J = 16.2, 8.0 Hz, 1 H), 3.28 (dd, J = 16.2, 8.0 Hz, 1 H), 4.31 (m, 1 H), 7.26 (m, 5 H.

B. With Iodine. An experiment similar to the one described above was carried out with the exception that iodine (12.5 mg, 0.05 mmol) was added to the mixture before the addition of DIS. An ^{1}H NMR spectrum recorded after 6 h at room temperature showed phenylacetone (2.16 and 3.70 ppm), 2-iodo-2-siloxy-1-phenylpropane (2.37 and 4.05 ppm), and 2-iodo-1-phenylpropane in a ratio of 18:22:60, respectively. It should be noted that the absorptions assigned to phenylacetone were unaffected by the presence of iodine.

C. With Iodine and *m*-Dintrobenzene. An experiment similar to the one described in **B** was carried out with the exception that *m*-dinitrobenzene (1.7 mg, 0.01 mmol) was added to the mixture after addition of iodine and before addition of DIS. An ^{1}H NMR spectrum recorded after 6 h at room temperature showed a mixture of the above-mentioned three compounds in a ratio of 24:21:55, respectively.

NMR Study of the Reaction between Acetone and DIS. A. DIS (300 mg, 1.03 mmol) was added to a solution of acetone (60 mg, 1.03 mmol) in $CDCl_3$ (0.4 mL). An ^{1}H NMR spectrum recorded after 10 min at room temperature showed acetone (s, 2.18 ppm), 2-iodo-2-siloxypropane (s, 2.31 ppm), 2-iodopropane (1.88, 4.35 ppm), and diisopropyl ether (1.19, 3.75 ppm) in a 63:27:5:5 ratio, respectively, as well as traces of 2-siloxypropane. Another ^{1}H NMR spectrum recorded 80 min later indicated the presence of the same four compounds in a ratio of 38:38:12:12, respectively. This composition was confirmed by a ^{13}C NMR spectrum (30.5 and 206.5; 37.8 and 60.7; 31.1 and 21.6; 22.7 and 66.2 ppm, respectively) that was recorded within 80 min (between the two ^{1}H NMR measurements).

Iodine (26 mg, 10 mol %) was then added to the NMR tube and the first ^{1}H NMR spectrum was recorded 5 min later. The above-mentioned components, acetone, 2-iodo-2-siloxypropane, 2-iodopropane, and diisopropyl ether, were observed in a ratio of 1:70:19:10, respectively. This situation was confirmed by a ^{13}C NMR spectrum that was recorded over 100 min (between 5 and 105 min after the addition of iodine). A second ^{1}H NMR spectrum recorded at 105 min from addition of iodine showed the above-mentioned four compounds in a 6:25:68:1 ratio, respectively. Another change observed in the second ^{1}H NMR spectrum was a significant line broadening of the signal at 2.31 ppm, assigned to 2-iodo-2-siloxypropane ($W_{1/2}$ = 6.5 Hz relative to 1 Hz of other signals).

B. An experiment similar to the one described above was carried out with the exception that iodine (10 mol %) was added to the mixture before DIS. An ^{1}H NMR spectrum recorded after 10 min at room temperature showed acetone, 2-iodo-2-siloxypropane, 2-iodopropane, and diisopropyl ether in a ratio of 7:82:10:1, respectively. This situation was confirmed by ^{13}C NMR, recorded over 80 min (between 10 and 90 min after the addition). Another ^{1}H NMR spectrum recorded at 90 min from addition indicated the presence of the above-mentioned four compounds in a ratio of 15:23:62:<1, respectively. Again, a significant line broadening of the signal at 2.31 ppm, ($W_{1/2}$ = 5 Hz) was observed in the second ^{1}H NMR spectrum.

Acknowledgment. D.P. thanks the postdoctoral fellowship program of the Consent Nacional de Investigaciones Cientificas y Tecnicas de la Rupublica Argentina for their generous financial support. M.S. is grateful to the Banaras Hindu University for his study leave.

Registry No. **1**, 4360-68-3; **2**, 99-90-1; **3**, 125763-63-5; **4**, 77-76-9; **5**, 2916-31-6; **6**, 4405-16-7; **7**, 1670-47-9; **8**, 177-10-6; **9**, 4362-18-9; **10**, 125763-64-6; **11**, 79449-69-7; **12**, 5406-60-0; **13**, 24856-58-4; **14**, 10602-01-4; **15**, 2403-50-1; **16**, 4359-49-3; **17**, 100847-13-0; **18**, 5420-89-3; **19**, 4359-31-3; **20**, 105-57-7; **21**, 933-40-4; **22**, 6581-66-4; **23**, 62606-31-9; **24**, 125763-65-7; **25**, 125763-66-8; **26**, 13760-02-6; **27**, 16029-98-4; MeCOMe, 67-64-1; *i*-$PrCOCH_3$, 563-80-4; $PhCH_2COCH_3$, 103-79-7; *p*-BrC_6H_4CHO, 1122-91-4; *p*-$MeOC_6H_4CHO$, 123-11-5; HI, 10034-85-2; $PhCOCH_2CH_3$, 93-55-0; $PhCHICH_2CH_3$, 4119-41-9; *p*-$MeOC_6H_4CH_2I$, 70887-29-5; PhCHO, 100-52-7; $PhCH_2I$, 620-05-3; $PhCH_2CHICH_3$, 29527-87-5; CH_3CHICH_3, 75-30-9; EtI, 75-03-6; $I(CH_2)_5I$, 628-77-3; $PhCOCH_3$, 1334-78-7; $H_3C(CH_2)_2CHO$, 123-72-8; $H_3C(CH_2)_4CHO$, 66-25-1; $H_3C(CH_2)_8CHO$, 112-31-2; $PhCHICH_3$, 10604-60-1; $PhCOCH_2CH(CH_3)Ph$, 1533-20-6; $H_3C(CH_2)_3I$, 542-69-8; $H_3C(CH_2)_5I$, 638-45-9; $H_3C(CH_2)_9I$, 2050-77-3; $H_3CCOCH{=}CHPh$, 122-57-6; $PhCH{=}CHCH_2OH$, 104-54-1; $PhCH{=}CHCHO$, 104-55-2; $ICH_2CH_2CH_2COCH_3$, 3695-29-2; cyclohexanone, 108-94-1; iodocyclohexane, 626-62-0; 2-iodotetrahydrofuran, 7429-25-6; 3,4-dimethoxybenzaldehyde, 120-14-9; 3,4-dimethoxybenzyl iodide, 76950-76-0; cyclopropyl methyl ketone, 765-43-5.

