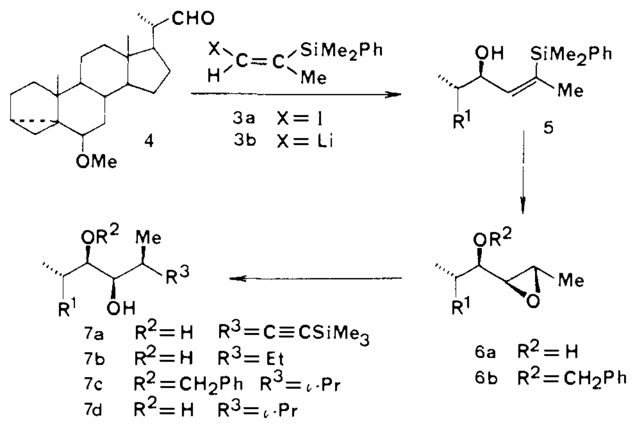
Scheme III



Palladium-catalyzed silylalumination of propyne followed by addition of iodine provided an 88:12 mixture of 2-(dimethylphenylsilyl)-1-iodo-1-propene (**3a**)[10] and its regioisomer. The desired 2-silylalkene **3a** was obtained in pure form by column chromatography. Treatment of a mixture of the aldehyde **4**[11] and iodoalkene **3a** with butyllithium at -78 °C gave, after chromatography, the (22*S*)-allylic alcohol **5**[12] in 48% yield along with the (22*R*) isomer (16% yield; Scheme III). Silyl-group-assisted stereoselective epoxidation[13] (VO(acac)$_2$-*t*-BuOOH) followed by elimination of PhMe$_2$Si group with *n*-Bu$_4$NF gave the key intermediate *threo*-α,β-epoxy alcohol **6a**[14] exclusively (65% yield). Regio- and stereoselective ring opening of epoxy alcohol with the organoaluminum compound Et$_2$AlC≡CSiMe$_3$[15] proceeded with inversion at the reacting center to give 1,2-diol **7a**[16] in 60% yield. Removal of Me$_3$Si group (KF, Me$_2$SO) and hydrogenation (H$_2$, PtO$_2$) provided **7b**.[17] Reaction of benzyl ether **6b** with the higher order mixed cuprate[18] (Me$_2$CH)$_2$Cu(CN)Li$_2$ afforded **7c**[19] (63% yield), which was transformed into **7d** (Li in liquid NH$_3$).[9b,20-22]

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[9] (a) Grove, M. D.; Spencer, G. F.; Rohwedder, W. K.; Mandava, N.; Worley, J. F.; Warthen, J. D., Jr.; Steffens, G. L.; Flippen-Anderson, J. L.; Cook, J. C. *Nature* (*London*) **1979**, *281*, 216. (b) Fung, S.; Siddall, J. B. *J. Am. Chem. Soc.* **1980**, *102*, 6581. (c) Ishiguro, M.; Takatsuto, S.; Morisaki, M.; Ikekawa, N. *J. Chem. Soc., Chem. Commun.* **1980**, 962. (d) Wada, K.; Marumo, S.; Ikekawa, N.; Morisaki, M.; Mori, K. *Plant Cell Physiol.* **1981**, *22*, 323.

[10] Pd(OAc)$_2$–phosphine combination was catalytically as effective as PdCl$_2$L$_2$ [L: phosphine ligand such as PPh$_3$, (*o*-CH$_3$C$_6$H$_4$)$_3$P]. Palladium(II) acetate (40 mg, 0.18 mmol) and (*o*-CH$_3$C$_6$H$_4$)$_3$P (0.16 g, 0.54 mmol) were combined in THF (3.0 mL). A solution of PhMe$_2$SiAlEt$_2$ derived from PhMe$_2$SiLi (12.5 mmol) and Et$_2$AlCl (12.5 mmol) in THF (20 mL) was added at 0 °C, and the whole was stirred for 10 min at 0 °C. The resulting mixture was added to propyne (neat, 4.0 mL) at -78 °C, and the mixture was stirred for 5 min at −78 °C, 2 h at 0 °C, then 30 min at 25 °C. A solution of iodine (3.2 g, 12.5 mmol) in THF (10 mL) was added dropwise at 0 °C, and the mixture was stirred for another 10 min at this temperature and poured into hexane (100 mL) containing NaF (2.0 g). Water (10 mL) was added, and the precipitate was filtered. The filtrate was washed with aqueous NaHSO$_3$ and brine and dried over Na$_2$SO$_4$. Purification by silica gel column chromatography (hexane) gave **3a** (2.8 g, 73% yield) as a clear oil: bp 85 °C (0.01 torr, bath temperature); IR (neat) 2960, 1555, 1430, 1250, 1110, 832, 814, 695 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.52 (s, 6 H), 1.80 (d, J = 1.5 Hz, 3 H), 6.72 (d, J = 1.5 Hz, 1 H), 7.07–7.61 (m, 5 H); MS, *m/e* (relative intensity) 302 (M$^+$, 2), 175 (19), 135 (100), 105 (47), 43 (76).

