1.00 (3 H), and 0.80 (6 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) $M^+$ absent, 365 ($M^+ - 15$, 2), 279 (18), 261 (21), 243 (26), 2 03 (7), 135 (30), 121 (15), 95 (20), 81 (22), 69 (20), 55 (32), 43 (100). Anal. Calcd for $C_{23}H_{40}O_4$: C, 72.59; H, 10.60. Found: C, 72.48; H, 10.53.

**(14*S*)-*ent*-3β-Acetoxy-8,13β:14,15-diepoxylabdane (3f).** A 246-mg sample of compound **3a** (0.715 mmol) was treated with 0.8 mmol of tosyl chloride in pyridine solution (12 mL) at room temperature during 24 h; workup in the usual manner yielded (14*S*)-*ent*-3β-acetoxy-15-(tosyloxy)-8,13β-epoxylabdan-14-ol (**3e**): $^1$H NMR δ 7.82 and 7.33 ($A_2B_2$ system, $J$ = 8 Hz, tosyl group), 4.50–3.80 (4 H, complex signal, H-3, H-14, and 2 H-15), 2.43 (3 H, s, MePh, tosyl group), 2.03 (3 H, s, OAc), CMe singlets at 1.10 (3 H), 1.05 (3 H), 0.85 (6 H), and 0.79 (3 H). Treatment of this last compound under reflux for 2 h with $Na_2CO_3$ in 90% aqueous EtOH solution (0.1%, w/v, 15 mL)[5] quantitatively yielded compound **3f**: mp 159–161 °C (MeOH); $[\alpha]^{18}_{\mathrm{D}}$ −34.1° (*c* 0.41, $CHCl_3$); IR (KBr) 3070 (oxirane), 1735, 1245 (OAc) $cm^{-1}$; $^1$H NMR δ 4.51 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), 3.12 (1 H, dd, $J_1$ = 3 Hz, $J_2$ = 4 Hz, oxirane), 2.80 (1 H, t, $J$ = 4 Hz, oxirane), 2.50 (1 H, dd, $J_1$ = 3 Hz, $J_2$ = 4 Hz, oxirane), 2.07 (3 H, s, OAc), CMe singlets at 1.43 (3 H), 1.11 (3 H), 0.89 (3 H), 0.85 (3 H), and 0.81 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) $M^+$ absent, 349 ($M^+ - 15$, 8), 321 (32), 251 (52), 243 (42), 203 (16), 201 (18), 135 (70), 121 (32), 109 (31), 95 (40), 81 (43), 69 (50), 55 (62), 43 (100). Anal. Calcd for $C_{22}H_{36}O_4$: C, 72.49; H, 9.96. Found: C, 72.39; H, 10.03.

**(14*S*)-*ent*-8,13β-Epoxylabdane-3β,14-diol (3g).** The (14*S*)-14,15-epoxy derivative (**3f**) was treated with $LiAlH_4$ in $Et_2O$ solution at room temperature for 3 h, yielding compound **3g**: mp 90–91 °C ($Me_2CO$–*n*-hexane); $[\alpha]^{18}_{\mathrm{D}}$ −15.5° (*c* 0.43, MeOH); IR (KBr) 3480, 3300 (br, OH) $cm^{-1}$; $^1$H NMR ($CDCl_3$–$C_5D_5N$, 9:1) δ 3.70 (1 H, q, $J$ = 6 Hz, H-14), 3.27 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), 1.17 (3 H, d, $J$ = 6 Hz, 3 H-15), CMe singlets at 1.23 (3 H), 1.17 (3 H), 1.05 (3 H), 0.85 (3 H), and 0.80 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) $M^+$ absent, 309 ($M^+ - 15$, 2) 279 (62), 261 (68), 243 (91), 203 (21), 135 (100), 121 (68), 95 (65), 81 (72). Anal. Calcd for $C_{20}H_{36}O_3$: C, 74.02; H, 11.18. Found: C, 73.96; H, 11.26.

**(14*S*)-*ent*-3β,14-Diacetoxy-8,13β-epoxylabdane (3h).** Acetylation of compound **3g** gave compound **3h**: mp 119–121 °C (MeOH); $[\alpha]^{18}_{\mathrm{D}}$ −33.3° (*c* 0.74, $CHCl_3$); IR (KBr) 1730, 1245 (OAc) $cm^{-1}$; $^1$H NMR δ 5.13 (1 H, q, $J$ = 6 Hz, H-14), 4.47 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), 2.07 (6 H, s, 2 OAc), 1.23 (3 H, d, $J$ = 6 Hz, 3 H-15), CMe singlets at 1.29 (3 H), 1.13 (3 H), 0.89 (3 H), 0.86 (3 H), and 0.82 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) $M^+$ absent, 393 ($M^+ - 15$, 1), 349 (3), 333 (9), 321 (20), 251 (52), 243 (38), 203 (11), 201 (14), 135 (54), 121 (18), 95 (21), 81 (26), 69 (32), 55 (41), 43 (100). Anal. Calcd for $C_{24}H_{40}O_5$: C, 70.55; H, 9.87. Found: C, 70.63; H, 9.57.

