Pergamon

Tetrahedron 58 (2002) 7043–7047

TETRAHEDRON

Reaction of 7,7-diphenyl-6-oxabicyclo[3.2.0]hept-1-ene with ROH; controlling factors on the regioselectivity in the nucleophilic addition reaction☆

Manabu Abe,* Takafui Minamoto, Yasunori Ino, Takanori Kawakami and Masatomo Nojima

Department of Materials Chemistry, Graduate School of Engineering, Osaka University, Yamadaoka 2-1, Suita 565-0871, Osaka, Japan

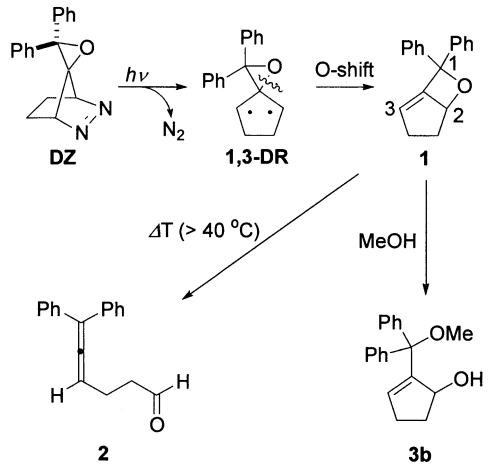
This paper is dedicated to Professor Waldemar Adam on the occasion of his 65th birthday

Received 14 February 2002; accepted 19 April 2002

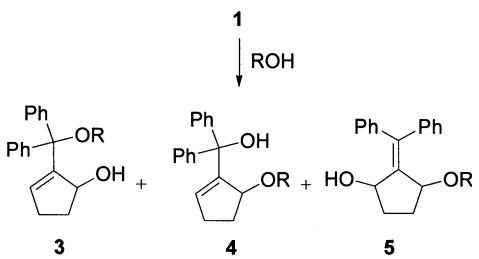
Abstract—ROH-induced decomposition of the strained 7,7-diphenyl-6-oxabicyclo[3.2.0]hept-1-ene **1** was investigated in detail. The selective formation of the *endo* double-bonded alkene **3** was observed for the reaction with H_2O or MeOH. Alternatively, the reaction with hexafluoro-2-propanol or acetic acid exclusively afforded the *exo* double-bonded alkene **5**. The dramatic ROH effect on the product distribution is rationalized in this study. Strain energy (SE=41.3 kcal/mol) of 6-oxabicyclo[3.2.0]hept-1-ene was calculated at RHF/6-31G* level of theory.

1. Introduction

The challenging investigations on the synthesis and reactivity of strained molecules have produced a number of important concepts and synthetic methodologies.[1] We have recently reported for the first time the quantitative formation of the 3-alkylideneoxetane derivative, 7,7-diphenyl-6-oxabicyclo[3.2.0]hept-1-ene **1**, via the kinetically favored CO-bond cleavage in 2-spiroepoxy-1,3-cyclopentanediyl 1,3-**DR** (1,3-diradical) generated by the photodenitrogenation of diazene **DZ**, and described some of its reactivity (Scheme 1):[2] (1) the thermal decomposition of **1** led to the allene derivative **2** (78%) via the retro [2+2] type of reaction; (2) the methanolysis was found to give selectively the adduct **3b** in high yield (>90%). The transformations under the mild conditions undoubtedly originate from the release of strain in compound **1** (vide infra). In this Symposia-in-Print work, we aim at clarifying the mechanism for the alcohol-trapping reaction of **1**. Why does the methanolysis occur selectively at C1, although the bond formation at C2 and/or C3 would also be possible to give the regioisomeric MeOH-adduct **4b** and/or **5b** (R=Me) (Scheme 2)? This pertinent question was addressed by investigating the reaction of **1** with a variety of ROH, i.e. water (H_2O), trifluoroethanol (TFE), hexafluoro-2-propanol (HFIP), and acetic acid (AcOH).



Scheme 1. Preparation and reactivity of 7,7-diphenyl-6-oxa-bicyclo[3.2.0]-hept-1-ene **1**.



a: R = H, **b**: R = Me, **c**: R = CH_2CF_3
d: R = $CH(CF_3)_2$, **e**: R = $COCH_3$

Scheme 2. ROH-induced decomposition of **1**.

Keywords: strained molecule; 3-alkylideneoxetane; ring-opening reaction; regioselectivity; stereoselectivity.

