alcohol are very similar. There are thus several good pieces of evidence to support the view that upon ionization of 3-phenyl-2-propen-1-ol isomerizes at least partly to the molecular ion of 3-phenylpropanal, possibly by the following route:

$$\underset{\text{I}}{(C_6H_5CH{=}CHCH_2OH)^{+\cdot}} \rightarrow \underset{\text{II}}{C_6H_5\dot{C}HCH_2CH{=}\overset{+}{O}H}$$

$$\swarrow$$

$$\underset{\text{III}}{(C_6H_5CH_2CH_2CHO)^{+\cdot}}$$

(Note that ion II is identical with one of the intermediates in Scheme II.) Considering decompositions in the same time window, it seems that ions III are slightly more excited than those generated directly from 3-phenylpropanal, since the ratio of the intensities of the metastable peaks in the first field-free region for the loss of C_2H_2O and of C_3H_4O are $\approx$150 for 3 phenyl-2-propen-1-ol and $\approx$200 for 3-phenylpropanal (AP m/e 78 − AP m/e 92 $\approx$ 1.4 eV in both cases).[23]

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Electroorganic Chemistry. 31. Reductive Cyclization of Nonconjugated Olefinic Ketones to Cyclic Tertiary Alcohols[1]

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Abstract: The electroreduction of a series of nonconjugated olefinic ketones in a mixed solvent of methanol and dioxane or in *N,N*-dimethylformamide gave intramolecular cycloaddition products, namely, cis-1,2-dialkyl alicyclic tertiary alcohols, in excellent yields. This reductive cyclization showed remarkable regio- and stereoselectivities, in which the reaction always took place between the inner carbon atom of the double bond and the carbonyl carbon atom, and the product was exclusively the cis isomer. Some bicyclic tertiary alcohols or nitrogen heterocycles were synthesized satisfactorily by this new cyclization.

The electrochemical reduction of organic compounds has been recognized as a promising method for the formation of a carbon–carbon bond.[2] For instance, the electroreductive coupling of a carbonyl group with ketones,[3] alkyl halides,[4] carbon dioxide,[4] activated olefins,[5,6] pyridine,[7] or cyanamide[8] has been reported to be a versatile tool to form a new carbon–carbon bond.

Although the reaction of organometallic reagents is also an effective method for bringing about carbon–carbon bond formation,[9] the attempts to synthesize cyclic tertiary alcohols by the intramolecular reactions of organometallic reagents formed from halo ketones are generally unsuccessful owing to the extreme difficulty of the generation of such organometallics.[10]

In the present study, we wish to describe a novel electrochemical method for syntheses of five- and six-membered cy-

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Table I. Electroreduction of Olefinic Ketones **1a–h** in MD Solvent

	Ketone 1		Yield, %[a]	
	R^1	R^2	**2**	**3**
1a	CH_3	H	98	0
b	C_2H_5	H	88	0
c	i-C_3H_7	H	89	0
d	n-C_4H_9	H	92	0
e	n-C_6H_{11}	H	90	0
f[b]	CH_3	CH_3	86	0
g[b]	CH_3	C_2H_5	78	5
h[b]	CH_3	i-C_3H_7	75	10

[a] Isolated. [b] The configuration of the olefinic part is trans.

Table II. Electroreduction of Olefinic Ketones **1f–k** in DMF

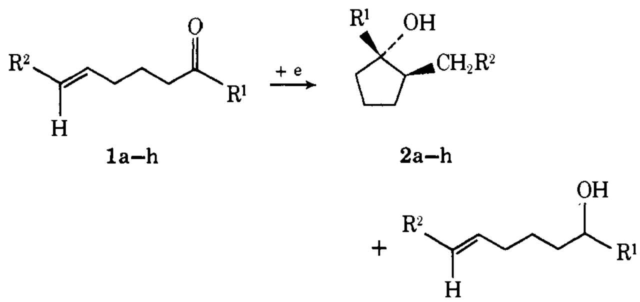
	Ketone 1		Yield, %[a]	
	R^1	R^2	**2**	**8**
1f	CH_3	H	77	0
g	C_2H_5	H	68	19
h	i-C_3H_7	H	71	15
i	CH_3	CH_3	54	19
j	C_2H_5	CH_3	23	18
k	i-C_3H_7	CH_3	26	37

[a] Isolated.

clic tertiary alcohols through the intramolecular cyclization of nonconjugated olefinic ketones initiated by the electron transfer from the electrode to the carbonyl group. This novel electroreductive cycloaddition is characterized by the remarkable regio- and stereoselectivities and excellent yields.

Results and Discussion

Reductive Cycloaddition Yielding a Five-Membered Ring. Cyclization in a Mixed Solvent of Methanol and Dioxane (MD Solvent). The electroreduction of a series of nonconjugated olefinic ketones **1a–h** in MD solvent containing tetraethylammonium *p*-toluenesulfonate (Et_4NOTs) as a supporting electrolyte was carried out with carbon rod electrodes under a constant current condition. *cis*-1,2-Dialkylcyclopentanols **2a–h** were isolated in excellent yields (Table I). The alkyl group

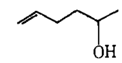
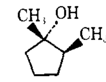
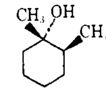
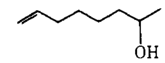
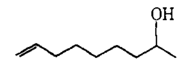
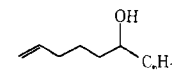


1a–h   2a–h   3a–h

on the terminal carbon atom of the starting olefinic ketones did not hinder the intramolecular cyclization, while the yield of **2g** or **2h** was slightly decreased and a small amount of the noncyclized product **3g** or **3h** was formed as the by-product. All the products mentioned hereafter were identified by spectroscopic (IR, NMR), gas chromatographic, and elemental analyses, and their stereochemistry was confirmed by comparison with the independently prepared samples.[11] The stereoselective formation of the cis isomer of the cyclic tertiary alcohols **2a–h** is quite interesting, since the corresponding alcohols prepared by the reaction of 2-alkylcyclopentanones with the Grignard reagents do not show any predominance in the formation of the cis isomer.