[11] Wiersig, J. R.; Waespe-Sarcevic, N.; Djerassi, C. *J. Org. Chem.* **1979**, *44*, 3374.

[12] ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.34 (s, 3 H), 0.38 (s, 3 H), 0.50 (s, 3 H), 0.88 (d, J = 6.0 Hz, 3 H), 0.97 (s, 3 H), 1.87 (d, J = 1.8 Hz, 3 H), 2.72 (m, 1 H), 3.29 (s, 3 H), 4.08 (d, J = 9.2 Hz, 1 H), 6.26 (dd, J = 9.2, 1.8 Hz, 1 H), 7.32 (m, 3 H), 7.50 (m, 2 H).

[13] Tomioka, H.; Suzuki, T.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 3387.

[14] ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.70 (s, 3 H), 0.98 (s, 3 H), 1.29 (d, J = 5.2 Hz, 3 H), 2.72 (m, 2 H), 2.88 (dq, J = 5.2, 2.3 Hz, 1 H), 3.29 (s, 3 H), 3.62 (dd, J = 7.5, 2.3 Hz, 1 H).

[15] Suzuki, T.; Saimoto, H.; Tomioka, H.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 3597.

[16] ^{1}H NMR (200 HMz, CDCl$_3$) δ 0.09 (s, 9 H), 0.69 (s, 3 H), 0.98 (s, 3 H), 1.15 (d, J = 8.0 Hz, 3 H), 2.57 (m, 1 H), 2.63 (m, 1 H), 2.74 (m, 1 H), 3.30 (s, 3 H), 3.48 (dd, J = 5.0, 5.0 Hz, 1 H), 3.80 (m, 1 H).

[17] ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.69 (s, 3 H), 0.80 (d, J = 6.4 Hz, 3 H), 0.91 (d, J = 6.0 Hz, 3 H), 0.93 (d, J = 7.5 Hz, 3 H), 0.98 (s, 3 H), 2.74 (m, 1 H), 3.29 (s, 3 H), 3.54 (m, 2 H); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 11.9, 12.0, 12.2, 12.3, 13.0, 19.3, 21.4, 22.8, 24.0, 24.9, 27.2, 27.9, 30.6, 33.3, 35.0, 35.2, 35.7, 37.0, 40.3, 42.6, 43.3, 47.9, 52.5, 56.4, 56.6, 74,6, 74.9, 82.4.

[18] Lipshutz, B. H.; Kozlowski, J.; Wilhelm, R. S. *J. Am. Chem. Soc.* **1982**, *104*, 2305.

[19] ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.68 (s, 3 H), 0.83 (d, J = 6.9 Hz, 3 H), 0.86 (d, J = 6.7 Hz, 3 H), 0.88 (d, J = 6.7 Hz, 3 H), 0.93 (d, J = 6.0 Hz, 3 H), 0.97 (s, 3 H), 2.72 (m, 1 H), 3.26 (s, 3 H), 3.40 (d, J = 8,0 Hz, 1 H), 3.68 (m, 1 H), 4.67 (dd, J = 17.5, 6.5 Hz, 2 H), 7.31 (m, 5 H). The regioisomer, 1,3-diol monobenzyl ether, could not be detected in the reaction mixture. The 23-oxo compound generated by the isomerization of epoxide **6b** was obtained (10% yield) as a byproduct.

