ia occurred after 5 h of refluxing in decalin, nor after 3 h of heating without solvent in a bath at 205°C. Adduct Ia did, however, evolve nitrogen when treated with methyl iodide in benzene, producing a 20% yield of trimethylsilyl iodide and unidentified organic solids.

Discussion

The relative inertness of trimethylsilyl azide as a 1,3-dipole toward olefins can be explained by a mismatch of orbital energies in the transition state for cycloaddition, which can be qualitatively assessed by the Fukui technique [13]. The present cycloadditions take place at a temperature where adducts from aryl- and sulfonyl-azides decompose; it is interesting to examine the reasons why a trimethylsilyltriazoline should be thermally stable. If the principal mode of decomposition of a triazoline is via the betaine intermediate [4], i.e.:
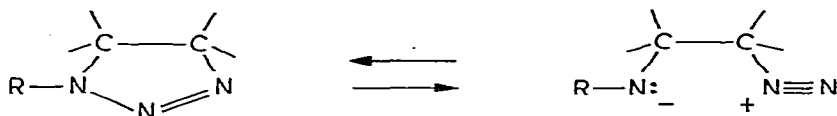
it would be expected that a $R = Me_3Si$ substituent would be less able to stabilize an adjacent negative charge than would a $R = Aryl$ or $R = SO_2Aryl$ group. However, the thermolysis of trimethylsilyltriazolines has not been investigated in detail, and the mechanism of thermolysis is still an open question [9].

The NMR parameters of the isolated adducts are in good accord with *exo* stereochemistry (Table 1) as previously determined for cycloaddition to norbornene type olefins. It should be noted that Ib, II and IV could exist as mixtures of regioisomers depending on the regiochemistry of addition, e.g. in Ib the trimethylsilyl could be *anti* or *syn* (as shown) to the methyl group. The broadness of the resonance lines of II indicated such a mixture of regioisomers, and IV exhibited two Me_3Si— resonances of unequal intensity implying two isomers with Me_3Si's *syn* and *anti* (shown). The facility of 1,3-rearrangement on the Si—N_3 framework, i.e. R_3Si—N—N=N ⇌ —N=N—N—SiR_3 [11], precluded our separation of the isomer pairs. As the proton NMR of the isomer pairs are very similar, a definitive answer to the regiochemistry of trimethylsilyl azide cycloaddition must await analysis of the ^{13}C NMR spectra of these adducts, which will be reported in a further paper.
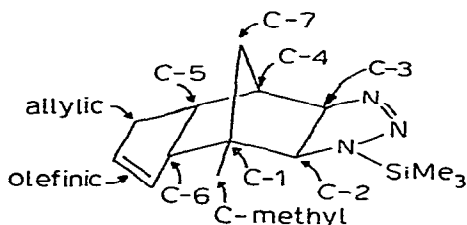
Experimental

General
   All reactions involving silicon compounds were carried out under an atmosphere of dry nitrogen in flame-dried glassware. NMR spectra were determined at 60 MHz on Varian A60A and/or T-60 spectrometers; elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. Trimethylsilyl azide (TMSA) was freshly distilled immediately before use.

TABLE 1

PROTON NMR RESONANCES OF 1-TRIMETHYLSILYL-1,2,3-TRIAZOLINE ADDUCTS

Proton Location	Resonance (ppm δ downfield from Me₄Si) in adduct of:			
	Norbornene (Ia)	1-Methylnorbornene (Ib)	Dicyclopentadiene (II)	Norbornadiene (IV)
Me₃Si—	0.30	0.26	0.32	0.31 & 0.37
C-7	1.06	0.88—1.30	1.20	1.03
C-1 & C-4	2.15 & 2.56	2.08	2.0—2.8	2.52
C-2	3.30	3.40	3.33	3.55
C-3	4.23	4.12	4.30	4.40
C-5 & C-6	0.97—1.68	0.88—1.30	2.0—2.8	
C-Methyl		1.28		
Olefinic			5.70	
Allylic			2.0—2.8	

KEY:

Reaction of norbornene with TMSA

A solution of 9.4 g (0.1 mol) of norbornene (Aldrich) and 11.5 g (0.1 mol) of TMSA was stirred at 140°C for 16 h. Distilation of the brown reaction mixture at 68—70°C afforded 19.2 g (92%) of Ia: IR (CCl₄) 2980, 2920, 1480, 1340, 1258, 1160, 1035, 990, 900, 842, and 725 cm⁻¹; NMR (CDCl₃) in Table 1. (Found: C, 57.40; H, 9.01; N, 20.29. C₁₀H₁₉N₃Si calcd.: C, 57.38; H, 9.13; N, 20.07%.)

