

- wt, 285. Found: C, 54.2; H, 6.3; Al, 9.3; Cl, 12.5; Ti, 16.9; mol wt, 310 (cryoscopic in benzene).
- (6) Characteristically the methylene hydrogens of **1** and its derivatives appear at low field in ¹H NMR spectra. The methylene carbon is also shifted to low field, approaching the region for metal carbene complexes (e.g. δ_{13C} 204 (Cp₂TiCH₂AlMe₃), 188 (Cp₂TiCH₂AlCIME₂), vs. 228 (Cp₂TaMe(=CH₂)).⁷ ¹H NMR data for **1** and its derivatives follow (C₆D₆ solvent, 22 °C, 220-MHz spectrometer, measurements from C₆D₅H τ 2.63): Cp₂TiCH₂AlMe₃ (present with Cp₂TiMe₂), τ 0.90 (2 H, s, CH₂), 4.40 (10 H, s, Cp), 10.18 (6 H, s, AlMe), 11.36 (3 H, s, TiMeAl); Cp₂TiCH₂AlCIME₂, τ 1.51 (2 H, s, CH₂), 4.16 (10 H, s, Cp), 10.06 (6 H, s, Me); Cp₂TiCH₂AlMeCH₂CMe₃, τ 1.51 (1 H, d, J = 6.7 Hz, TiCH₂Al), 1.57 (1 H, d, J = 6.7 Hz, TiCH₂Al), 4.12 (5 H, s, Cp), 4.15 (5 H, s, Cp), 8.57 (s, 9 H, CMe₃), 9.28 (1 H, d, J = 13.8 Hz, AlCH₂CMe₃), 9.37 (1 H, d, J = 13.8 Hz, AlCH₂CMe₃), 10.04 (3 H, s, AlMe). ¹H NMR data for the TiCH₂Zn species follow: product of Cp₂TiMe₂ and Me₂Zn, τ 1.32 (s, TiCH₂Zn); product of Cp₂TiCl₂ and Me₂Zn, τ 1.69 (s, TiCH₂Zn).
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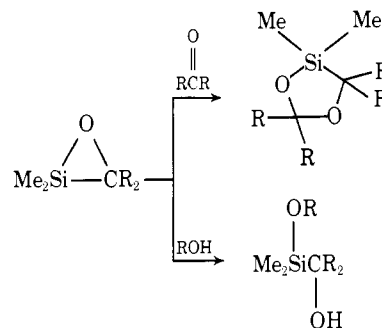
Chemistry of Oxasilacyclopropane. 2.¹ Formations of Dioxasilacyclopentanes in the Reaction of Oxasilacyclopropane Derivatives with Adamantanone and Norbornone

Sir:

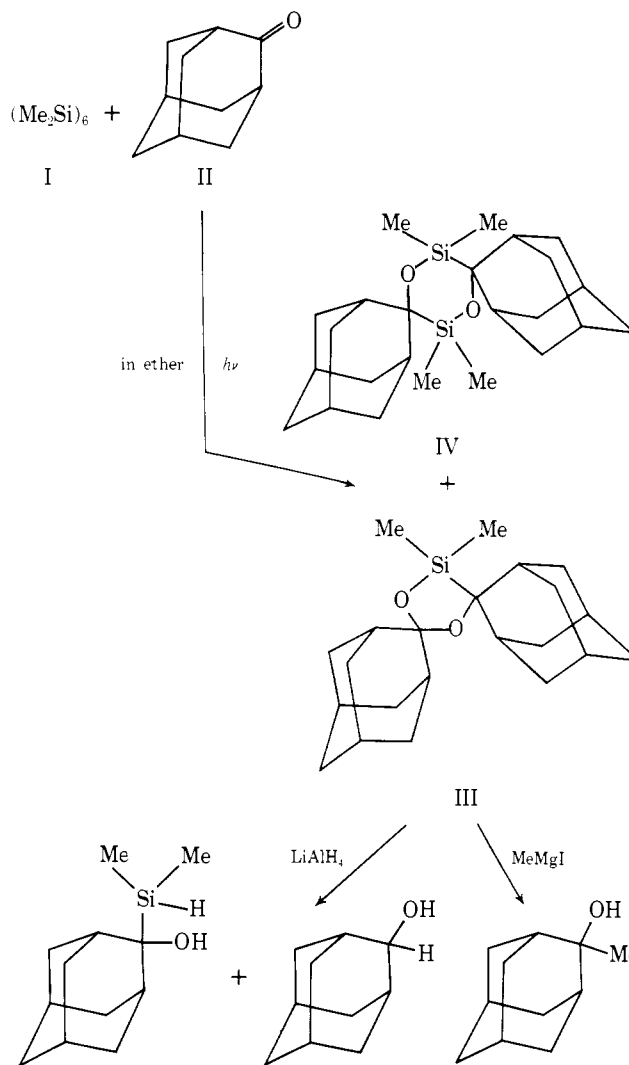
Interest has quickened over last few years in the chemistry of strained ring system containing a silicon atom. In contrast to rather extensive studies of chemistry of silacyclopropane,^{2,3} and silacyclopentene,^{4,5} very little is known about the chemistry of oxasilacyclopropane.^{1,6} Recently, we reported that generation of dimethylsilylene by 1,2-dimethoxytetramethyldisilane pyrolysis in the presence of benzophenone gave 1,1-dimethyl-1-sila-2-oxa-3-phenyl-4,5-benzocyclopentene, which we can be best rationalized by assumption of oxasilacyclopropane intermediate followed by skeletal rearrangement via a cleavage of silicon-carbon bond.

