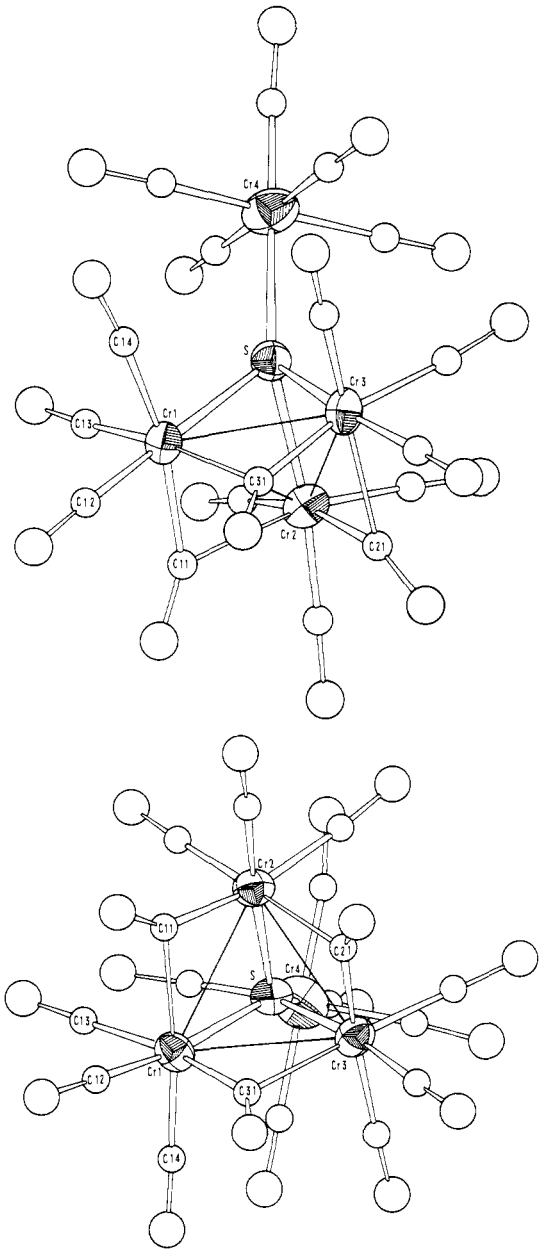

Figure 1. Molecular geometry of **2**. View from the side and from below. The anisotropically refined chromium and sulfur atoms are designated as 50% probability thermal ellipsoides.

Table I. Selected Anion Bond Lengths (ppm) and Bond Angles (deg) of Compound **2**

Cr-Cr	285.0 (9) mean	
Cr1,2,3-S	230.5 (5) mean	
Cr4-S	246.8 (3)	
Cr4-C_a	174.8 (14)	Δ = 10.6
Cr4-C_e	185.4 (15)	
Cr1-C14	184.1 (13) (trans to C11)	
Cr1-C13	178.6 (12) (trans to C31)	
Cr1-C12	178.7 (13) (trans to S)	
Cr1-C31	233.8 (11)	Δ = 39.4
Cr3-C31	194.4 (13)	
Cr2-C21	196.8 (12)	Δ = 26.5
Cr3-C21	223.3 (14)	
Cr1-C11	192.3 (12)	Δ = 39.6
Cr2-C11	231.9 (15)	
Cr1,2,3-S-Cr1,2,3	76.40 (3) mean	
Cr1-S-Cr4	134.20 (16)	
Cr2-S-Cr4	138.23 (15)	
Cr3-S-Cr4	130.59 (14)	
C12-Cr1-S	175.40 (4)	
C13-Cr1-C31	173.70 (5)	
C14-Cr1-C11	163.50 (6)	