Electrochemical Oxidation of Polycyclic Cyclopropanes and Camphene.[1] Novel Synthesis of *exo*-5,5-Dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol (Nojigiku Alcohol)

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Anodic oxidation of tricyclene (**1a**) in acetic acid containing triethylamine, followed by hydrolysis, provides a facile and efficient synthesis of *exo*-5,5-dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol (**2a**), named "nojigiku alcohol", which was isolated from the essential oil of *chrysanthemum japonese*. Furthermore, a method for large-scale production of **2a** starting from the readily available impure starting tricyclene (**1a**) has been developed by appropriate selection of reaction conditions. Similar electrooxidation of the related naturally occurring polycyclic methylcyclopropanes, cyclofenchene (**1b**) and longicyclene (**1c**), followed by hydrolysis also brought about stereo- and regioselective cleavage of carbon–carbon bonds of the cyclopropane rings to give the corresponding homoallylic alcohols **2b**,**c** in good yields.

exo-5,5-Dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol (**2a**) was isolated by Matsubara and co-workers[3] from the essential oil of *chrysanthemum japonese* in 1974 and was called "nojigiku alcohol". This alcohol was shown to be

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[†] Kinki University.

[‡] Kuraray Co. Ltd.

(1) A part of this work was reported in a preliminary communication, see: Matsubara, Y.; Uchida, T.; Ohnishi, T.; Kanehira, K.; Fujita, Y.; Hirashima, T.; Nishiguchi, I. *Tetrahedron Lett.* **1985**, 4513.

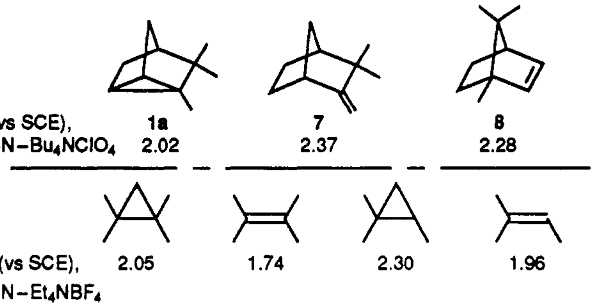
0022-3263/90/1955-2938$02.50/0

Table I. Anodic Oxidation of Tricyclene (1a) in Acetic Acid[a]

run	supporting electrolyte[b]	content of water, wt %	reaction temp, °C	product yield,[c] %			
				2a	**3**	**4a**	**4b**
1	KOAc	0	25–30	58	6	5	2
2	KOAc	2.50	25–30	54	5	4	1
3	NEt_3	0	25–30	70	8	8	3
4	NEt_3	2.50	25–30	68	7	7	3
5	NEt_3[d]	10.0	25–30	38	3	3	1
6	NEt_3	0	15–20	76	9	10	5
7	NEt_3	5.0	8–10	77	4	9	3
8	28% aq NH_3[e]	–	25–30	68	7	6	2
9	$NaHPO_4 \cdot 12H_2O$[e]	–	25–30	60	6	5	1
10	$LiClO_4 \cdot 3H_2O$[e]	–	25–30	45	5	5	1
11	$(NH_4)_2SO_4$	0	25–30	65	6	6	1
12	Et_4NOTs	0	25–30	57	4	8	1

[a] Anodic oxidation was continued until 4.0 F/mol of electricity was passed. [b] Concentration of each supporting electrolyte was 0.375 M. [c] Isolated yield. [d] Approximately 45% of the starting **1a** was recovered. [e] Any additional amount of water was not needed.

Chart I. Oxidation Potential of Tricyclene (1a), Camphene (7), and Bornylene (8)



[a] Reference 9.

an important olfactory component of floral perfume and fragrance compositions.[4]

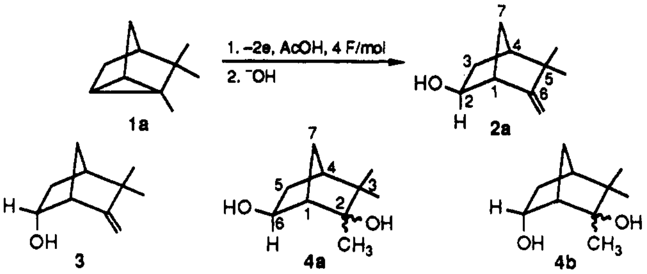
Although several syntheses of this alcohol have been reported,[5-7] the methods and yields are poor, the starting materials are expensive, and many of reagents used to effect the conversion are toxic.

We report a highly selective and efficient method for the synthesis of nojigiku alcohol (**2a**) using anodic oxidation of even impure tricyclene (**1a**), the latter compound being available from α- or β-pinene; the method was shown to be applicable to industrial production.

Furthermore, it has been found that anodic oxidation of related polycyclic cyclopropanes, cyclofenchene (**1b**) and longicyclene (**1c**), also brought about stereo- and regioselective cleavage of carbon–carbon bonds of the cyclopropane rings to give the corresponding homoallylic alcohols (**2b,c**) in good yields.