We now report here the entirely new photochemical addition of silylene⁷ to ketone in solution and study the intermolecular reactions of oxasilacyclopropane with ketones and alcohols.

An ether solution of dodecamethylcyclohexasilane (**I**, 0.3 mmol) and 2-adamantanone (**II**, 1.5 mmol) in quartz tube was irradiated with a low pressure mercury lamp for 4 h under a nitrogen atmosphere. Evaporation followed by GLC gave two main products, dispiro[adamantane-2,1'-(2',5'-dioxo-3'-



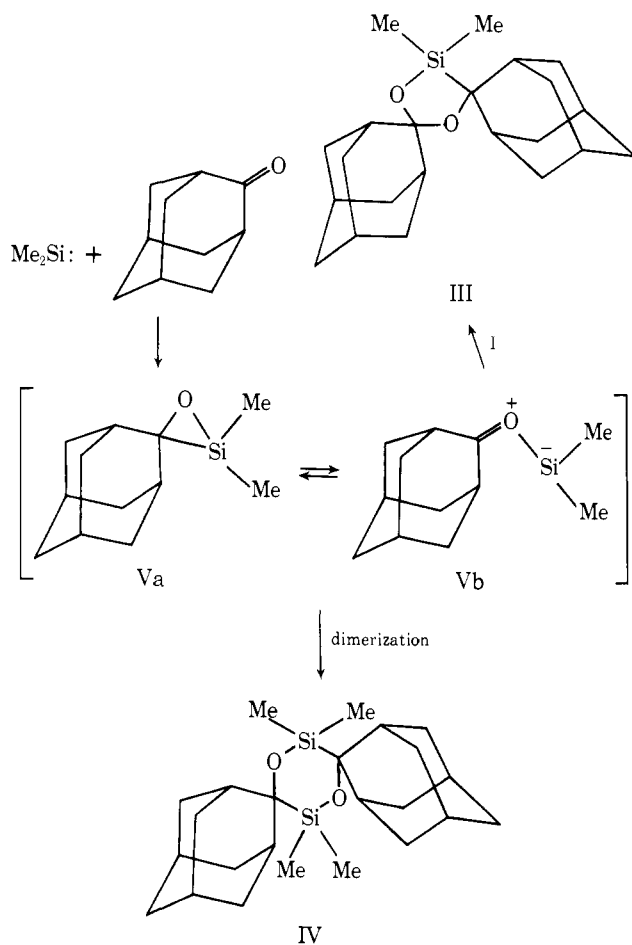
dimethylsilacyclopentane)-4',2''-adamantane] (**III**, mp 131-131.5 °C) and dispiro[adamantane-2,1'-(2',5'-dioxo-3',6'-tetramethyldisilacyclohexane)-4',2''-adamantane] (**IV**, mp 230-231 °C), in 165 and 18% yields, respectively (based on the number of moles of **I**). The assigned structure is com-



patible with spectral data of **III**, as well as the reaction with lithium aluminum hydride⁸ to 2-adamantanol (70%) and 2-dimethylsilyl-2-adamantanol (78%), and the reaction with methylmagnesium iodide⁹ to 2-methyl-2-adamantanol (47%). The mass spectrum (70 eV) of **III** showed a relatively strong molecular ion at *m/e* 358, and no higher species, confirming that the five-membered ring was in hand. The ¹H NMR spectra of **III** showed in CDCl₃ a singlet for Si-Me at 0.25 (6 H) and broad adamantyl protons at 1.28-2.6 ppm (28 H). Its IR spectrum shows bands of medium intensity at 1090-1115 (Si-O and C-O bands) and at 1250 cm⁻¹ (Si-Me band).