(to C11) compared to 233.8 (11) pm (to C31). Since we have a terminal CO in an opposite position in each case, we are able to look for a trans effect of asymmetric CO bridges for the first time, and indeed, the distance C13-Cr1 is considerably shorter than C14-Cr1 (Table I). The electron-donating abilities of the sulfur atom can be evaluated from the $(CO)_5Cr$ group. The difference between equatorial and axial Cr-C bonds amounts to 10.6 pm. Comparable large effects are shown solely by ligands (sulfur as ligator), which are regarded as possessing only donor but no acceptor abilities.[10] If sulfur donates two electrons to each of the four chromium atoms, both parts of the molecule are electronically saturated.[11] Therefore, the sulfur ligand can be regarded formally as an eight-electron-donating sulfide ligand. In most other cases, where a bare sulfur atom is tetrahedrally surrounded by four metal atoms, it is best considered as a formal six-electron donor.[12]

As there is not apparent electronic reason for the observed deviation of the cluster part from C_{3v} symmetry as well as for the asymmetric arrangement of the $Cr(CO)_5$ group, we think that this is caused by package effects.

Infrared spectra, taken in THF and in KBr, show that the structure as determined in the solid state is essentially the same persistent in solution. In the CO valency region, seven bands are observed at 2061 vw, 2014 vw, 1968 vs, 1932 m, 1914 s, 1868 s, and 1796 vw(broad) cm^{-1} (THF solution). The habitus of the latter band is characteristic for the considered type of asymmetric CO bridges.[13] At -60 °C, we find two signals at 221.9 and 216.7 ppm (intensity ratio 1:3) in the ^{13}C NMR spectra, which are attributable to the cluster part of **2**. At -10 °C, there is already total carbonyl scrambling in this part of the molecule, as now only one signal is observed at 216.8 ppm. The $Cr(CO)_5$ group gives rise to two signals at 232.6 (cis) and 224.4 (trans) ppm with a 4:1 ratio (δ values relative to external Me_4Si, $THFd_8$ as solvent). The large downfield shift of the signal of the cis CO ligands ($Cr(CO)_5$ group) is interesting, since with other $LCr(CO)_5$ compounds, the resonance signal of the cis CO ligands is located at higher field than that of the trans CO.[14]

Acknowledgment. We are indebted to Fonds der Chemischen Industrie and to Prof. Dr. Th. Kruck for their support of this work, as well as to Dr. R. Froehlich for technical assistance.

Supplementary Material Available: Seven tables listing details of the structural work, three figures with numbering schemes, and two drawings, showing the packing (20 pages). Ordering information is given on any current masthead page.

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Effective Route to Azetidines from Azetidin-2-ones Using Hydroalanes as Specific Reducing Agents

Mitsuo Yamashita and Iwao Ojima*[1]

Sagami Chemical Research Center
Nishi-Ohnuma 4-4-1, Sagamihara
Kanagawa 229, Japan

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Although the chemistry and biochemistry of azetidin-2-ones have been extensively studied with regard to various β-lactam antibiotics,[2] less attention has been drawn to those of azetidines.

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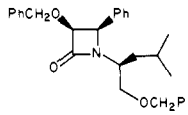
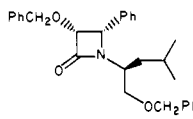
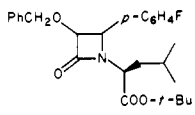
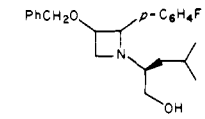
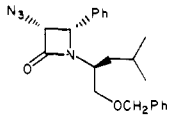
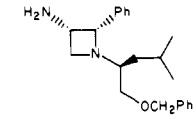
Table I. Reduction of Azetidin-2-ones with Hydroalanes Giving Azetidines

