2566 *J. Org. Chem.* **1993,** *58,* 2566–2572

Solvolyses of 3-Oxo- and 3-Methylenebicyclo[2.2.2]oct-1-yl Triflates: Through-Bond Interaction of a β-Carbonyl Lone Pair with a Cationic p Orbital

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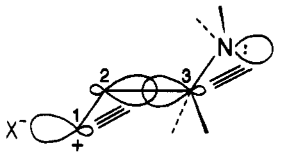
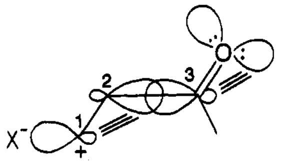
The rates of solvolysis of 3,3-dimethyl-2-oxobicyclo[2.2.2]oct-1-yl triflate (1b), 2-methylenebicyclo-[2.2.2]oct-1-yl triflate (2b), 5,5-dimethyl-3-oxobicyclo[2.2.2]oct-1-yl triflate (3b), 3-oxobicyclo[2.2.2]-oct-1-yl triflate (4b), 3-methylenebicyclo[2.2.2]oct-1-yl triflate (5b), 3,3-dimethylbicyclo[2.2.2]oct-1-yl triflate (6b), and bicyclo[2.2.2]oct-1-yl triflate (7b) have been determined in 80% ethanol at 25 °C. The ^{18}O- and deuterium-labeling studies exclude both carbonyl addition and the enolization processes in the solvolyses of 3b and 4b. The rate ratios 1b/6b and 2b/7b are $10^{-9.1}$ and $10^{-3.9}$, respectively, indicating that the oxo substituent at the C(2) position is more electron withdrawing than the methylene substituent at the same position. In contrast, the rate ratios 3b/6b and 5b/7b, $10^{-2.3}$ and $10^{-2.2}$, respectively, are comparable with each other. Moreover, the rate ratio 4b/5b is 2.3, suggesting that the 3-oxo substituent is less electron withdrawing than the 3-methylene substituent with respect to the cationic center. Evaluation of the inductive effect of the oxo substituent at the C(3) position by means of the reported rates of solvolysis of various 2- or 3-substituted and unsubstituted bicyclo[2.2.2]oct-1-yl *p*-nitrobenzenesulfonates (14, 13, and 15, respectively) indicates a rate enhancement of 10^3–10^4 for 3b and 4b. This marked enhancement is interpreted as evidence of the stabilization of the 3-oxo carbocation by a through-bond interaction between the β-carbonyl lone pair and the cationic p orbital. The *mY* relationships and the formation of fragmentation products 11 (9%) and 12 (20%) in the methanolyses of 3-oxo compounds 3b and 4b, respectively, support the through-bond interaction.

Interactions between two orbitals through framework σ orbitals have been studied not only for their theoretical interest but also for their application to synthetic organic chemistry. In the 1960s, the stabilization of an incipient carbocation by the lone pair of an amino nitrogen attached to the C(3) position was first demonstrated by Grob, and the effect was named the "frangomeric effect" (Scheme I).[1] In several reports published since 1978, Vogel and co-workers have reported that a carbonyl oxygen has a similar effect on regioselective electrophilic additions to the C═C bond of bicyclo[2.2.1]hept-5-en-2-one and related enones (Scheme II), and the results have been explained in terms of a through-bond $pC(1)^+ \leftrightarrow \sigma C(2)C(3) \leftrightarrow n(CO)$ hyperconjugative interaction in a $C(1)^+$—C(2)—C(3)═O species.[2] This explanation is based on the concept of through-bond interaction recognized by Hoffmann: the lone pair of a carbonyl group interacts with the σ* orbital of an adjacent C–C σ bond.[3] Lajunen and his co-workers used this concept to rationalize the preferred protonation of bicyclo[2.2.1]hept-5-en-2-one at the C(5) position.[4]

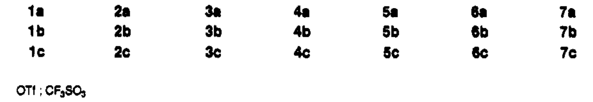
Scheme I



Scheme II



This sort of through-bond electronic effect can be best assessed quantitatively by the study of the solvolyses of appropriate compounds. In a recent communication,[5] we described the solvolyses in 80% EtOH of 2-oxo-, 2-methylene-, 3-oxo-, and 3-methylene-substituted bicyclo[2.2.2]-oct-1-yl systems (1b–5b) as well as the unsubstituted compounds (6b and 7b). The bridgehead substrates have the advantage that nucleophilic solvent assistance and carbonyl participation from the rear side of the bridgehead carbon are prohibited. 3-Oxobicyclo[2.2.2]oct-1-yl compounds (3b and 4b) were found to solvolyze in 80% EtOH at 25 °C at a rate 10^3–10^4 faster than that predicted from the inductive electron-withdrawing effect of the carbonyl group.[5] The marked stabilization of the incipient 3-oxobicyclo[2.2.2]oct-1-yl cation was interpreted as evidence for the above-mentioned through-bond interaction.



L=OH	**1a**	**2a**	**3a**	**4a**	**5a**	**6a**	**7a**
L=OTf	**1b**	**2b**	**3b**	**4b**	**5b**	**6b**	**7b**
L=OCH_3	**1c**	**2c**	**3c**	**4c**	**5c**	**6c**	**7c**

OTf ; CF_3SO_3

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[1] (a) Grob, C. A.; Schiess, P. W. *Angew. Chem.* **1967,** *79,* 1. (b) Grob, C. A. *Angew. Chem.* **1969,** *81,* 543.

[2] (a) Carrupt, P.-A.; Avenati, M.; Quarroz, D.; Vogel, P. *Tetrahedron Lett.* **1978,** 4413. (b) Avenati, M.; Carrupt, P.-A.; Quarroz, D.; Vogel, P. *Helv. Chim. Acta* **1982,** *65,* 188. (c) Carrupt, P.-A.; Vogel, P. *Helv. Chim. Acta* **1989,** *72,* 1008.

[3] Hoffmann, R. *Acc. Chem. Res.* **1971,** *4,* 1.

[4] (a) Lajunen, M. *Acc. Chem. Res.* **1985,** *18,* 254. (b) Lajunen, M.; Lahti, M.; Heimo, S. *Acta Chem. Scand.* **1989,** *43,* 771.

[5] Takeuchi, K.; Yoshida, M. *J. Org. Chem.* **1989,** *54,* 3772.