**Application of Horeau's method to compounds 3d and 3g** was performed in the usual manner.[8] Compound **3d** (59.81 mg, 0.1574 mmol) and (±)-α-phenylbutyric anhydride (148.54 mg, 0.4792 mmol) in pyridine solution (2.00 mL): $\alpha_1 - 1.1\alpha_2 = +0.335$, 3*R* configuration. Compound **3g** (51.000 mg, 0.1574 mmol) and (±)-α-phenylbutyric anhydride (148.54 mg, 0.4792 mmol) in pyridine solution (2.00 mL): $\alpha_1 - 1.1\alpha_2 = +0.128$ for the two 3*R* and 14 centers. Thus, $0.128 - 0.335 = -0.207$ for the C(14)-hydroxyl group, configuration 14*S*. This experiment was performed with identical time reaction (16 h) and temperature (18 °C) for the two compounds.

**(14*R*)-*ent*-3β,14,15-Triacetoxy-8,13β-epoxylabdane (4b).** Acetylation of compound **4a** gave compound **4b**: mp 199–200 °C (MeOH); $[\alpha]^{25}_{\mathrm{D}}$ +7.4° (*c* 0.39, $CHCl_3$); IR (KBr) 1750, 1740, 1735 (OAc) $cm^{-1}$; $^1$H NMR δ 5.05 (1 H, dd, X part of an ABX system, $J_{XA}$ = 9 Hz, $J_{XB}$ = 2.5 Hz, H-14), 4.53 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), 4.47 (1 H, dd, B part of an ABX system, $J_{BA}$ = 11.5 Hz, H-15), 4.07 (1 H, dd, A part of an ABX system, H′-15), 2.10, 2.04, and 2.01 (3 H each, singlets, 3 OAc), CMe singlets at 1.23 (6 H), 0.87 (3 H), 0.85 (3 H), and 0.82 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) $M^+$ absent, 451 ($M^+ -$ 15, 3), 407 (2), 391 (2), 331 (1), 321 (34), 261 (100), 243 (65), 203 (15), 201 (21), 135 (62). Anal. Calcd. for $C_{26}H_{42}O_7$: C, 66.92; H, 9.07. Found: C, 66.98; H, 8.96.

**(14*R*)-*ent*-8,13β-Epoxylabdane-3β,14,15-triol (4c).** Alkaline hydrolysis of compound **4b** gave compound **4c**: mp 132–134 °C ($Me_2CO$–*n*-hexane); $[\alpha]^{18}_{\mathrm{D}}$ −13.0° (*c* 0.115, MeOH); IR (KBr) 3450, 3200 (br, OH) $cm^{-1}$; $^1$H NMR ($CDCl_3$–$C_5D_5N$, 9:1) δ 3.80–3.40 (3 H, complex singal, H-14 and 2 H-15), 3.27 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), CMe singlets at 1.29 (3 H), 1.17 (3 H), 1.07 (3 H), 0.85 (3 H), and 0.79 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensty) $M^+$ absent, 325 ($M^+ - 15$, 8), 291 (6), 279 (34), 261 (40), 243 (62), 203 (26), 135 (100), 121 (61), 95 (68), 81 (72), 69 (83). Anal. Calcd for $C_{20}H_{36}O_4$: C, 70.54; H, 10.66. Found: C, 70.43; H, 10.46.