* Corresponding author. Tel.: +81-6-6879-7929, fax: +81-6-6879-7928; e-mail: abe@ap.chem.eng.osaka-u.ac.jp

0040–4020/02/$ - see front matter
PII: S0040-4020(02)00700-7

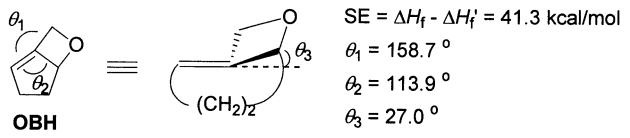


Figure 1. Strain energy of 6-oxabicyclo[3.2.0]hept-1-ene **OBH** and its structural analysis at RHF/6-31G* level of theory.

2. Results and discussion

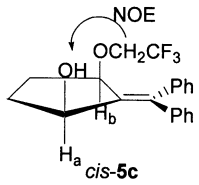
Prior to discussing the mechanism for the ROH-induced decomposition of **1**, we would like to indicate briefly the strain energy (SE) of the parent 6-oxabicyclo[3.2.0]hept-1-ene **OBH** and its origin, which have not been reported until now. The strain energy of **OBH**, SE=41.3 kcal/mol, was computed using the heat of formation (ΔH_f=18.4 kcal/mol) calculated by Wiberg's method[3] at RHF/6-31G* level[4] and Franklin group equivalents[5] for the energy ($\Delta H_f'$=−22.9) of the corresponding unstrained models (Fig. 1).[6]

The strain energy exceeded the sum of the energies of the oxetane (SE=25.7 kcal/mol)[1b] and cyclopentene (SE=6.8 kcal/mol)[7] by ca. 9 kcal/mol. As can be easily imagined from the calculated angles θ_{1-3}, the deviation from the additivity role should be due to the expansion of the double-bond angle θ_1 (=159°, deviation from 20°) and the torsional strain (or pyramidalization) θ_3(=27°, deviation from 0°).[8]

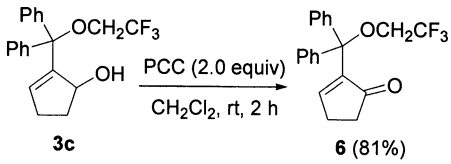
2.1. ROH-induced decomposition of 7,7-diphenyl-6-oxabicyclo[3.2.0]hept-1-ene (1)

The products and yields (%) of the ROH-induced decomposition of the 3-alkylideneoxetane **1** were summarized in Table 1. The reaction of **1** with H_2O (R=H) selectively afforded the diol **3a** (=**4a**) in 88% (entry 1). It was impossible to determine the regioselectivity of the nucleophilic H_2O addition, i.e. C1 vs C2. However, the selective formation of the MeOH-adduct **3b** (entry 2) suggests that the reaction site is at C1.

The dramatic ROH effects on the product distributions were observed for the reactions with TFE, HFIP, and AcOH (entries 3–5). When TFE was used for the reaction (entry 3), the regioisomeric TFE-adduct **5c** (R=CH_2CF_3) was obtained as a minor product in a significant amount (25%, **3c/5c**=74/26). It should be noted that one of the possible stereoisomers was selectively formed, >90/10, as judged by the NMR spectroscopic analysis. To determine the configuration of the TFE-adduct **5c**, the ^{1}H NMR (600 MHz) NOE measurements were performed for the isolated adduct. The NOE measurement between H_a (δ 4.42 ppm) and H_b (δ 4.47 ppm) protons was difficult due to the closely positioned chemical shifts. Fortunately, the NOE enhancements (1.4 and 1.0%) between the methylene protons (δ 3.40 and 3.65 ppm) of the $-CH_2CF_3$ moiety and the alcoholic proton (δ 2.26 ppm) were observed.



The small but significant NOE-enhancements clearly suggest the *cis*-configuration between −OH and $-OCH_2CF_3$ groups; thus, the *cis*-isomer **5c** was stereoselectively formed in the reaction with TFE. Before going to the appropriate discussion for the notable ROH effects on the product distribution, we had to confirm perfectly the structure of **3c**, since the spectroscopic data for the regioisomeric TFE-adduct **4c**, which is also one of the possible candidates of the TFE-adducts, would be quite similar to those of **3c**. The structural assignment of **3c** was unambiguously achieved by the chemical transformation of **3c** to ketone **6**. A similar transformation was also useful for confirming the structure of **3b**[2a] (Eq. (1)). The TFE-adduct **4c** should be intact under the oxidation conditions.



