tortion results in a pseudoaxial methyl group at C-2 protecting the same α or ρ face in the *E* rotamer that the *t*-Bu group protects in the *Z* rotamer. We suggest that for $\mathbf{R} = t$ -Bu both alkene or radical C(O)-N rotamers must favor the formation of the same product diastereomer, while this bias is apparently not guaranteed for other R substituents (e.g. α selectivity for $\mathbf{R} = \mathbf{Ph}$ is 1.1:1).



The ease of preparation of the oxazolidines and the high selectivities observed for these auxiliaries make them attractive candidates for further study. It is noteworthy that the *t*-Busubstituted compound gives the highest selectivity reported to date in a variety of free radical addition reactions.

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Supplementary Material Available: Experimental details for acrylamide and trisubstituted alkene preparations and free radical addition reactions (3 pages). Ordering information is given on any current masthead page.

Intramolecular Reaction of 1,5-Disila-1,4-pentadiene: Formation of 2,4,5-Trisilabicyclo[1.1.1]pentane and 2,3,5-Trisilabicyclo[2.1.0]pentane

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The recent surge of interest in strained compounds has resulted in reports of constructing polycyclic system with group 14 elements, Si, Ge, and Sn.¹ A bulky substituent is indispensable to the usual method, since the methodology is based on the intermolecular oligomerization reaction. Our recent studies of silene chemistry via silyldiazomethane² encouraged the synthesis of the polysilabicyclo system by new methodology. We report here the fruitful procedure for the formation of strained compounds by intramolecular reaction of 1,5-disila-1,4-diene **2**.

Benzene solution of bis(silyldiazomethyl) compound $1a^3$ with excess 'BuOH was allowed to irradiate for 4.5 h, producing 3 in 47% yield, which is the 2 mol of 'BuOH adduct (eq 1).⁶ This

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(3) The starting material 1 was prepared in 83% (R = Me) and 85% (R = Ph) crude yield, respectively.⁴ An analytically pure sample was obtained by alumina column chromatography and GPC. 1a: yellow oil; MS m/e 400 (M⁺); ¹H NMR (C₆D₆) δ 0.340 (s, 6 H), 0.297 (s, 12 H), 0.126 (s, 18 H); IR (neat) ν/cm^{-1} 2042 (C=N₂). 1b: yellow oil; MS m/e 524 (M⁺); ¹H NMR (C₆D₆) δ 7.27-7.17 (m, 10 H), 0.36 (s, 12 H), 0.26 (s, 16 H), 0.17 (s, 12 H); IR (neat) ν/cm^{-1} 2042 (C=N₂). (4) (a) Sekiguchi, A.; Ando, W. Organometallics 1987, 6, 1857. (b) Ando,

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Figure 1. X-ray structure of 4b. Selected bond lengths (Å) and angles (deg) are as follows: Si(3)-C(1), 1.92; Si(4)-C(1), 1.95; Si(5)-C(1), 1.97; Si(3)-C(2), 1.84; Si(4)-C(2), 1.90; Si(5)-C(2), 1.90; Si(3)-Si(4), 2.54; C(1)-Si(3)-C(2), 81.1; C(1)-Si(4)-C(2), 78.9; C(1)-Si(5)-C(2), 78.2; Si(3)-C(1)-Si(4), 82.1.



result shows that 1,³ upon irradiation, serves as a disiladiene synthon and raises, the possibilities of intramolecular reaction in the absence of a trapping reagent.



The photolysis of 1 without trapping reagent yielded mainly polymeric compounds, with the main interest compound, trisilabicyclo[1.1.1]pentane 4: yield 4a, 0.39%,⁷ and 4b, 1.4%.^{8,9}

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⁽⁶⁾ The product 3 was isolated by preparative GLC. 3: MS m/e 477 (M-15); ¹H NMR (C₆D₆) δ 1.48 (s, 18 H), 0.45 (br s, 18 H), 0.34 (s, 18 H), 0.24 (s, 2 H).

