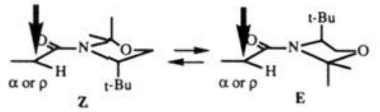
tortion results in a pseudoaxial methyl group at C-2 protecting the same α or ρ face in the *E* rotamer that the *t*-Bu group protects in the *Z* rotamer. We suggest that for R = *t*-Bu both alkene or radical C(O)–N rotamers must favor the formation of the same product diastereomer, while this bias is apparently not guaranteed for other R substituents (e.g. α selectivity for R = 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*-Bu-substituted compound gives the highest selectivity reported to date in a variety of free radical addition reactions.

Acknowledgment. Support for this research from NIH (HL17921) and NSF is gratefully acknowledged. J.D.B. and I.J.R. thank the Burroughs Wellcome Foundation for support. We thank Professor D. P. Curran for a sample used to correlate the stereochemistry of **9** with products formed in Curran's labs, ref 4.

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

Wataru Ando,* Hitoaki Yoshida, Katsuaki Kurishima, and Mitsuru Sugiyama

Department of Chemistry, University of Tsukuba
Tsukuba, Ibaraki 305, Japan

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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 silyldiazomethane[2] 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 ^{t}BuOH was allowed to irradiate for 4.5 h, producing **3** in 47% yield, which is the 2 mol of ^{t}BuOH adduct (eq 1).[6] This 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.

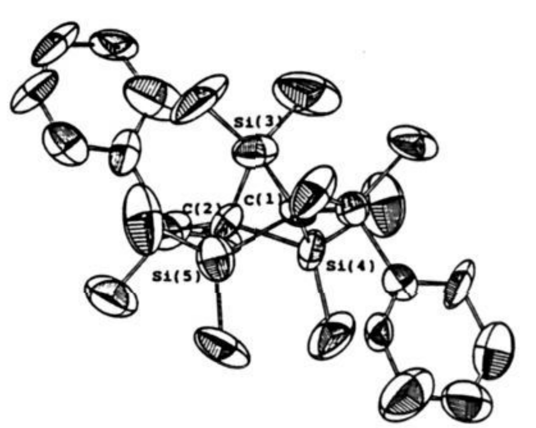
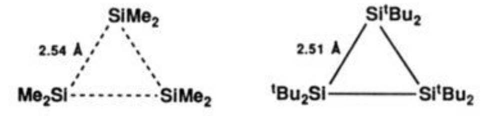


Figure 1. X-ray structure of **4b**. Selected bond lengths (Å) and angles (deg) are as follows: Si(3)–C(1), 1.92; Si(4)–C(1), 1.95; Si(5)–C(1), 1.97; Si(3)–C(2), 1.84; Si(4)–C(2), 1.90; Si(5)–C(2), 1.90; Si(3)–Si(4), 2.54; C(1)–Si(3)–C(2), 81.1; C(1)–Si(4)–C(2), 78.9; C(1)–Si(5)–C(2), 78.2; Si(3)–C(1)–Si(4),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

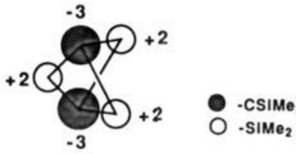
Chart I

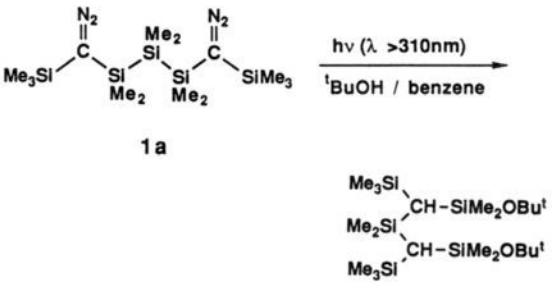


4b this work

ref. 23

Chart II





1a

(1)

3

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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(1) Scheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*, Patai, S., Rappoport, Z.; Ed.: John Wiley & Sons Ltd., 1989; Part 1, Chapter 3. Bock, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1627. Sita, L. R.; Kinoshita, I. *J. Am. Chem. Soc.* **1990**, *112*, 8839. Sita, L. R.; Kinoshita, I. *Organometallics* **1990**, *9* 2865 and references cited therein. Sekiguchi, A.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 55.