entry	azetidin-2-one[a] X	R¹	R²	reducing[b] agent	conditions temp, °C	time, h	solvent	product[c] (isolated yield, %)
1	$PhCH_2O$	Ph	Ph (1a)	Dibal-H (3.0)	65	2	THF, *n*-hexane	2a (73), 3a (11)
2	$PhCH_2O$	Ph	furyl (1b)	Dibal-H (3.0)	65	2	THF, *n*-hexane	2c (54), 3b (27)
3	$PhCH_2O$	Ph	thienyl (1c)	Dibal-H (3.0)	65	2	THF, *n*-hexane	2d (72), 3c (17)
4	$PhCH_2O$	Ph	3,4-$(MeO)_2C_6H_3$ (1d)	Dibal-H (3.0)	65	2	THF, *n*-hexane	2e (77), 3d (<1)
5		1a		AlH_2Cl (2.4)	34	1.5	Et_2O	2a (94)
6		1a		$AlHCl_2$ (12.0)	34	1	Et_2O	2a (94)
7	$PhCH_2O$	Ph	*p*-C_6H_4F (1e)	AlH_2Cl (2.4)	34	1.5	Et_2O	2e (94)
8	$PhCH_2O$	PhMeCH	Ph (1f)[d]	$AlHCl_2$ (2.4)	34	1.5	Et_2O	2f (100)
9	$PhCH_2O$	$PhCH_2$	Ph (1g)	AlH_2Cl (2.4)	34	1.5	Et_2O	2g (96)
10	 (1h)[e]			AlH_2Cl (1.4)	34	1.5	Et_2O	2h[f] (85)
11	 (1i)[g]			AlH_2Cl (1.2)	34	1.5	Et_2O	2i[h] (92)
12	PhO	*t*-Bu	Ph (1j)	AlH_2Cl (2.4)	34	4	Et_2O	2j (97)
13	PhO	*t*-Bu	Ph (1k)	AlH_2Cl (2.4)	34	1.5	Et_2O	2k (91)
14	 (1l)			AlH_2Cl (4.6)	34	4	Et_2O	 (72) 21
15	N_3	Ph	Ph (4a)	AlH_2Cl (4.0)	34	4	Et_2O	5a (90)
16		4a		$AlHCl_2$ (16)	34	2	Et_2O	5a (79)
17	N_3	Ph	*p*-FC_6H_4 (4b)	AlH_2Cl (3.5)	34	2	Et_2O	5b (100)
18	N_3	*t*-Bu	Ph (4c)	AlH_2Cl (4.0)	34	2	Et_2O	5c (87)
19			(4d)[i]	AlH_2Cl (4.4)	34	2	Et_2O	 (88) 5d[j]
20	N_3	$PhCH_2$	3,4-$(MeO)_2C_6H_3$ (4e)	AlH_2Cl (3.0)	34	2	Et_2O	5e (83)
21	N_3	*t*-Bu	Ph (4f)	AlH_2Cl (4.1)	34	2	Et_2O	5f (81)

[a] The relative stereochemistry of C_3 and C_4 carbons is cis unless otherwise noted. [b] The value in the parentheses is the molar ratio of reducing agent toward azetidin-2-one. [c] The relative stereochemistry of C_2 and C_3 carbon is cis unless otherwise noted. Spectral and microanalytical data were consistent with the assigned structure in every case. [d] The relative stereochemistry is trans. [e] $[\alpha]^{20}_D$ −44.61° (*c* 0.777, $CHCl_3$). [f] $[\alpha]^{20}_D$ −56.62° (*c* 0.773, $CHCl_3$). [g] $[\alpha]^{20}_D$ +51.57° (*c* 0.877, $CHCl_3$). [h] $[\alpha]^{20}_D$ +89.02° (*c* 0.720, $CHCl_3$). [i] $[\alpha]^{20}_D$ +133.4° (*c* 1.04, $CHCl_3$). [j] $[\alpha]^{20}_D$ +120.5° (*c* 0.501, $CHCl_3$).

However, azetidines are an interesting class of four-membered heterocyclic compounds, and it has been shown that a variety of azetidines exhibit various biological activities.[3-7] Accordingly, exploitation of effective general methods for the synthesis of azetidines are of significant value. It has been shown that azetidines can be synthesized by several methods[4,8] including the cyclization of γ-halogenopropylamines[6,8] or by the reduction of azetidin-2-ones with the use of $LiAlH_4$[3,7] and B_2H_6.[7,9] As various azetidin-2-ones can be prepared by using several established methods,[1] the latter method seems to be an attractive approach to the general synthesis of azetidines. However, the applicability of the latter method has been restricted to a couple of 1-unsubstituted azetidin-2-ones: It has been reported[3] that the reduction of N-substituted azetidin-2-ones with $LiAlH_4$,[7] B_2H_6,[7,10] Raney

(1) Present address: Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794.