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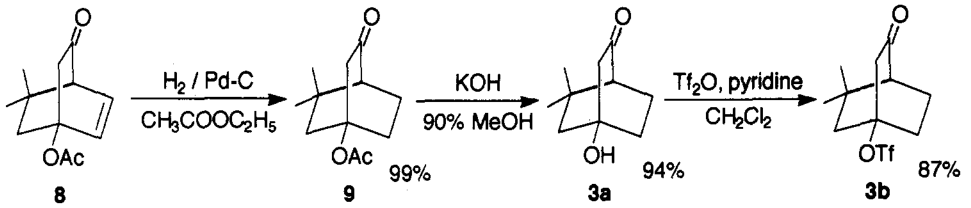
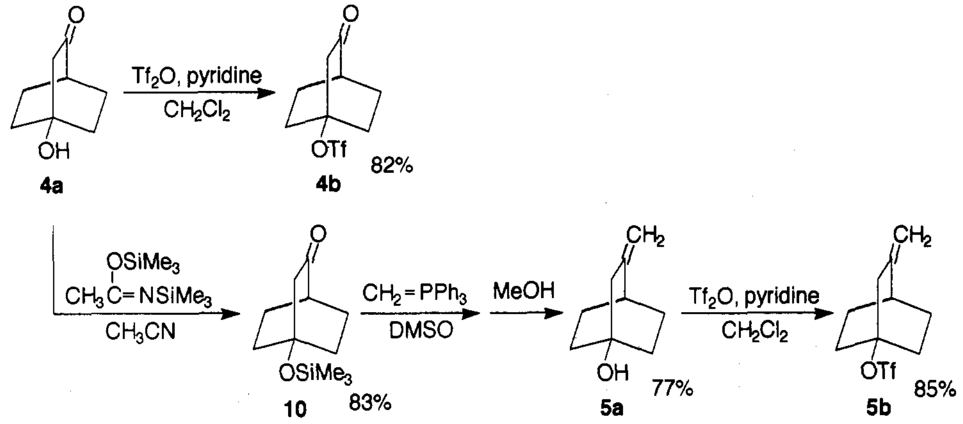
Scheme III



Scheme IV



Recent quantum mechanical calculations by Carrupt and Vogel confirmed our interpretation.[6] Furthermore, the stereoelectronic nature of this interaction was supported by a study of the rates and products of the solvolyses of 4-oxo-2-adamantyl derivatives.[7] This paper describes the details of the solvolysis of the bicyclo[2.2.2]oct-1-yl system (**1b**–**7b**) in various solvents. The rates, solvolysis products, and solvent effects are presented to support the through-bond interaction in the solvolyses of 3-oxo compounds **3b** and **4b**.

Results

Synthesis of Solvolysis Substrates. The 2-oxo, 2-methylene, and parent bridgehead triflates (**1b**, **2b**, **6b**, and **7b**) were described previously.[8] The 3-oxo and 3-methylene bridgehead triflates (**3b**, **4b**, and **5b**) were synthesized as follows (Schemes III and IV). Hydrogenation of 1-acetoxy-8,8-dimethylbicyclo[2.2.2]oct-2-en-5-one[9] followed by saponification afforded new precursor alcohol **3a**. Precursor alcohol **4a** was prepared according to a literature method.[10] New precursor alcohol **5a** was obtained by means of a modified Wittig reaction[11] on the trimethylsilyl ether of **4a**. All the bridgehead alcohols were converted to the corresponding triflates by treatment with triflic anhydride in methylene chloride in the presence of pyridine.

Solvolysis Rates. Most of the substrates were very unstable to both water and column chromatography.[12] The unstable substrates were used for solvolysis studies without further purification. All the substrates were essentially pure (>97%) on the basis of their ^{13}C NMR spectra; the sole impurity, if any, was the starting alcohol, which did not influence the solvolysis rates. The solvolyses were conducted in the presence of 2,6-lutidine, and the rates were determined either titrimetrically or conductimetrically. All the substrates followed good first-order kinetics ($r > 0.999$) till 80–90% completion. The rate data and activation parameters for the solvolyses of 3-oxo and 3-methylene compounds in ethanol, methanol, trifluoroethanol, aqueous ethanol, aqueous methanol, and aqueous acetone are summarized in Table I. In addition, for the purpose of comparison with the data for the 3-oxo and 3-methylene compounds, the rate data and activation parameters for the solvolyses of the 2-oxo and 2-methylene compounds as well as the parent compounds in 80% ethanol are summarized in Table II.

Solvolysis Products. The methanolyses of the 3-oxo and 3-methylene compounds (0.040 M) containing 2,6-lutidine (0.050 M) were carried out at 25.0 °C for a period longer than 10 half-lives. The product distribution was determined by GLC (PEG 20M) of the reaction mixture. Although 3-methylene compound **5b** gave the corresponding bridgehead methyl ether **5c** exclusively, 3-oxo compound **3b** afforded a mixture of bridgehead methyl ether **3c** (91%) and fragmentation product **11** (9%) (Scheme V). Triflate **4b** also afforded a mixture of bridgehead methyl ether **4c** (74%) and fragmentation product **12** (20%) (Scheme V).[13]

Evidence against Carbonyl Addition and Enolization Processes. When the solvolyses of carbonyl-containing substrates are studied, it is necessary to examine the possibility of the mechanism involving solvent addition to the carbonyl group and subsequent solvolysis of the resulting tetrahedral adduct.[14] For this purpose, the solvolysis of **3b** was conducted in 90% MeOH–10% $H_2{}^{18}O$

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[6] Carrupt, P.-A.; Vogel, P. *J. Org. Chem.* **1990**, *55*, 5696.

[7] Yoshida, M.; Mitsuhashi, K.; Kimura, T.; Takeuchi, K.; Fukuyo, E., Yanagi, K. *Chem. Lett.* **1992**, 1771.

[8] (a) Takeuchi, K.; Akiyama, F.; Ikai, K.; Shibata, T.; Kato, M. *Tetrahedron Lett.* **1988**, *29*, 873. (b) Takeuchi, K.; Yoshida, M.; Ohga, Y.; Tsugeno, A.; Kitagawa, T. *J. Org. Chem.* **1990**, *55*, 6063. (c) Takeuchi, K.; Kitagawa, T.; Ohga, Y.; Yoshida, M.; Akiyama, F.; Tsugeno, A. *J. Org. Chem.* **1992**, *57*, 280.

[9] Cimarusti, C. M.; Wolinsky, J. *J. Am. Chem. Soc.* **1968**, *90*, 113.

[10] Duddeck, H.; Wolff, P. *Org. Magn. Reson.* **1977**, *9*, 528.

[11] Greenwald, R.; Chaykovsky, M.; Corey, E. J. *J. Org. Chem.* **1963**, *28*, 1128.

[12] Compound **1b** was a stable solid (mp 111.5–112.0 °C) and showed satisfactory microanalytical and spectral data: see ref 8a.

[13] An unidentified product amounting to 6% was also detected in addition to **4c** and **12**.

[14] Creary, X. *Acc. Chem. Res.* **1985**, *18*, 3.