(1)

Next, we performed the control experiments. The adduct **3c** (R=CH_2CF_3) did not convert to the regioisomer **5c** under the reaction conditions, and vice versa. The control experiments strongly suggest that **3c** and **5c** are not the thermodynamically controlled products but the primary products in the ROH-induced decomposition of 3-alkylideneoxetane **1**.

For the reaction with HFIP or AcOH, the exclusive formation of the adduct **5d** (R=$CH(CF_3)_2$) or **5e** ($COCH_3$) was observed (entries 4 and 5). We could not detect any trace of **3**,**4** <5%. The NOE enhancements (1.0 and 1.2%, 600 MHz) between H_a (for **5d**; δ 4.43, for **5e**; δ 4.63) and H_b

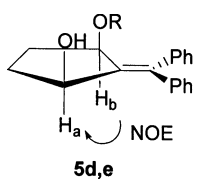


Table 1. The reactions of 3-alkylideneoxetane **1** with ROH

Entry	ROH	pK_a[a]	Time (h)	Products and yields (%)[b]			**3/5**[c]
				3	**4**	**5**[d]	
1[e]	H_2O	15.7	24	**3a** (88)	–	**5a** (<5)	>95/5
2[e]	MeOH	15.5	20	**3b** (91)	**4a** (<5)	**5b** (<5)	>95/5
3[e]	TFE	12.4	18	**3c** (63)	**4a** (< 5)	**5c** (25)	74/26
4	HFIP	9.2	<1	**3d** (<5)	**4a** (<5)	**5d** (92)	<5/95
5	AcOH	4.8	<1	**3e** (<5)	**4a** (<5)	**5e** (82)	<6/94

To a solution of 3-alkylideneoxetane **1** (0.05 M) in benzene (20 mL) was added a solution of ROH (1.0 M) in benzene (20 mL) at rt (ca. 15°C), except for H_2O. H_2O was added as a solution in THF.

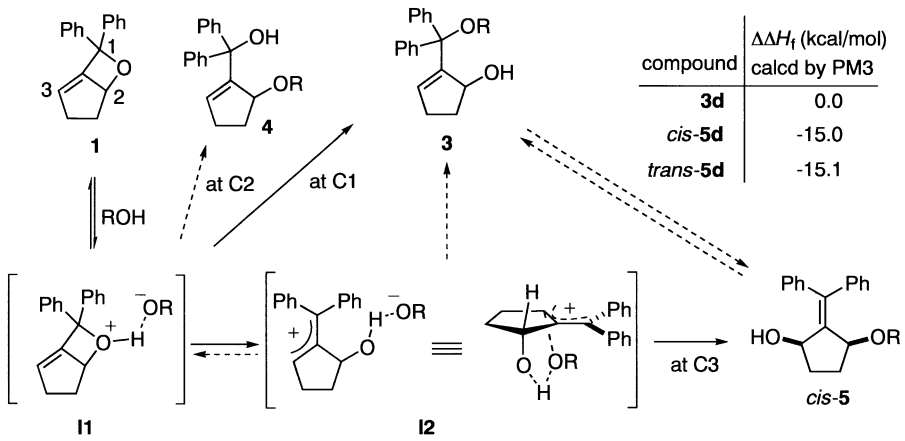
[a] Data taken from Ref. 9, which were measured in H_2O at 25°C.

[b] Isolated yields, after column chromatography on silica gel. The expression, <5, means that the compound did not detect under the isolation conditions.

[c] The ratios, **3/5**, were normalized to 100%.

[d] *cis*-**5** was selectively formed, *cis*-**5**/*trans*-**5**=>90/10.

[e] Allene **2** was obtained, ca. 5%.



compound	ΔΔH_f (kcal/mol) calcd by PM3
3d	0.0
cis-**5d**	-15.0
trans-**5d**	-15.1

Scheme 3. Mechanism of the reaction of **1** with ROH.

(for **5d**; δ 4.85, for **5e**; δ 5.55) again confirmed the *cis*-configuration of the substituents, as depicted for **5d**,**e**.

As shown in Table 1, the product ratios (**3**/**5**) and the reaction time (h) were closely related to the acidity of ROH, i.e. pK_a.[9] Namely, the stronger the acidity of ROH, the faster the reaction was detected, and the higher the chemical yield of **5** was observed, in spite of lowering the nucleophilicity of ROH. The clear phenomena suggest that the formation of the ROH-adduct **5** was initiated by the acid-induced ring-opening of the oxetane **1** (see, Scheme 3).