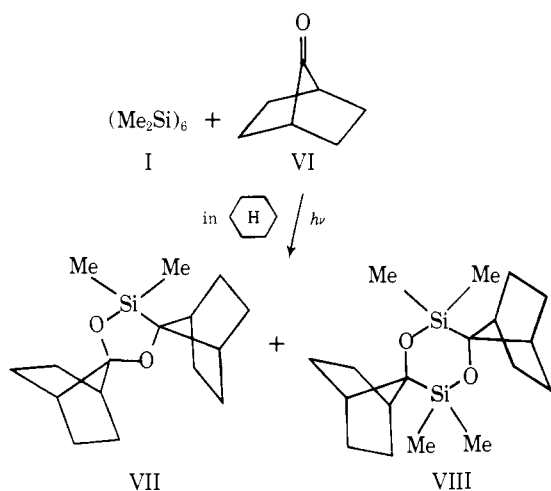
Compound IV could be isolated by preparative GLC and its structure was confirmed by mass spectrum (m/e 416), IR (KBr) (1015 and 1250 cm^{-1}), and $^1\text{H NMR}$ in CDCl_3 (0.3 (12 H, singlet for Si-Me) and 1.2–2.6 ppm (28 H, multiplet for ring protons)).

An attractive mechanism for the reaction of dimethylsilylene with 2-adamantanone may involve a 2-adamantylidenesilene oxides V which either react with 2-adamantanone to product



III or dimerize to IV via cleavage of the silicon-oxygen bond (Va) or a silacarbonyl ylide (Vb). With regard to the observed ketone insertion into the oxasilacyclopropane ring, analogous ketone and aldehyde insertion into silacyclopropane has been reported by Seyferth.¹⁰

Similar studies on the photolysis of I (0.31 mmol) in 7-norbornone (VI, 1.5 mmol) in dry cyclohexane afforded di-

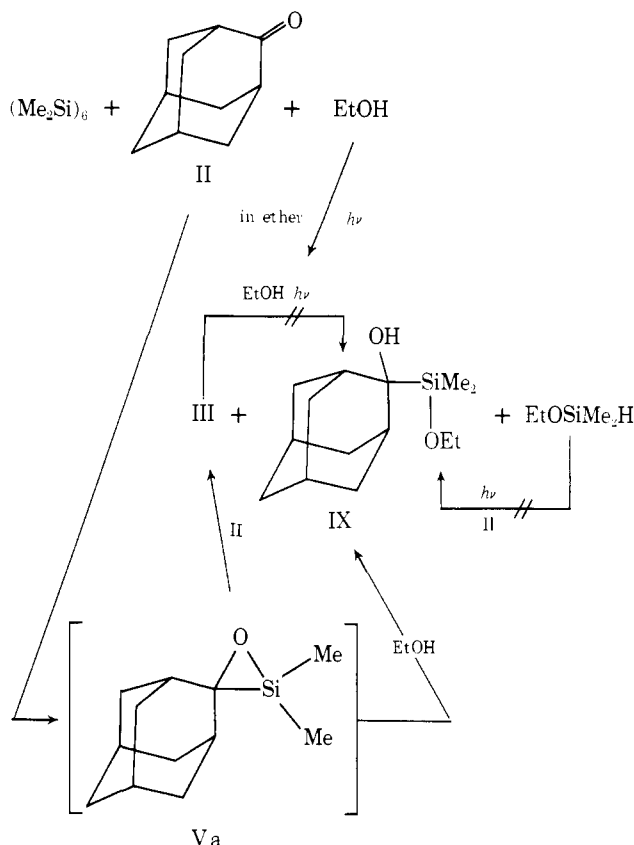


spiro[norbornane-7,1'-(2',5'-dioxo-3'-dimethylsilacyclopentane)-4',7''-norbornane] (VII, mp 94–94.5 $^\circ\text{C}$, 97% yield) and dispiro[norbornane-7,1'-(2',5'-dioxo-3',6'-tetramethyldisilacyclohexane)-4',7''-norbornane] (VIII, mp 142.5–143 $^\circ\text{C}$, 56% yield).¹¹

Photolysis of I in di-*tert*-butyl ketone under the similar conditions was carried out, but the product which reacted with the ketone was not observed by GLC analysis.¹² The reason is not certain, but steric factors may be responsible.