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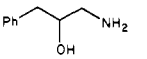
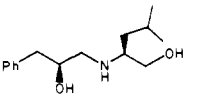
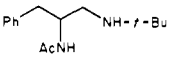
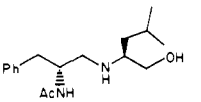
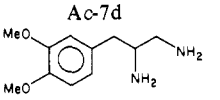
Table II. Reductive Cleavage of 2-Arylazetidines[a]

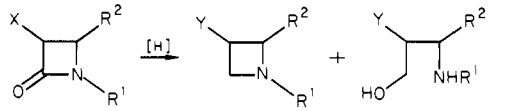
entry	azetidine	catalyst	conditions: temp, °C	conditions: time, h	conditions: solvent	product	isolated yield, %
1	2g	10% Pd-C	50	19	MeOH	 6g	94
2	2h	10% Pd-C	50	24	EtOH	 6h	84
3	Ac-5c[b]	10% Pd-C	50	48	EtOH	 Ac-7c	90
4	Ac-5c[b]	Raney Ni[c]	78	2	EtOH	Ac-7c	88
5	Ac-5d[b]	10% Pd-C	50	48	EtOH	 Ac-7d	100
6	5e	10% Pd-C	50	48	EtOH	 7e	81

[a] Reactions were run with 0.5 mmol of azetidine and 600 mg of 10% Pd-C in 10 mL of ethanol or methanol under an atmospheric pressure of hydrogen. [b] Ac-5 were prepared by the acetylation of 5 with acetic anhydride in pyridine. [c] Reaction was run with 0.553 mmol of Ac-5d and 1 mL of Raney Ni in 10 mL of ethanol under nitrogen atmosphere.

Nickel, $LiAlH_4$–$AlCl_3$ (AlH_3), and $NaBH_4$–$AlCl_3$ all result in cleavage of the 1,2-bond to give the substituted 3-aminopropanols.

We chose 3-benzyloxy-1,4-diphenylazetidin-2-one (**1a**) as a typical substrate and examined various metal hydride reducing agents. Attempted reduction by BH_3·THF (22 h in refluxing dioxane) and $NaBH_4$–$AlCl_3$ (3.5 h in refluxing ether) resulted in the complete recovery of the starting substrate and the reduction with $LiAlH_4$, $LiBEt_3H$, or LiB-*sec*-Bu_3H gave 3-(phenylamino)-3-phenyl-2-(benzyloxy)propanol (**3a**) exclusively through 1,2-bond fission (25 °C in THF). However, *i*-Bu_2AlH (DiBAL-H) was found to undergo the desired reduction successfully to give 3-(benzyloxy)-1,2-diphenylazetidine (**2a**) in 73% yield although small amount (16%) of **3a** was also produced, which was easily separated on a silica gel column. Thus, we carried out the reductions of a variety of 3-(benzyloxy)azetidin-2-ones (**1**) with the use of DiBAL-H in THF as shown in Table I and obtained the corresponding azetidines (**2**) in 54–77% yields (entries 1–4).[11]

Next, we employed monochloroalane (AlH_2Cl) and dichloroalane ($AlHCl_2$) since Brown's selective hydroboration with thexylchloroborane[12] inspired us to examine the reactivities of chloroalanes toward azetidin-2-ones. To our happy surprise, AlH_2Cl and $AlHCl_2$ prepared in situ from $LiAlH_4$ and $AlCl_3$ in ether[13] converted **1** into **2** in quite high yields (85–100%) without being accompanied by **3** (entries 5–13). Similarly, 3-azidoazetidin-2-ones (**4**) were converted to 3-aminoazetidines (**5**) in high yields (79–100%) (eq 1): In these cases, the reduction of



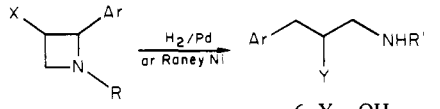
(1)

1, X = $PhCH_2O$ 2, Y = $PhCH_2O$ 3, Y = $PhCH_2O$
4, X = N_3 5, Y = NH_2

carbonyl and azide functionalities proceeded at once (entries 15–21).[14] The use of alane (AlH_3) itself for the reduction of **1a** resulted in the formation of a mixture of **2a** (29%) and **3a** (59%).