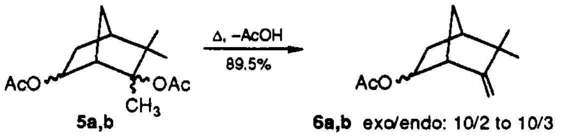
Results and Discussion

Anodic Oxidation of Tricyclene (1a). Anodic oxidation of tricyclene (**1a**) was usually carried out in acetic acid using an undivided cell equipped with carbon rod electrodes as the anode and cathode. The solution was stirred under constant-current conditions (current density: 17–20 mA/cm^2), until 4.0 F/mol of electricity passed. The resulting mixture was subsequently subjected to base-catalyzed hydrolysis to give the desired *exo*-5,5-dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol (**2a**) as a main product, accompanied by small amounts (>10%) of the corresponding endo isomer (**3**) of **2a**, 2,3,3-trimethylbicyclo[2.2.1]heptane-2,6(*exo*)-diol (**4a**) and 2,3,3-trimethylbicyclo[2.2.1]heptane-2,6(*endo*)-diol (**4b**) as side products. The yield and selectivity for formation of each product were found to be dependent upon the nature of the supporting electrolyte and the reaction temperature, as shown in Table I.



Data from Table I shows that the presence of a small amount (2.5–5.0 wt %) of water in acetic acid had little influence on the yield of **2a**. The current efficiency, however, was observed to decrease considerably when more than 10 wt % of water was added to the solvent. Nojigiku alcohol (**2a**) was obtained in a 76–77% yield under the optimum conditions (run 6, 7: acetic acid containing triethylamine as a supporting electrolyte, 10–15 °C).

It is noteworthy that treatment of a stereoisomeric mixture of the diacetates **5a** and **5b** with acetic acid at reflux brought about selective elimination of acetic acid to give a stereoisomeric mixture of 2-acetoxy-5,5-dimethyl-6-methylenebicyclo[2.2.1]heptanes (exo isomer **6a** and endo isomer **6b**, ratio of **6a**/**6b** = 10/2 to 10/3), which could be hydrolyzed to a mixture of **2a** and **3**. Therefore, taking into account this transformation, the isolated yield of **2a** was over 80%.



The starting tricyclene (**1a**) is usually prepared by acid-catalyzed isomerization[8] of α- or β-pinene followed by fractional distillation of the resulting product mixture of tricyclene (**1a**), camphene (**7**), and bornylene (**8**). It is quite easy to obtain highly pure tricyclene (**1a**) in relatively

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(2) Author to whom correspondence should be addressed at Osaka Municipal Technical Research Institute.

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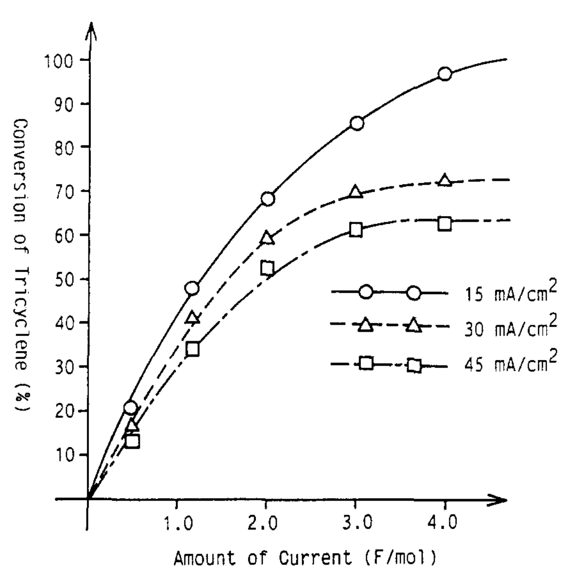
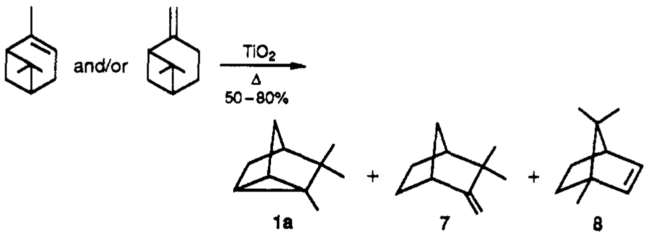


Figure 1. Effect of current density on conversion of tricyclene: anodic oxidation of a mixture of **1a**, **7**, and **8** in the ratio of 75%, 16%, 9%, respectively, was carried out in 97 wt % aqueous acetic acid containing triethylamine as a supporting electrolyte at 20–25 °C.

small amounts by repeated fractional distillation. It is, however, quite difficult to obtain a large amount of **1a** with high purity for a large-scale electrooxidation. This situation has required the development of an alternative method for large-scale electrooxidation using readily available but impure tricyclene (**1a**) (70–75% purity).



As shown in Chart I, measurement of the oxidation potential of **1a**, **7**, and **8** clearly indicates that **1a** is easier to oxidize than **7** and **8**. This phenomenon may be due to the higher strain energy[9] of the polycyclic cyclopropane ring of **1a**, since monocyclic cyclopropanes were shown to be more difficult to oxidize than the corresponding olefins.[10]

Furthermore, the effect of current density on the consumption rate of **1a** was studied for the anodic oxidation of a mixture containing 75% **1a**, 16% **7**, and 9% **8**. The result showed that **1a** was almost quantitatively consumed in the electrooxidation with 15 mA/cm^2 of current density. On the other hand, consumption of **1a** stopped at about 60–70% conversion. Some tarry material was deposited on the surface of the anode after passage of more than 4.0 F/mol with 30 and 45 mA/cm^2 current density, as shown in Figure 1.

