Electrolysis of *N*-(Benzyloxycarbonyl)-2-phenylproline (4). The proline (1.63 g, 5 mmol) was electrolyzed in 20 mL of aqueous tetrahydrofuran (water/tetrahydrofuran = 3:1) containing 0.25 mL of 1 N potassium hydroxide at 8–10 °C at a constant current of 0.5 A. The electrolysis was discontinued when the theoretical amount of current was passed. The electrolyzed solution was concentrated to about 15 mL under reduced pressure. The solution was shaken with two 50-mL portions of ethyl acetate. The combined ethyl acetate layers were dried over magnesium sulfate and then evaporated to dryness in vacuo to afford 1.2 g (81%) of colorless crystals of 4-(benzyloxycarbonylamino)butyrophenone (**5**). Recrystallization from ethyl acetate–hexane gave the pure compound: mp 86–87 °C; IR (Nujol) 3350, 1710, 1670 cm^{-1}; NMR ($CDCl_3$) δ 1.8–2.3 (m, 2 H), 2.9–3.5 (m, 4 H), 4.8–5.2 (m, 1 H), 5.10 (s, 2 H), 7.30 (s, 5 H), 7.1–8.1 (m, 5 H). Anal. Calcd for $C_{18}H_{19}O_3N$: C, 72.70; H, 6.44; N, 4.71. Found: C, 72.23; H, 6.43; N, 4.64.

Compound 7a. Compound **6** (5.16 g, 0.04 mol) was electrolyzed according to the general electrolysis procedure. The electrolyzed solution was evaporated to dryness in vacuo below 30 °C. The residue was extracted with ethyl acetate, and the solution was treated with activated charcoal and filtered. The filtrate was evaporated to dryness in vacuo below 30 °C to afford 4.5 g (98%) of compound **7a**, which was recrystallized from ethyl acetate–hexane: mp 59–60.5 °C; IR (Nujol) 3180, 1710–1660 (broad) cm^{-1}; NMR ($CDCl_3$) δ 1.8–2.6 (m, 4 H), 3.30 (s, 3 H), 4.8–5.0 (m, 1 H), 8.70 (broad s, 1 H). Anal. Calcd for $C_5H_9O_2N$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.17; H, 7.89; N, 12.21.

Compound 7b. Compound **6** (5.16 g, 0.04 mol) was oxidized in aqueous tetrahydrofuran. After the theoretical amount of current was passed, the electrolyzed solution was evaporated to dryness in vacuo below 30 °C. The residue was dissolved in a mixture of acetonitrile (100 mL) and tetrahydrofuran (100 mL). The solution was dried over magnesium sulfate and then evaporated to dryness in vacuo below 30 °C. The resulting syrup (4.2 g) was washed with ether and ethyl acetate. The resulting crystals were recrystallized from ethanol–tetrahydrofuran to afford 0.5 g (13%) of compound **7b**: mp 146–148 °C (prism); IR (Nujol) 3180, 3110, 1690 cm^{-1}; NMR (Me_2SO-d_6) δ 1.5–2.6 (m, 4 H), 3.4 (broad s, 1 H), 4.9–5.2 (m, 1 H), 8.56 (broad s, 1 H). Anal. Calcd for $C_4H_7NO_2$: C, 47.52; H, 6.98; N, 13.86. Found: C, 47.66; H, 7.11; N, 13.59. From the filtrate of the recrystallized solution was recovered 0.8 g of the starting material.

Acknowledgment. We would like to thank Professor Mituyosi Kawanisi, Kyoto University, for his valuable suggestions. We are also grateful to Dr. Ichiro Chibata, Director of our Research Laboratory, for his encouragement.