The formation of a six-membered ring from the cyclization

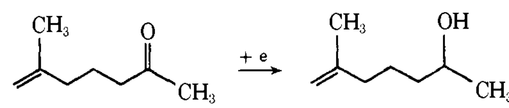
Table III. Electroreduction of $CH_2{=}CH(CH_2)_nCOR$ in MD Solvent

	Ketone		Product		Yield, %[a]
	R	*n*			
12	CH_3	2		**15**	33
1a	CH_3	3		**2a**	98
9	CH_3	4		**10**	70 (75)[b]
				**11**	8 (0)[b]
13	CH_3	5		**16**	25
14	C_6H_5	3		**17**	51

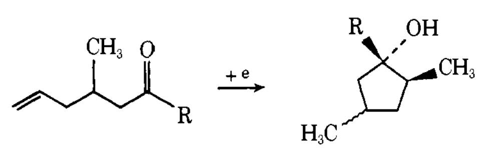
[a] Isolated. [b] In DMF.

of the starting olefinic ketones **1** may be another possible route. The results, however, clearly show that this cyclization always takes place regioselectively between the carbonyl carbon atom and the inner carbon atom of the double bond.

The alkyl substituent on the inner carbon atom of the double bond inhibited the cyclization, while the substituent located on the carbon atom between the double bond and the carbonyl group did not obstruct the cyclization.

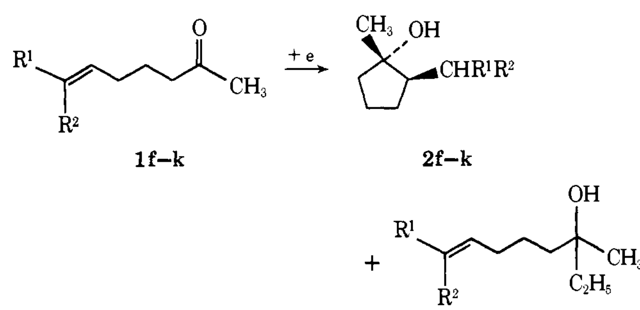


4   5 12%



6a, R = CH_3 7a 90%
b, R = i-C_3H_7 b 92%

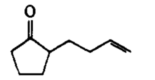
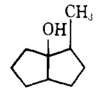
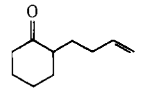
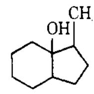
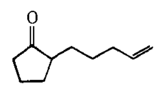
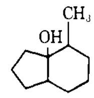
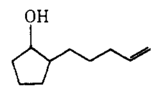
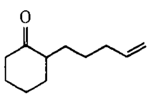
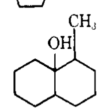
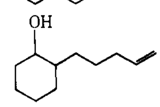
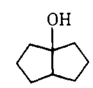
Cyclization in *N,N*-Dimethylformamide (DMF). The reduction in DMF using a diaphragm is another promising method to bring about the cyclization. The expected *cis*-1,2-dialkylcyclopentanols **2f–k** were obtained from **1f–k** as the main products in moderate to good yields (Table II). Noncyclized tertiary alcohols **8f–k** were also formed as by-products,



1f–k   2f–k   8f–k

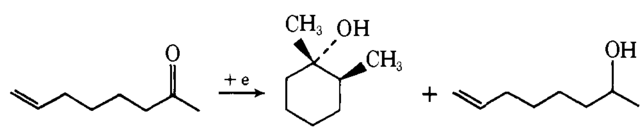
which probably resulted from the nucleophilic attack of the intermediate anionic species to Et_4NOTs used as the supporting electrolyte. Owing to the steric crowding, two alkyl groups on the terminal carbon atom of the starting olefinic ketones hindered the cyclization to a certain extent.

Table IV. Electroreductive Synthesis of Bicyclic Alcohols

Olefinic ketone		Product		Yield, %[a] MD Solvent	Yield, %[a] DMF
	20		25	87	70
	21		26	61	67
	22		27	65	51
			30	5	0
	23		28	37	32
			31	8	0
	24		29[13]	69	

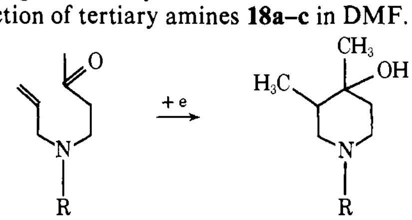
[a] Isolated.

Formation of Other Than Five-Membered Rings. The electroreduction of 7-octen-2-one (**9**) in MD solvent gave *cis*-1,2-dimethylcyclohexanol (**10**) in a 70% yield together with a small amount (yield 8%) of a noncyclized product, 7-octen-2-ol (**11**). The substitution of MD solvent by DMF brought



	9	10	11
MD solvent		70%	8%
DMF		75%	0%

about the exclusive formation of **10** in a slightly increased yield. The results shown in Table III, however, indicate that the formation of cyclic tertiary alcohols other than five- and six-membered rings, and of the cyclic alcohol from the aromatic ketone, can hardly be expected in this cathodic reaction. Six-membered nitrogen heterocycles **19a–c**[12] were also formed from the reduction of tertiary amines **18a–c** in DMF.