**(14*R*)-*ent*-8,13β-Epoxy-14,15-(isopropylidenedioxy)labdan-3β-ol (4d).** Obtained from compound **4c** as prevously described for the preparation of compound **3d**. Compound **4d** had mp 72–75 °C (*n*-hexane): $[\alpha]^{18}_{\mathrm{D}}$ −9.6° (*c* 0.42, $CHCl_3$); IR (KBr) 3350 (OH) $cm^{-1}$; $^1$H NMR δ 4.20–3.70 (3 H, complex signal, H-14 and 2 H-15), 3.23 (1 H, dd, $J_{aa'}$ = 9 *Hz*, $J_{ae'}$ = 6 *Hz*, H-3), CMe singlets at 1.47 and 1.37 (acetonide), 1.30 (3 H), 1.18 (3 H), 1.00 (3 H), 0.83 (3 H), and 0.78 (3 H); mass spectrum (75 eV, direct inlet), *m/z* (relative intensity) $M^+$ absent, 365 ($M^+ - 15$, 6), 347 (2), 307 (2), 289 (2), 279 (46), 261 (52), 243 (71), 203 (15), 135 (81), 121 (42), 95 (53), 81 (59), 69 (62), 55 (76), 43 (100). Anal. Calcd for $C_{23}H_{40}O_4$: C, 72.59; H, 10.60. Found: C, 72.62; N, 10.57.

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**Registry No. 1**, 42895-91-0; **2**, 82398-41-2; **3a**, 82351-54-0; **3b**, 82351-55-1; **3c**, 82351-56-2; **3d**, 82351-57-3; **3e**, 82351-58-4; **3f**, 82351-59-5; **3g**, 82351-60-8; **3h**, 82351-61-9; **4a**, 82398-42-3; **4b**, 82398-43-4; **4c**, 82398-44-5; **4d**, 82398-45-6; **5**, 76549-11-6; **6**, 52591-03-4.

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# Epoxidation of Olefins by a Polymeric Reagent Electrochemically Generated and Recycled in Situ

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Recently we have developed a novel method of oxidation of alcohols by a polymeric reagent of electrochemically generated and recycled in situ (Scheme I).[1] Cross-linked poly(4-vinylpyridine) hydrobromide is an excellent precursor of the polymeric reagent. This method does not consume any chemical oxidant and does not produce any contaminating reduced product. Since oxidation of olefins is also an essential reaction in synthetic organic chemistry, we have directed our attention to the oxidation of olefins[2,3] using this methodology. During the investigation, we were somewhat surprised to find that the use of polymeric quaternary ammonium bromide as a precursor of the polymeric reagent resulted in a facile epoxidation of olefins,

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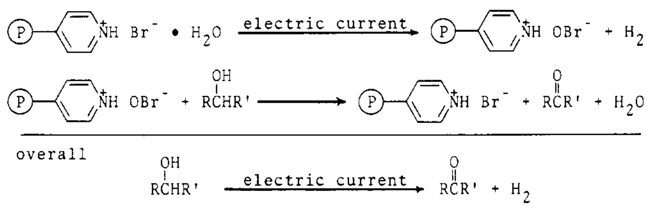
(1) Yoshida, J.; Nakai, R.; Kawabata, N. *J. Org. Chem.* **1980**, *45*, 5269.

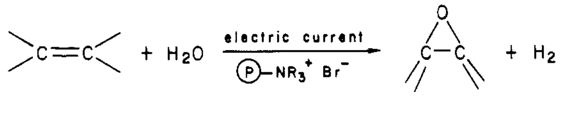
(2) Epoxidation of olefins by polymeric reagent (polymeric peroxy acid) has been reported: (a) Harrison, C. R.; Hodge, P. *J. Chem. Soc., Chem. Commun.* **1974**, 1009. (b) Harrison, C. R.; Hodge, P. *J. Chem. Soc., Perkin Trans. 1* **1976**, 605. (c) Frêchet, J. M. J.; Haque, K. E. *Macromolecules* **1975**, *8*, 130.

(3) An elegant indirect electrochemical epoxidation of olefins with bromide ion as mediator has been reported: (a) Torii, S.; Uneyama, K.; Ono, M.; Tazawa, H.; Matsunami, S. *Tetrahedron Lett.* **1979**, 4661. (b) Torii, S.; Uneyama, K.; Matsunami, S. *J. Org. Chem.* **1980**, *45*, 16. (c) Torii, S.; Uneyama, K.; Tanaka, H.; Yamanaka, T.; Yasuda, T.; Ono, M.; Kohmoto, Y. *Ibid.* **1981**, *46*, 3312. Indirect electrochemical epoxidation of propylene with chloride ion as mediator has also been developed: (d) Rifi, M. R.; Covitz, F. H. "Introduction to Organic Electrochemistry"; Marcel Dekker: New York, 1974; Chapter 5.

Scheme I



whereas poly(4-vinylpyridine) hydrobromide was much less effective in spite of its higher activity for the oxidation of alcohols.



