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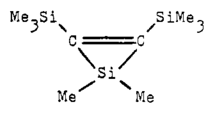
Received December 7, 1977

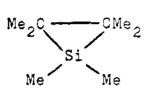
Reactions of 1,1-Dimethyl-2,3-bis(trimethylsilyl)-1-silirene and Hexamethylsilirane with Dimethyl Sulfoxide. Insertion of Dimethylsilanone into the Silirene and Silirane Rings

Sir:

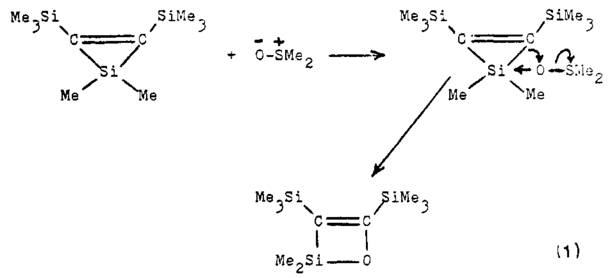
In a continuation of our recent investigations of the highly strained and hyperreactive silirene and silirane ring systems,[1] we have examined their reactions with dimethyl sulfoxide. In view of the propensity of both silirenes and siliranes to undergo attack at the ring silicon atom by nucleophilic reagents, we expected that the reaction of dimethyl sulfoxide with the SiC_2 cyclics I and II would follow the course shown for I in eq 1. The 1-oxa-2-silacyclobutene III would be a new ring system of some interest, one which we have sought without success as a product of the autoxidation of I. The actual course of the reaction of silirene I with dimethyl sulfoxide, however, proceeded differently, although the initial step could well be that shown in eq 1. The reaction is of particular significance and interest in that dimethylsilanone (or dimethylsilylene oxide), $Me_2Si{=}O$, appears to be an intermediate.



I



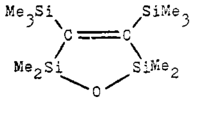
II



III

(1)

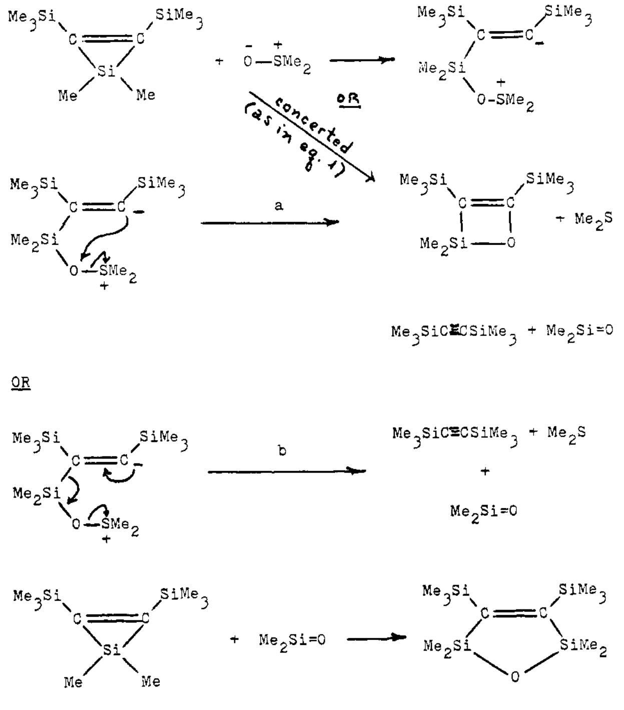
In one such reaction, 0.5 mmol of dimethyl sulfoxide was added slowly, under argon to a cold (0 °C) solution of silirene I (1.54 mmol) in 1 mL of dry benzene in a flame-dried, 10 mL, one-necked flask. The mixture was stirred and kept at 0 °C for 5 min and then was allowed to warm to room temperature.[2] After 1 h, gas-liquid chromatographic (GLC) analysis showed the presence of dimethyl sulfide, bis(trimethylsilyl)acetylene (94%, based on Me_2SO), and the unsaturated, cyclic siloxane IV in 66% yield (assuming that it requires 2 mol of I to produce 1 mol of IV). The latter, a solid of mp 74.5-75.5 °C, was identified by combustion analysis and by comparison of its IR and NMR spectra with those of an authentic sample obtained by autoxidation of 1,1,2,2-tetramethyl-3,4-bis(trimethylsilyl)-1,2-disilacyclobut-3-ene.[1b,3] The formation of these products can be rationalized as shown in Scheme I. Whether a cyclic intermediate is involved (path a) or not (path b), in either case, a dimethylsilanone, $Me_2Si{=}O$, intermediate is generated and this then inserts into the Si—C bond of the strained, highly reactive silirene to give IV.