[20] ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.66 (s, 3 H), 0.78 (d, J = 7.0 Hz, 3 H), 0.83 (d, J = 6.3 Hz, 3 H), 0.87 (d, J = 6.7 Hz, 3 H), 0.89 (d, J = 6.7 Hz, 3 H), 0.96 (s, 3 H), 2.72 (m, 1 H), 3.26 (s, 3 H), 3.51 (d, J = 8.9 Hz, 1 H), 3.67 (d, J = 8.9 Hz, 1 H); ^{13}C NMR (50.3 MHz, CDCl$_3$) δ 10.2, 11.9, 12.1, 13.1, 19.3, 20.7, 20.9, 21.4, 22.8, 24.0, 24.9, 27.9, 30.5, 30.7, 33.3, 35.0, 35.1, 36.8, 40,0, 40,3, 42.6, 43.3, 47.9, 52.5, 56.4, 56.5, 73.4, 74.9, 82.3.

[21] Alternatively **7d** was obtained in 42% yield from **7a** by the following series of procedures: acetylation of diol, hydration of silylacetylene (HgSO$_4$) to ketone, Wittig methylenation (Ph$_3$P=CH$_2$), hydrogenation, and final deacetylation.

[22] Financial support by the Ministry of Education, Science, and Culture, Japanese Government (Grant-in-Aid for Special Project Research 57118006) is acknowledged.

Nitroxyl-Mediated Electrooxidation of Alcohols to Aldehydes and Ketones

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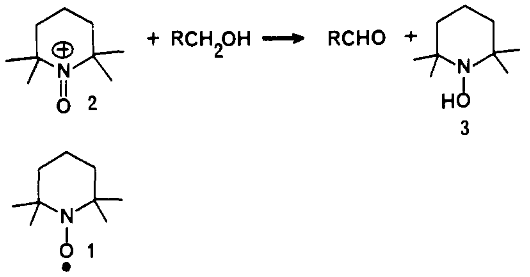
Chemically mediated[1,2] electrooxidation of alcohols can be achieved with 2,2,6,6-tetramethylpiperidine nitroxyl (**1**); oxoammonium **2** is the active oxidizing agent and hydroxylamine **3** is the byproduct.[3] The process occurs at low potential (ca. +0.4



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[1] Direct electrooxidation of alcohols cannot be achieved because of the high overpotential of the hydroxyl group. Simple alcohols do not show oxidation waves under polarographic analysis in neutral solution at a platinum electrode out to +2.0 V vs. the saturated calomel electrode.

[2] Mediators previously reported required +1.0–1.3 V to recycle. (a) Thioanisole: Shono, T. *Tetrahedron Lett.* **1979**, *20*, 3861–3864. (b) Bromide anion: Shono, T.; Matsumura, Y.; Hayashi, J. *Ibid.* **1980**, *21*, 1867–1870. (c) Iodide anion: Shono, T.; Matsumura, Y.; Hayashi, J.; Mizoguchi, M. *Ibid.* **1979**, *20*, 164–168. (d) nitrate: Leonard, J. E.; Scholl, P. C.; Steckel, T. P.; Lentsch, S. E.; van de Mark, M. R. *Ibid.* **1980**, *21*, 4695–4699. (e) Poly(4-vinylpyridine): Yoshida, J.-I.; Nakai, R.; Kawabata, N. *J. Org. Chem.* **1980**, *45*, 5269.

[3] Cation **2** is easily formed by oxidation of the readily available nitroxyl **1** with, for example, chlorine,[4] peracid,[5] and electrooxidation.[6] The hydroxylamine intermediate, **3**, is known,[7] but neither preparative electrolysis nor voltammetric studies have appeared. We have now shown that the cyclic voltammetry oxidation peak potential for **3** in acetonitrile is ca. +0.8 V vs. Ag/AgNO$_3$; direct recycling would require high positive potential. However, **3** reacts with **2** to generate **1** and a proton, and **1** reenters the cycle. Therefore, the catalytic cycle can be set up at potentials just sufficient for conversion of **1** to **2** (+0.4 V vs. Ag/AgNO$_3$).