Registry No.—**1a**, 13200-83-4; **1b**, 68-95-1; **1c**, 23500-13-2; **1d**, 5874-58-8; **1e**, 5700-74-3; **1f**, 69352-26-7; **1g**, 1160-54-9; **1h**, 28697-09-8; **2a**, 61020-06-2; **2b**, 63050-21-5; **2c**, 68471-61-4; **2d**, 69001-12-3; **2e**, 69352-20-1; **2f**, 69352-21-2; **2g**, 69352-22-3; **2h**, 66893-75-2; **2i**, 69001-13-4; **2j**, 69352-23-4; **2k**, 69352-24-5; **2l**, 69352-25-6; **2m**, 69622-67-9; *cis*-**3**, 69352-27-8; *trans*-**3**, 69352-28-9; **4**, 69352-29-0; **5**, 69352-30-3; **6**, 98-79-3; **7a**, 63853-74-7; **7b**, 62312-55-4; (*S*)-proline, 147-85-3; (*R*)-pipecolic acid, 1723-00-8; *N*-(benzyloxycarbonyl)glycine, 1138-80-3; proline ethyl ester, 5817-26-5.

Supplementary Material Available: IR, NMR, and mass spectral data for compounds **2a–m** and **3** (4 pages). Ordering information is given on any current masthead page.

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Electrosynthesis of Hetero–Hetero Atom Bonds. 3. Sodium Bromide Promoted Electrolytic Cross-Coupling Reaction of Imides with Disulfides. Convenient Synthesis of *N*-(Cyclohexylthio)phthalimide, an Important Prevulcanization Inhibitor

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In our preceding paper, we reported the synthesis of 2-benzothiazolyl- and thiocarbamylsulfenamides from the corresponding disulfides and amines by electrolytic cross-coupling.[1] However, extension to the preparation of thiophthalimides (**1a**) and thiosuccinimides (**1b**) (sulfenimides)[2] by cross-coupling of imides **2** with disulfides **3** under similar conditions gave only ~20% yields of **1** even after passage of 5–10 equiv of electricity. This result can be ascribed to lack of an equilibrium reaction between imides **2**–disulfides **3** and sulfenimides **1**.[1] In an effort to find a more suitable electrochemical procedure for the cross-coupling of **2** and **3**,[3]

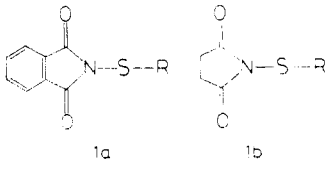

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Table I. Electrolytic Cross-Coupling of Phthalimide with Dicyclohexyl Disulfide[a]

entry	halide salts (mg)	current, mA/cm²	time, h	electricity passed, faraday/mol	sulfenimide **1a**[d] (R = cyclohexyl) yield, %[b]
1		4.0–0.3	46	10	17
2	NaBr (1)	1.7–0.3	24	7	71
3	NaBr (10)	1.5–0.3	18	2.4	99
4	NaBr (20)[c]	1.2–0.3	40	2.5	94
5	NaI (20)	7.5–0.3	24	3	85
6	NaCl (20)	10.8–0.3	24	3	36
7	LiBr (30)	5.0–0.7	22	4	66
8	KBr (50)	4.3–0.7	22	4	39
9	$MgBr_2$ (100)	6.0–0.8	20	4	30
10	NH_4Br (50)	7.5–0.6	20	4	trace

[a] Carried out under a constant voltage of 3 V at 15–20 °C in MeCN (20 mL) containing Et_4NClO_4 (100 mg). [b] Isolated yield. [c] Carried out without using Et_4NClO_4. [d] Registry no., 17796-82-6.

Table II. Electrolytic Cross-Coupling of Imides with Disulfides[a]

entry	imide **2**	disulfide **3** (RSSR), R	registry no.	current, mA/cm²	time, h	electricity passed, faraday/mol	sulfenimide **1** yield,[b] %	registry no.
1	phthalimide	phenyl	882-33-7	3.3–0.3	18	3	93	14204-27-4
2	phthalimide	benzyl	150-60-7	3.7–0.7	20	3	94	14204-26-3
3	phthalimide	*o*-nitrophenyl	1155-00-6	3.8–0.2	20	4	3	61639-74-5
4	succinimide	cyclohexyl	2550-40-5	3.3–0.2	20	3	99	17796-91-7
5	succinimide	phenyl		3.7–0.3	22	6	94	14204-24-1
6	succinimide	benzyl		1.7–0.3	22	3	93	14204-23-0

[a] Carried out under a constant voltage of 3 V at 15–20 °C in acetonitrile (20 mL) containing Et_4NClO_4 (100 mg) using two Pt electrodes (2 × 3 cm²). [b] Isolated yields.

we have studied the effect of halide salt on the electrosynthesis of sulfenimides **1** and found a potentially useful electrolytic cross-coupling reaction of **2** with **3**, assisted by sodium bromide in acetonitrile.