Optically active azetidin-2-ones can be transformed to the corresponding azetidines without loss of optical activities, which were checked by HPLC analyses. When an azetidin-2-one *tert*-butyl ester (**1l**) was employed as substrate for AlH_2Cl reduction, the corresponding azetidine alcohol (**2j**) was obtained, i.e., *tert*-butyl ester was not tolerant of this reduction (entry 14).

Among the azetidines thus obtained, 2-arylazetidines, **2**, **5**, and Ac-**5**, were found to undergo 1,2-bond fission accompanied by removal of benzyl group through hydrogenolysis on palladium catalyst or Raney nickel to give 3-arylpropylamines, **6**, **7**, and Ac-**7**, respectively, in high yields (eq 2). These compounds may serve as versatile chiral building blocks for organic syntheses. Results are listed in Table II.



(2)

2, X = $PhCH_2O$ 6, Y = OH
5, X = NH_2 7, Y = NH_2
Ac-5, X = AcNH Ac-7, Y = AcNH

Further studies on the usage of chiral 3-amino- and 3-hydroxyazetidines as reagents for organic synthesis and the

(11) A typical procedure for the DiBAL-H reduction of **1** is as follows: To a refluxing solution of **1a** (207 mg, 0.629 mmol) in 5 mL of THF was added 2.5 mL of 1 M DiBAL-H solution in *n*-hexane (2.5 mmol), and the mixture was refluxed for 2 h with stirring. Then, 50 mL of water was added to the reaction mixture and extracted with CH_2Cl_2 (70 mL). After the extract was dried over anhydrous $MgSO_4$, the solvent was removed and the residue was submitted to a column chromatography on silica gel (AcOEt/*n*-hexane 1/5) to give **2a** (144 mg, 73%) and **3a** (34 mg, 16%).

(12) (a) Brown, H. C.; Sikorski, J. A.; Kulkarni, S. U.; Lee, H. D. *J. Org. Chem.* **1982**, *47*, 863–873. (b) Sikorski, J. A.; Brown, H. C. *Ibid.* **1982**, *47*, 872–876.

(13) Monochloroalane and dichloroalane were prepared by refluxing 1:1 and 1:3 mixture of $LiAlH_4$ and $AlCl_3$ in ether for 30 min, respectively. Cf.: (a) Fieser, L. F.; Fieser, M. In "Reagents for Organic Syntheses"; Wiley: New York, 1967; Vol 1, pp 595–599 and references cited therein. (b) Ferles, M. *Chem. Listy* **1968**, *62*, 1045–1065.

(14) A typical procedure for the AlH_2Cl reduction of 4 is as follows: A mixture of $AlCl_3$ (267 mg, 2.00 mmol) and $LiAlH_4$ (79 mg, 2.08 mmol) in 15 mL of ether was refluxed for 30 min with stirring. To the AlH_2Cl solution thus prepared was added **4d** (171 mg, 0.45 mmol), and the mixture was stirred under reflux for 2 h. Then, 50 mL of water was added to the reaction mixture and extracted with CH_2Cl_2 (90 mL). A centrifugal separation was helpful for this extraction. The extract was dried over anhydrous $MgSO_4$ and the solvent was removed to give **5d** (134 mg, 88%) as colorless oil.

syntheses of polyazetidines, polyamines, and polyamino ethers and the mechanisms of these reactions are actively underway.