18a, R = $CH_2CH{=}CH_2$ **19a**, 36%
b, R = $n\text{-}C_3H_7$ **b**, 34%
c, R = $n\text{-}C_4H_9$ **c**, 26%

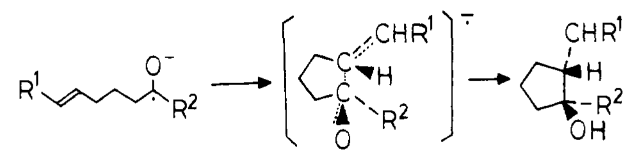
Syntheses of Bicyclic Alcohols. This cathodic intramolecular cyclization is a powerful tool in the syntheses of tertiary bicyclic alcohols possessing a hydroxyl group on the bridgehead. These products are difficult to obtain by other methods[13] (Table IV). The stereochemistry of the products listed in Table IV was not determined, though spectroscopic and gas chromatographic analyses clearly indicated that each product was a single isomer.

Table V. Reduction of 6-Octen-2-one (**1f**)

Reducing agent	Solvent system	Yield, %[a] 2f	34f	3f
Electroreduction	MD solvent	75	0	0
	DMF	77	0	0
Al(Hg)	Benzene	6	0	19
Na	Wet ether	0	0	65
Na	Liquid ammonia-THF	6	1	71
Na	HMPA-THF	63	15	0
$TiCl_4$-Mg(Hg)[b]	THF	0	59	0

[a] Isolated. [b] From the reduction of **1h** under the similar reaction conditions, *trans*-1-methyl-2-isobutylcyclopentanol (**34h**) and an acyclic olefinic alcohol **3h** were obtained in 35 and 13% yields, respectively.

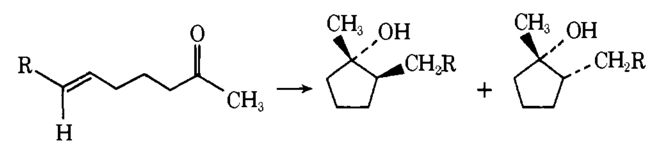
Scheme I



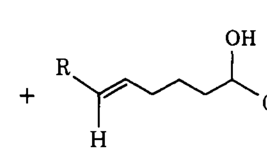
32 33 2

Reaction Pathway. Although the detail of the regio- and stereoselectivities of this novel electroreductive cyclization does not seem simple, the following explanation may show one of the most plausible mechanisms (Scheme I). The first electron transfer from the cathode to the starting olefinic ketone **1** generates a radical anion species **32,** which subsequently interacts with the olefinic part. The exclusive formation of the five-membered ring rather than the six-membered ring may be explained in a similar way to the homolytic intramolecular coupling reaction between a radical and a double bond.[14] In the cyclic intermediate **33,** which is formed by the interaction of the radical anion with the inner carbon atom of the double bond, both the oxygen atom and the CHR^1 group carry some negative charge which keeps both moieties away from each other and brings about the formation of the cis isomer **2.**

Comparison with Other Reductive Methods. Finally, it is instructive to compare this electrochemical reduction with other reductions with the reducing agents used usually in the pinacolic coupling (Table V). The reduction of **1f** with sodium in wet ether[15a] or in liquid ammonia-tetrahydrofuran (THF)[15b] or with aluminum amalgam in benzene[16] gave the noncyclized acyclic alcohols **3f** as the sole or predominant product. A mixture of cis and trans 1,2-dialkyl cyclic alcohols **2f** and **34f** was obtained from the reduction of **1f** with sodium



1f, R = CH_3 **2f,h** **34f,h**
h, R = $i\text{-}C_3H_7$



3f,h

in hexamethylphosphoric triamide (HMPA)-THF.[15b] On the other hand, the stereoselective formation of trans 1,2-dialkyl cyclic alcohols **34f,h** was observed in the reduction of **1f,h** with magnesium amalgam-titanium tetrachloride in THF.[17] The remarkable features of this electroreductive cyclization, namely, the high regio- and stereoselectivities and the excellent yields, clearly show the wide potentiality of this new cyclization in organic syntheses.

Experimental Section

Preparation of Nonconjugated Olefinic Ketones. Nonconjugated olefinic methyl ketones **1a, 1f–k, 4, 6a, 9, 12,** and **13** and 2-alkenylcycloalkanones **20–24** were prepared from acetoacetic ester condensation[18] followed by acid-catalyzed decarboxylation.[19] The Grignard reaction[21] of 4-pentenylmagnesium bromide[20] with the corresponding nitriles gave pentenyl alkyl or pentenyl phenyl ketones **1b–e, 6b,** or **14** in satisfactory yields. 4-(Alkylallylamino)butan-2-ones **18a–c** were obtained in 71–76% yields according to the reported procedure.[22] **6-Hepten-2-one (1a),**[23] **6-nonen-2-one (1g),**[24] **7-methyl-6-octen-2-one (1i),**[25] **7-methyl-6-nonen-2-one (1j),**[26] **6-methyl-6-hepten-2-one (4),**[27] **7-octen-2-one (9),**[28] **5-hexen-2-one (12),**[29] **8-nonen-2-one (13),**[30] **1-phenyl-5-hexen-2-one (14),**[31] **2-(3-butenyl)cyclopentanone (20),**[32] **2-(3-butenyl)cyclohexanone (21),**[30] **2-(4-pentenyl)cyclopentanone (22),**[33] **2-(4-pentenyl)cyclohexanone (23),**[30] and **cyclooct-4-en-1-one (24)**[34] were characterized by comparison of their gas chromatographic and spectroscopic behaviors with those of authentic samples. the other nonconjugated olefinic ketones were identified by spectroscopic and elemental analyses as shown below.