Electrosynthesis of Sulfenimides 1. Electrolysis of a mixture of phthalimide (**2a**) and dicyclohexyl disulfide (**3**, R = cyclohexyl) in acetonitrile containing a catalytic amount of sodium bromide was carried out under a constant voltage of 3 V, 0.7–0.9 V vs. SCE, using two platinum electrodes at 18–20 °C. During the electrolysis, the current varied from ~2 to 0.3 mA/cm². Passage of ~0.25 F/mol of electricity, based on disulfide **3**, afforded the desired **1a** (R = cyclohexyl) in quantitative yield (Table I, entry 3). Remarkably, without using sodium bromide (entry 1) the electrolysis provided **1a** in only 17% yield, indicating that the presence of sodium bromide is indispensable for the efficient S–N bond-making reaction. Sodium iodide can also be used for the present purpose (entry 5), but sodium chloride gives only a poor yield of **1** (~36%) along with undesired byproducts[4] (entry 6). The striking effect of the counterions for the cross-coupling reaction was found since the yields of **1a** increase in the order as follows: $Na^+ > Li^+ > K^+ > Mg^{2+} > NH_4^+$ (entries 7–10). Apparently, sodium bromide is a highly effective catalyst as well as an efficient supporting electrolyte for the sulfenimide synthesis. In contrast to ammonium bromide, alkali bromides reword on the formation of **1**, which can be explained by assuming that alkali metals provided by cathodic reaction of alkali ions would, in turn, react with imides **2** to give imide anions **a** as precursors of **4** (Scheme I). However, the reaction of ammonia, derived from the discharge of ammonium ion on the cathode, with imides **2** cannot be expected at all (entry 10). The electrolyses of two series of sulfenimides **1** derived from phthalimide (**2a**) and succinimide (**2b**) are summarized in Table II.

Scheme I

$$\underset{\mathbf{2}}{2R'(CO)_2NH} + 2e^- \xrightarrow{\text{at the cathode}} \underset{\mathbf{a}}{2R'(CO)_2N^-} + H_2 \quad (1)$$

$$2Br^- \xrightarrow{\text{at the anode}} Br_2 + 2e^- \quad (2)$$

$$R'(CO)_2N^- + Br_2 \longrightarrow \underset{\mathbf{4}}{R'(CO)_2NBr} + Br^- \quad (3)$$

$$\underset{\mathbf{3}}{R'(CO)_2NBr} + RSSR \longrightarrow \underset{\mathbf{1}}{R'(CO)_2NSR} + RSBr \quad (4)$$

$$RSSR + Br_2 \longrightarrow \underset{\mathbf{b}}{2RSBr} \quad (5)$$

$$R'(CO)_2N^- + RSBr \longrightarrow R'(CO)_2NSR + Br^- \quad (6)$$

$$2R'(CO)_2NH + RSSR \xrightarrow{2\ F/mol} 2R'(CO)_2NSR + H_2 \quad (7)$$

$R'(CO)_2NH$ = phthalimide (**2a**) or succinimide (**2b**)

Mechanistic Consideration of S–N Bond Formation. The current-potential curves of a mixture of **2a** and **3** (R = cyclohexyl) in acetonitrile containing Et_4NClO_4 (curve A, entry 1 of Table I) and Et_4NClO_4–NaBr (curve B, entry 3) are shown in Figure 1. Curve B reveals that the current begins to pass at 0.5 V vs. SCE, close to the discharge potential of bromide ion (~0.6 V vs. SCE).[5] Obviously, under the conditions employed (0.7–0.9 V vs. SCE), bromide ion would be oxidized to bromine or bromonium ion by loss of two electrons on the anode. On the other hand, the imides **2** would be reduced cathodically to give the corresponding imide anions (**a**, eq 1 in Scheme I), which would give the *N*-bromoimides **4** by reaction with either bromine (eq 3 in Scheme I) or bromonium ion. Independently, electrolysis of succinimide (**2b**) in ace-