Even more convincing is the evidence for oxasilacyclopropane intermediate when alcohols are used as traps for intermediate V. Silacyclopropanes¹³ and silacyclopropenes^{4,5} are known to react with alcohol to give alkoxysilane derivatives.

Photolysis of an ether solution of I (0.11 mmol) in the presence of 2-adamantanone (2.0 mmol) and ethanol (0.42 mmol) leads to the formation of ethoxydimethylsilane (216%), III (16%), and 2-ethoxydimethylsilyl-2-adamantanone (IX, 35% yield based on the number of moles of I). These results are



consistent with the intermediacy of oxasilacyclopropane (Va) which is trapped by addition of alcohol to silicon-oxygen bond. Alternative interpretations, namely that III reacts with ethanol to yield IX, and also the reaction of ethoxydimethylsilane with 2-adamantanone, were ruled out by control experiments. Thus, III and IV were shown to be stable to ethanol in the presence and absence of light.

Related works are in progress and will be reported elsewhere.

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 (11) Spectral data for VII: NMR (CCl₄) 0.27 (6 H, s, Si-Me), 1.0–2.2 ppm (20 H, m, ring protons); IR (KBr) 1060–1080 (Si-O and C-O bands), 1260 cm⁻¹ (Si-Me band); mass spectrum *m/e* 278. Anal. Calcd for C₁₈H₂₈SiO₂: C, 69.01, H= 9/4/ Found: C, 68.9, H, 9.3. Spectral data for VIII: NMR (CCl₄) 0.17 (12 H, s, Si-Me), 1.0–2.1 ppm (20 H, m, ring protons); IR (KBr) 1080 (Si-O band), 1260 cm⁻¹ (Si-Me band); mass spectrum *m/e* 336. Anal. Calcd for C₁₈H₃₈Si₂O₂: C, 64.23; H, 9.58. Found: C, 63.9, H, 9.3.
 (12) Photolysis of I in the presence of acetone, diethyl ketone, and cyclohexanone resulted in the formation of corresponding silyl enol ethers in high yields. These reactions were analogous to ref 6.
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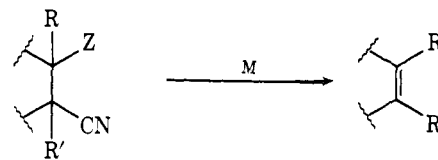
Stereochemistry of Vicinal Cyanohydrin Reduction-Elimination

Sir:

We recently described a method for converting vicinal cyanohydrins to olefins (Scheme I) through reduction-elimination of their methanesulfonate or methyl ether derivatives (Ia, Ib) with dissolving metals (M = Li or Ti).^{1,2} We now wish to report findings with methylthiomethyl ether sulfones (Ic) and sodium naphthalenide which extend the synthetic potential of this reaction and shed light on its stereochemistry.

The starting cyanohydrins **1a** and **5a** for these studies were prepared in 91% yield as a 55:45 mixture by reduction of cyanocyclododecanone **4** with sodium borohydride (Chart I). The methylthiomethyl ether derivatives **2a** and **6a** (obtained in quantitative yield using dimethyl sulfoxide-acetic anhydride-acetic acid⁴) could be readily separated by chromatography. Oxidation with *m*-chloroperoxybenzoic acid yielded

Scheme I



- Ia, R, R' = H or alkyl; Z = OMs
 Ib, R, R' = H or alkyl; Z = OMe
 Ic, R, R' = H or alkyl; Z = OCH₂SO₂Me