A large amount (2.25 kg) of the readily available mixture referred to above was oxidized in 31.4 kg of acetic acid with 15 mA/cm^2 of current density using a semipilot scale electrolysis instrument, as shown in Figure 2. Figure 3 shows plots of the percentage composition of the reaction mixture vs the amount of electricity passed through the system. It indicates that **1a** is converted to *exo*- and *endo*-2-acetoxy-5,5-dimethyl-6-methylenebicyclo[2.2.1]heptanes (**6a** and **6b**) (**6a**/**6b** = ca. 10/1) after consumption of 4.0 F/mol of electricity. Under these conditions, however, compounds **7** and **8** were essentially unchanged.

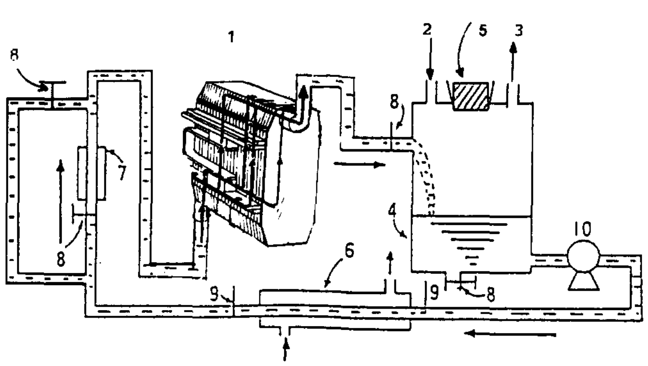


Figure 2. Semipilot scale electrolysis instrument (equipped at Osaka Municipal Technical Research Institute). (1) Undivided cell (Modified ElectroSyn Cell purchased from ElectroCell AB Co. Ltd.); anode, carbon plate; cathode, stainless steel plate. (2) N_2 gas inlet. (3) Gas outlet. (4) Feeding tank (30 L). (5) Stopper for safety. (6) Heat exchanger (Freon gas). (7) Flow meter. (8) Bulb. (9) Thermometer. (10) Recycle pump.

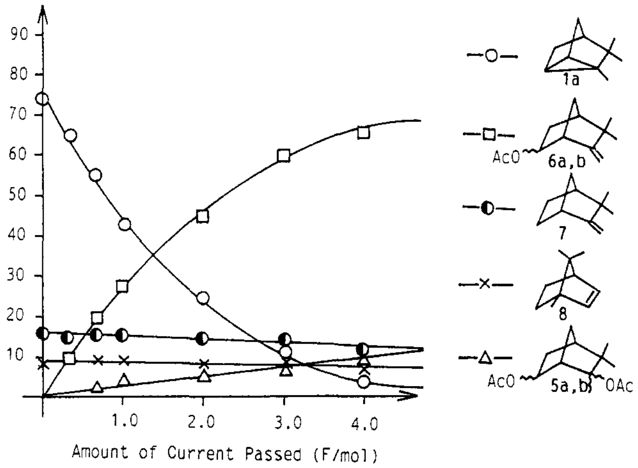


Figure 3. Plot of percentage composition of the reaction mixture vs the amount of current passed.

This method may be applicable to the industrial-scale production of **2a**. The acetates **6a,b** were initially separated from the reaction mixture after the passage of 2–3 F/mol of electricity and were subsequently subjected to hydrolysis. The recovered hydrocarbon distillate was converted to the starting mixture containing 75% **1a**, 16% **7**, and 9% **8** by acid-catalyzed isomerization[8] followed by fractional distillation, and was reused for the next run of the anodic oxidation.

Anodic Oxidation of Camphene (7). Anodic oxidation of camphene (**7**), a related isomeric monoterpene, was carried out using a procedure similar to that described above for tricyclene (**1a**). 2-(2,2-Dimethyl-3-methylenecyclopentyl)ethanol (isocampholenol) (**9**), camphene glycol (**10**), and bornane-2,10-diol (**11**) were obtained as the major products after subsequent hydrolysis of the product mixture. *exo*-5,5-Dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol (**2a**) formed only in a small amount (5–9% yield).

Yields of these major products (**9**–**11**) were affected by the nature of the supporting electrolyte, as shown in Table II. In sharp contrast with the results obtained from anodic oxidation of **1a**, use of triethylamine as the supporting electrolyte brought about low conversion of **7** and formation of much tarry product. Furthermore, the diol **11** was

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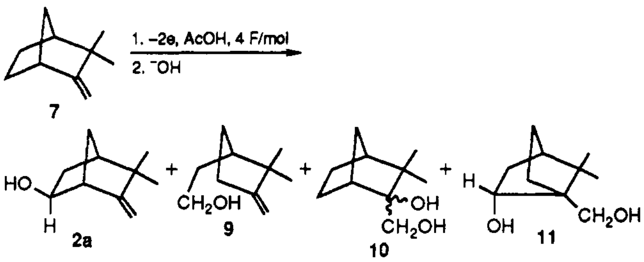
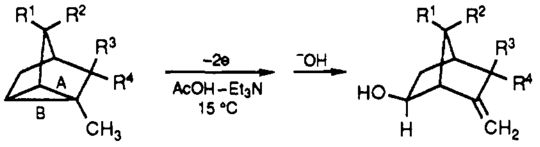
(9) It was found that the oxidation potentials of strained polycyclic hydrocarbons is a reflection of the level of the HOMO of these systems. See: Gassman, P. G.; Yamaguchi, R. *J. Am. Chem. Soc.* **1979**, *101*, 1308.

(10) Shono, T.; Matsumura, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2861.



selectively obtained in a 70% yield when the concentration of tetrabutylammonium tetrafluoroborate as a supporting electrolyte was increased.