(2) (a) Ando, W.; Hagiwara, T.; Migita, M. *J. Am. Chem. Soc.* **1973**, *95*, 7518. (b) Ando, W.; Sekiguchi, A.; Migita, T.; Kammula, S.; Green, M.; Jones, M., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 3818. (c) Sekiguchi, A.; Ando, W. *J. Am. Chem. Soc.* **1981**, *103*, 3579. (d) Ando, W.; Sekiguchi, A.; Sato, T. *J. Am. Chem. Soc.* **1981**, *103*, 5573. (e) Sekiguchi, A.; Ando, W. *J. Am. Chem. Soc.* **1984**, *106*, 1486.

(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^+); ^{1}H NMR (C_6D_6) δ 0.340 (s, 6 H), 0.297 (s, 12 H), 0.126 (s, 18 H); IR (neat) ν/cm^{-1} 2042 ($C{=}N_2$). **1b**: yellow oil; MS *m/e* 524 (M^+); ^{1}H NMR (C_6D_6) 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 ($C{=}N_2$).

(4) (a) Sekiguchi, A.; Ando, W. *Organometallics* **1987**, *6*, 1857. (b) Ando, W.; Sekiguchi, A.; Migita, T. *Chem. Lett.* **1976**, 779. (c) Sekiguchi, A.; Ando, W. *Chem. Lett.* **1986**, 2025.

(5) Ando, W. IXth International Symposium on Organosilicon Chemistry, Edinburg, I-17, 1990.

(6) The product **3** was isolated by preparative GLC. **3**: MS *m/e* 477 (M-15); ^{1}H NMR (C_6D_6) δ 1.48 (s, 18 H), 0.45 (br s, 18 H), 0.34 (s, 18 H), 0.24 (s, 2 H).

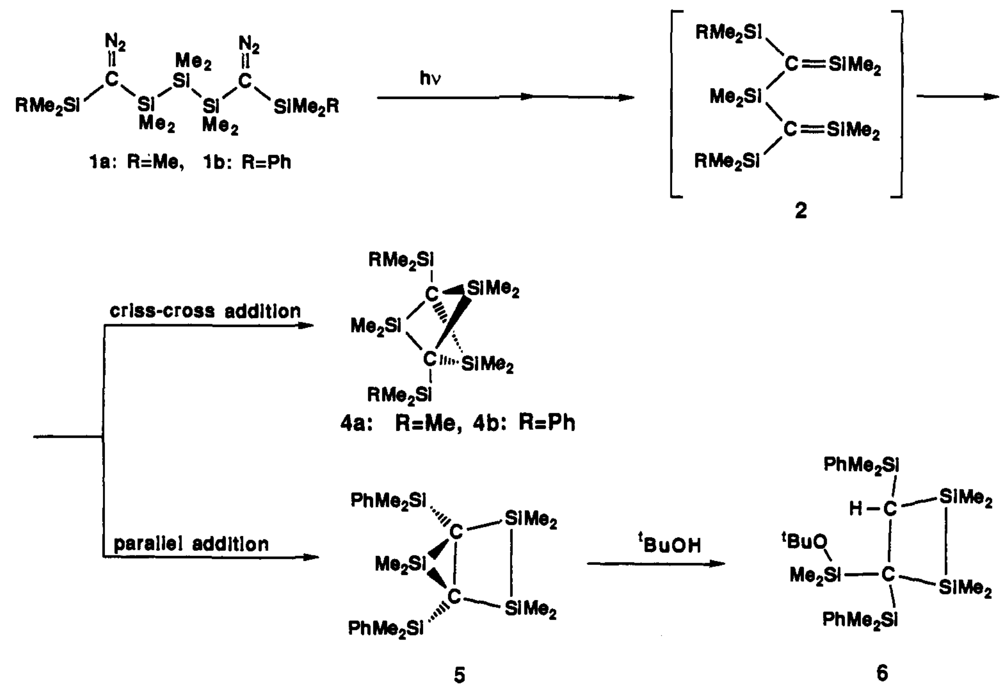
(7) THF was used as solvent. **4a**: colorless crystals; MS *m/e* 344 (M^+); ^{1}H NMR (C_6D_6) δ 0.44 (s, 18 H), 0.06 (s, 18 H); ^{13}C NMR (C_6D_6) δ 17.03 (s), 7.56 (q), 1.98 (q); ^{29}Si NMR (C_6D_6) δ –4.9 ($SiMe_2$), –11.4 ($SiMe_3$); exact MS found 329.1403, calcd for $C_{13}H_{33}Si_5$ (M – 15) 329.1428.