The plausible mechanism of the ROH-induced decomposition of 3-alkylideneoxetane **1** can be summarized as shown in Scheme 3. When ROH (R=H, Me) is a relatively strong nucleophile (entries 1 and 2), the nucleophilic attack at C1 position is dominant to give the ROH-adduct **3** via the protonated intermediate **I1**, before converting to the allylic cation **I2**. Alternatively, when the acidity of the ROH increases with decreasing the nucleophilicity, R=$CH(CF_3)_2$, Ac, the allylic cation **I2** becomes an important intermediate for the nucleophile trapping reactions. The intervention of the hydrogen-bonded intermediate **I2** can reasonably explain the *cis*-selective formation of the adduct **5** (R=CH_2CF_3, $CH(CF_3)_2$, Ac), as depicted in the structure **I2**. In principle, the formation of the regioisomeric adduct **3** is possible from the allylic cation **I2**. However, as suggested by the PM3-calculated heat of formations (ΔH_f),[10,11] $\Delta\Delta H_f$=ΔH_f (**5d**)−ΔH_f (**3d**)≈−15 kcal/mol, the nucleophilic attack at C1 carbon in the intermediate **I2**, which leads to the adduct **3**, is expected to be less energetically favored process, compared with the attack at C3 carbon leading to the adduct **5**. The regioselective C1–O bond cleavage, which observed in this study, can be reasonably explained by the presence of the adjacent phenyl-rings which stabilize effectively the positive charge at C1 carbon.

In this paper, we describe the reactivity of the strained bicyclic-3-alkylideneoxetane **1** in the reaction with ROH. The regioselectivity observed in this study is quite sensitive to the acidity and the nucleophilicity of ROH. The origin of the strain is suggested to be the coexistence of small ring and unsaturation.

3. Experimental

3.1. General

^{1}H and ^{13}C NMR (DEPT) spectra were recorded on JEOL JNM-EX-270 spectrometer at 270 MHz and 67.8 MHz. NOE measurements at 600 MHz were performed on Brucker AM-600, UNITY-INOVA600. ^{1}H NMR chemical shifts were reported in ppm (δ) using the residual $CHCl_3$ (δ 7.26) in $CDCl_3$. ^{13}C NMR chemical shifts were reported in ppm (δ) relative to the internal standard $CDCl_3$ (δ 77.0). IR spectra were recorded on a HORIBA FT-720 spectrometer. Mass spectrometric data were obtained by using a JEOL JNS-DX303 mass spectrometer. Elemental analyses were carried out at the Analytical Center of Osaka University, Faculty of Engineering.

3.2. Preparation of 3-alkylideneoxetane 1[2]

A degassed solution of **DZ** (0.05 M) in benzene (20 mL) was irradiated with a high-pressure Hg lamp (500 W) through a Pyrex filter (>290 nm) at ca. 10°C. The quantitative formation of 3-alkylideneoxetane **1** was confirmed by the NMR measurement after 3 h.

3.3. General procedure for the reaction of 3-alkylideneoxetane 1 with ROH

To a solution of 3-alkylideneoxetane **1** (0.05 M) in benzene (20 mL) was added a solution of ROH (1.0 M) in benzene (20 mL) at rt (ca. 15°C), except for H_2O. H_2O was added as a solution in THF. After the completion of the reaction, which was checked by TLC analyses, the mixture was washed with sat. $NaHCO_3$ aqueous solution (50 mL×2). The organic phase was separated and the solvent was removed under the reduced pressure by using a rotary evaporator. Separation of the products by using the column chromatography on silica gel (EtOAc/hexanes as eluent) afforded the ROH-adduct **3** and/or **5**. The yields were listed in Table 1. The MeOH-adduct **3b** (R=Me) was already identified in the previous study.[2a] The spectroscopic data for new compounds obtained in this study are as follows.

3.3.1. 2-(1′-Hydroxy-1′,1′-diphenylmethyl)cyclopent-2-enol (3a). White powder: mp 109–110°C; FTIR (KBr)

3255, 2946, 2892, 1442, 1311, 1049 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 1.80–1.86 (m, 1H), 2.15–2.58 (m, 3H), 2.96 (br s, 1H, OH), 4.78 (br s, 1H, OH), 4.85–4.87 (m, 1H), 5.34 (br s, 1H), 7.24–7.46 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 29.5 (t), 33.9 (t), 78.3 (d), 80.2 (s), 127.0 (4×d), 127.1 (d), 127.3 (2×d), 127.6 (d), 128.0 (2×d), 134.5 (d), 144.8 (s), 145.7 (s), 148.2 (s). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.38; H, 6.78.