Reaction of 1-methylnorbornene with TMSA

A solution of 5.8 g (0.05 mol) of TMSA and 5.4 g (0.05 mol) of 1-methylnorborn-2-ene (Pfaltz & Bauer) was stirred at 150°C for 16 h. Distillation at 64—65°C (0.1 mm) afforded 9.3 g (83%) of Ib; IR (film) 2985, 2910, 1475, 1460, 1255, 1158, 1040, 993, 840, and 760 cm⁻¹; NMR (CDCl₃) in Table 1. (Found: C, 59.16; H, 9.61; N, 19.09. C₁₁H₂₁N₃Si calcd.: C, 59.14; H, 9.48; N, 18.81%.)

Reaction of dicyclopentadiene with TMSA

A solution of 6.6 g (0.05 mol) of dicyclopentadiene (MC & B) and 5.8 g (0.05 mol) of TMSA was heated with stirring in a bath at 140°C for 16 h; at which time the yellow reaction mixture has ceased to reflux. Triazoline II, 10.9 g (89%) was collected at 96—99°C (0.1 mm) as a pale yellow liquid: IR (film) 3050, 2960, 2900, 1478, 1258, 1160, 1040, 987, 840, and 729 cm⁻¹;

NMR (CCl$_4$) in Table 1. (Found: C, 63.11; H, 8.56; N, 16.98. C$_{13}$H$_{21}$N$_3$Si calcd.: C, 62.95; H, 8.44; N, 17.19%.)

Reaction of norbornadiene with TMSA

A solution of 17.3 g (0.15 mol) of TMSA and 9.2 g (0.1 mol) of norbornadiene (Aldrich) was stirred at 125—130°C for 36 h. Distillation of the reaction mixture afforded first a liquid, b.p. 49—50°C (10 mm), which upon fractionation through a jacketed Widmer column yielded 11.3 g (80%) of triazole V, b.p. 147—149°C: IR (CCl$_4$) 3060, 2970, 2880, 1470, 1255, 1150, 1035, 983, 900, 880, 840, and 715 cm^{-1}; NMR (CDCl$_3$) δ 0.53 (9H, s) and 7.64 (2H, s) ppm (Found: C, 42.19; H, 7.91; N, 29.52. C$_5$H$_{11}$N$_3$Si calcd.: C, 52.52; H, 7.85; N, 29.75%). Further distillation of the reaction mixture gave the cyclopentadiene adduct II, 1.1 g (9%), b.p. 90—96°C (0.07 mm), followed by 2.3 g (9%) of bis-triazoline (IV), b.p. 156—160°C (0.05 mm); IR (CCl$_4$) 2990, 2960, 1475, 1330, 1255, 1150, 1045, 990, 875, and 845 cm^{-1}; NMR (CDCl$_3$) in Table 1. (Found: C, 48.54; H, 7.91; N, 26.28. C$_{13}$H$_{26}$N$_6$Si$_2$ calcd.: C, 48.43; H, 8.13; N, 26.06%.)

Attempted reaction of α-pinene with TMSA

A mixture of 6.8 g (0.05 mol) of α-pinene (Aldrich) and 6.8 g (0.05 mol) of TMSA were stirred for 20 h in a bath at 130°C. Distillation of the reaction mixture afforded unreacted starting materials. No other materials were detected by GLPC or IR.

Thermal decomposition studies

A sample of norbornene adduct Ia was placed in a flask connected through a dry-ice/acetone trap to a gas-measuring buret and heated for 3 h in a bath at 205°C. No gas was evolved, and the IR and NMR spectra of the heated material were unchanged. In another experiment using the same reaction setup, 5.6 g (0.025 mol) of Ia in 50 ml of decalin (Aldrich) was heated at reflux for 5 h, GLPC, IR, and NMR analysis indicated that no reaction had taken place.

Reaction of norbornene adduct with methyl iodide

To a solution of 5.2 g (0.025 mol) of Ia in 20 ml of benzene was added 14.2 g (0.1 mol) of methyl iodide over a 5 min period. The reaction mixture frothed and refluxed spontaneously, yellowed, and deposited white solids. The solids were removed by filtration. Distillation of the filtrate afforded 1.0 g (20%) of trimethyliodosilane, identical with an authentic sample.

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