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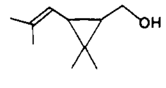
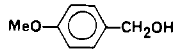
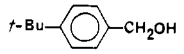
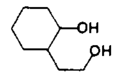
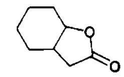
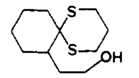
V vs. $Ag/AgNO_3$),[8] with no tendency for over-oxidation of aldehydes to acids.[10] Rapid reaction at −60 °C, a strong selectivity for primary over secondary alcohols, and electrorecycling of the oxidizing agent (5–40 turnovers) are special features.

In the stoichiometric process,[15] electrogeneration of **2** from **1** at 20 °C followed by addition of excess of 2,6-lutidine[16] and 0.5 mol equiv of *n*-dodecanol led to rapid consumption of alcohol (91%/5 min; 98%/10 min; 100%/30 min) and gave *n*-dodecanal in 100% yield. Primary alcohols react fast even at −60 °C. A solution of **1** (10 mmol),[15] using dichloromethane/acetonitrile (3:2 v:v) and lutidine (2.5 mL), and 0.2 M in lithium perchlorate converted 3-phenylpropanol (5 mmol) to 3-phenylpropanal in 90% yield after 3.0 h at −60 °C.[17]

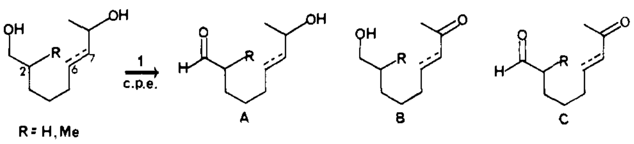
Secondary alcohols react more slowly than primary, and base-promoted loss of oxidizing agent interferes. When 5-dodecanol (0.5 mol equiv) is oxidized as above, the conversion is only 30% after 23 h. Cyclohexanol is oxidized slowly at 25 °C, with only 80% conversion (79% yield of cyclohexanone) after 4 h at 25 °C. The secondary benzylic alcohol, 1-phenyl-1-ethanol, reacts slightly faster, giving 70% conversion (100% yield of actophenone) after 2 h at 25 °C. In each of these cases, longer reaction time does not significantly increase the degree of conversion.[18]

Table I. Electrooxidation of Alcohols Mediated by TEMPO

alcohol	1, mol equiv	reaction time,[a]	yield of aldehyde,[b] %
1. *n*-$C_{12}H_{25}OH$	0.2[d]	4	81 (97)[c]
2. $Ph(CH_2)_3OH$	0.2[d]	6	78
3. 	0.3[e]	2	59 (72)[c]
4. 	0.05[f]	24	83
5. $C_3H_7CH{=}CHCH_2OH$	0.1[d]	4	56 (72)[c]
6. 	0.05[g]	7	78
7. $PHS(CH_2)_3OH$	0.33[e]	4	25
8. 	0.5[e]	1.5	 88
9. 	0.33[e]	1.25	40

[a] The reactions were carried out on 1–2-mmol scale under continuous controlled electrolysis conditions according to the typical procedure.[15] [b] The yields are based on isolated, homogeneous, weighed products unless otherwise noted. [c] This yield was determined by calibrated quantitative GLPC analysis using an internal standard. [d] 10-mmol scale. [e] 2–4-mmol scale. [f] 50-mmol scale. [g] 20-mmol scale.

Table II. Selectivity in Oxidation of Diols **4**–**7**



4, 1,8-dihydroxynonane
5, 1,8-dihydroxy-2-methylnonane
6, 1,8-dihydroxy-(*E*)-6-nonene
7, 1,8-dihydroxy-2-methyl-(*E*)-6-nonene

diol	conversion,[a] %	% of total[b] A	B	C	combined yield,[c] %
4	100	100 (75)[d]	0	0	75
5	96	93 (67)[d]	7	0	86
6	89[e]	53	13	33	69
6	100[f]	0	7	93	61
6	92[g]	81 (58)[d]	0	19	68
7	75[e]	81	3	16	74
7	100[g]	11	0	89	88

[a] Unless otherwise noted, each reaction involved 30 mol % of 1 under standard conditions.[15] [b] Ratio of product peaks by GLPC. [c] Yield by calibrated GLPC analysis. [d] Yield based on weight of pure component after chromatography. [e] Reaction Interrupted after passage of 1.0 C/mol of diol. [f] Reaction allowed to proceed until current decayed. [g] The diol was added to 2 mol equiv of preformed 1 at −60 °C.