7-Octen-3-one (1b): bp 76 °C (30 mm); NMR (CCl_4) τ 4.01–4.85 (m, 1 H), 4.90–5.33 (m, 2 H), 7.47–8.80 (m, 8 H), 9.00 (t, 3 H, J = 6.9 Hz); IR (neat) 3090, 1710, 1640, 990, and 910 cm^{-1}. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.32; H, 11.21.

2-Methyl-7-octen-3-one (1c): bp 97 °C (4 mm); NMR (CCl_4) τ 4.01–4.81 (m, 1 H), 4.90–5.35 (m, 2 H), 7.15–8.60 (m, 7 H), 8.95 (d, 6 H, J = 7.0 Hz); IR (neat) 3090, 1710, 1640, 990, and 910 cm^{-1}. Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.92; H, 11.58.

9-Decen-5-one (1d): bp 115 °C (40 mm); NMR (CCl_4) τ 4.00–4.82 (m, 1 H), 4.91–5.32 (m, 2 H), 7.81 (t, 4 H, J = 6.0 Hz), 8.00 (t, 2 H, J = 7.0 Hz), 8.21–8.81 (m, 6 H), 9.10 (t, 3 H, J = 6.0 Hz); IR (neat) 3090, 1710, 1640, 990, and 910 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.98; H, 11.79.

11-Dodecen-7-one (1e): bp 108 °C (5 mm); NMR (CCl_4) τ 4.01–4.81 (m, 1 H), 4.91–5.34 (m, 2 H), 7.15–8.70 (m, 16 H), 9.12 (t, 3 H, J = 6.1 Hz); IR (neat) 3080, 1710, 1640, 990, and 910 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.15; H, 12.19.

6-Octen-2-one (1f): bp 89 °C (60 mm); NMR (CCl_4) τ 4.55–4.80 (m, 2 H), 7.70 (t, 2 H, J = 7.0 Hz), 7.90–8.65 (m, 4 H), 8.01 (s, 3 H), 8.27–8.51 (m, 3 H); IR (neat) 965 and 1710 cm^{-1}. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.08; H, 11.29.

8-Methyl-6-nonen-2-one (1h): bp 106 °C (44 mm); NMR (CCl_4) τ 4.63–5.11 (m, 2 H), 7.45–8.71 (m, 7 H), 7.98 (s, 3 H), 9.05 (d, 6 H, J = 6.2 Hz); IR (neat) 965 and 1710 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.59; H, 11.68.

7,8-Dimethyl-6-nonen-2-one (1k): bp 54 °C (2 mm); NMR (CCl_4) τ 4.60–5.18 (m, 1 H), 7.62 (t, 2 H, J = 6.5 Hz), 7.81–8.27 (m, 1 H), 8.01 (s, 3 H), 8.12 (t, 2 H, J = 6.0 Hz), 8.40 (s, 3 H) 8.30–8.75 (m, 2 H), 9.02 (d, 6 H, J = 6.5 Hz); IR (neat) 1715 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.48; H, 11.99.

4-Methyl-6-hepten-2-one (6a): bp 141 °C; NMR (CCl_4) τ 4.06–4.67 (m, 1 H), 4.98–5.34 (m, 2 H), 7.81 (d, 2 H, J = 6.0 Hz), 8.01 (s, 3 H), 7.85–8.50 (m, 3 H), 9.01 (d, 3 H, J = 6.3 Hz); IR (neat) 3080, 1710, 1640, 990, and 910 cm^{-1}. Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.25; H, 11.15.

2,5-Dimethyl-7-octen-3-one (6b): bp 67 °C (20 mm); NMR (CCl_4) τ 4.05–4.65 (m, 1 H), 4.95–5.35 (m, 2 H), 7.05–7.78 (m, 3 H), 7.85–8.50 (m, 3 H), 8.95 (d, 6 H, J = 6.0 Hz), 9.01 (d, 3 H, J = 6.2 Hz); IR (neat) 3085, 1710, 1640, 990, and 910 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.98; H, 11.85.

4-(Diallylamino)butan-2-one (18a): bp 95 °C (20 mm); NMR (CCl_4) τ 3.87–4.60 (m, 2 H), 4.71–5.20 (m, 4 H), 7.01 (d, 4 H, J = 6.2 Hz), 7.46 (t, 4 H, J = 4.2 Hz), 7.54 (t, 2 H, J = 4.3 Hz), 7.99 (s, 3 H); IR (neat) 3080, 1704, 1640, 995, and 920 cm^{-1}. Anal. Calcd for $C_{10}H_{17}NO$: C, 71.81; H, 10.25; N. 8.38. Found: C, 71.95; H, 10.31; N, 8.41.

4-(Allyl-*n*-propylamino)butan-2-one (18b): bp 98 °C (22 mm); NMR (CCl_4) τ 3.93–4.63 (m, 1 H), 4.75–5.21 (m, 2 H), 7.05 (d, 2 H, J = 6.0 Hz), 7.23–7.89 (m, 6 H), 7.98 (s, 3 H) 8.35–8.94 (m, 2 H), 9.18 (t, 3 H, J = 6.1 Hz); IR (neat) 3080, 1703, 1640, 995, and 920 cm^{-1}. Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.32; N, 8.28. Found: C, 71.01; H, 11.50; N, 8.35.