(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.

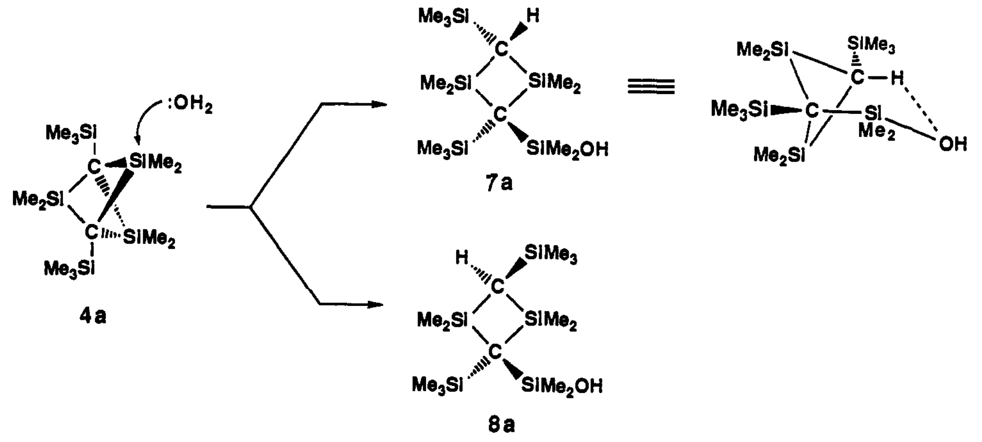
(9) **4b**: colorless crystals; mp 128–129 °C; MS *m/e* 453 (M – 15); ^{1}H NMR (C_6D_6) δ 7.5–7.1 (m, 10 H), 0.30 (s, 12 H), 0.29 (s, 18 H); ^{13}C NMR (C_6D_6) δ 142.0 (s), 133.4 (d), 128.0 (d), 126.7 (d), 7.36 (q), 0.11 (q); ^{29}Si NMR (C_6D_6) δ 31.9, –51.0; exact MS found 468.1952, calcd for $C_{24}H_{40}Si_5$ 468.1976.

0002-7863/91/1513-7790$02.50/0

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 ^{29}Si NMR signals at −54 ppm strongly suggest the existence of the silirane.[11] After the photolysis, large excess ᵗBuOH was added to the reaction mixture. The compound was trapped by ᵗBuOH 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% yield[10]).

The proposed mechanism of the photoreaction of **1b** was shown in Scheme I. It is interesting to obtain both the crisscross addition product[13] 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, PBL[17]) of **4b**, 2.54 Å, is somewhat

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[10] **5**: ^{1}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); ^{29}Si NMR (*n*-hexane-d_{14}, 18 MHz, at 218 K) δ −21.711 ($SiMe_2SiMe_2$), −5.8 ($SiMe_2Ph$), −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*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd., 1989; Part 1, Chapter 8.