IV

If $Me_2Si{=}O$ is an actual intermediate, other substrates which are known to react with this species might be added to the reaction mixture to intercept it.[4] Accordingly, a Me_2SO-I reaction (4 mmol of Me_2SO, 1.7 mmol of I) was carried out in the presence of dimethyldimethoxysilane. The silirene was added slowly to a solution of Me_2SO in dimethyldimethoxysilane (4 mL) to give an exothermic reaction in which the following products were formed: dimethyl sulfide, bis(trimethylsilylacetylene (86%), and *sym*-tetramethyldimethoxydisiloxane (81%), n^{25}_D 1.3815 (lit.[8] n^{25}_D 1.3811), ^1H NMR (CCl_4)

Scheme I



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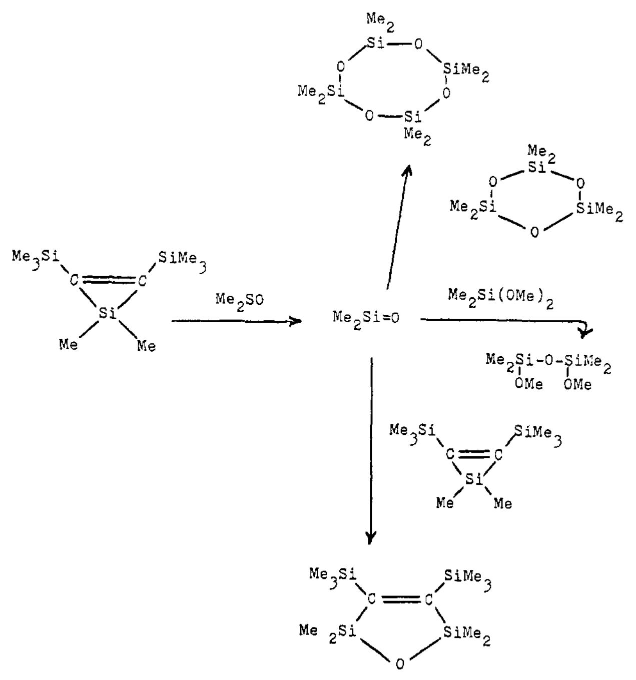
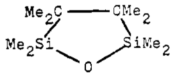
Scheme II



δ 0.04 (s, 12 H) and 3.40 ppm (s, 6 H). In a similar Me_2SO/I reaction carried out in the presence of an excess of hexamethylcyclotrisiloxane (D_3) in benzene at 0 °C, dimethyl sulfide (93%) and bis(trimethylsilyl)acetylene again were formed as well as the $Me_2Si{=}O$ trapping product, octamethylcyclotetrasiloxane (D_4) (66% yield, based on I), and IV (32%). Thus $Me_2Si{=}O$ is an intermediate in these reactions which can be trapped (Scheme II). The insertion of $Me_2Si{=}O$ into the Si—O bonds of D_3[5,6] and of dimethyldimethoxysilane[7] are known processes, but its insertion into a strained three-membered ring had not been reported to date.