4-(Allyl-*n*-butylamino)butan-2-one (18c): bp 108 °C (20 mm); NMR (CCl_4) τ 3.94–4.61 (m, 1 H), 4.63–5.20 (m, 2 H), 7.03 (d, 2 H, J = 5.6 Hz), 7.21–7.85 (m, 6 H), 7.95 (s, 3 H), 8.51–8.95 (m, 4 H), 9.13 (t, 3 H, J = 5.8 Hz); IR (neat) 3080, 1710, 1638, 990, and 915 cm^{-1}. Anal. Calcd for $C_{11}H_{21}NO$: C, 72.08; H, 11.55; N, 7.64. Found: C, 72.13; H, 11.58; N, 7.71.

General Procedure for the Electroreduction of Nonconjugated Olefinic Ketones in MD Solvent. In a 100-mL undivided electrolysis cell equipped with carbon rod electrodes[35] and a reference electrode was placed a solution of 0.01 mol of nonconjugated olefinic ketone and 30 g (0.10 mol) of Et_4NOTs in 50 mL of MD solvent (1:9 v/v methanol-dioxane). Stirred with a magnetic bar and cooled with running water, the solution was electrochemically reduced at the constant current of 200 mA,[36] because the stable connection between the working and reference electrodes in this solvent system was not sufficiently kept throughout the reaction, though the initial cathode potential, −2.8 V vs. SCE, was measurable. After almost complete consumption of the starting ketone was observed by VPC analysis (about 10 F/mol of electricity was passed),[37] the reaction mixture was poured into 200 mL of saturated solution of sodium chloride and extracted with three 100-mL portions of ether. The combined ethereal solution was dried over anhydrous magnesium sulfate and evaporated. The residue was distilled in vacuo.

All the products were isolated by preparative VPC. Among them, gas chromatographic and spectroscopic behaviors of ***cis*-1,2-dimethylcyclopentanol (2a),**[11] **6-methyl-6-hepten-2-ol (5),**[39] ***cis*-1,2-dimethylcyclohexanol (10),**[40] **7-octene-2-ol (11),**[41] **5-hexen-2-ol (15),**[42] **1-phenyl-5-hexen-1-ol (17),**[31] and **bicyclo[3.3.0]octan-1-ol (29)**[13] were identical with those of authentic samples. Satisfactory spectroscopic and elemental analyses were obtained for the other products, **2b–h, 3g,h, 7a,b, 16,** and **25–31,** as shown below. The cis stereoconfiguration of 1,2-dialkyl cyclic tertiary alcohols, **2a–k, 7a,b, 10,** was confirmed by the comparison with the samples prepared independently by the hydroboration method,[11] and/or the Grignard reaction of the corresponding cyclic ketones. The stereochemistry of the products **25–29** was not determined, though IR, NMR, and VPC analyses clearly indicated that each product was a single stereoisomer.

Isolated yields of the products, **2a–h, 3g,h, 10, 11, 15–17,** and **25–31** are summarized in Tables I, III, and IV.

***cis*-1-Ethyl-2-methylcyclopentanol (2b):** bp 77 °C (17 mm); NMR (CCl_4) τ 7.91 (br s, 1 H), 8.01–8.80 (m, 9 H), 9.12 (t, 3 H), 9.15 (d, 3 H, J = 7.5 Hz); IR (neat) 3360 and 1110 cm^{-1}; mass spectrum m/e 128 (M^+). Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.75; H, 12.41.

***cis*-1-Isopropyl-2-methylcyclopentanol (2c):** bp 85 °C (18 mm); NMR (CCl_4) τ 7.81–8.80 (m, 8 H), 8.10 (br s, 1 H), 9.11 (d, 6 H, J = 6.5 Hz), 9.20 (d, 3 H, J = 7.6 Hz); IR (neat) 3410 and 1115 cm^{-1}; mass spectrum m/e 142 (M^+). Anal. Calcd for $C_9H_{18}O$: C, 75.99; H, 12.76. Found: C, 75.85; H, 12.86.

***cis*-1-*n*-Butyl-2-methylcyclopentanol (2d):** bp 105 °C (18 mm); NMR (CCl_4) τ 8.13 (br s, 1 H), 7.51–8.90 (m, 13 H), 9.10 (t, 3 H, J = 6.2 Hz), 9.17 (d, 3 H, J = 7.4 Hz); IR (neat) 3400 and 1120 cm^{-1}; mass spectrum m/e 156 (M^+). Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C. 76.96; H, 12.86.

***cis*-1-*n*-Hexyl-2-methylcyclopentanol (2e):** bp 76 °C (5 mm); NMR (CCl_4) τ 8.15 (br s, 1 H), 7.49–8.93 (m, 17 H), 9.15 (t, 3 H, J = 6.3 Hz), 9.21 (d, 3 H, J = 7.5 Hz); IR (neat) 3400 and 1120 cm^{-1}; mass spectrum m/e 184 (M^+). Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 78.01; H, 13.31.

***cis*-1-Methyl-2-ethylcyclopentanol (2f):** bp 70 °C (14 mm); NMR (CCl_4) τ 7.35 (br s, 1 H), 7.81–8.80 (m, 9 H), 8.90 (s, 3 H), 9.05 (t, 3 H, J = 6.0 Hz); IR (neat) 3420 and 1120 cm^{-1}; mass spectrum m/e 128 (M^+). Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.84; H, 12.32.

***cis*-1-Methyl-2-*n*-propylcyclopentanol (2g):** bp 79 °C (16 mm); NMR (CCl_4) τ 7.90 (br s, 1 H), 8.05–8.80 (m, 11 H), 8.91 (s, 3 H), 9.10 (t, 3 H, J = 6.1 Hz); IR (neat) 3400 and 1120 cm^{-1}; mass spectrum m/e 142 (M^+). Anal. Calcd for $C_9H_{18}O$: C, 75.99; H, 12.76. Found: C, 75.74; H, 12.62.