Table I. Rate Data for the Solvolyses of 3-Oxo and 3-Methylene Bridgehead Compounds in Various Solvents[a]

compd	solvent	temp (°C)	k_1 (s^{-1})[b]	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
3b	EtOH	25.0	1.41×10^{-4} [c]	22.6	−0.2
		0.0	3.89×10^{-6} [c]		
	80% EtOH	25.0	2.92×10^{-3} [d]	20.9	0.0
		40.0	1.66×10^{-2} [d]		
	60% EtOH	25.0	1.52×10^{-2} [d]		
	MeOH	25.0	7.48×10^{-4} [d]		
	90% MeOH	25.0	2.50×10^{-3} [d]		
4b	EtOH	25.0	1.06×10^{-4} [c]	22.1	−2.5
		0.0	3.17×10^{-6} [c]		
	80% EtOH	25.0	2.43×10^{-3} [d]	21.1	0.2
		40.0	1.40×10^{-2} [d]		
	60% EtOH	25.0	1.14×10^{-2} [d]	19.9	−0.7
		40.0	5.97×10^{-2} [d]		
	MeOH	25.0	5.46×10^{-4} [c]	20.8	−3.5
		40.0	3.09×10^{-3} [d]		
	TFE	25.0	1.02×10^{-3} [d,e]	22.4	3.1
		40.0	6.57×10^{-3} [d,e]		
	80% acetone	25.0	2.63×10^{-3} [d]	19.6	−4.5
		40.0	1.35×10^{-2} [d]		
	60% acetone	25.0	1.40×10^{-2} [d]	19.3	−2.1
		40.0	7.02×10^{-2} [d]		
5b	EtOH	25.0	1.72×10^{-5} [c]	24.9	3.2
		50.0	4.81×10^{-4} [c]		
	80% EtOH	25.0	1.06×10^{-3} [d]	21.8	0.9
		40.0	6.47×10^{-3} [d]		
	60% EtOH	25.0	8.61×10^{-3} [d]	21.3	3.4
		40.0	5.05×10^{-2} [d]		
	MeOH	25.0	1.36×10^{-4} [d]	23.8	3.5
		40.0	9.75×10^{-4} [d]		
	TFE	25.0	1.27×10^{-2} [d,e]	19.0	−3.6
		40.0	6.17×10^{-2} [d,e]		
	80% acetone	25.0	9.95×10^{-4} [d]	20.4	−3.7
		40.0	5.45×10^{-3} [d]		
	60% acetone	25.0	9.70×10^{-3} [d]	19.4	−2.6
		40.0	4.89×10^{-2} [d]		

[a] Buffered with 0.025 M 2,6-lutidine except in TFE. [b] Determined by a single run. In all cases the correlation coefficient for the first-order plot was greater than 0.999. [c] Determined titrimetrically on 0.020 M substrate within an experimental error of ±2%. [d] Determined conductimetrically on 2×10^{-4} M substrate within an experimental error of ±0.5%. [e] Buffered with 1.2×10^{-3} M 2,6-lutidine.

Table II. Rate Data for the Solvolyses of 2-oxo, 2-Methylene, and Parent Bridgehead Compounds in 80% Ethanol[a]

compd	temp (°C)	k_1 (s^{-1})[b]	$\Delta H^{\ddagger}$ (kcal/mol)	$\Delta S^{\ddagger}$ (eu)
1b	25.0	4.54×10^{-10} [c]	30.6	1.3
	75.0	8.73×10^{-7} [d]		
	100.0	1.79×10^{-5} [d]		
2b	25.0	1.99×10^{-5} [d]	24.5	2.0
	50.0	5.24×10^{-4} [d]		
6b	25.0	0.60[c]	19.4	5.4
	5.15	5.37×10^{-2} [e]		
	−3.30	1.79×10^{-2} [e]		
	−10.30	6.43×10^{-3} [e]		
7b	25.0	0.15[c]	18.8	1.0
	15.10	5.06×10^{-2} [e]		
	5.15	1.47×10^{-2} [e]		
	−3.30	5.01×10^{-3} [e]		

[a] Buffered with 0.025 M 2,6-lutidine. [b] Determined by a single run. In all cases the correlation coefficient for the first-order plot was greater than 0.999. [c] Extrapolated from data at other temperatures. [d] Determined titrimetrically on 0.020 M substrate within an experimental error of ±2%. [e] Determined conductimetrically on 2×10^{-4} M substrate within an experimental error of ±0.5%.

Scheme V

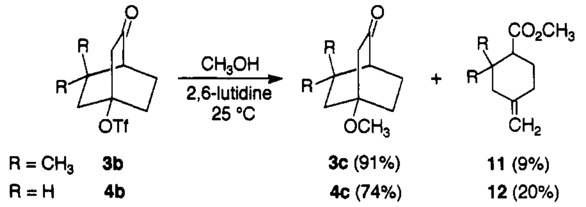
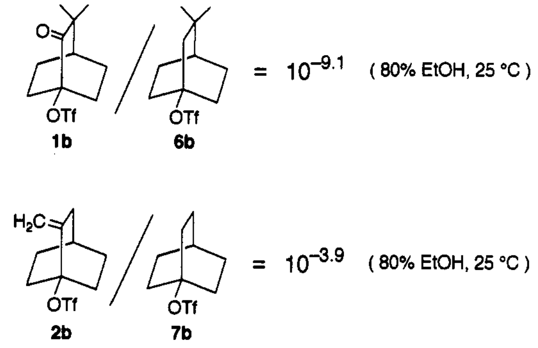


Chart I



(27 atom % ^{18}O) in the presence of excess 2,6-lutidine for 10 half-lives at 25 °C, and the ^{18}O content at the carbonyl group in the methyl ether product (**3c**) was determined by comparing the intensities of the mass spectral peaks at M (182) and M + 2 (184). The intensity ratio M:(M + 2) was 100:1.1, which was consistent with the theoretical natural abundance.[15] If **3b** had solvolyzed via the carbonyl addition process, the intensity of M + 2 relative to M would have been higher than that of the natural abundance because of the incorporation of ^{18}O in the carbonyl group. In addition, control experiments starting with **3c** enriched at the carbonyl oxygen (**3c-^{18}*O***, M:(M + 2) = 100:33.5[16]) showed no exchange during workup (see Experimental Section). Consequently, the involvement of the carbonyl addition process was ruled out.

Another possible mechanism for the solvolysis of **3b** is the solvolysis of the enol form of the triflate,[14] 5,5-dimethyl-3-hydroxybicyclo[2.2.2]oct-2-en-1-yl triflate. In order to determine if this mechanism was involved, the solvolysis of **3b** was conducted in methanol-d_4 in the presence of excess 2,6-lutidine for 10 half-lives at 25 °C in an NMR tube. If **3b** had solvolyzed via the enolization process, deuterium would have been incorporated at the C(2) position of the methyl ether product (**3c-*d*$_3$**). However, the integrals for the ^1H NMR spectrum showed no incorporation of deuterium (<5%) in the C(2) position of **3c-*d*$_3$**. Therefore, the involvement of the enolization process was ruled out.