Similar chemistry was observed with hexamethylsilirane, although it appeared to be less reactive toward Me_2SO than the silirene. Thus a reaction of 1.65 mmol of II with 0.75 mmol of Me_2SO under argon resulted in an only mildly exothermic reaction which produced cyclic siloxane V (n^{25}_{D} 1.4524 (lit.[1b]


V

n^{25}_{D} 1.4531)) in 53% yield, based on Me_2SO, tetramethylethylene (97%, based on Me_2SO), as well as dimethyl sulfide. The dimethylsilanone generated in the Me_2SO-II interaction also could be intercepted when this reaction was carried out in the presence of an excess of dimethyldimethoxysilane. *sym*-Tetramethyldimethoxydisiloxane was formed in 69% yield. When a mixture of ~1 molar equiv each of silirene I and silirane II was treated with 1 molar equiv of Me_2SO at 0 °C, followed by 1-h reaction time at room temperature, the yield of bis(trimethylsilyl)acetylene was 36%, of dimethyl sulfide, 66%, of IV, 17%, and of V, 29%, a finding in line with the already observed greater reactivity of I as compared with that of II.

Pyridine *N*-oxide and trimethylamine *N*-oxide also reacted with silirene I to give dimethylsilanone. Such reactions, carried out in dimethyldimethoxysilane at room temperature, were mildly exothermic and gave *sym*-tetramethyldimethoxydisiloxane in 59% yield in the case of pyridine *N*-oxide and in 32% yield in the case of the reaction with anhydrous trimethylamine *N*-oxide. The lower yield in the latter case may be due to the fact that trimethylamine *N*-oxide is only poorly soluble in the dimethyldimethoxysilane medium.

The insertion of dimethylsilanone into the Si—C bonds of silirane II and silirene I bears a formal similarity to the insertion of aldehydes and ketones into these ring systems.[1a,c] However, in terms of mechanism, the $RCH{=}O$ and $R_2C{=}O$ insertion reactions, believed to be radical processes on the basis of limited evidence,[1a] may be quite different from the $Me_2Si{=}O$ insertion reactions. The evidence which has accumulated thus far suggests that the species containing silicon-heteroatom double bonds are quite polar,[5,6] $R_2Si^{\delta+}{=}Y^{\delta-}$, and so the $Me_2Si{=}O$ insertion may well be a polar, not a radical, process.

We have pictured the formation of $Me_2Si{=}O$ in the Me_2SO-I reaction as shown in Scheme I. We note, however, that Weber and his coworkers have reported that dimethylsilylene deoxygenates Me_2SO, giving $Me_2Si{=}O$, which they intercepted with D_3.[6b] This possibility, Me_2Si extrusion prior to reaction with Me_2SO, is unlikely in the case of silirene I. This compound is thermally very stable and resistant to extrusion of dimethylsilylene. Only upon photolysis or transition metal catalysis does this process occur,[1a,c,9] conditions which are absent in the present reactions.

The reactions of silirene I and silirane II with other 1,2-dipolar reagents are under active investigation.

Acknowledgment. The authors are grateful to the U.S. Air Force Office of Scientific Research (NC)-AFSC for generous support of this research under Grant AF-AFOSR-76-2917 and to Union Carbide Corporation for gifts of chemicals.

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(2) A reaction carried out at room temperature was exothermic and product yields were lower.

(3) The melting point of IV in ref 1b was erroneously reported as 62–64 °C. It should read 72–74 °C.

(4) The generation and the chemistry of $Me_2Si{=}O$ has been the subject of several reports by Sommer,[5] Weber,[6] and Ando.[7]

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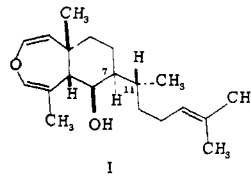
Received October 17, 1977

Stereorational Total Synthesis of the Marine Diterpene Dictyolene and Its C-11 Epimer

Sir:

Recently Erickson et al. reported the isolation of two novel diterpenoids, dictyoxepin (I) and dictyolene (II), from antibiotic extracts of the marine alga *Dictyota acutiloba.*[1]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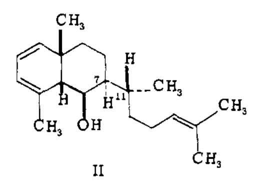
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