Registry No. 1a, 64468-52-6; **1b**, 86863-57-2; **1c**, 86863-58-3; **1d**, 75957-95-8; **1e**, 75958-03-1; **1f**, 86863-61-8; **1g**, 86863-62-9; **1h**, 86863-63-0; **1l**, 86940-70-7; **1j**, 86863-64-1; **1l**, 86863-65-2; **2a**, 86863-66-3; **2c**, 86863-59-4; **2d**, 86863-60-7; **2e**, 86863-67-4; **2f**, 86863-68-5; **2g**, 86863-69-6; **2h**, 86863-70-9; **2l**, 86940-71-8; **2j**, 86863-71-0; **2l**, 86863-72-1; **3a**, 86863-73-2; **3b**, 86863-74-3; **3c**, 86863-75-4; **3d**, 86863-76-5; **4a**, 16311-94-7; **4b**, 16312-06-4; **4c**, 86863-77-6; **4d**, 82166-23-2; **4e**, 86863-78-7; **5a**, 86863-79-8; **5b**, 86863-80-1; **5c**, 86863-81-2; Ac-**5c**, 86863-87-8; **5d**, 86863-82-3; Ac-**5d**, 86863-88-9; **5e**, 86863-83-4; **6g**, 50411-26-2; **6h**, 86863-84-5; Ac-**7c**, 86863-85-6; Ac-**7d**, 86863-86-7; **7e**, 31595-02-5; DiBAL-H, 1191-15-7; AlH_2Cl, 14644-71-4; $AlHCl_2$, 13497-97-7.

Intramolecular 1,1-Cycloaddition Reaction of Allyldiazomethane: Electrophilic Nature of the Terminal Nitrogen of Diazomethane and Geometrical Requirement[1]

Tsutomu Miyashi,* Katsuyoshi Yamakawa, Masaki Kamata, and Toshio Mukai

Photochemical Research Laboratory and Department of Chemistry, Faculty of Science Tohoku University, Sendai 980, Japan

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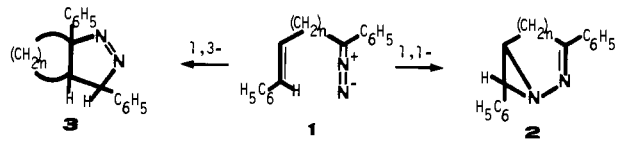
We previously reported that allyldiazomethanes undergo a formal nitrene-type 1,1-cycloaddition reaction to give 1,2-diazabicyclo[3.1.0]hex-2-enes,[2] which occurs reversibly with retention of configuration.[3] It was also of interest to know whether this novel cycloaddition is limited to allyldiazomethanes. We have now compared the reactivities of the homologous diazomethanes **1b** ($n = 2$), **1c** ($n = 3$), and **1d** ($n = 4$) to that of **1a** ($n = 1$), which is known to afford the 1,1-cycloadduct **2a** ($n = 1$) (Scheme I).[3] It was found that **1b**, **1c**, and **1d** do not undergo the 1,1-cycloaddition to give **2b** ($n = 2$), **2c** ($n = 3$), and **2d** ($n = 4$) but undergo 1,3-dipolar cycloadditions giving **3c** ($n = 3$)[4] and **3d** ($n = 4$)[5] from **1c** and **1d**, respectively.[6] This indicates that the 1,1-cycloaddition can compete with the 1,3-dipolar cycloaddition only when the HOMO(dizomethane)–LUMO(olefin) controlled parallel-plane approach required for the 1,3-dipolar cycloaddition becomes geometrically unfavorable, especially in allyldiazomethane. Therefore, the 1,1-cycloaddition reaction of allyldiazomethane is a suitable model to investigate the latent nature of the terminal nitrogen of diazomethane, which is responsible for the 1,1-cycloaddition. Herein we report results obtained from the rate analyses on the reversible 1,1-cycloaddition between 1,2-diazabicyclo[3.1.0]hex-2-enes **4** and allyldiazomethanes **5**, which prove the electrophilic nature of the terminal nitrogen of diazomethane in contrast with the nucleophilic nature[7] of diazomethane as a 1,3-dipole (Scheme II).