Discussion

Effect of the 3-Oxo Substituent on the Solvolysis Rates. In 80% ethanol at 25 °C, the 2-oxo and 2-methylene compounds solvolyzed more slowly than the corresponding parent compounds (Chart I); the rate ratios were $10^{-9.1}$ (**1b**/**6b**) and $10^{-3.9}$ (**2b**/**7b**), respectively.[17] Since the π system in **1b** and **2b** is essentially perpendicular to the developing cationic p orbital, the rate decelerations were ascribed to the purely inductive effect of the 2-oxo and 2-methylene substituents.[8a,18] Consequently, the 2-oxo

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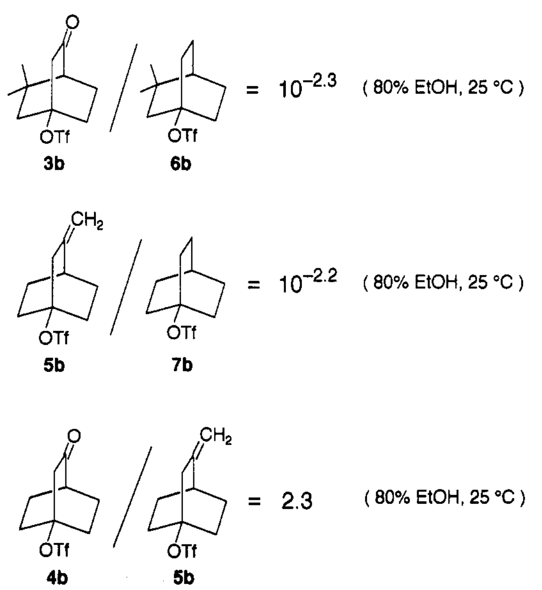
(15) The theoretical natural abundance ratio M:(M + 2) is 100:1.1: Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. In *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 1963. The observed intensity ratio M:(M + 2) for **3c** without enrichment of ^{18}O was 100:1.2, showing little experimental error in the experiment.

(16) If **3c** were completely enriched by 27 atom % ^{18}O, the intensity ratio M:(M + 2) would be (100−27):(1.1 + 27) = 100:38.5.

(17) The rate ratios **1b**/**6b** and **2b**/**7b** in ethanol at 25 °C are $10^{-8.4}$ and $10^{-3.9}$, respectively: see ref 8a.

(18) However, see: Creary, X. *Chem. Rev.* **1991**, *91*, 1625.

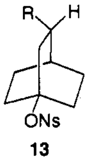
Chart II



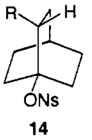
substituent is markedly more electron withdrawing than the 2-methylene substituent.

In contrast, when the oxo or the methylene substituent was attached to the C(3) position, the rate-decelerating effects were comparable, as evidenced by the rate ratios for **3b**/**6b** ($10^{-2.3}$) and **5b**/**7b** ($10^{-2.2}$) in 80% ethanol at 25 °C (Chart II). Moreover, a comparison of the rate of solvolysis of 3-oxo compound **4b** with that of the corresponding 3-methylene compound **5b** resulted in a rate ratio of 2.3 for **4b**/**5b** in 80% ethanol at 25 °C. In this case, the 3-oxo substituent appeared to be less electron withdrawing than the 3-methylene substituent with respect to the cationic center. Since the 3-oxo substituent does not appear to exert any steric acceleration, the unexpectedly fast rates for the 3-oxo compounds could be ascribed to the electronic effect. As the most probable interpretation of these results, we adopt the through-bond electron donation from the carbonyl lone pair to the developing cationic p orbital[2] as shown in Scheme II.

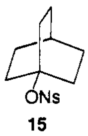
Quantitative Evaluation of the Through-Bond Stabilization. For the purpose of quantitative evaluation of the unexpectedly fast solvolysis rate of **3b**, we compared the rate ratios **3b**/**6b** and **5b**/**7b** to the ratios **1b**/**6b** and **2b**/**7b**, respectively, in a logarithmic plot of the rate ratios **13**/**15** against **14**/**15** (Figure 1). These particular rate ratios were employed to cancel out the effects of the dimethyl substituent and the leaving group. The rate data for the solvolyses of bicyclo[2.2.2]oct-1-yl *p*-nitrobenzenesulfonates **13** and **14** in 80% ethanol have been reported by Grob and his co-workers for 10 substituents at C(2) or C(3) position, and the rates have been found to be controlled only by the inductive effect of the substituent R.[19]



13



14



15

ONs; $p\text{-}NO_2C_6H_4SO_3$

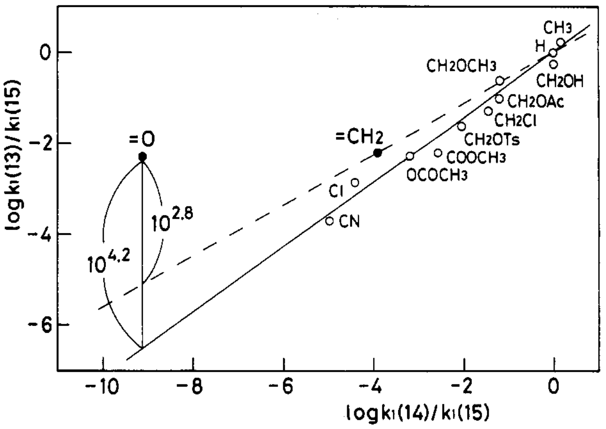


Figure 1. Plot of log $k_1(\mathbf{13})/k_1(\mathbf{15})$ vs log $k_1(\mathbf{14})/k_1(\mathbf{15})$ for the solvolysis in 80% ethanol at 25 °C. Closed circles indicated by =O and $=CH_2$ stand for the plots of log $k_1(\mathbf{3b})/k_1(\mathbf{6b})$ vs log $k_1(\mathbf{1b})/k_1(\mathbf{6b})$ and log $k_1(\mathbf{5b})/k_1(\mathbf{7b})$ vs log $k_1(\mathbf{2b})/k_1(\mathbf{7b})$, respectively. For the rate data for **13**–**15**, see ref 19.

As Figure 1 shows, the point for the methylene compounds conforms fairly well to the plot, indicating that the methylene group can be treated as an ordinary electron-withdrawing substituent. In contrast, the point for the oxo compounds deviates significantly upward. The most reasonable explanation for the upward deviation is the unexpectedly fast solvolysis rate of **3b**. The deviation from the regression line indicates a rate enhancement of $10^{4.2}$ in 80% ethanol at 25 °C. When a straight line passing through the points for R = H and for methylene is used (see Figure 1), the enhancement is evaluated to be $10^{2.8}$. When the rate ratio **4b**/**7b** is plotted in the place of **3b**/**6b**, the rate acceleration of **4b** is evaluated to be $10^{3.3}$–$10^{4.7}$. Consequently, we estimate that the through-bond stabilization of the incipient 3-oxobicyclo[2.2.2]oct-1-yl cation amounts to a solvolysis rate factor of 10^3–10^4, which corresponds to a 4–5 kcal/mol stabilization.