The easy regeneration of **2** from **1** and **3** suggests a simple catalytic cycle. Table I presents examples where an alcohol is mixed with **1** with the anode maintained at +0.4 V. Several

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(4) Golubev, V. A.; Rozantsev, E. G.; Neiman, M. B. *Bull. Acad. Sci. USSR* **1965**, *1927*–1936.

(5) Cella, J. A.; Kelley, J. A.; Kenehan, E. F. *Tetrahedron Lett.* **1975**, 2869–2872.

(6) Sümmermann, W.; Deffner, U. *Tetrahedron* **1975**, *31*, 593–596.

(7) (a) Paleos, C. M.; Dais, P. *J. Chem. Soc., Chem. Commun.* **1977**, 345–346. (b) Rozantsev, E. G.; Golubev, V. A. *Bull. Acad. Sci. USSR* **1966**, 852. (c) Miura, Y.; Masuda, S.; Kinoshita, M. *Makromol. Chem.* **1972**, *160*, 243.

(8) This potential is well below that for electrooxidation of most common functional groups.[9]

(9) For a comprehensive list of redox potentials for organic compounds, see: Meites, L.; Zuman, P. "Electrochemical Data"; Wiley: New York, 1974; Part 1, Vol. A.

(10) It has been known since the work of Golubev and co-workers that oxoammonium ions (e.g., **2**) convert methyl, ethyl, and isopropyl alcohols into the corresponding carbonyl compounds.[4] While this work has been described in subsequent papers from the same group as establishing the usefulness of the reagent in synthesis, reaction with only the simplest alcohols was reported, no yields or weights were given, and the products were simply detected as 2,4-dinitrophenylhydrazone derivatives. More recently, Cella[12] and Ganem[13] have shown that a combination of *m*-chloroperoxybenzoic acid and nitroxyl **1** is capable of oxidizing alcohols. It is suggested by both authors to be useful for secondary alcohols (see also ref 5). Indeed, over-oxidation of simple primary alcohols to acids is significant.[12] Cella has shown that at low pH, *m*-chloroperoxybenzoic acid alone is capable of oxidation of secondary alcohols.[14] It is important to note that Ganem pointed out clearly the possibility of an electrocatalytic process mediated by **1**.[13]

(11) Golubev, V. A.; Rozantsev, E. G.; Neiman, M. B. *Bull. Acad. Sci. USSR* **1978**, 1874–1881.

(12) Cella, J. A.; Kelley, J. A.; Kenehan, E. F. *J. Org. Chem.* **1975**, *40*, 1860–1862.

(13) Ganem, B. *J. Org. Chem.* **1975**, *40*, 1998–1999.

(14) Cella, J. A.; McGrath, J. P.; Regen, S. L. *Tetrahedron Lett.* **1975**, 4115–4118.

(15) A typical procedure follows: A mixture of 2,6-lutidine (1.5 mL), TEMPO (**1**, 0.260 g, 1.6 mmol), and 25 mL of 0.2 M lithium perchlorate (Alfa Chemical Co.) in acetonitrile (reagent grade used without further purification) was placed in the "working electrode" chamber of a standard two-compartment cell. The compartments were separated by a medium-grade sintered glass frit. In the "counterelectrode" chamber were placed a mixture of 0.2 M lithium perchlorate in acetonitrile and a large molar excess of 1,2-dibromoethane to act as depolarizer. The reference electrode was a solution of 0.1 M $AgNO_3$ in acetonitrile in contact with the electrolysis medium through a small piece of Thirsty Glass (Corning Glass) attached to the end of the electrode and connected to the power supply with a silver wire. The working electrode was 2-cm^2 Pt gauge and the counterelectrode either Pt or Cu wire. The power was supplied by a Wenking Model 68FR-05 potentiostat at controlled potential, usually +0.35 V. The cell was immersed in a large water bath at 23 °C. The potential was applied for 30 min, during which time the current decreased to 10–15 mA from an initial value of 250–300 mA. The initial red color of the radical **2** deepened as cation **1** formed. Then, a mixture of 1-dodecanol (0.8 mmol) and GC standard was added. Aliquots were removed and quenched by partitioning between 10% aqueous HCl and ether, and the ether solution was analyzed for 1-dodecanol and dodecanal by carefully calibrated GLPC. Because of the reaction between **1** and **3** to generate **2**, the stoichiometry of the reaction is 2 mol of **1** (or **2**)/mol of alcohol.