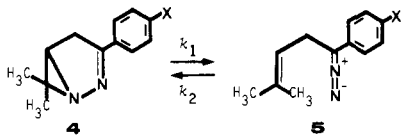
Scheme I



3 1 2

a: n=1; b: n=2; c: n=3; d: n=4

Scheme II



4 5

a: X=NO_2; b: X=Br; c: X=Cl
d: X=H; e: X=CH_3; f: X=OCH_3

Table I. First-Order Rate Constants, Equilibrium Constants, and Free Energy Change at 50 °C

substituent	$10^3 k_1$, s^{-1}	$10^3 k_2$, s^{-1}	K^b	ΔG,[c] kcal/mol
NO_2	10.71	2.88	3.71	−0.84
Br	0.59	1.89	0.32	0.75
Cl	0.49	1.80	0.28	0.84
H	0.40	1.49	0.26	0.86
CH_3	0.18	1.23	0.16	1.22
OCH_3	0.06[a]	1.16[a]	0.05	1.92

[a] Estimated from $\log k_2^X/k_2^H = 0.38\sigma_p$ ($r = 0.996$) and $K^{OCH_3} = 0.05$. [b] Obtained by $\log K$ vs. $1/T$ plots. [c] Calculated from equilibrium constants at 50 °C.

The 1,2-diazabicyclo[3.1.0]hex-2-ene derivatives **4a–f**[8] were synthesized in good yields by the same procedure[3] we reported previously. In particular, the *p*-nitro derivative **4a** was quantitatively isolated by freeze-dry evaporation of carbon tetrachloride at −30 °C after decomposition followed by cooling at −20 °C for 3 days. The rate analyses were performed by monitoring the disappearance of **4b–e** and the appearance of **5b–e** while heating a degassed sealed tube containing a carbon tetrachloride solution of **4** in the preheated 90-MHz NMR probe and vice versa for the *p*-nitro derivatives **4a** and **5a**.[10] The equlibrium constants (K) were measured at temperature ranges between 20 and 75 °C for **4a**, 42 and 76 °C for **4b**, 45 and 65 °C for **4c**, 45 and 75 °C for **4d**, 50 and 80 °C for **4e**, and 60 and 85 °C for **4f**. In all cases

(1) Organic Thermal Reaction. 56. Part 55, see: Satake, K.; Kumagai, T.; Mukai, T., *Chem. Lett.* **1983**, 743.

(2) Nishizawa, Y.; Miyashi, T.; Mukai, T. *J. Am. Chem. Soc.* **1980**, *102*, 1176.

(3) Miyashi, T.; Fujii, Y.; Nishizawa, Y.; Mukai, T. *J. Am. Chem. Soc.* ***103***, 725. see also: Padawa, A.; Ku, H. *Tetrahedron Lett.* **1980**, 1009. Padawa, A.; Rodriguez, A. *Ibid.* **1981**, 187.

(4) **3c**: mp 54.5 °C (dec 105 °C); *m/e* 262 (M^+, 3%), 234 (100%); UV λ_{max} (cyclohexane) 254 (ε 440), 260 (ε 480), 265.5 (ε 300), 333 (ε 230) nm; ^{1}H NMR ($CDCl_3$), δ 0.85–1.53 (1 H, m), 1.60–2.25 (4 H, m), 2.50–2.85 (2 H, m), 5.35 (1 H, d, $J = 4.0$ Hz), 6.85–7.09 (2 H, 7), 7.10–7.53 (8 H, m).

(5) **3d**: mp 119 °C; *m/e* 276 (M^+, 4.5%), 248 (100%); UV λ_{max} (cyclohexane) 254 (ε 740), 259 (ε 630), 265 (ε 390), 340 (ε 230) nm; ^{1}H NMR ($CDCl_3$) δ 1.10–2.24 (8 H, m), 2.35–2.56 (1 H, m), 5.16 (1 H, d, $J = 11.5$ Hz), 7.08–7.60 (8 H, m), 7.62–7.90 (2 H, m).

(6) Padwa and Fukunaga reported that **1b** undergoes complex reactions upon heating in benzene.[11] We found that **1b** is very stable even under refluxing in CCl_4 and did not change for more than 2 months at ambient temperatures when kept under N_2 atmosphere. Chemical behavior of **1b** will be separately reported soon.