[12] **6**: oil; cis/trans = 51/49 mixture, the stereochemistry was determined by NOESY NMR spectroscopy;[29] MS *m/e* 542 (M^+); ^{1}H NMR (C_6D_6, 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**.

[13] (a) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309, and references cited therein. (b) Gleiter, R.; Sander, W. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 566, and references cited therein. (c) Srinivasan, R.; Carlough, K. H. *J. Am. Chem. Soc.* **1967**, *89*, 4932.

[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 Å^3, Z = 2, space group $P2_1$, ρ = 1.07 g/cm^3, μ = 2.5 cm. The 1863 independent observed reflections ($2\theta \leq 50°$; $|F_o| > 3\sigma|F_o|$) were measured on an Enraf-Nonius CAD4 diffractometer using Mo Kα irradiation and ω-2θ 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, S.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1988**, 1063. (c) Streitwieser, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1261. (d) Schleyer, P. R.; Janoschek, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1267. (e) Kitchen, D. B.; Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1990**, *112*, 3408.

shorter than a calculated value (2.59 Å).[19] Three Si atoms form an imaginary three-membered ring with three phantom bonds[16] (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 H_2O 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–$SiMe_2R$ groups are represented by the point charge −3 and the bridge $SiMe_2$ 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 $\theta = 80°$;[16c] this value is very close to the C–Si–C angle of **4b** (79.5°).[31] The NMR signal of the cage ^{29}Si 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.

Acknowledgment. This work was supported by the Grant-in-Aid for Scientific Research on Priority Area of Molecular Design by heteroatom and for General Scientific Research from the Ministry of Education, Science and Culture, Japan.

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.

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(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 bonding has been a very recently proposed alternative.[18]

(18) (a) Liang, C.; Allen, L. C. *J. Am. Chem. Soc.* **1991**, *113*, 1878. (b) Jackson, J. E.; Allen, L. C. *J. Am. Chem. Soc.* **1984**, *106*, 591.

(19) The value was calculated by trigonometry using the data of ref 16e.

(20) Michalczyk, M. J.; Fink, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1986**, *5*, 531.

(21) Shāfer, A.; Weidenbruch, M.; Peters, K.; Schnering, H. G. v. *Angew. Chem.* **1984**, *96*, 311. The **PBL** is shorter than the Si–Si bond of 1,3-diiodotetra-*tert*-butyltrisilane (2.581, 2.644 Å)[23] and hexa-*tert*-butyldisilane (2.697 Å).[24]

(22) Weidenbruch, M.; Flintjer, B.; Schnering, H. G. v.; Peters, K. *Angew. Chem.* **1984**, *98*, 1090.

(23) Wiberg, N.; Schuster, H.; Simon, A.; Peters, K. *Angew. Chem.* **1986**, *98*, 100.

(24) Kabe, Y.; Kawase, T.; Okada, J.; Yamashita, O.; Goto, M.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 794.

(25) The isomers could be easily separated by TLC; it suggests the notable difference between their polarities. ^{1}H NMR signal of the methylene proton 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 carbon acidity of CH_4 and $(H_3Si)_3CH$, the silyl substitutions increased the acidity by 289 kJ/mol.[26] **7a**: MS *m/e* 347 (M − 15); ^{1}H NMR (C_6D_6) 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 (CCl_4 solution) ν/cm^{-1} 3690 (Si–OH). **8a**: MS *m/e* 347 (M − 15); ^{1}H NMR (C_6D_6) 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 (CCl_4 solution) ν/cm^{-1} 3694 (Si–OH). The compound **4b** also reacted with H_2O in EtOH to give the mixture of corresponding hydrolized products, which were detected by GC-MS and ^{1}H NMR spectroscopy (see supplementary material). The stereochemistry of these isomers was determined by NOESY NMR spectroscopy.[27]

(26) Glidewell, C.; Thompson, C. *J. Comput. Chem.* **1982**, *3*, 495.