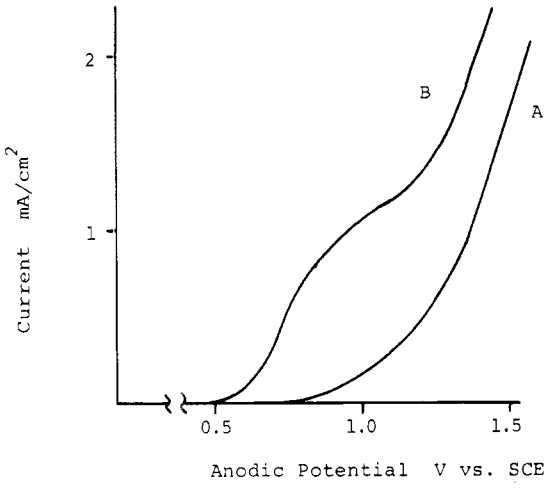
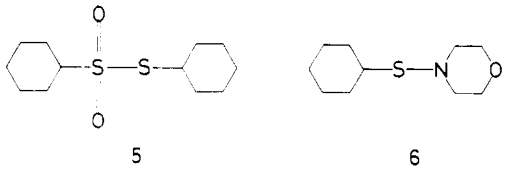


Figure 1. Current–potential curves: (A) **2a** (4 mmol), **3** (R = cyclohexyl; 2 mmol), Et_4NClO_4 (100 mg), and MeCN (20 mL); (B) in the presence of NaBr (10 mg).

tonitrile containing sodium bromide without the presence of **3** afforded the corresponding *N*-bromosuccinimide **4**[6] in 80% yield. The bromides **4** would react with the disulfides **3** to afford sulfenimides **1** as well as sulfenyl bromides (b, eq 4 in Scheme I). A plausible mechanism for the electrolytic S–N bond formation is shown in equations 1–7 in Scheme I. In the course of electrosynthesis of **1**, 2 faradays of electricity must be consumed for conversion of 2 mol of the imides **2** and 1 mol of the disulfides **3** into 2 mol of the sulfenimides **1** (see summary eq 7 in Scheme I) since sulfenyl bromides (b), which would also be provided by the reaction shown in eq 5, can react with a to give **1**. The electrolysis would proceed by the repeated anodic oxidation of bromide ion as well as by the cathodic reduction of imides **2** (eq 1 and 2). Apparently, sodium bromide would circulate in the electrolysis solution as a redox catalyst.

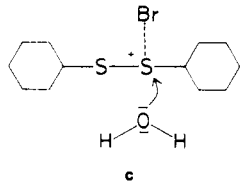
On the other hand, electrolytic coupling of bis(*o*-nitrophenyl) disulfide (**3**, R = *o*-nitrophenyl) with phthalimide (**2a**) yielded the desired sulfenimide **1a** in ~3% yield (Table II, entry 3), indicating that the electron-withdrawing nature of the *o*-nitro group would inhibit electrophilic attack of *N*-bromophthalimide (**4**) to the disulfide **3**.

When a suspension of phthalimide (**2b**) and disulfide **3** (R = cyclohexyl) was electrolyzed in aqueous acetonitrile, the corresponding thiosulfonate **5** was obtained in 61% yield along with recovered **2b**. Apparently, the above solvent system can provide the sulfur-oxidized product **5** by nucleophilic attack of water on the cation c.



5

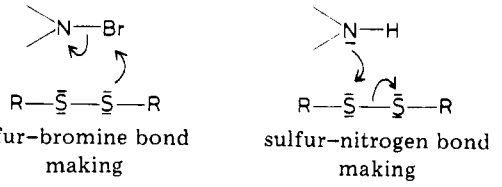
6



c

The halide salt promoted electrosynthesis can be distinguished from the previously reported results[1] of electrolytic cross-coupling reaction of disulfides **3** and amines. The present reaction is thought to proceed initially by nucleophilic attack of the sulfur atom of **3** on the cationic bromine atom as shown