Selective Cleavage of Polycyclic Methylcyclopropanes (1a–c) by Electrooxidation. The selective formation of *exo*-5,5-dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol (**2a**) in anodic oxidation of tricyclene (**1a**) followed by hydrolysis has tempted us to examine the electrochemical behavior[11–14] of the related polycyclic methylcyclopropanes. Electrochemical oxidation of cyclofenchene (**1b**) and longicyclene (**1c**) under similar conditions to those used for **1a** resulted in stereo- and regioselective cleavage of a carbon–carbon bond of the cyclopropane ring to give the corresponding homoallylic *exo*-alcohols, *exo*-7,7-dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol (**2b**) and *exo*-3,3,7-trimethyl-8-methylenetricyclo[5.4.0.0^{2,9}]undecan-10-ol (**2c**) in 77% and 85% yields, respectively.

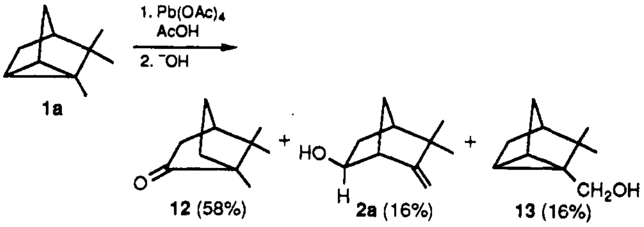


1a: $R^1 = R^2 = H$; $R^3 = R^4 = CH_3$ (*tricyclene*)
b: $R^1 = R^2 = CH_3$; $R^3 = R^4 = H$ (cyclofenchene)
c: $R^1 = H$; $R^4 = CH_3$;
R^2–R^3 = $-C(CH_3)_2CH_2CH_2CH_2-$ (longicyclene)

2a: Y = 76%
b: Y = 77%
c: Y = 85%

The electrochemical oxidation shows sharp contrast to conventional oxidations using a metal–salt oxidizing agent.[15] Thus, oxidation of tricyclene (**1a**) in acetic acid with lead tetraacetate followed by hydrolysis gave camphor (**12**), *exo*-5,5-dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol (**2a**), and tricyclenyl alcohol (**13**) as principle products in 58%, 16%, and 16% yields, respectively.[16] Therefore, high stereo- and regioselectivity in cleavage of a carbon-carbon bond of a cyclopropane ring in polycyclic compounds **1a–c** may be a characteristic of this anodic oxidation, though the reasons for the observed selectivity are not clear.

It has been reported by Shono and co-workers[12] that a carbon–carbon bond of a cyclopropane ring with high electron density is exclusively cleaved in anodic oxidation of bicyclic cyclopropyl compounds. Therefore, one attractive explanation for the regioselectivity suggests that the higher electron density of the more substituted carbon–carbon bond of the cyclopropane ring of **1a–c** makes it most reactive.



Differentiation between the two trisubstituted carbon–carbon bonds, A and B, of **1b** and **1c**, with selective cleavage of the B bond, may be attributed to steric repulsion between the bulky dialkyl groups of **1b–c** and an anode on electron transfer from the substrate to the anode. Stereoselectivity caused by steric repulsion between a bulky alkyl group and an anode has been observed in similar electrochemical oxidations.[17,18]

Stereoselective formation of *exo*-olefinic alcohols **2a–c** may be rationalized by generation of a norbornyl-type cationic intermediate after electron transfer, followed by predominant exo attack of an acetate anion from the reverse side toward the carbon–carbon bond to be cleaved (see Figure 4), as was observed in solvolysis of *exo*-2-norbornyl brosylate.[19]

It is also interesting to note that the homoallylic alcohols possessing an *exo*-methylene group, **2a** and **3**, were obtained in preference to saturated dialcohols, **4a** and **4b**, in the anodic oxidation of tricyclene (**1a**) (according to run 3 in Table I, the ratio of [**2a** + **3a**]/[**4a** + **4b**] is ca. 7–8).

Experimental Section

General Procedure for Anodic Oxidation of Tricyclene (1a), Cyclofenchene (1b), Longicyclene (1c), and Camphene (7). Into 80 mL of glacial acetic acid containing 3.03 g (0.03 mol) of triethylamine (or other supporting electrolyte) was added 0.02 mol of **1a–c** or **7**. The substrate was oxidized in an undivided beaker equipped with a carbon rod anode and cathode at 25–30 °C with magnetic stirring under the constant current conditions (current density, 17–20 mA/cm^2). After 4.0 F/mol of electricity passed through the system, the reaction mixture was poured into 200 mL of ice–water and was extracted three times with diethyl ether. The combined ethereal solution was neutralized with 10% aqueous sodium bicarbonate. After removal of the solvent by evaporation, the residual oily material was dissolved in 50 mL of 90% aqueous ethanol containing 4.0 g (0.10 mol) of sodium hydroxide, and the solution was refluxed for 2 h. The mixture was neutralized with 5% aqueous sulfuric acid solution and was again extracted with diethyl ether. The combined ethereal solution was washed with 10% aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. Filtration of the drying agent and removal of the solvent by evaporation gave a product mixture that was analyzed by chromatographic and spectroscopic methods.

Yields of the products from anodic oxidation of **1a–c** and **7** under various conditions are summarized in Table I and Chart I, respectively.

All of the product isolated by gas or thin-layer chromatographic technique were identified by comparison of their chromatographic and spectroscopic behaviors with those of authentic samples, or by spectroscopic methods and elemental analyses, as shown below.

***exo*-5,5-Dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol (nojigiku alcohol) (2a)**: mp 55.0–56.5 °C (lit. mp 52–53 °C,[3] 54–55 °C[7]).

***endo*-5,5-Dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol (isonojigiku alcohol) (3)**: mp 67.0–68.0 °C (lit.[20] mp 67.5–68.5 °C).

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[11] For recent electrochemical oxidation of cyclopropane rings, see ref 9, 10, and 12–14.