(16) In the absence of lutidine, the consumption of alcohol is very slow (<10% in 8 h at 20 °C). Other bases such as triethylamine, metal hydrides, sodium carbonate, etc., were tested and generally were somewhat effective. Work continues to develop the optimum base.

(17) Aliquots were taken periodically and gave the following results: 2 min, 0%; 1 h, 50%; 2 h, 75%.

(18) The reaction stops due to slow inactivation of **2** by the lutidine. The disappearance of **2** is monitored by the characteristic IR band at 1615 cm^{-1}.[19] The oxidizing power of the solution can be regenerated by renewed electrooxidation at +0.4 V as before.

(19) A value of 1630 cm^{-1} (KBr) was assigned to the N=O stretch in the chloride salt: Atovmzan, L. O.; Golubev, V. A.; Golovina, N. I.; Klitskaya, G. A. *Zh. Strukt. Khim.* **1975**, *16*, 92.

generalizations can be drawn. The method is most successful for primary alcohols. The approximate rates of oxidation suggest that the process is sensitive to steric factors and relatively insensitive to electronic features such as an allylic double bond. Secondary alcohols are driven to completion in a reasonable time (12–18 h) only with a full equivalent of **1**. The diol in entry 8 is oxidized preferentially at the primary hydroxyl and is subsequently converted to the lactone, presumably via the cyclic hemiacetal. At the same time, the presence of 10 mol equiv of water in the electrolysis medium does not lead to further oxidation of aldehydes to acids. Benzylic primary alcohols react particularly fast, producing turnover numbers in excess of 40 (e.g., entry 4, 0.05 mol equiv of **1**). At least 0.2 mol equiv of **1** (10 turnovers) is needed for complete conversion of typical aliphatic alcohols.

The compatibility of the electrochemical system with other functional groups should be high,[9] but little is known about the functional group compatibility of **2**. We find that a 1:1 mixture of *n*-dodecanol and thioanisole under the conditions of entry 1 in Table I produces *n*-dodecanal (90%) and recovered thioanisole (>90%). However, entries 7 and 9 suggest *intra*molecular selectivity is less efficient.

An equimolar mixture of 1-dodecanol and 5-dodecanol under the conditions of entry 1 of Table I leads to complete conversion of the primary alcohol (83% yield of *n*-dodecanal) and <3% yield of the ketone (93% recovery of the secondary alcohol). This selectivity for primary over secondary alcohols is also easily demonstrated in the intramolecular test cases, **4–7**.[20] Table II displays results with diol substrates that were chosen to test for the steric effect of α- and β-methyl substituents and the allylic double bond.[21] In the competition of simple primary vs. secondary (**4**, **5**) selectivity for the primary site is nearly quantitative. In the more difficult test of primary vs. secondary allylic (**6**, **7**), catalytic electrooxidation at 25 °C shows a good preference for the primary hydroxyl, but oxidation of both hydroxyls is significant even at just 90% conversion for **6** and 75% conversion for **7**. At −40 °C with preformed **2** in equivalent amount, better selectivity is observed, allowing isolation of (*E*)-8-hydroxy-2-methylnon-6-enal in 58% yield (63% when corrected for **7** not reacted). We are unaware of other methods that produce comparable selectivity.[22,23] Work is in progress to devise nitroxyl catalysts with better turnover numbers and to further define the scope and origins of the selectivity.

Acknowledgment. Financial support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowled. We thank Professor Andrew Bocarsly (Princeton) for technical suggestions.