3.3.2. 2-[1′,1′-Diphenyl-1′-(2,2,2-trifluoroethoxy)-methyl]cyclopent-2-enol (3c). Viscous oil; FTIR (liquid film) 3522, 1449, 1277, 1166, 1107 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.86–1.90 (m, 1H), 2.11–2.17 (m, 1H), 2.21 (br s, 1H), 2.30–2.35 (m,1H), 2.63–2.69 (m, 1H), 3.41–3.65 (m, 2H), 4.71 (d, J=7.2 Hz, 1H), 5.95 (t, J=2.4 Hz, 1H), 7.18–7.53 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 30.3 (t), 32.6 (t), 61.8 ($-CH_2CF_3$, $^2J_{CF}$=34.1 Hz), 77.1 (d), 86.6 (s), 124.2 ($-CF_3$, $^1J_{CF}$=276 Hz), 127.8 (4×d), 128.2 (2×d), 129.3 (4×d), 135.0 (d), 140.1 (s), 141.1 (s), 146.4 (s). Anal. Calcd for $C_{20}H_{19}F_3O_2$: C, 68.96; H, 5.50. Found: C, 68.96; H, 5.65.

3.3.3. 2-Benzhydrylidene-3-(2′,2′,2′-trifluoroethoxy)cyclopentanol (5c). Viscous oil; FTIR (liquid film) 2561, 3027, 2940, 1599, 1449, 1368, 1285, 1228, 1195, 1104 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.82–1.90 (m, 1H), 1.95–2.05 (m, 1H), 2.07–2.15 (m, 2H), 2.26 (d, J=9.0 Hz, OH), 3.36–3.43 (m, 1H), 3.61–3.78 (m, 1H), 4.42 (br s, 1H), 4.47 (m, 1H), 7.31–7.44 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 28.9 (t), 33.3 (t), 65.4 ($-CH_2CF_3$, $^2J_{CF}$=34.1 Hz), 72.5 (d), 81.8 (d), 123.8 ($-CF_3$, $^1J_{CF}$=278 Hz), 127.6 (d), 127.9 (d), 128.1 (2×d), 128.3 (2×d), 129.3 (2×d), 129.4 (2×d), 140.3 (s), 140.7 (s), 141.1 (s), 144.2 (s). Anal. Calcd for $C_{20}H_{19}F_3O_2$: C, 68.96; H, 5.50. Found: C, 69.15; H, 5.71.

3.3.4. 2-Benzhydrylidene-3-(2′,2′,2′-trifluoro-1′-trifluoromethylethoxy)cyclopentanol (5d). Viscous oil; FTIR (liquid film) 3560, 3060, 3026, 2939, 1491, 1448, 1368, 1284, 1194, 1104 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.85–1.90 (m, 1H), 1.95–2.04 (m, 1H), 2.05–2.13 (m, 3H), 3.78 (sept, J_F=6.0 Hz, 1H), 4.45 (m, 1H), 4.85 (m, 1H), 7.09–7.35 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 29.1 (t), 33.6 (t), 72.6 (d), 72.9 ($-CH(CF_3)_2$, $^2J_{CF}$=31.8 Hz), 83.8 (d), 124.2 (CF_3×2, ^1JCF=276 Hz), 127.9 (d), 128.1 (4×d), 128.5 (2×d), 129.1 (2×d), 129.3 (d), 140.0 (s), 140.0 (s), 140.6 (s), 145.5 (s). Anal. Calcd for $C_{21}H_{18}F_6O_2$: C, 60.58; H, 4.36. Found: C, 60.33; H, 4.56.

3.3.5. 2-Benzhydrylidene-3-acetoxycyclopentanol (5e). White powder: mp 108–109°C; FTIR (KBr) 3420, 3020, 2870, 1730, 1600, 1240 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.84 (s, 3H), 1.85–1.89 (m, 1H), 1.94–1.98 (m, 1H), 2.01–2.06 (m, 1H), 2.07–2.14 (m, 1H), 2.30 (br s, OH), 4.61–4.64 (m, 1H), 5.55 (t, J=5.6 Hz, 1H), 7.13–7.43 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 21.5 (q), 30.4 (t), 33.4 (t), 72.9 (d), 76.0 (d), 127.8 (d), 128.2 (d), 128.7 (2×d), 128.8 (2×d), 128.9 (2×d), 129.3 (2×d), 141.1 (2×s), 141.3 (s), 145.0 (s), 170.8 (s); EI MS (m/z, relative intensity) 308 (M^+, 4), 205 (31), 220 (48), 248 (100); HRMS (EI) Calcd for $C_{20}H_{20}O_3$ 308.1413. Found 308.1418. Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.90; H, 6.54. Found: C, 77.67; H, 6.45.