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Table II. Anodic Oxidation of Camphene (7) in Acetic Acid[a]

supporting electrolyte	concn, M	product yield, %			
		2a	**9**	**10**	**11**
NEt_3[b]	0.375	5	2	18	6
Et_4NOTs	0.10	9	20	31	10
Bu_4NBF_4	0.10	0	0	39	10
Bu_4NBF_4	0.40	0	0	2	70

[a] Concentration of 7 was 0.2 M. After 4.0 F/mol of electricity passed, the mixture was hydrolyzed in 90% aqueous EtOH containing 10 wt % NaOH. [b] Approximately 35% of 7 was recovered.

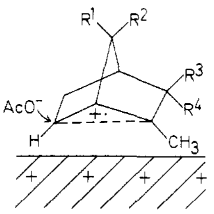

Figure 4. Specific adsorption of polycyclic cyclopropanes on an anode in electrooxidation.

2,3,3-Trimethylbicyclo[2.2.1]heptane-2,6(*exo*)-diol (4a): mp 143–144 °C; ^1H NMR ($CDCl_3$, ppm) 0.82, 0.97 (2 s, 6 H, *gem*-CH_3), 1.08 (ddd, 1 H, J = 3.5, 7.0, 14.0 Hz, C_7-H_{syn}), 1.13 (s, 3 H, C_3-(OH)CH_3), 1.42 (d, 1 H, J = 10.0 Hz, C_6-H_{endo}), 1.69 (dd, 1 H, J = 1.5, 3.5 Hz, C_1-H), 1.91 (s, 1 H, C_4-H), 2.00 (ddd, 1 H, J = 1.5, 3.5, 10.0 Hz, C_6-H_{exo}), 2.09 (ddd, 1 H, J = 3.5, 7.0, 14.0 Hz, C_7-H_{anti}), 3.94 (d, 1 H, J = 3.5 Hz, C_5-(OH)*H*); ^{13}C NMR ($CDCl_3$, ppm) 21.61 (q, CH_3), 23.65, 25.46 (two q, *gem*-CH_3), 31.18 (t, C_7), 37.14 (t, C_6), 43.74 (s, C_2), 50.28 (d, C_1), 60.79 (d, C_4), 70.43 (d, C_5), 78.95 (s, C_3); IR (KBr) 3320, 1030 cm^{-1} (–OH); mass *m/e* 152 ($M^+ - H_2O - CH_3$). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.63; H, 10.80.

2,3,3-Trimethylbicyclo[2.2.1]heptane-2,6(*endo*)-diol (4b): mp 105–108 °C; ^1H NMR ($CDCl_3$, ppm) 0.89, 1.01 (2 s, 6 H, *gem*-CH_3), 1.13 (s, 3 H, C_3-(OH)CH_3), 1.20–1.40 (m, 2 H, C_7-H_2), 1.55 (dd, 1 H, J = 3.0, 8.5 Hz, C_6-H_{exo}), 1.73 (br d, 1 H, J = 3.0 Hz, C_1-H), 1.88–2.02 (m, 2 H, C_4-H and C_6-H_{endo}), 4.15 (d, 1 H, J = 6.5 Hz, C5-(OH)*H*); IR (KBr) 3320, 1045 cm^{-1} (–OH); mass *m/e* 155 ($M^+ - CH_3$), 152 ($M^+ - H_2O$), 137 ($M^+ - H_2O - CH_3$). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.71; H, 10.84.

Although the stereochemistry of the C_2-hydroxy group in **4a** and **4b** has not been determined as yet, gas chromatographic analysis (column: 10% Silicon SE-30 on Chromosorb B, at 180 °C) indicated that both of products consist of their corresponding stereoisomers in the ratio of ca. 4/1 to 5/1.

***exo*-7,7-Dimethyl-6-methylenebicyclo[2.2.1]heptan-2-ol (2b)**: mp 60–62 °C (3,5-dinitrobenzoate mp 115–116 °C); ^1H NMR ($CDCl_3$, ppm) 0.94, 1.24 (2 s, 6 H, *gem*-CH_3), 2.30 (d, 1 H, J = 6.0 Hz, C_5-H), 3.95 (dd, 1 H, J = 3.5, 8.0 Hz, C_6-(OH)*H*), 4.72, 4.93 (2 dd, 2 H, J = 1.5, 4.0 Hz, $=CH_2$); ^{13}C NMR ($CDCl_3$, ppm) 22.13, 22.83 (2 q, *gem*-CH_3), 35.86 (t, C_5), 41.23 (t, C_3), 45.73 (d, C_4), 45.96 (s, C_7), 61.96 (d, C_1), 76.15 (d, C_6), 105.76 (t, C_2), 152.07 (s, C_8); mass *m/e* 152 (M^+), 137 ($M^+ - CH_3$), 134 ($M^+ - H_2O$), 119 ($M^+ - CH_3 - H_2O$). Anal. Calcd for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.01; H, 10.53.

***exo*-3,3,7-Trimethyl-8-methylenetricyclo[5.4.0.0^{2,9}]undecan-10-ol (2c)**: mp 79–80 °C (3,5-dinitrobenzoate mp 150–151 °C); ^1H NMR ($CDCl_3$, ppm) 1.00 (three s, 9 H, CH_3), 2.60–2.68 (m, 1 H, C_9-H), 3.55–3.85 (m, 1 H, C_{10}-(OH)*H*), 4.55, 4.90 (2 s, 2 H, $=CH_2$); ^{13}C NMR ($CDCl_3$, ppm) 21.14 (t, C_{10}), 29.43, 30.31, 30.54 (3 q, CH_3), 31.59 (s, C_8), 33.29 (s, C_2), 36.91 (t, C_9), 38.48 (t, C_{11}), 43.21 (t, C_6), 44.97 (d, C_1), 57.52 (d, C_7), 57.94 (d, C_4), 74.46 (d, C_5), 102.55 (t, C_{12}), 163.22 (s, C_3); IR (KBr) 3300, 1052 (–OH), 980, 882 cm^{-1} ($=CH_2$); mass *m/e* 220 (M^+). Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.58; H, 10.89.