Registry No. 4, 61448-29-1; **4A**, 85926-51-8; **5**, 85926-47-2; **5A**, 85926-52-9; **5B**, 85926-53-0; **6**, 85926-48-3; **6A**, 85926-54-1; **6B**, 85926-55-2; **6C**, 85926-56-3; **7**, 85926-49-4; **7A**, 85926-57-4; **7C**, 79971-12-3; benzenepropanol, 122-97-4; 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanemethanol, 5617-92-5; 4-methoxybenzenemethanol, 105-13-5; 2-hexen-1-ol, 2305-21-7; 4-*tert*-butylbenzenemethanol, 877-65-6; 3-(phenylthio)propanol, 24536-40-1; 2-hydroxycyclohexaneethanol, 24682-42-6; 1,5-dithiaspiro[5.5]undecane-7-ethanol, 85926-46-1; TEMPO, 2564-83-2; benzenepropanol, 104-53-0; 2,2-dimethyl-3-(2-methyl-1-propenyl)cyclopropanecarboxaldehyde, 7427-85-2; 4-methoxybenzaldehyde, 123-11-5; 2-hexenal, 505-57-7; 4-*tert*-butylbenzaldehyde, 939-97-9; 3-(phenylthio)propanal, 27098-65-3; octahydrobenzofuran-2-one, 6051-03-2; 1,5-dithiaspiro[5.5]undecane-7-ethanal, 85926-50-7; dodecanol, 112-53-8; dodecanal, 112-54-9.

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(20) The synthesis of diols **4–7** follows that previously reported: Stork, G.; Shiner, C. S.; Winkler, J. D. *J. Am. Chem. Soc.* **1982**, *104*, 310.

(21) A pure sample of each of the products A–C from each of the diols **4–7** was prepared, fully characterized, and used for calibration of GLPC analysis of the electrooxidation procedure. The electrooxidations were carried out according to the typical procedure.[15]

(22) Catalytic oxidation using PtO_2 and oxygen is an effective method for oxidation of primary alcohols in the presence of secondary. However, the process is not generally effective at producing simple aldehydes. Further oxidation to carboxylic acids or lactones is the most effective application. (a) Heyns, K.; Paulsen, H. In "Newer Methods of Preparative Organic Chemistry"; Academic Press: New York, 1963; Vol. 2, pp 303 ff. For specific recent applications in lactone synthesis, see: (b) Lansbury, P. T. Hangauer, D. G.; Vacca, J. P. *J. Am. Chem. Soc.* **1980**, *102*, 3964. (c) Kretchmer, A.; Thompson, W. J. *Ibid.* **1976**, *98*, 3379. (d) Fried, J.; Sih, J. C. *Tetrahedron Lett.* **1973**, 3899.

(23) A recent report describes an oxidation procedure that is effective for primary alcohols in the presence of secondary. A test of primary vs. allylic secondary was not included. the system requires stoichiometric amounts of the oxidizing agent tris(triphenylphosphine)trichlororuthenium(II). Tomioka, N.; Takai, K.; Oshima, K.; Nozak, H. *Tetrahedron Lett.* **1981**, *22*, 1605–1608.

Tris(trimethylsilyl)aluminum and Transition-Metal Catalysts. Silylation of Allyl Acetates

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The burgeoning use of allylsilanes as synthetic intermediates[1] opens the question of their methods of preparation.[2–4] In attempting to synthesize new conjunctive reagents, we sought a method to effect an "umpolung" of allyl acetates, i.e., to convert these electrophilic partners into nucleophilic ones by transforming them into allylsilanes. Limitations associated with generating trimethylsilylcuprates[3] led us to examine tris(trimethylsilyl)aluminum (**1**)[5] as an alternative. Unfortunately, direct reaction of allyl acetates with **1** normally proceeded very slowly, if at all, at room temperature and was accompanied by substantial elimination at elevated temperature. We report that palladium[6] and molybdenum[7] catalysts facilitate the transfer of the trimethylsilyl residue from aluminum to carbon with surprising regioselectivity and the first example of the use of "hard" nucleophiles in molybdenum-catalyzed coupling.

The reactions were very simple to perform. In a palladium-catalyzed reaction, an aliquot of a standardized pentane solution of $(Me_3Si)_3Al$·etherate[8] (0.5 mol) was added to a solution of 1.0 mol of allyl acetate and 4–6 mol % of the palladium catalyst in benzene or THF. After being stirred at room temperatue or below

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(8) Prepared according to ref 5 from aluminum powder and granular aluminum activated by adding iodine in ether and then adding mercury and trimethylchlorosilane. After completion, filtration, and removal of ether, the solid residue was stirred with pentane and filtered to form the stored solutions. These solutions were conveniently titrated by adding an aliquot to a known excess of iodine in toluene and back-titrating the excess iodine with sodium thiosulfate.

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