⁽M-15); H HARC ($c_6 D_6$) of the (H 12) 0.24 (s, 2 H). (7) THF was used as solvent. **4a**: colorless crystals; MS m/e 344 (M⁺); ¹H NMR ($C_6 D_6$) δ 0.44 (s, 18 H), 0.06 (s, 18 H); ¹³C NMR ($C_6 D_6$) δ 17.03 (s), 7.56 (q), 1.98 (q); ²⁹Si NMR ($C_6 D_6$) δ –4.9 (SiMe₂), –11.4 (SiMe₃); exact MS found 329.1403, calcd for $C_{13}H_{33}Si_5$ (M – 15) 329.1428. (2) Colorbarane was used as solvent for routine work and *n*-hexane- d_{14} for

⁽⁸⁾ Cyclohexane was used as solvent for routine work and *n*-hexane- d_{14} for low-temperature NMR study. For the reaction of 1b, UV-35 filter was used to cut the light of $\lambda < 350$ nm.

⁽⁹⁾ **4b**: colorless crystals; mp 128–129 °C; MS m/e 453 (M – 15); ¹H NMR (C₆D₆) δ 7.5–7.1 (m, 10 H), 0.30 (s, 12 H), 0.29 (s, 18 H); ¹³C NMR (C₆D₆) δ 142.0 (s), 133.4 (d), 128.0 (d), 126.7 (d), 7.36 (q), 0.11 (q); ²⁹Si NMR (C₆D₆) δ 31.9, –51.0; exact MS found 468.1952, calcd for C₂₄H₄₀Si₅ 468.1976.

Scheme I

Scheme II



Low-temperature NMR study (at -55 °C) revealed one more product in the photolysis of **1b**, which was easily polymerized at 25 °C ($\tau_{1/2}$ = 99 min).¹⁰ The NMR data suggest the structure 5; particularly ²⁹Si NMR signals at -54 ppm strongly suggest the existence of the silirane.¹¹ After the photolysis, large excess 'BuOH was added to the reaction mixture. The compound was trapped by 'BuOH to give 6 in 67% yield.¹² These results show that trisilabicyclo[2.1.0]pentane 5 was produced in the photolysis of **1b** (7.6% yield¹⁰).

The proposed mechanism of the photoreaction of **1b** was shown in Scheme I. It is interesting to obtain both the crisscross addition product¹³ and the parallel addition product.

A thermal reaction of 1a at 720 K gave only the compound 4a in 24.6% yield.¹⁴

The X-ray structure of **4b** was shown in Figure 1.¹⁵ The bond lengths and angles are nearly the same as the predicted values,^{16e} but the angle of C-Si-C (79.5°) in the cage is larger than the predicted value (77.5°) and closer to an optimal value of Streitwieser's model^{16c} (ca. 80°, vide infra). Moreover, the Si...Si distance (phantom bond length, PBL¹⁷) of **4b**, 2.54 Å, is somewhat

^{(10) 5: &}lt;sup>1</sup>H NMR (c-hexane- d_{12} , 500 MHz, at 298 K) δ 7.6–7.1 (m, 10 H), 0.579 (s, 6 H), 0.556 (s, 3 H, silirane SiMe), 0.460 (s, 3 H, silirane SiMe), 0.322 (s, 6 H), 0.293 (s, 6 H), -0.238 (s, 6 H); ²⁹Si NMR (n-hexane- d_{14} , 18 MHz, at 218 K) δ -21.711 (SiMe₂SiMe₂), -5.8 (SiMe₂Ph), -54.1 (silirane). The yield and $\tau_{1/2}$ of **5** were determined on NMR data. (11) Williams, E. A. In *The Chemistry of Organic Silicon Compounds*;