2-(2,2-Dimethyl-3-methylenecyclopentyl)ethanol (iso-α-campholenol) (9): bp 93–94 °C (5 mm); ^1H NMR ($CDCl_3$, ppm) 0.83, 1.05 (2 s, 6 H, *gem*-CH_3), 2.38 (m, 2 H, C_4-H_2), 3.71 (m, 2 H, C_1-(*OH*)H_2), 4.76, 4.78 (2 d, 2 H, J = 2.5 Hz, $=CH_2$); ^{13}C NMR ($CDCl_3$, ppm) 23.42, 26.57 (2 q, *gem*-CH_3), 28.36 (t, C_5'), 30.78 (t, C_2), 33.17 (t, C_4'), 43.97 (s, C_2'), 46.89 (d, C_1'), 62.43 (t, C_1), 103.01 (t, $=CH_2$), 162.23 (s, C_3'); mass *m/e* 154 (M^+), 139 ($M^+ - CH_3$), 136 ($M^+ - H_2O$), 121 ($M^+ - CH_3 - H_2O$). Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 78.01; H, 11.52.

Camphere glycol (10): mp 140.5–141.0 °C; ^1H NMR ($CDCl_3$, ppm) 0.94, 1.02 (2 s, 6 H, *gem*-CH_3), 2.12 (m, 1 H, C_4-H), 3.66 (ddd, J = 3.5, 5.5, 11.0 Hz, 2 H, C_3-CH_2OH); IR (KBr, cm^{-1}) 3425, 1070, 990 (–OH); mass *m/e* 170 (M^+), 152 ($M^+ - H_2O$), 139 ($M^+ - CH_2OH$). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.49; H, 10.71.

Bornane-2,10-*diol* (*11*): mp 172–173.5 °C; ^1H NMR ($CDCl_3$, ppm) 0.88, 1.14 (2 s, 6 H, *gem*-CH_3), 3.65, 3.94 (2 d, 2 H, J = 11.0 Hz, C_{10}-(OH)H_2), 3.94 (dd, J = 4.0, 7.5 Hz, 1 H, C2-(OH)*H*); IR (KBr, cm^{-1}) 3350, 1045 (–OH); mass *m/e* 152 ($M^+ - H_2O$), 137 ($M^+ - H_2O - CH_3$). Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.54; H, 10.66. Found: C, 70.81; H, 10.59.

Elimination of Acetic Acid from a Stereoisomeric Mixture of 2,3,3-Trimethyl-2,6-diacetoxybicyclo[2.2.1]heptanes (5a,b). In 30 mL of glacial acetic acid was dissolved 5.08 g (0.02 mol) of a stereoisomeric mixture of the title diacetates **5a,b**, obtained directly from anodic oxidation of tricyclene (**1a**), and the solution was refluxed for 10 h. After the acetic acid was removed under reduced pressure, the residue was poured into 50 mL of 10% aqueous sodium carbonate solution and extracted with ether three times. The combined ethereal solution was washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Filtration of the drying agent and evaporation of the solvent gave an oily material, which was subjected to fractional distillation to give 3.47 g of a stereoisomeric mixture of *exo*- and *endo*-2-acetoxy-5,5-dimethyl-6-methylenebicyclo[2.2.1]heptane (**6a,b**) in the ratio of 10 to 2–3 (89.5%).

2,3,3-Trimethyl-2,6-diacetoxybicyclo[2.2.1]heptanes (5a,b): bp 168–173 °C (2 mm); ^1H NMR (CCl_4, ppm) 0.92, 1.03, 1.47 (s, 9 H, CH_3), 1.90, 1.94 (s, 6 H, OCOCH_3), 2.72 (br s, 1 H, CH), 4.62–4.83 (m, 1 H, C(H)OCO); IR (neat, cm^{-1}) 1740 (C=O), 1250–1230 (C—O); mass *m/e* 152 ($M^+ - OCOCH_3 - COCH_3$), 137 ($M^+ - OCOCH_3 - COCH_3 - CH_3$). Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.48; H, 8.81.

***exo*-2-Acetoxy-5,5-dimethyl-6-methylenebicyclo[2.2.1]heptane (nojigiku acetate) (6a)**: bp 74–75 °C (1 mm) (lit.[4] bp 60–61 °C (0.75 mm)).

***endo*-2-Acetoxy-5,5-dimethyl-6-methylenebicyclo[2.2.1]heptane (isonojigiku acetate) (6b)**: bp 76–78 °C (1 mm); ^1H NMR (CCl_4, ppm) 1.10 (s, 6 H, CH_3), 2.00 (s, 3 H, $OCOCH_3$), 2.68 (br s, 1 H, CH), 4.5–4.7 (m, 1 H, C(H)OCO), 4.53, 4.93 (s, 2 H, $=CH_2$); IR (neat, cm^{-1}) 1740 (C=O), 1250, 1230, 1030 (C—O), 1660, 890 ($=CH_2$); mass *m/e* 194 (M^+) 179 ($M^+ - CH_3$). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.31; H, 9.28.

Measurement of Oxidation Potential of Tricyclene (1a), Camphene (7), and Bornylene (8). Measurement of the half-wave potential for **1a**, **7**, and **8** was carried out by single-sweep voltammetry (sweep rate 100 mV/s) in anhydrous acetonitrile containing 0.1 M tetrabutylammonium perchlorate using a Hokuto Denko polarographic analyzer system equipped with a potentiostat HA-303, a function generator HB-104, and a rotating platinum electrode. A saturated calomel electrode (SCE) was used as a reference electrode. The results are summarized in Chart I.