(27) Macura, S.; Ernst, R. R. *Mol. Phys.* **1980**, *41*, 95. Jeener, J.; Meier, B. H.; Bachmann, P.; Ernst, R. R. *J. Chem. Phys.* **1979**, *71*, 4546.

(28) Devine, A. M.; Haszeldine, R. N.; Tipping, A. E. *J. Chem. Soc., Dalton Trans.* **1975**, 1832, 1837 and references cited therein.

(29) Allen, C. L. *J. Am. Chem. Soc.* **1989**, *111*, 9003, 9115, and private communication; Lewis–Langmuir atomic charges were calculated to be $CSiMe_3(O) = -0.4221$ and $SiMe_2(O) = +0.2818$.

(30) Nagase also reported the polarization. Reference 16a,b and Kudo, T.; Nagase, S. *J. Am. Chem. Soc.* **1985**, *107*, 2589.

(31) The replacement by point charges is a gross approximation; fractional not proportional charges would give an identical result.[16c]

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

Guo-Fei Chen and Ffrancon Williams*

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37996-1600

Received June 24, 1991

Both mass spectrometric studies[1] and theoretical calculations[2] have concluded that the ion–molecule reaction of 1,3-butadiene proceeds through an acyclic intermediate to form the 4-vinylcyclohexene radical cation ($1^{\bullet +}$), the overall transformation being regarded as the classical example of an indirect radical cation Diels–Alder reaction.[3] Here we report that when $1^{\bullet +}$ 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 ($3^{\bullet +}$) on annealing to 140 K. The observation of this novel cycloaddition indicates that $3^{\bullet +}$ is a more stable isomer than $1^{\bullet +}$ on this important $C_8H_{12}^{\bullet +}$ potential energy surface.[1-3,5]

Evidence for the thermal rearrangement of $1^{\bullet +}$ to $3^{\bullet +}$ was obtained by ESR spectroscopy. After the radiolytic oxidation of **1** in $CFCl_3$ at 77 K, the initial spectrum observed with optimal resolution at 95 K can be assigned to $1^{\bullet +}$ 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 $1^{\bullet +}$ (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 $CFCl_3$ was identified as $3^{\bullet +}$ 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 $CFCl_3$.[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 $CFCl_2CFCl_2$ (Figure 1a). This spectrum has precisely the same total width as that obtained in $CFCl_3$ but the much-improved resolution now allows all the coupling constants greater than ca. 5 G to be

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(1) Groenewold, G. S.; Gross, M. L. *J. Am. Chem. Soc.* **1984**, *106*, 6569.

(2) (a) Bauld, N. L.; Bellville, D. J.; Pabon, R. A.; Chelsky, R.; Green, G. *J. Am. Chem. Soc.* **1983**, *105*, 2378. (b) Bellville, D. J.; Bauld, N. L. *Tetrahedron* **1986**, *42*, 6167.

(3) Bauld, N. L. *Tetrahedron* **1989**, *45*, 5307.

(4) (a) Shida, T.; Kato, T. *Chem. Phys. Lett.* **1979**, *68*, 106. (b) Shida, T.; Haselbach, E.; Bally, T. *Acc. Chem. Res.* **1984**, *17*, 180.

(5) For neutral C_8H_{12} isomers: Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981; Chapter 8, Section IV, pp 271–286.

(6) (a) Shida, T.; Egawa, Y.; Kubodera, H.; Kato, T. *J. Chem. Phys.* **1980**, *73*, 5963. (b) Blackstock, S. C.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 2484. (c) Guo, Q.-X.; Qin, X.-Z.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1988**, *110*, 1974. (d) Williams, F.; Guo, Q.-X.; Petillo, P. A.; Nelsen, S. F. *J. Am. Chem. Soc.* **1988**, *110*, 7887.

(7) Matching spectra from the oxidation of **1** and **3** were also observed in the $CF_2ClCFCl_2$ and CF_3CCl_3 matrices.

0002-7863/91/1513-7792$02.50/0