Scheme II



in the sulfur–bromine bond-making mechanism of eq 4 and 5, whereas the previous results can be explained by considering a sulfur–nitrogen bond-making mechanism (Scheme II). Therefore, the disulfide **3** bearing strong electron-withdrawing groups, such as 2-benzothiazolyl, thiocarbamyl, and *o*-nitrophenyl, can be used for the direct electrosynthesis of sulfenamides.[1] Indeed, electrosynthesis of *N*-phenylthiomorpholine (**6**) from diphenyl disulfide (**3**, R = phenyl) and morpholine in the absence of halide salts failed. But the halide salt promoted electrosynthesis of **6** was successful since the electrolysis of sodium iodide in a solution of **3** (R = phenyl) and morpholine in acetonitrile afforded **6** in 92% yield.

Experimental Section

All melting points are uncorrected. IR spectra were determined with a JASCO Model IRA-1 grating spectrometer. ^1H NMR spectra were obtained with Hitachi R-24 and/or JEOL MH-100 spectrometers. Chemical shifts (δ) are expressed in parts per million downfield from internal Me_4Si. Current–potential measurements were carried out by using a Kowa Electronics Model PGS-1550 potentio-galvanostat and a FG-102A function generator.

Electrolysis Apparatus. Electrolysis was carried out in an undivided cell (3.5-cm d., height 10 cm) fitted with a gas lead pipe, a thermometer, a magnetic stirrer, and two platinum foil electrodes (2 × 3 cm^2) placed parallel to each other 7 mm apart. Regulated dc power was supplied by a Metronix Model 543B instrument.

Electrosynthesis of Sulfenimides 1 from Imides 2 and Disulfides 3. Unless otherwise noted, a suspension of imide **2** (4.4 mmol), disulfide **3** (2.0 mmol), and NaBr (10 mg) in acetonitrile (20 mL) containing Et_4NClO_4 (100 mg) was electrolyzed under a constant applied voltage of 3 V. A typical procedure is as follows (Table I, entry 3). A suspension of phthalimide (**2a**; 650 mg, 4.4 mmol) and dicyclohexyl disulfide (**3**, R = cyclohexyl; 468 mg, 2.0 mmol) in acetonitrile (20 mL) in the presence of NaBr (10 mg) and Et_4NClO_4 (100 mg) was electrolyzed at 3 V (applied voltage), 0.7–0.9 V vs. SCE, 1.5–0.3 mA/cm^2, at 18–20 °C. After the passage of 4.8×10^{-3} faradays of electricity for 18 h, most of the solvent was removed. The residue was chromatographed (SiO_2, benzene) to give 1050 mg (99%) of **1a** (R = cyclohexyl): mp 92–93 °C (acetone) (lit.[3b] mp 93–94 °C); IR (Nujol) 1780, 1740, 1730, 1707 (C=O), 1607 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90–2.30 (m, 10, CH_2), 2.80–3.50 (m, 1, HCS), 7.60–8.20 (m, 4, HC=C).

Details of the reaction conditions and results are given in Tables I and II. Physical and spectral data of the products **1** are as follows.

1a (R = phenyl): mp 160–161 °C (acetone) (lit.[3b] mp 160–161 °C); IR (Nujol) 3020 (HC=C), 1780, 1744, 1729, 1706 (C=O), 1607 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.05–8.06 (m, 9).

1a (R = benzyl): mp 163.5–164.5 °C (acetone) (lit.[3b] mp 167–167.5 °C); IR (Nujol) 3100 (HC=C), 1783, 1747, 1714 (C=O), 1608 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.11 (s, 2, CH_2), 7.24 (broad s, 5, HC=C), 7.80 (broad s, 4, HC=C).

1b (R = cyclohexyl): mp 104.5–105 °C (EtOH) (lit.[3b] mp 99 °C); IR (Nujol) 1716 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 1.00–2.05 (m, 10, CH_2), 2.87 (s, 4, CH_2CO), 3.20 (broad, 1, HCS).

1b (R = phenyl): mp 114.5–115.5 °C (EtOH) (lit.[3b] mp 115–116 °C); IR (Nujol) 3200 (HC=C), 1720 (shoulder), 1708, 1686 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.80 (s, 4, CH_2CO), 7.20–7.80 (m, 5, HC=C).