Solvolysis Intermediates. The most notable feature of the methanolyses of the 3-oxo compounds (**3b** and **4b**) is that the fragmentation products (**11** and **12**) are formed in addition to the normal substitution products (**3c** and **4c**). Since 3-methylene compound **5b** gives only normal substitution product **5c**, the fragmentation observed for the oxo compounds indicates that the C(2)–C(3) σ bond is weakened by the special electronic effect of the 3-oxo substituent, i.e., the through-bond interaction.[20] Recent quantum mechanical calculations by Carrupt and Vogel on the 3-oxobicyclo[2.2.2]oct-1-yl cation supported the weakening of the C(2)–C(3) σ bond by a through-bond interaction.[6] A similar fragmentation that occurs concurrently with the electrophilic addition of 2,4-dinitrobenzenesulfenyl chloride to the C=C bond of bicyclo[2.2.1]hept-5-en-2-one has been explained in terms of the through-bond interaction.[2c,21] Consequently, fragmentation product **11** is most probably formed via acyl cation **17**, which is generated from bridgehead cation **16** as shown

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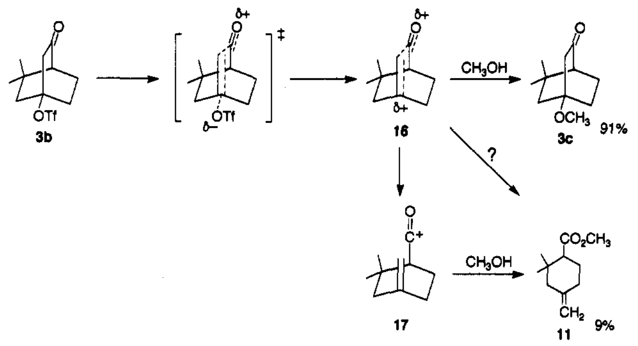
[19] Bielmann, R.; Grob, C. A.; Küry, D.; Yao, G. W. *Helv. Chim. Acta* **1985**, *68*, 2158.

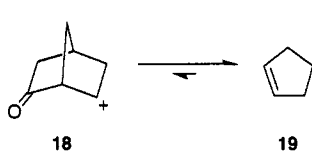
[20] For the theoretical study of a fragmentation caused by through-bond interaction, see: Gleiter, R. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 696.

[21] The reported formation of a fragmentation product in other reactions can also be explained similarly. The acetolysis of 3,3-dimethyl-2-oxobicyclo[2.2.1]hept-7-yl tosylate gives (Δ^2-cyclopentenyl)-2,2-dimethylacetic acid in 67% yield: Gassmann, P. G.; Hornback, J. M. *J. Am. Chem. Soc.* **1969**, *91*, 5817. It has also been reported that the reaction of 4-methyl-3-oxobicyclo[2.2.2]oct-1-yl tosylate with titanium tetrachloride gives 4-methylene-1-methylcyclohexanecarbonyl chloride in trace amounts: Kraus, W.; Gräf, H.-D. *Angew. Chem.* **1975**, *87*, 878.

Scheme VI



Scheme VII



in the mechanism in Scheme VI. The formation of acyl cation **17** from bridgehead cation **16** is supported by the results of ab initio MO calculations by Carrupt and Vogel, in which the acyl cation **19** was found to be 11.3 kcal/mol more stable than cation **18** (Scheme VII).[22,23] Direct formation of **17** from **3b** appears unlikely since **11** is a minor product. The formation of **11** by direct capture of **16** by solvent might also be occurring, but there is no evidence to support such a mechanism.

Effect of Solvent on Solvolysis Rates. The mY relationship provides useful information about the solvolysis mechanisms.[24] In Figure 2 are shown the correlations of the logarithms of the solvolysis rates for **3b**, **4b**, and **5b** in various solvents (EtOH, MeOH, TFE, aqueous EtOH, aqueous MeOH, and aqueous acetone) at 25 °C vs $Y_{\text{2-AdOTf}}$.[25]

The linearity of the $mY_{\text{2-AdOTf}}$ relationship ($r = 0.999$) for 3-methylene compound **5b** over all the solvents shows the S_N1 nature of the solvolysis of **5b**: the m value is 0.97 and allows the solvolysis of the 3-methylene compound to be classified as a k_C process. The correlations for 3-oxo compounds **3b** and **4b** give nicely linear $mY_{\text{2-AdOTf}}$ relationships (**3b**, $r = 0.999$; **4b**, $r = 1.000$) (excluding the trifluoroethanol data). The linearity provides a piece of evidence for the S_N1 nature of the solvolyses of **3b** and **4b**. The m values for **3b** and **4b** are 0.74 and 0.75, respectively. These values are somewhat smaller than the value for 3-methylene compound **5b**. It has been proposed that substrates reacting by neighboring group participation (k_Δ process) give m values significantly smaller than 1.00, probably because of delocalization of positive charge.[26] Therefore, the smaller m values for **3b** and **4b** are

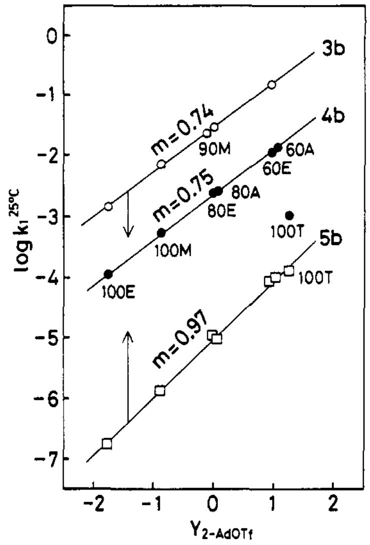


Figure 2. Plots of log k_1 for solvolyses of **3b**, **4b**, and **5b** vs $Y_{\text{2-AdOTf}}$ at 25 °C. Open circles are for **3b** ($r = 0.999$) shifted upward by 1 unit. Closed circles are for **4b** ($r = 1.000$). Open squares are for **5b** ($r = 0.999$) shifted downward by 2 units. A, E, M, and T stand for acetone, ethanol, methanol, and TFE, respectively, and the attached numbers correspond to their vol percentages in aqueous solutions.

presumably attributed to delocalization of the positive charge to the 3-oxo group by means of the through-bond interaction. It is also notable that the trifluoroethanol point for 3-oxo compound **4b** deviates downward from the correlation line. This deviation can probably be ascribed to destabilization of the intermediate carbocation by a hydrogen-bonding interaction between the carbonyl oxygen and trifluoroethanol (pK_a 12.37[27]). Such a hydrogen-bonding interaction of a highly acidic solvent with a carbonyl oxygen has been demonstrated by the IR absorption shift for the carbonyl stretching vibration of camphor in hexafluoro-2-propanol.[28] Similar hydrogen-bonding interactions with ether oxygen,[29] sulfur,[30] and amino nitrogen[30] have also been reported to cause deviations in mY.

Through-Bond Interaction in the Ground State. Duddeck and Wolff reported the interaction between the substituent X and the carbonyl group of 3-oxobicyclo[2.2.2]oct-1-yl compound **20** on the basis of the ^{13}C NMR chemical shifts.[10] The discrepancies between the observed and the calculated[31] chemical shifts ($\Delta\delta = \delta_{\text{obs}} - \delta_{\text{calc}}$) of C(1) and C(3) for X = Br were −11.7 and −8.5 ppm, respectively. These values were more negative than those of C(5,8) (−0.5 ppm). Duddeck and Wolff concluded that these results could be attributed to "a special interaction between the substituent X and the carbonyl group via σ bond framework." [10,32]

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[22] Carrupt, P.-A.; Vogel, P. *J. Phys. Org. Chem.* **1988**, *1*, 287.

[23] AM1 semiempirical molecular orbital calculations on (4-methylenecyclohex-1-yl)carbonyl cation with a twist-boat structure showed that this cation is more stable by 9 kcal/mol than 3-oxobicyclo[2.2.2]oct-1-yl cation, with respect to their heats of formation (158.4 and 167.3[6] kcal/mol, respectively). More rigorous calculations on the fragmentation pathway would be required.