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^{(12) 6:} oil; cis/trans = 51/49 mixture, the stereochemistry was determined by NOESY NMR spectroscopy;²⁹ MS m/e 542 (M⁺); ¹H NMR (C₆D₆, 60 MHz) δ 6-trans, 7.68-7.66 (m, 4 H), 7.30-7.16 (m, 6 H), 1.145 (s, 9 H), 0.621 (s, 6 H), 0.599 (s, 1 H), 0.581 (br s, 6 H), 0.301 (s, 6 H), 0.165 (br s, 6 H), 0.123 (br s, 6 H); 6-cis, 7.63-7.57 (m, 4 H), 7.30-7.16 (m, 6 H), 1.199 (s, 9 H), 0.596 (s, 6 H), 0.502 (s, 6 H), 0.466 (s, 6 H), 0.375 (s, 6 H), 0.195 (s, 6 H), 0.165 (s, 1 H); IR (neat) ν/cm^{-1} 1044, 1019. The yield was determined on the basis of the yield of 5.

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⁽¹⁴⁾ The *n*-hexane solution of the diazo compound 1 was pyrolized by FVP. The cage compound 4 was detected with GC-MS as the almost sole volatile product.

⁽¹⁵⁾ Compound 4b: $C_{24}H_{40}Si_5$, fw 469.02, monoclinic, a = 11.828 (3), b = 13.448 (1), c = 9.173 (2) Å, V = 1458.4 Å³, Z = 2, space group P_21 , $\rho = 1.07$ g/cm³, $\mu = 2.5$ cm. The 1863 independent observed reflections ($2\theta \le 50^\circ$; $F_{02}i > 3\sigma [F_{02}i]$) were measured on an Enraf-Nonius CAD4 diffractometer using Mo K α irradiation and $\omega - 2\theta$ scan. No absorptions correction was made. The structures were solved by direct methods and were refined anisotropically to R = 0.076 and $R_w = 0.084$. (16) (a) Nagase, S.; Kudo, T. Organometallics 1987, 6, 2456. (b) Nagase,

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shorter than a calculated value (2.59 Å).¹⁹ Three Si atoms form an imaginary three-membered ring with three phantom bonds¹⁶ (Chart I). The average PBL is almost the same value as the Si-Si bond length of hexa-tert-butyltrisilane.²¹

The isolation of the trisilabicyclo[1.1.1]pentane 4 was very exciting (without any bulky groups), because 2,4,5-trisilabicyclo[1.1.1]pentane (strain energy 54.2 kcal/mol) is calculated to be more strained than pentasilabicyclo[1.1.1]pentane (strain energy 37.4 kcal/mol)^{16e} whose derivative was isolated very recently.24

The cage C-Si bond of 4 showed a high reactivity to moisture. The compound 4a reacted with H₂O in MeOH or EtOH at room temperature to give ring-opening products 7a and 8a (Scheme II),²⁵ although normal disilacyclobutanes do not show such a reactivity.28

The high reactivity of the cage Si-C bond to the nucleophile may be rationalized in terms of the polarization of the cage.²⁹ If Streitwieser's ionic model can apply to this system, the polarization can be accounted for by a model shown in Chart II.^{16c,30} The bridgehead C-SiMe₂R groups are represented by the point charge -3 and the bridge SiMe₂ groups as point charge +2. The net Coulomb interaction of this model acts as the attraction; it resulted in the shortening of the atomic distance (or the bond length). The energy minimum of Streitwieser's model is found at about θ = 80°;^{16c} this value is very close to the C-Si-C angle of 4b (79.5°).³¹ The NMR signal of the cage ²⁹Si was observed at the lower field (4a, -4.9 ppm; 4b, 31.9 ppm), compared with that of the substituent (4a, -11.4 ppm; 4b, -5.10 ppm). From these results we concluded that the bonds of 2,4,5-trisilabicyclo[1.1.1]pentane, 4, have considerable ionic character.