1b (R = benzyl): mp 158–159.5 °C (acetone) (lit.[3b] mp 165–166 °C); IR (Nujol) 3180 (HC=C), 1752, 1714, 1695 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.66 (s, 4, CH_2CO), 4.13 (s, 2, CH_2), 7.33 (s, 5, HC=C).

Preparation of 1b (R = Phenyl) via *N*-Bromosuccinimide (4). A mixture of **2b** (200 mg, 2.0 mmol) and NaBr (103 mg, 1.0 mmol) in acetonitrile (20 mL) containing Et_4NClO_4 (100 mg) was electrolyzed at 4 V, 3.7–0.3 mA/cm^2, at 15–20 °C for 17 h (3.5 F/mol based on NaBr). To the electrolysis solution was added 3 (R = phenyl; 113 mg, 0.5 mmol) without passing electric current. The mixture was stirred

at room temperature for 3 h. After evaporation of the solvent, the residue was chromatographed (SiO_2, benzene) to give **1b** (R = phenyl; 210 mg, 98%), mp 114.5–116 °C (lit.[3b] mp 115–116 °C).

When the electrolysis solution was worked up without addition of **3** (R = phenyl), there was obtained *N*-bromosuccinimide (**4**; 71 mg, 80% based on NaBr), mp 176–178 °C (lit.[6] mp 178.5 °C).

Electrolysis of a Mixture of 2a and 3 (R = Cyclohexyl) in Acetonitrile–Water. A suspension of **2a** (650 mg, 4.4 mmol), **3** (R = cyclohexyl; 460 mg, 2.0 mmol), and NaBr (30 mg) in a mixed solvent of acetonitrile (5 mL) and water (20 mL) was electrolyzed at 3 V, 2.0–1.2 mA/cm^2, at 23–27 °C. After the passage of 6.26×10^{-3} faradays of electricity for 24 h, the mixture was filtered and the solids were washed twice with water and once with benzene and air-dried to give **2a** (562 mg, 86%). The filtrate and washing were combined and extracted with ether. The extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed (SiO_2, benzene) to give **3** (14 mg) and **5**[7] (321 mg, 61%): IR (neat) 1450, 1317, 1123 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.0–2.5 (m, 20, CH_2), 2.65–3.10 (m, 1, CH), 3.10–3.72 (m, 1, CH).

Electrolytic Cross-Coupling Reaction of Morpholine with Diphenyl Disulfide (3, R = Phenyl). A mixture of **3** (R = phenyl; 437 mg, 2.0 mmol) and morpholine (400 mg, 4.6 mmol) in acetonitrile (20 mL) containing NaI (30 mg) and Et_4NClO_4 (100 mg) was electrolyzed at 3 V, 5–1.2 mA/cm^2, at 15–22 °C for 18 h. Evaporation of the solvent followed by column chromatography (SiO_2, benzene–AcOEt) gave 718 mg (92%) of sulfenamide **6**:[8] IR (neat) 3150 (HC=C), 1585 (C=C), 1256, 1112, 927 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.86–3.10 (m, 4, CH_2N), 3.58–3.85 (m, 4, CH_2O), 1.18–7.61 (m, 5, HC=C).

Registry No.—**5**, 4837-39-2; **6**, 42267-53-8; morpholine, 110-91-8; phthalimide, 85-41-6; succinimide, 123-56-8.

References and Notes

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Facile Syntheses of Optically Active Terpene Sulfonic Acids. Application to the Resolution of (±)-Phenylglycine

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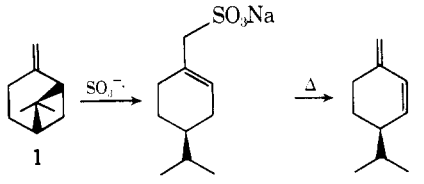
Although the resolution of racemic carboxylic acids by optically active amines is well documented, only two optically active sulfonic acids are available for the resolution of amines.[1] The availability of other optically active sulfonic acids, which could resolve amino acids, is desirable. The chirality of natural products such as terpenes makes these molecules suitable percursors for such synthesis. While the literature abounds with methods for the sulfonation of organic compounds[2] there exists a paucity of procedures for the simple preparation of optically active sulfonates, especially from olefins. Normal sulfonation reactions use SO_2, SO_3, $ClSO_3H$, oleum, etc., conditions which do not lend themselves readily to the preparation of sulfonates containing labile alternate functionalities. We wish to describe a new sulfonation reaction of β-pinene (**1**) as well as a remarkably facile synthesis of β-hydroxy sulfonates from optically active terpene epoxides.