[24] Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1.

[25] The $Y_{\text{2-AdOTf}}$ values for EtOH, MeOH, TFE, 80% EtOH, 60% EtOH, 90% MeOH, 80% acetone, and 60% acetone are −1.756, −0.878, 1.227, 0, 0.948, −0.098, 0.04, and 1.03, respectively, see: (a) Kevill, D. N.; Anderson, S. W. *J. Org. Chem.* **1985**, *50*, 3330. (b) Bentley, T. W.; Roberts, K. *J. Org. Chem.* **1985**, *50*, 4821.

[26] Bentley, T. W.; Llewellyn, G. In *Progress in Physical Organic Chemistry*; Taft, R. W., Ed.; John Wiley & Sons: New York, 1990; Vol. 17, pp 121–158 and references cited therein.

[27] Ballinger, P.; Long, F. A. *J. Am. Chem. Soc.* **1959**, *81*, 1050.

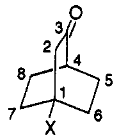
[28] Laurence, C.; Berthelot, M.; Lucon, M.; Helbert, M.; Morris, D. G.; Gal, J.-F. *J. Chem. Soc., Perkin Trans. 2* **1984**, 705.

[29] Jursic, B.; Ladika, M.; Sunko, D. E. *Tetrahedron* **1986**, *42*, 911.

[30] McManus, S. P.; Sedaghat-Herati, M. R.; Karaman, R. M.; Neamati-Mazraeh, N.; Cowell, S. M.; Harris, J. M. *J. Org. Chem.* **1989**, *54*, 1911.

[31] The calculated chemical shifts were obtained by means of a simple additivity rule: see ref 10.

[32] For other examples and detailed discussion, see: Duddeck, H.; Feuerhelm, H.-T. *Tetrahedron* **1980**, *36*, 3009.



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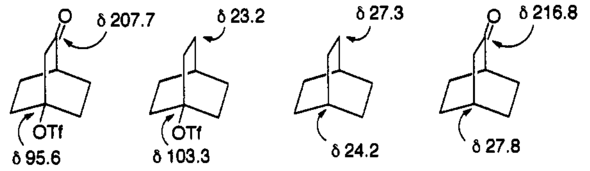
We applied this methodology to the examination of the through-bond interaction in our system. The Δδ values of C(1) and C(3) for 3-oxo compound **4b** were calculated



4b **7b**

by means of the ^{13}C NMR chemical shifts of **4b**, **7b**, bicyclo[2.2.2]octane, and bicyclo[2.2.2]octanone. The Δδ values of C(1) and C(3) for **4b** were calculated to be −11.3 and −5.0 ppm from eqs 1 and 2, respectively.

$$\Delta\delta(\text{ppm}) = 95.6 - (27.8 + 103.3 - 24.2) = -11.3 \quad (1)$$

$$\Delta\delta(\text{ppm}) = 207.7 - (216.8 + 23.2 - 27.3) = -5.0 \quad (2)$$

Interestingly, these Δδ values show the same large negative shift mentioned by Duddeck and Wolff. These results indicate a special interaction between the leaving group OTf and the carbonyl gorup via the σ bond framework. Presumably, the through-bond interaction in **4b** is at work not only in the transition state of the ionization but also in the ground state.

The ground-state stability might contribute to the rapid solvolysis of **4b**. However, the C(1) carbon in the transition state for the ionization of **4b** is much more positive than that in the ground state, resulting in the greater contribution of the through-bond interaction in the transition state than in the ground state. In addition, recent quantum mechanical calculations by Carrupt and Vogel on 3-oxobicyclo[2.2.2]oct-1-yl and related cations supported the remarkable through-bond stabilization in the transition state of the ionization of **4b**.[6] Consequently, although the through-bond interaction in **4b** is effective not only in the transition state of the ionization but also in the ground state, the ground-state stability is probably a small factor in determining the rate of formation of the carbocation.

Experimental Section

Melting points are uncorrected. IR spectra were recorded on a Hitachi 215 spectrophotometer. ^{1}H NMR spectra were recorded on a Hitachi R-24 (60 MHz) or JEOL FX90A (89.55 MHz) spectrometer. ^{13}C NMR spectra were obtained on a JEOL FX90A (22.5 MHz) spectrometer. In all NMR measurements TMS was used as an internal standard. Mass spectra were recorded on a JEOL JMS-01SG spectrometer. Elemental analyses were performed by the Microanalytical Center, Kyoto University, Kyoto. Triflates **1b**, **2b**, **6b**, and **7b** were described previously.[8] 1-Acetoxy-8,8-dimethylbicyclo[2.2.2]oct-2-en-5-one[9] (**8**) and 4-hydroxybicyclo[2.2.2]octan-2-one[10] (**4a**) were prepared according to literature procedures. Ethanol and methanol were refluxed over the corresponding magnesium alkoxides and distilled. Acetone and trifluoroethanol were stored over 4- and 5-Å sieves, respectively, and distilled. All the anhydrous solvents used for synthetic work were purified by standard procedures. The purities of the unstable substrates for rate studies were generally higher than 97% on the basis of their ^{13}C NMR spectra. Commercially available methyltriphenylphosphonium bromide was dried at 95–100 °C in vacuo for 1 h before use. Other commercially available reagents were of a reagent-grade quality and used as received. Medium-pressure liquid chromatography (MPLC) was conducted on Merck silica gel (230–400 mesh).

1-Acetoxy-5,5-dimethylbicyclo[2.2.2]octan-3-one (9). A mixture of 1-acetoxy-8,8-dimethylbicyclo[2.2.2]oct-2-en-5-one[9] (**8**) (2.15 g, 10.3 mmol) and palladium-on-carbon (0.18 g, 10%) in ethyl acetate (30 mL) was placed in a hydrogenation vessel, and the mixture was vigorously stirred under hydrogen. The hydrogenation was complete in 30 min. After the reaction mixture had been filtered, the ethyl acetate was removed by rotary evaporation to give **9** (2.15 g, 99%) as a pale yellow liquid: ^{1}H NMR (60 MHz, CCl_4) δ 0.93 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 1.5–2.2 (m, 7 H), 1.91 (s, 3 H, CH_3 of acetate), 2.57 (s, 2 H).

6,6-Dimethyl-4-hydroxybicyclo[2.2.2]octan-2-one (3a). A solution of **9** (2.02 g, 9.61 mmol) and KOH (1.10 g, 19.6 mmol) in 90% MeOH (60 mL) was stirred at room temperature for 12 h. After most of the methanol had been evaporated, $CHCl_3$ (40 mL) was added. The aqueous layer was extracted with $CHCl_3$ (3 × 10 mL). The combined extracts were dried ($MgSO_4$) and evaporated to give a white semisolid (1.74 g). Adding pentane (15 mL) to the semisolid and scratching afforded **3a** (1.53 g, 94%) as white crystals. An analytical sample was obtained by sublimation of the crystals at 85–90 °C (2 mmHg): mp 158.5–159.5 °C (after sublimation); IR (CCl_4) 3600, 3450 br, 1720, 1330, 1085 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 0.90 (s, 3 H, CH_3), 1.10 (s, 3 H, CH_3) 1.3–1.9 (m, 7 H), 2.17 (s, 2 H), 3.50 (br, 1 H, OH); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 31.0, 70.2 (C), 53.4 (CH), 18.4, 30.8, 49.1, 49.6 (CH_2), 28.5, 31.1 (CH_3), 214.1 (C=O). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.28; H, 9.89.