(7) Huisgen, R.; Geittner, J. *Heterocycles* **1978**, *11*, 105.

(8) **4a**: mp 98 °C dec; ^{1}H NMR (CCl_4) δ 0.92 (s, 3 H), 1.37 (s, 3 H), 2.58 (dd, 1 H, $J = 3.0$, 9.0 Hz), 2.96 (dd, 1 H, $J = 3.0$, 18.0 Hz), 3.30 (dd, *1* H, $J = 9.0$, 18.0 Hz), 7.84 (d, 2 H, $J = 9.0$ Hz), 8.20 (d, 2 H, $J = 9.0$ Hz); *m/e* 231 (M^+, 1.7%), 203 (100%), 156 (23%). **4b**: mp 76 °C; ^{1}H NMR (CCl_4) δ 0.90 (s, 3 H), 1.32 (s, 3 H), 2.47 (dd, 1 H, $J = 3.0$, 8.2 Hz), 2.85 (dd, 1 H, $J = 3.0$, 18.0 Hz), 3.25 (dd, 1 H, $J = 8.2$, 18.0 Hz); *m/e* 266 ($M^+ + 2$, 2.2%), 264 (M^+, 2.0%), 238 (32.3%), 236 (42.2%), 221 (16.2%), 142 (100%). **4c**: mp 67 °C; ^{1}H NMR (CCl_4) δ 0.93 (s, 3 H), 1.3[illegible] (s, 3 H), 2.47 (dd, 1 H, $J = 3.0$, 8.1 Hz), 2.85 (dd, 1 H, $J = 3.0$, 18.0 Hz), 3.21 (dd, 1 H, $J = 8.1$, 18.0 Hz), 7.31 (d, 2 H, $J = 8.7$ Hz), 7.64 (d, 2 H, $J = 8,7$ Hz); *m/e* 222 ($M^+ + 2$, 1.8%), 194 (15%), 177 (100%). **4d**: see ref 3. **4e**: mp 63.5 °C; ^{1}H NMR (CCl_4) δ 0.90 (s, 3 H), 1.29 (s, 3 H), 2.35 (s, 3 H), 2.47 (dd, 1 H, $J = 3.0$, 8.2 Hz), 2.85 (dd, 1 *H*, $J = 3.0$, 18.0 Hz), 3.19 (dd, 1 H, $J = 8.2$, 18.0 Hz), 7.08 (d, 2 H, $J = 8.1$ Hz), 7.54 (d, 2 H, $J = 8.1$ Hz); *m/e* 200 (M^+, 3.0 %), 172 (28%), 157 (100%). 4f: mp 102 °C; ^{1}H NMR (CCl_4) δ 0.91 (s, 3 H), 1.30 (s, 3 H), 2.41 (dd, 1 H, $J = 3.0$, 8.2 Hz), 2.82 (dd, 1 H, $J = 3.0$, 18.0, Hz), 3.19 (dd, 1 H, $J = 8.2$, 18.0 Hz), 3.79 (s, 3 H), 6.79 (d, 2 H, $J = 8.7$ Hz), 7.59 (d, 2 H, $J = 8.7$ Hz); *m/e* 216 (M^+, 3.2%) 188 (12%), 173 (100%). The precursors tosylhydrazones were prepared from the corresponding ketones, which were synthesized according to the procedures reported by Steglich.[9]

(9) Engel, S.; Borries, K.; Steglich, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 394.

(10) Rate constants $k_1^{NO_2}$ and $k_2^{NO_2}$ were measured by monitoring the disappearance of **5a** and the appearance of **4a** using a mixture containing ca. 80% of **5a** and 20% of **4a**, which was prepared by heating a carbon tetrachloride solution of **4a** at 72 °C for 10 min in a degassed sealed NMR tube. The rate constants $k_1^{OCH_3}$ and $k_2^{OCH_3}$ could not be accurately measured because of a low conversion of **4f** to **5f** and were estimated from $\log k_2^X/k_2^H = 0.38\sigma_p$ ($r = 0.996$, X = NO_2, Br, Cl, H, and CH_3) and $K = 0.05$.

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