(17) We use the term "a phantom bond" in imitation of Nagase's paper and to avoid a term "nonbonded distance". We do not think that there is chemical bonding between bridge silicon atoms. It is natural to postulate chemical bonding between spatially closing atom. It may be that there is some special bond which has considerable ionic character, otherwise σ -bridged- π

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 (25) The isomers could be used by the total second with the second se of 7a is shifted to low field by δ 0.4 ppm, compared with 8a. Both isomers showed the very sharp IR absorption of O-H stretching, and the absorption of 7a was slightly shifted to low wave number. These results suggested that the difference of the polarity of these isomers could result in the intramolecular hydrogen bond type interaction shown in Scheme II. Glidewell calculated the involution acidity of CH₄ and (H₃Si)₃CH, the silv substitutions increased the acidity by 289 kJ/mol.²⁶ **7a**: MS m/e 347 (M - 15); ¹H NMR (C₆D₆) δ 0.463 (s, 6 H), 0.413 (s, 6 H), 0.207 (s, 6 H), 0.166 (s, 9 H), 0.085 (s, 9 H), 0.287 (s, 1 H); IR (CCl₄ solution) ν/cm^{-1} 3690 (Si–OH). **8a**: MS m/e 347 (M - 15); ¹H NMR (C₆D₆) δ 0.480 (s, 6 H), 0.393 (s, 6 H), 0.244 (s, 9 H), 0.168 (s, 6 H), 0.097 (s, 9 H), -0.115 (s, 1 H); IR (CCl₄ solution) ν/cm^{-1} 3694 (Si-OH). The compound 4b also reacted with H₂O in EtOH to give the mixture of corresponding hydrolized products, which were detected by GC-MS and ¹H NMR spectroscopy (see supplementary material). The stereochemistry of these isomers was determined by NOESY NMR spectroscopy.²⁷
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Supplementary Material Available: Complete spectral data of all new compounds and detailed information of the X-ray crystal analysis (32 pages); table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

Radical Cation Rearrangement of 4-Vinylcyclohexene to Bicyclo[3.2.1]oct-2-ene: A Matrix-Isolation ESR Study

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Both mass spectrometric studies¹ and theoretical calculations² have concluded that the ion-molecule reaction of 1.3-butadiene proceeds through an acyclic intermediate to form the 4-vinylcyclohexene radical cation (1^{•+}), the overall transformation being regarded as the classical example of an indirect radical cation Diels-Alder reaction.³ Here we report that when 1^{•+} is generated by radiolytic oxidation in Freon matrices at 77 K,⁴ it undergoes a further rearrangement to the bicyclo[3.2.1]oct-2-ene radical cation (3^{*+}) on annealing to 140 K. The observation of this novel cycloaddition indicates that 3^{•+} is a more stable isomer than 1^{•+} on this important C₈H₁₂^{•+} potential energy surface.^{1-3,5}

Evidence for the thermal rearrangement of 1^{•+} to 3^{•+} was obtained by ESR spectroscopy. After the radiolytic oxidation of 1 in CFCl₃ at 77 K, the initial spectrum observed with optimal resolution at 95 K can be assigned to 1⁺⁺ with the positive hole localized at the ene group. This assignment rests on the similarity of the spectrum to that of the cyclohexene radical cation,⁶ their common features including the diagnostic ca. 8-9 G triplet splitting from the two cycloolefinic hydrogens in the wing lines and approximately the same total spectral width. A detailed analysis by simulation showed that the conformationally dependent β hydrogen couplings for 1^{•+} (Table I) are not equivalent in pairs, presumably due to the absence of C_2 symmetry. On annealing of the sample to 140 K, a much narrower pattern grew in irreversibly, the spectrum obtained on recooling to 95 K having the same profile as that of the 140 K spectrum except for poorer resolution. This new signal carrier produced in CFCl₃ was identified as 3^{•+} from studies in other matrices (vide infra), and the assignment was then corroborated by finding that its spectrum matched precisely with that resulting from the direct oxidation of 3 in CFCl₃.7

A solution to the problem of identifying the species formed on annealing only became feasible when a spectrum of higher resolution was obtained following the oxidation of 1 in CFCl₂CFCl₂ (Figure 1a). This spectrum has precisely the same total width as that obtained in CFCl₃ but the much-improved resolution now allows all the coupling constants greater than ca. 5 G to be

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