5,5-Dimethyl-3-oxobicyclo[2.2.2]oct-1-yl Triflate (3b). To a solution of **3a** (0.600 g, 3.57 mmol) and pyridine (0.593 g, 7.50 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added a solution of triflic anhydride (1.207 g, 4.28 mmol) in CH_2Cl_2 (10 mL) with stirring over 10 min, and then stirring was continued for 2.5 h. The reaction mixture was diluted with CH_2Cl_2 (10 mL), washed at 0 °C with water (3 × 20 mL), 5% aqueous HCl (5 × 20 mL), and water (3 × 20 mL), and dried ($MgSO_4$). Evaporation of solvent with a rotary evaporator afforded **3b** (0.937 g, 87%) as a pale yellow unstable oil, which was used for solvolysis studies without further purification: ^{1}H NMR (60 MHz, CCl_4) δ 1.00 (s, 3 H, CH_3), 1.17 (s, 3 H, CH_3), 1.5–2.4 (m, 7 H), 2.77 (s, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 31.7, 96.1 (C), 52.6 (CH), 18.2, 29.1, 46.7, 47.8 (CH_2), 28.4, 31.0 (CH_3) 117.7 (q, CF_3, J = 318 Hz), 207.3 (C=O).

3-Oxobicyclo[2.2.2]oct-1-yl Triflate (4b). The procedure described for the preparation of **3b** was followed. Treatment of 4-hydroxybicyclo[2.2.2]octan-2-one[10] (**4a**) (0.070 g, 0.499 mmol) with triflic anhydride (0.183 g, 0.649 mmol) and pyridine (0.083 g, 1.05 mmol) in CH_2Cl_2 (6 mL) at 0 °C for 3 h followed by the usual workup at 0 °C afforded **4b** (0.111 g, 82%) as a pale yellow oil, which was used for solvolysis studies without further purification: IR (CCl_4) 1735, 1405, 1240, 1210, 1140, 920 cm^{-1}; ^{1}H NMR (60 MHz, CCl_4) δ 1.2–2.7 (m, 9 H), 2.85 (s, 2 H); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 95.6 (C), 40.6 (CH), 22.0, 30.4, 49.6 (CH_2), 117.9 (q, CF_3, J = 319 Hz), 207.7 (C=O).

3-Oxobicyclo[2.2.2]oct-1-yl Trimethylsilyl Ether (10). Affording to a procedure described for the trimethylsilylation of 2-hydroxy-2-methylpentan-3-one,[33] a solution containing 4-hydroxybicyclo[2.2.2]octan-2-one[10] (**4a**) (0.400 g, 2.85 mmol) and *N*,*O*-bis(trimethylsilyl)acetamide (0.872 g, 4.29 mmol) in CH_3CN (4.3 mL) was heated at reflux for 3 h under N_2. After evaporation of solvent, the crude product was subjected to MPLC (SiO_2, hexane–ether (9:1)) to give **10** (0.500 g, 83%) as a pale yellow oil: ^{1}H NMR (60 MHz, CCl_4) δ 0.20 (s, 9 H), 1.4–2.3 (m, 11 H).

3-Methylenebicyclo[2.2.2]octan-1-ol (5a). Trimethylsilyl ether **10** (0.500 g, 2.35 mmol) was treated in DMSO (13 mL) with methylenetriphenylphosphorane, which was generated from methyltriphenylphosphonium bromide (1.68 g, 4.70 mmol) and NaH (60% dispersion, 0.188 g, 4.70 mmol) in DMSO, at 70 °C for 4 h under N_2. After the reaction mixture was cooled to 15

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(33) Young, S. D.; Buse, C. T.; Heathcock, C. T. *Organic Syntheses*; John Wiley & Sons: New York, 1990; Collect. Vol. VII, p 381.

°C, methanol (0.5 mL) was added. The reaction mixture was poured into ice–water (40 mL) and extracted with ether (4 × 30 mL). The combined extracts were washed with water (3 × 30 mL) and 10% aqueous NaCl (3 × 30 mL) and dried ($MgSO_4$). Evaporation of the ether followed by MPLC (SiO_2, hexane–ether (1:1)) gave **5a** (0.250 g, 77%) as a white powder: mp 57.0–58.0 °C (from pentane); IR (CCl_4) 3620, 3350 br, 1650, 1330, 1095, 925, 880 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 1.3–2.5 (m, 12 H), 4.53 (d, 1 H, J = 2.0 Hz), 4.70 (d, 1 H, J = 2.0 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 70.1, 150.5 (C), 34.8 (CH), 26.8, 33.4, 42.9, 105.5 (CH_2). Analytical data were unsatisfactory probably because of the highly sublimating nature. Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.69; H, 10.46.

3-Methylenebicyclo[2.2.2]oct-1-yl Triflate (5b). The procedure described for the preparation of **3b** was followed. Treatment of **5a** (0.150 g, 1.09 mmol) with triflic anhydride (0.371 g, 1.31 mmol) and pyridine (0.181 g, 2.29 mmol) in CH_2Cl_2 (6 mL) at 0 °C for 2 h followed by the usual workup at 0 °C afforded **5b** (0.251 g, 85%) as a pale yellow, unstable oil, which was used for solvolysis studies without further purification: ^1H NMR (60 MHz, CCl_4) δ 1.5–2.5 (m, 9 H), 2.90 (s, 2 H), 4.65 (d, 1 H, J = 1.0 Hz), 4.80 (d, 1 H, J = 1.0 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 100.6, 147.2 (C), 33.8 (CH), 27.1, 31.2, 40.8, 107.4 (CH_2), 118.0 (q, CF_3, J = 320 Hz).