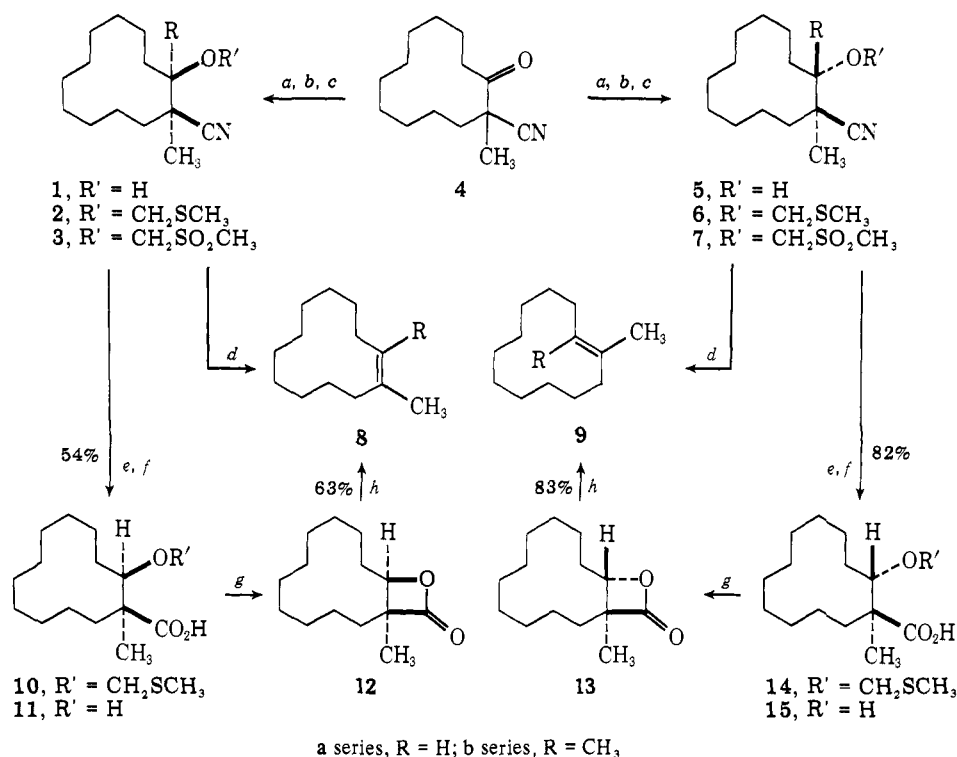
the crystalline sulfones **3a** (mp 94–95 °C, 84% yield) and **7a** (mp 96–97 °C, 67% yield). Reduction of the former with sodium naphthalenide in hexamethylphosphoramide (HMPA) gave *cis*-1-methylcyclododecene (**8a**, 85% yield) while the latter afforded the *trans* isomer **9a** (60% yield).

The stereochemistry of cyanohydrins **1a** and **5a** was ascertained as follows. Hydrolysis of the protected nitriles **2a** and **6a** followed by mercuric-catalyzed cleavage of the hemithioacetal acids **10** and **14** afforded the hydroxy acids **11** and **15**. Direct saponification of nitriles **1a** and **5a** could not be effected owing to their facile retroaldolization.

Hydroxy acids **11** and **15** were converted to the β-lactones **12** and **13** by treatment with benzenesulfonyl chloride.⁵ Thermal decarboxylation of such lactones is known to proceed by *syn* elimination.⁵ Consequently, the formation of *cis*-1-methylcyclododecene (**8a**)⁶ from the former and *trans*-1-methylcyclododecene (**9a**) from the latter constitutes a proof of stereochemistry for both the hydroxy acids and their cyanohydrin precursors as well. These findings show that the conversion of cyano ethers **3a** and **7a** to olefins **8a** and **9a** must likewise proceed by a pathway involving *syn* elimination.

We have also examined the reduction decyanation of the 1,2-dimethylcyclododecyl cyanohydrin methylthiomethyl ether sulfones **3b** and **7b**. These isomers were secured via addition of methyl lithium to cyano ketone **4** to give a 1:3 mixture of cyanohydrins **1b** and **5b** in 88% yield. Treatment, as before,

Chart I.



^a NaBH₄. ^b Me₂SO, Ac₂O, AcOH. ^c *m*-ClC₆H₄CO₃H. ^d NaC₁₀H₈, HMPA. ^e KOH, HCl. ^f HgCl₂, H₂O, CdCO₃. ^g PhSO₂Cl. ^h 150 °C.