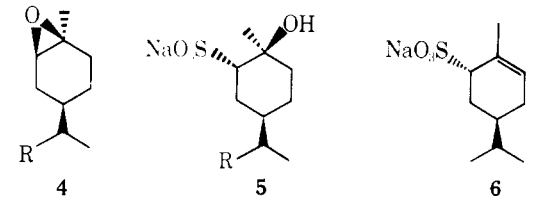
The radical addition of bisulfite at 110 °C and 45 psig to (−)-β-pinene (90.7% ee) (**1**) in the presence of an initiator and potassium nitrate[3] gave (−)-sodium (4*S*)-*p*-menth-1-ene-7-sulfonate (**2**) in ~50% yield. The ring opening of the bicyclic skeleton of β-pinene (**1**) is well known in attack by carbon



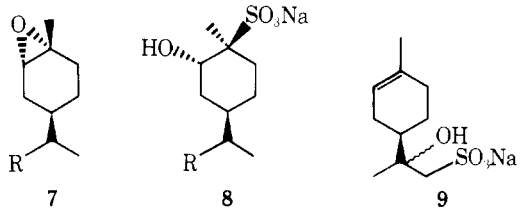
1 2 3

radicals;[4] however, sulfur-based radicals such as thiols and thioacetates yield shorter lived radical intermediates in which the integrity of the pinane structure is usually retained.[5] Acid ion-exchange chromatography gave the sulfonic acid of **2** as a brown syrup. The sulfonation of α-pinene[6] or camphene by this procedure proved less successful, the former undergoing competitive acid isomerization and hydration to α-terpineol and other products while the latter was recovered unchanged. The optical integrity of **2** was estimated by pyrolysis at 260 °C under reduced pressure, which gave (−)-β-phellandrene (**3**), $[\alpha]_d$ − 10.33°, as the major (90% GLC) menthadiene. This represents an optical purity of 65.0% for **3** or 71.6% retention of optical purity from **1**.[7] The partial racemization of **3** could arise by allylic hydrogen abstraction in **1** or **2** under free-radical conditions[8] or by a prototropic shift in **2** during pyrolysis. The formation of β-phellandrene (**3**) from **2** represents one of the few syntheses of optically active **3** in high chemical purity.[9] The cyclohexenylidene **3** is a product of kinetic control in the acid isomerization of *p*-menthadienes, from which it is usually obtained as a minor isomer.[10]

The preparation of a series of optically active β-hydroxy sulfonates was achieved by nucleophilic epoxide opening with sodium sulfite.[11] Thus (+)-*trans*-limonene oxide (**4a**) and (+)-*trans*-1,2-epoxy-*p*-menthane (**4b**, 97% ee) gave the hydroxy sulfonates (+)-(1*S*,2*S*,4*R*)-**5a** and (+)-(1*S*,2*S*,4*R*)-**5b**



4 5 6



7 8 9

a, R = H_2C=
b, R = H_3C–

in 40.3 and 64% yield, respectively, after reflux with aqueous sodium sulfite. Analysis[12] of the white crystalline hydrates of **5a** and **5b** by NMR failed to show any evidence for products of reverse addition, unlike the nucleophilic addition of alkyl amines to these epoxides.[13] Similarly, (+)-*cis*-limonene oxide (**7a**) and (+)-*cis*-1,2-epoxy-*p*-menthane (**7b**) gave the hydroxy sulfonates (−)-(1*S*,2*S*,4*R*)-**8a** and (−)-(1*S*,2*S*,4*R*)-**8b** in 28 and 44.2% yield, respectively.[14] The (+)-limonene 8,9-epoxides

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