Product of Solvolysis of 3b in Methanol: A Typical Procedure. A solution of **3b** (0.876 g, 2.92 mmol) in 0.050 M 2,6-lutidine in methanol (73.0 mL) was kept at 25.0 °C in a constant temperature bath for 2.8 h (10.9 half-lives). Analysis of the reaction mixture by GLC (PEG 20M, 3 mm × 2 m) showed the formation of two products (91%, 9%). After most of the methanol had been removed with a rotary evaporator, the residue was dissolved in ether (100 mL). The ether solution was washed with 10% aqueous NaCl (50 mL), 10% aqueous HCl (50 mL), 10% aqueous NaCl (50 mL), and saturated aqueous $NaHCO_3$ (50 mL) and dried ($MgSO_4$). Evaporation of the ether afforded a pale yellow liquid. MPLC (SiO_2, hexane–ether (9:1, 7:3)) gave methyl 2,2-dimethyl-4-methylenecyclohexanecarboxylate (**11**) (0.034 g, 6.4%) and 6,6-dimethyl-4-methoxybicyclo[2.2.2]octan-2-one (**3c**) (0.360 g, 68%), both as colorless liquids, in that order. The low yields of the products were due to their high volatility. **3c**: ^1H NMR (60 MHz, CCl_4) δ 0.93 (s, 3 H, CH_3), 1.12 (s, 3 H, CH_3), 1.3–2.4 (m, 9 H), 3.10 (s, 3 H, OCH_3); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 30.6, 74.8 (C), 53.4 (CH), 18.3, 27.0, 45.0, 45.8 (CH_2), 28.7, 31.3, 49.2 (CH_3), 212.6 (C=O). **11**: IR (CCl_4) 3015, 1735, 1650, 1155, 895 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 0.85 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3), 1.5–2.5 (m, 7 H), 3.55 (s, 3 H, OCH_3), 4.50 (d, 1 H, J = 1.0 Hz), 4.60 (d, 1 H, J = 1.0 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 34.5, 145.6 (C), 50.9 (CH), 26.0, 33.2, 49.2, 109.2 (CH_2), 21.4, 29.8, 51.9 (CH_3), 174.8 (C=O).

Product of Solvolysis of 4b in Methanol. From **4b** (0.694 g, 2.55 mmol) in 0.050 M 2,6-lutidine in methanol (63.7 mL) at 25.0 °C for 3.7 h (10.4 half-lives) was obtained a pale yellow oil. MPLC (SiO_2, hexane–ether (9:1, 7:3)) afforded methyl 4-methylenecyclohexanecarboxylate (**12**) (0.040 g, 10%) as a colorless liquid and 4-methoxybicyclo[2.2.2]octan-2-one (**4c**) (0.091 g, 23%) as a pale yellow liquid, in that order. The low yields of the products were due to their high volatility. The spectral data of **4c**[10] and **12**[34] were consistent with reported data.

Product of Solvolysis of 5b in Methanol. From **5b** (0.064 g, 0.237 mmol) in 0.050 M 2,6-lutidine in methanol (5.9 mL) at 25.0 °C for 22 h (15.5 half-lives) was obtained 1-methoxy-3-methylenebicyclo[2.2.2]octane (**5c**) (0.020 g, 55%) as a colorless liquid. The low yield of the product was due to its high volatility: ^1H NMR (60 MHz, CCl_4) δ 1.3–2.6 (m, 11 H), 3.07 (s, 3 H, CH_3), 4.48 (d, 1 H, J = 2.0 Hz), 4.64 (d, 1 H, J = 2.0 Hz); ^{13}C NMR (22.5 MHz, $CDCl_3$) δ 74.4, 150.5 (C), 49.0 (CH), 26.7, 29.0, 38.6, 105.7 (CH_2), 34.8 (CH_3).

Natural Abundance of ^{18}O for 6,6-Dimethyl-4-methoxybicyclo[2.2.2]octan-2-one (3c). The natural abundance of ^{18}O for **3c** was determined by analysis of the mass spectral peaks at M (182) and M + 2 (184); the intensity ratio M:(M + 2) was 100:1.2 (theoretical ratio is 100:1.1[15]).

6,6-Dimethyl-4-methoxybicyclo[2.2.2]octan-2-one Containing Oxygen-18 at Carbonyl Site (3c-^{18}O). A mixture of **3c** (0.253 g, 1.39 mmol) in hexane (5.0 mL) and 5% H_2SO_4–95% $H_2{}^{18}O$ (27 atom % ^{18}O) (1.6 mL) was heated at reflux for 20 h. The hexane layer was separated, and then the aqueous layer was extracted with ether (2 × 5 mL). To the combined extracts was added a small amount of solid $NaHCO_3$, and the mixture was dried ($MgSO_4$). Evaporation of solvent with a rotary evaporator afforded **3c-^{18}O** (0.217 g, 86%) as a colorless liquid. The isotopic composition of the product was determined by analysis of the mass spectral peaks at M (182) and M + 2 (184), whose ratio was 100:33.5.

Product of Solvolysis of 3b in 90% MeOH–10% $H_2{}^{18}O$ (27 Atom % ^{18}O). A solution of **3b** (0.565 g, 1.88 mmol) in 0.100 M 2,6-lutidine in 90% MeOH–10% $H_2{}^{18}O$ (27 atom % ^{18}O) (23.52 mL) was kept at 25.0 °C in a constant temperature bath for 70 min (15.1 half-lives). After ether (80 mL) had been added, the mixture was washed with saturated aqueous NaCl (3 × 80 mL) and dried ($MgSO_4$). After evaporation of solvent, the crude product was subjected to MPLC (SiO_2, hexane–ether (9:1, 7:3)) to give **11** (0.016 g, 4.7%) as a colorless liquid, a mixture (0.224 g) of **3c** and 2,6-lutidine (86:14 in mol) as a colorless liquid, and **3a** (0.039 g, 12%) as a white powder, in that order. The isotopic composition of **3c** (containing 2,6-lutidine) was determined by analysis of the mass spectral peaks at M (182) and M + 2 (184); the intensity ratio M:(M + 2) was 100:1.1, showing no incorporation of ^{18}O in the carbonyl group.

Control Experiment for Workup in Product Study. Compound **3c-^{18}O** (M:(M + 2) = 100:33.5) in ether (15 mL) was washed with saturated aqueous NaCl (2 × 10 mL) and dried ($MgSO_4$). The ether was evaporated, and the residual liquid was passed through a MPLC column (SiO_2, hexane–ether (9:1, 7:3)) to give **3c-^{18}O** (0.157 g, 84%). The isotopic composition of the obtained **3c-^{18}O** was determined by analysis of the mass spectral peaks at M (182) and M + 2 (184); the intensity ratio M:(M + 2) was 100:36.8, showing no exchange of the enriched carbonyl oxygen during workup.

Product of Solvolysis of 3b in Methanol-d_4. Compound **3b** (0.068 g, 0.226 mmol) and 2,6-lutidine (0.060 g, 0.560 mmol) were dissolved in methanol-d_4 (1 mL) in an NMR tube. After 155 min (10.0 half-lives) at 25 °C, the integrals for the ^1H NMR (89.55 MHz) spectrum showed no incorporation of deuterium (<5%) in the C(2) position of the produced methyl-d_3 ether **3c-d_3**.

Kinetic Studies. The preparation of solvents and kinetic methods were described previously.[35] Titrimetric measurements were conducted in the presence of 0.025 M 2,6-lutidine with 0.020 M substrate concentrations. Conductimetric measurements were conducted in the presence of 2,6-lutidine (1.2 × 10^{-3} M in trifluoroethanol and 0.025 M in the other solvents) with 2 × 10^{-4} M substrate concentrations. The first-order rate constants were calculated by the least-squares method on a microcomputer. The results are summarized in Tables I and II.

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Supplementary Material Available: ^1H NMR spectra for compounds **9** and **10** and ^{13}C NMR spectra for **3a, 3b, 4b, 5a, 5b, 3c, 5c,** and **11** (10 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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