3.4. Oxidation of the TFE-adduct 3c

To a solution of PCC (0.19 g, 0.87 mmol) in dry CH_2Cl_2 (3 mL) was added a solution of **3c** (0.15 g, 0.43 mmol) in dry CH_2Cl_2 (3 mL) at room temperature under Ar. After stirring for 2 h, diethyl ether (20 mL) and $MgSO_4$ (5 g) was added and the mixture was filtrated over Celite. The filtrate was concentrated under the reduced pressure by using the rotary evaporator. Column chromatography on silica gel (30% EtOAc/hexanes, R_f=0.5) afforded 0.12 g (81%) of ketone **6**. White powder: mp 84–85°C; FTIR (KBr) 2927, 1710, 1286, 1168, 1115 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 2.45–2.48 (m, 2H), 2.63–2.68 (m, 2H), 3.52 (q, J_{HF}=8.5 Hz, 2H), 7.32–7.45 (m, 10H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 26.2 (t), 36.1 (t), 61.9 (tq, $^2J_{CF}$=34.1 Hz, $-CH_2CF_3$), 84.1 (s), 124.2 (q, $^1J_{CF}$=276.6 Hz, $-CH_2CF_3$), 128.2 (4×d), 128.3 (4×d), 128.7 (2×d), 139.3 (2×s), 148.3 (s), 161.9 (d), 206.0 (s). Anal. Calcd for $C_{20}H_{17}F_3O_2$: C, 69.35; H, 4.95. Found: C, 69.21; H, 5.02.

Acknowledgments

This research was supported in part by a grant-in-aid for Scientific Research on Priority Areas 'Molecular Physical Chemistry' from the ministry of Education, Science, Sports, and Culture of Japan. We thank Mrs T. Muneishi at Analytical Center of Faculty of Engineering, Osaka University, for measuring the 600 MHz NMR spectra.

References

1. (a) Liebman, J. F.; Greenberg, A. *Chem. Rev.* **1976**, *76*, 311. (b) Greenberg, A.; Liebman, J. F. *Strained Organic Molecules*. Academic: New York, 1978. (c) *Chem. Rev.* **1989**, *5*, 89; special issue for Strained Organic Compounds.
2. (a) Abe, M.; Adam, W.; Nau, W. M. *J. Am. Chem. Soc.* **1998**, *120*, 11304. (b) Abe, M.; Adam, W.; Ino, Y.; Nojima, M. *J. Am. Chem. Soc.* **2000**, *122*, 6508.
3. Wiberg, K. B. *J. Org. Chem.* **1985**, *50*, 5285.
4. The ab initio calculations at RHF/6-31G* level of theory were performed with GAUSSIAN 98W: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revision A.11*; Gaussian, Inc.: Pittsburgh PA, 2001.
5. Franklin, J. L. *J. Chem. Phys.* **1953**, *21*, 2029.
6. The strain energies of 3-alkylideneoxetane (SE=22.6 kcal/mol), 7-oxabicyclo4.2.0.oct-1-ene (SE=24.6 kcal/mol), and

5-oxabicyclo2.2.0.hex-1-ene (SE=87.1 kcal/mol) were calculated by the same procedure.

7. Schleyer, P. V. R.; Williams, Jr. J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.
8. (a) Borden, W. T. *Chem. Rev.* **1989**, *89*, 1067. (b) Warner, P. M. *Chem. Rev.* **1989**, *89*, 1095. (c) Chou, P. K.; Kass, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 697. (d) Branan, B. M.; Paquette, L. A.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 774. (e) Staneke, P. O.; Ingemann, S.; Eaton, P.; Nibbering, N. M. M.; Kass, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 6445. (f) Sauers, R. R.; Harris, J. *J. Org. Chem.* **2001**, *66*, 7951.
9. DeTar, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 7205.
10. The PM3 calculations (Ref. 11) were performed within *SPARTAN'02*; Wavefunction, Inc., 2001.
11. Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.