***cis*-1-Methyl-2-isobutylcyclopentanol (2h):** bp 91 °C (15 mm); NMR (CCl_4) τ 7.73 (br s, 1 H), 7.95–8.95 (m, 10 H), 8.95 (s, 3 H), 9.03 (d, 3 H, J = 6.0 Hz), 9.15 (d, 3 H, J = 6.0 Hz); IR (neat) 3400 and 1115 cm^{-1}; mass spectrum m/e 156 (M^+). Anal. Calcd for

$C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.69; H, 12.73.

6-Nonen-2-ol (3g): bp 99 °C (23 mm); NMR (CCl_4) τ 4.55–4.90 (m, 2 H), 6.15–6.65 (m, 1 H), 7.25 (br s, 1 H), 7.75–8.30 (m, 4 H), 8.40–8.70 (m, 2 H), 9.02 (d, 3 H, J = 6.0 Hz), 9.12 (t, 3 H, J = 7.5 Hz); Ir (neat) 3400, 1125, and 965 cm^{-1}. Anal. Calcd for $C_9H_{18}O$: C, 75.99; H, 12.76. Found: C, 76.10; H, 12.67.

8-Methyl-6-nonen-2-ol (3h): bp 103 °C (20 mm); NMR (CCl_4) τ 4.57–4.95 (m, 2 H), 6.05–6.70 (m, 1 H), 7.15 (br s, 1 H), 7.65–8.25 (m, 3 H), 8.25–8.78 (m, 4 H), 8.87 (d, 3 H, J = 6.3 Hz), 9.05 (t, 3 H, J = 6.8 Hz); IR (neat) 3400, 1120, and 965 cm^{-1}. Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.93; H, 12.98.

1,2,4-Trimethylcyclopentanol (7a): bp 72 °C (25 mm); NMR (CCl_4) τ 7.20 (br s, 1 H), 7.90–8.60 (m, 6 H), 8.90 (s, 3 H), 9.05 (d, 3 H, J = 6.8 Hz), 9.14 (d, 3 H J = 7.0 Hz); IR (neat) 3500 and 1120 cm^{-1}. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.89; H, 12.42.

1-Isopropyl-2,4-dimethylcyclopentanol (7b): bp 74 °C (24 mm); NMR (CCl_4) τ 8.64 (br s, 1 H), 7.81–8.60 (m, 7 H), 9.05 (d, 3 H, J = 7.1 Hz), 9.10 (d, 6 H, J = 6.0 Hz), 9.20 (d, 3 H, J = 6.8 Hz); IR (neat) 3480 and 1120 cm^{-1}. Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.98; H, 12.95.

8-Nonene-2-ol (16): bp 72 °C (15 mm); NMR (CCl_4) τ 3.91–4.82 (m, 1 H), 4.87–5.30 (m, 2 H), 6.11–6.62 (m, 1 H), 7.15 (br s, 1 H), 7.68–8.16 (m, 2 H), 8.25–8.80 (m, 8 H), 8.20 (d, 3 H, J = 6.1 Hz); IR (neat) 3400, 3080, 1640, 1110, 990, and 910 cm^{-1}. Anal. Calcd for $C_9H_{18}O$: C, 75.99; H, 12.76. Found: C, 76.12; H, 12.81.

2-Methylbicyclo[3.3.0]octan-1-ol (25): bp 108 °C (18 mm); NMR (CCl_4) τ 7.73 (br s, 1 H), 7.60–8.93 (m, 12 H), 9.08 (d, 3 H, J = 6.0 Hz); IR (neat) 3360 and 1110 cm^{-1}. Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.28; H, 11.42.

9-Methylbicyclo[4.3.0]nonan-1-ol (26): bp 82 °C (12 mm); NMR (CCl_4) τ 8.20 (br s, 1 H), 7.90–8.91 (m, 14 H), 9.15 (d, 3 H, J = 6.1 Hz); IR (neat) 3400 and 1115 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.96; H, 11.62.

2-Methylbicyclo[4.3.0]nonan-1-ol (27): bp 83 °C (12 mm); NMR (CCl_4) τ 8.25 (br s, 1 H), 7.90–8.91 (m, 14 H), 9.10 (d, 3 H, J = 6.0 Hz); IR (neat) 3400 and 1115 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.67; H, 11.89.

2-Methylbicyclo[4.4.0]decan-1-ol (28): bp 94 °C (4 mm); NMR (CCl_4) τ 8.23 (br s, 1 H), 7.75–9.35 (m, 17 H), 9.01 (d, 3 H, J = 6.8 Hz); IR (neat) 3480 and 1120 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.37; H, 11.84.

2-(4-Pentenyl)cyclopentanol (30): bp 71 °C (3 mm); NMR (CCl_4) τ 3.91–4.82 (m, 1 H), 4.87–5.31 (m, 2 H), 6.11–6.42 (m, 1 H), 6.63–7.15 (m, 2 H), 8.31 (br s, 1 H), 7.68–9.30 (m, 11 H); IR (neat) 3400, 3080, 1640, 1115, 990, and 910 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 78.01; H, 11.85.

2-(4-Pentenyl)cyclohexanol (31): bp 83 °C (3 mm); NMR (CCl_4) τ 3.91–4.80 (m, 1 H), 4.91–5.30 (m, 2 H), 6.11–6.35 (m, 1 H), 6.63–7.17 (m, 2 H), 8.12 (br s, 1 H), 7.76–9.24 (m, 13 H); IR (neat) 3400, 3080, 1640, 1115, 990, and 910 cm^{-1}. Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.73; H, 11.81.