Anodic Oxidation of Tricyclene (1a) in a Large-Scale Using a Flow System Electrolysis Instrument. Into a mixture of 31.5 kg of acetic acid and 1.0 kg of water was added carefully 1.22 kg (12.2 mol) of triethylamine and 2.25 kg (16.5 mol) of the starting hydrocarbon mixture consisting of tricyclene (**1a**), camphene (**7**), and bornylene (**8**) in the ratio of 75%, 16%, and 9%, respectively. The solution was oxidized under the constant current conditions, keeping current density at 15 mA/cm^2 and the flow rate of the solution 15–18 L/min, at 25–35 °C using a semipilot scale electrolysis instrument equipped with a modified ElectroSyn Cell of ElectroCell AB Co. Ltd. (carbon plate as an anode and stainless plate as a cathode), as shown in Figure 2. The composition of the reaction mixture was monitored by periodically sampling for the amount of current passed. The results are shown in Figure 3.

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Registry No. **1a**, 508-32-7; **1b**, 488-97-1; **1c**, 1137-12-8; **2a**, 54672-39-8; **2b**, 125948-46-1; **2b** (3,5-dinitrobenzoate), 125846-50-6; **2c**, 64854-50-8; **2c** (3,5-dinitrobenzoate), 125846-51-7; **3**, 83290-63-5; **4a** (isomer 1), 104462-63-7; **4a** (isomer 2), 104528-33-8; **4b** (isomer 1), 104459-12-3; **4b** (isomer 2), 104528-34-9; **5**, 97090-49-8; **6a**, 87422-04-6; **6b**, 125948-47-2; **7**, 79-92-5; **8**, 464-17-5; **9**, 99977-70-5; **10**, 466-12-6; **11**, 1925-39-9; α-pinene, 80-56-8; β-pinene, 127-91-3.

The Conversion of an Aziridine to a β-Lactam

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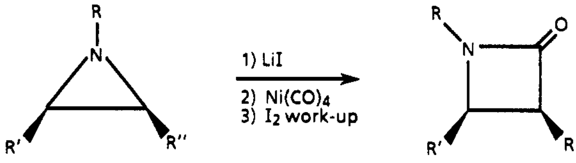
A one-pot, inert atmosphere conversion of an aziridine to a β-lactam using nickel tetracarbonyl as the carbonyl source is described. In this reaction it is the less substituted carbon–nitrogen bond which is carbonylated. The proposed mechanism for this reaction requires that a nickel acylate complex attack an alkyl iodide with inversion of configuration. Iron carbonyl complexes are unsuccessful in this carbonylation process.

Because of the ready availability of aziridines[1] and the great importance of β-lactams,[2] we have recently developed[3] a one-pot, low-pressure reaction, using nickel tetracarbonyl, for the conversion of an aziridine to a β-lactam. In this reaction, it is the *less* substituted carbon–nitrogen bond which is carbonylated. This result is complementary to a previously known,[4] high-pressure reaction, using rhodium, in which the *more* substituted carbon–nitrogen bond is carbonylated.



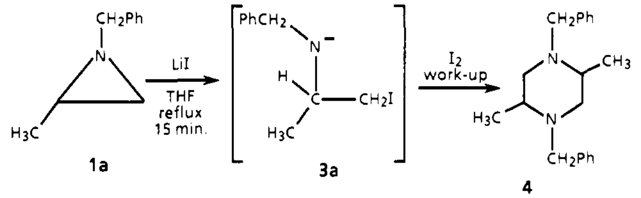
1 2

In this paper, we discuss a variety of substituents which are compatible with this chemistry (Table I) and those which are not, we report full experimental details, and we propose a mechanism of this nickel-promoted carbonylation reaction. In addition, we show that iron carbonyl complexes do not act as a carbonyl source for this transformation.

Results

Carbonylation of 1-Benzyl-2-methylaziridine (1a). Because the first step in the conversion of aziridine **1a** to β-lactam **2a** (Table I) is the S_N2 ring opening of the aziridine by lithium iodide in refluxing tetrahydrofuran (THF), the thermal stability of aziridine **1a** must be determined. Therefore, it was allowed to reflux in THF for over 3 h, and then subjected to the iodine workup conditions. 1-Benzyl-2-methylaziridine (**1a**) was recovered almost quantitatively from this sequence.

Next, **1a** was treated with lithium iodide in refluxing THF to effect a ring opening, which is complete in 15 min. To confirm this point and to observe the putative intermediate **3a**, NMR spectroscopy was attempted on the reaction mixture; however, the reaction solution is too dilute to see peaks other than those due to solvent. Upon concentration, only a mixture of stereoisomers of the six-membered ring dimer **4**[5] and the starting aziridine **1a** could be observed. If, instead, the solution is subjected to an iodine workup, again only a mixture of the six-membered ring dimer **4** and a very small amount of the starting aziridine **1a** could be observed. When the LiI reaction is allowed to proceed for a longer period, the results are very similar to the results for the 15 min reaction.



Because lithium iodide may be contaminated by iodine, the effect of iodine on the starting material was determined. When aziridine **1a** is allowed to reflux in THF for 15 min with added iodine, only benzyl iodide and bibenzyl are isolated. Thus, the ring opening of the aziridine is due to lithium iodide and is complete in 15 min.

After ring-opening, the next step of the carbonylation sequence is the reaction of the proposed intermediate **3a** with nickel tetracarbonyl. After **1a** and lithium iodide were allowed to reflux in THF, the reaction solution was cooled to room temperature, nickel tetracarbonyl was added, and the solution was heated to reflux for an additional 3 h under an inert atmosphere. Alternatively, once the ring-opening reaction was allowed to cool to room temperature, the solution was saturated with carbon monoxide, nickel

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