General Procedure for the Electroreduction of Olefinic Ketones 1f–k, 4, and 18a–c in Anhydrous DMF. The electrolysis apparatus was a divided cell in which the diaphragm was ceramic, and the cathodic and anodic chambers were 120 and 30 mL, respectively.[43] The electrolyte, that is, a solution of 20 g (0.067 mol) of Et_4NOTs in 80 mL of anhydrous DMF, was placed in the cathodic and anodic chambers, and 0.01 mol of an olefinic ketone was added to the catholyte. Under the external cooling with running water, the electrolysis was carried out at the cathode potential of −2.70 V vs. SCE until 4 F/mol of electricity was passed. The catholyte was stirred with a magnetic bar during the electrolysis.

Isolation of products from the catholyte was performed according to the method described above. All the products were identified by spectroscopic and elemental analyses, as shown below. Isolated yields of the products **2f–k** and **8f–k** from **1f–k** are summarized in Table II.

***cis*-1-Methyl-2-isopropylcyclopentan-1-ol (2i):** bp 80 °C (17 mm); NMR (CCl_4) τ 8.11 (br s, 1 H), 8.80 (s, 3 H), 8.21–8.70 (m, 8 H), 9.01 (d, 3 H, J = 5.1 Hz), 9.14 (d, 3 H, J = 5.0 Hz); IR (neat) 3360 and 1115 cm^{-1}. Anal. Calcd for $C_9H_{18}O$: C, 75.90; H, 12.76. Found: C, 76.15; H, 12.58.

***cis*-1-Methyl-2-*sec*-butylcyclopentan-1-ol (2g):** bp 80 °C (15 mm); NMR (CCl_4) τ 8.10 (br s, 1 H), 8.91 (s, 3 H), 8.18–8.78 (m, 10 H), 9.08 (t, 3 H, J = 6.8 Hz), 9.13 (d, 3 H, J = 6.1 Hz); IR (neat) 3340 and 1120 cm^{-1}. Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.68; H, 12.71.

***cis*-1-Methyl-2-(1,2-dimethylpropyl)cyclopentan-1-ol (2k):** bp 117 °C (16 mm); NMR (CCl_4) τ 8.12 (br s, 1 H), 8.92 (s, 3 H), 8.21–8.71 (m, 10 H), 9.12 (d, 3 H, J = 6.0 Hz), 9.23 (d, 3 H, J = 6.8 Hz), 9.30 (d, 3 H, J = 6.1 Hz); IR (neat) 3375 and 1125 cm^{-1}. Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.30; H, 13.32.

3-Methyl-7-decen-3-ol (8g): bp 105 °C (15 mm); NMR (CCl_4) τ 4.67–4.97 (m, 2 H), 7.72–8.37 (m, 4 H), 8.40–8.90 (m, 6 H), 8.57 (br s, 1 H), 8.92 (s, 3 H), 9.12 (t, 6 H, J = 6.5 Hz); IR (neat) 3400, 1120, and 966 cm^{-1}. Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.71; H, 13.01.

3,9-Dimethyl-7-decen-3-ol (8h): bp 125 °C (30 mm); NMR (CCl_4) τ 4.71–5.05 (m, 2 H), 7.31–8.26 (m, 3 H), 8.52 (br s, 1 H), 8.46–8.80 (m, 3 H), 8.93 (s, 3 H), 9.06 (d, 6 H, J = 6.1 Hz), 9.12 (t, 3 H, J = 6.8 Hz); IR (neat) 3400, 1120, and 965 cm^{-1}. Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 78.25; H, 13.26.

3,8-Dimethyl-7-nonen-3-ol (8i): bp 90 °C (17 mm); NMR (CCl_4) τ 4.91–5.10 (m, 1 H), 8.20 (br s, 1 H), 8.31 (s, 3 H), 8.40 (s, 3 H), 7.82–8.81 (m, 8 H), 8.92 (s, 3 H), 9.11 (t, 3 H, J = 6.1 Hz); IR (neat) 3350 and 1115 cm^{-1}. Anal. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.39; H, 12.98.

3,8-Dimethyl-7-decen-3-ol (8j): bp 95 °C (15 mm); NMR (CCl_4) τ 4.70–5.15 (m, 1 H), 7.93 (br s, 1 H), 8.48 (s, 3 H), 7.81–8.26 (m, 4 H), 8.55–8.82 (m, 6 H), 8.91 (s, 3 H), 9.19 (t, 6 H, J = 6.7 Hz); IR (neat) 3360 and 1115 cm^{-1}. Anal. Calcd for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 78.08; H, 13.12.

3,8,9-Trimethyl-7-decen-3-ol (8k): bp 126 °C (16 mm); NMR (CCl_4) τ 4.60–5.14 (m, 1 H), 7.51–8.22 (m, 3 H), 8.04 (br s, 1 H), 8.40 (s, 3 H), 8.53–8.80 (m, 6 H), 8.90 (s, 3 H), 9.07 (d, 6 H, J = 6.8 Hz), 9.12 (t, 3 H, J = 6.1 Hz); IR (neat) 3375 and 1120 cm^{-1}. Anal. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.89; H, 13.19.

1-Allyl-3,4-dimethyl-4-hydroxypiperidine (19a): bp 74 °C (3 mm); NMR (CCl_4) τ 3.91–4.54 (m, 1 H), 4.65–5.14 (m, 2 H), 6.20 (br s, 1 H), 7.08 (d, 2 H, J = 6.7 Hz), 7.25–8.60 (m, 7 H), 8.98 (s, 3 H), 9.08 (d, 3 H, J = 5.8 Hz); IR (neat) 3400, 3090, 1640, 1110, 995, and 920 cm^{-1}. Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.32; N, 8.28. Found: C, 71.03; H, 11.35; N, 8.31.

1-*n*-Propyl-3,4-dimethyl-4-hydroxypiperidine (19b): bp 72 °C (3 mm); NMR (CCl_4) τ 6.18 (br s, 1 H), 7.06–8.76 (m, 11 H), 9.01 (s, 3 H), 9.14 (d, 3 H, J = 6.8 Hz), 9.17 (t, 3 H, J = 5.4 Hz); IR (neat) 3380 and 1010 cm^{-1}. Anal. Calcd for $C_{10}H_{21}NO$: C, 70.12; H, 12.36; N, 8.18. Found: C, 70.09; H, 12.29; N, 8.16.

1-*n*-Butyl-3,4-dimethyl-4-hydroxypiperidine (19c): bp 89 °C (3 mm); NMR (CCl_4) τ 6.15 (br s, 1 H), 7.15–8.80 (m, 13 H), 9.01 (s, 3 H), 9.08 (d, 3 H, J = 6.8 Hz), 9.11 (t, 3 H, J = 5.5 Hz): IR (neat) 3390 and 1005 cm^{-1}. Anal. Calcd for $C_{11}H_{23}NO$: C, 71.30; H, 12.51; N, 7.56. Found: C, 71.54; H, 12.58; N, 7.61.

Reduction of 1f with Sodium in Moist Ether. The olefinic ketone **1f** was reduced with sodium using Eakin's method,[15a] and the acyclic alcohol **3f** was obtained as a sole product in a 75% yield.

Reduction of 1f with Sodium in Liquid Ammonia–THF. The reduction of **1f** with sodium was carried out according to the procedure of House,[15b] and the yield of the main product **3f** was 71% and the by-products **2f** and **34f** were formed in the yields of 6 and 1%, respectively.

Reduction of 1f with Aluminum Amalgam. The reduction of **1f** with aluminum amalgam by the reported procedure[16] gave the mixture of ***cis*-1-methyl-2-ethylcyclopentanol (2f)** and **6-octen-2-ol (3f)** in 6 and 19% yields, respectively. **6-Octen-2-ol (3f):** bp 87 °C (23 mm); NMR (CCl_4) τ 4.51–4.75 (m, 2 H), 6.10–6.61 (m, 1 H), 6.91 (br s, 1 H), 7.81–8.30 (m, 2 H), 8.31–9.01 (m, 7 H), 8.90 (d, 3 H, J = 6.1 Hz); IR (neat) 3350 and 965 cm^{-1}. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 75.05; H, 12.73.

Reduction of 1f with Sodium in HMPA–THF. The reported procedure[15b] was applied to the reduction of **1f**, and the products **2f** and **34f** were formed in 63 and 15% yields, respectively.

***trans*-1-Methyl-2-ethylcyclopentanol (34f):** bp 81 °C (47 mm); NMR (CCl_4) τ 7.81 (br s, 1 H), 7.91–8.90 (m, 10 H), 8.81 (s, 3 H), 9.01 (t, 3 H, J = 6.0 Hz); IR (neat) 3450 and 1105 cm^{-1}. Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.85; H, 12.61.

Reduction of 1f or 1h with Magnesium Amalgam–Titanium Tetrachloride. According to Corey's method,[17] the trans cyclic alcohol **34f** was obtained as a sole product in a 59% yield from the reduction of **1f** with the title reducing agent. The reduction of **1h** under similar conditions gave the mixture of ***trans*-1-methyl-2-isobutylcyclopentanol**

(**34h**) (35%) and an acyclic olefinic alcohol **3h** (13%).

***trans*-1-Methyl-2-isobutylcyclopentanol (34h)**: bp 104 °C (51 mm); NMR (CCl_4) τ 7.90 (br s, 1 H), 8.01–9.05 (m, 10 H), 8.90 (s, 3 H), 9.05 (d, 6 H, J = 6.0 Hz); IR (neat) 3450 and 1110 cm^{-1}. Anal. Calcd for $C_{10}H_{20}O$: C, 76.86; H, 12.90. Found: C, 76.98; H, 12.95.

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Ring-Closure Reactions. 11.[1] The Activation Parameters for the Formation of Four- to Six-Membered Lactones from ω-Bromoalkanoate Ions. The Role of the Entropy Factor in Small- and Common-Ring Formation[2]

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Abstract: Previous work on the kinetics of formation of 3- to 23-membered lactones from ω-bromoalkanoate anions in 99% Me_2SO has been completed with the inclusion of precise rate constants and thermodynamic activation parameters for the formation of four- to six-membered rings. The kinetics were followed by a stopped-flow spectrophotometric technique by the device of introducing a visual indicator into the reaction systems. The pattern observed for the enthalpies of activation leads to the suggestion that they closely follow the strain energies of the rings to be formed. The dependence of the entropy factor upon ring size is discussed in some detail with particular reference to the small- and common-ring regions, for which available literature data for comparison purposes are more abundant.

In recent studies[3] on the kinetics of formation of 3- to 23-membered lactones from ω-bromoalkanoate ions in 99% aqueous Me_2SO (eq 1) accurate rate data and activation parameters have been reported for the formation of most ring compounds in the given range. However, the rate of formation of four-, five-, and six-membered lactones was too high to be

$$Br(CH_2)_{n-2}CO_2^- \xrightarrow{k_{intra}} \overbrace{(CH_2)_{n-2}\text{—}C(=O)\text{—}O}^{\text{ring}} + Br^- \quad (1)$$

followed by our conventional technique. Only a crude estimation of the rate constants could be made by an indirect