The epoxidation of olefins was carried out in an undivided electrochemical cell equipped with platinum electrodes in a mixture of *N,N*-dimethylformamide (DMF) and benzene in the presence of a small amount of water. When a strong-base anion-exchange resin containing the quaternary ammonium group (Amberlite IRA-900) in the bromide form was used as a precursor of the polymeric reagent, the epoxides were obtained in good yields as shown in Table I. Use of cross-linked poly(4-vinylpyridine) hydrobromide as a precursor, however, resulted in very low yields of the epoxides. In the case of the hydrobromide of a weak-base anion-exchange resin containing tertiary amino groups (Amberlite IRA-94), the yields of the epoxides were also low. These results may indicate the importance of the quaternary ammonium group in the polymer for the epoxidation. We have also investigated the reaction with tetraethylammonium bromide as the monomeric analogue of the strong-base anion-exchange resin in the bromide form. The monomeric analogue was much less effective, indicating that the polymer effect was important.

When a strong-base anion-exchange resin in the chloride form (Amberlite IRA-900(Cl)) was used instead of the corresponding bromide form, the current did not flow smoothly. The strong-base anion-exchange resin in the nitrate form (Amberlite IRA-900($NO_3$)) was scarcely effective for the epoxidation, although the current flowed smoothly. Therefore, the bromide ion bound to the polymer seemed to play a crucial role in the epoxidation. Since a gelular resin (Amberlite IRA-400(Br)) showed similar activity as the macroporous resin (Amberlite IRA-900(Br)), the bromide ion bound to the surface of the polymer beads appeared to play an important role.

It is worth noting that the yield of the epoxide was greatly influenced by the amount of water in the reaction system (Table II). With no added water, the electric current did not flow appreciably. Addition of water up to 20 mmol (for the reaction with 5 mmol of olefin) remarkably increased the yield of epoxide. However, further addition of water resulted in the decrease of the yield, although the current flowed very smoothly.

In the case of the alcohol oxidation, the current efficiency was high, and only 2.4 F/mol of electricity was required.[1] In the present case, however, the reaction was carried out with 7.0 F/mol of electricity while only 2.0 F/mol are theoretically required for the epoxidation. The low efficiency of the present reaction may be ascribed to the competing electrolysis of water, although the detailed mechanism is not clear at present.

Easy separation, recovery, and reuse of the reagent are merits of the polymeric reagent. In the present case, polymer beads could be separated from the reaction mixture by simple filtration and reused at least three times with no loss of activity.

**Table I. Epoxidation of Olefins by a Polymeric Reagent Electrochemically Generated and Recycled in Situ[a]**

| olefin | precursor | yield, %<br>epoxide[b] | <br>unchanged olefin[c] |
|---|---|---|---|
| 1-decene | IRA-900(Br)[d] | 81 | 1 |
| | | 77[e] | 3 |
| | | 83[f] | 1 |
| | IRA-900(Cl)[g] | 8[h] | 81 |
| | IRA-900($NO_3$)[i] | 0 | 98 |
| | IRA-400(Br)[j] | 80 | 1 |
| | IRA-94(HBr)[k] | 47 | 12 |
| | PVP·HBr[l] | 29 | 18 |
| | $Et_4NBr$[m] | 21 | 49 |
| 2-octene | IRA-900(Br)[d] | 73 | *n* |
| cyclododecene | | 64 | 11 |
| styrene | | 21 | *n* |
| methyl 10-undecenoate | | 61 | 4 |
| *N,N*-diethyl-10-undecenamide | | 62 | 0 |
| 11-chloro-1-undecene | | 62 | 5 |

[a] Unless otherwise noted, the reactions were carried out with 1.0 g of dry resin, 5.0 mmol of olefin, 1.5 mL of DMF, 1.0 mL of benzene, and 20 mmol of water, and the electricity passed was 7.0 F/mol (based on the olefin). [b] Determined by GLC and based on the total amount of the olefin. [c] Determined by GLC. [d] A macroporous strong-base anion-exchange resin (Amberlite IRA-900) in the bromide form containing 3.01 mmol/g of $Br^-$. [e] Second use of the resin. [f] Third use of the resin. [g] Amberlite IRA-900 in the chloride form containing 3.54 mmol/g of $Cl^-$. [h] Enough current to perform the reaction did not flow under the usual conditions, and the electricity passed was 1.4 F/mol. [i] Amberlite IRA-900 in the nitrate form containing 4.21 mmol/g of $NO_3^-$. [j] A gelular strong-base anion-exchange resin (Amberlite IRA-400) in the bromide form containing 2.74 mmol/g of $Br^-$. [k] Hydrobromide of a macroporous weak-base anion-exchange resin (Amberlite IRA-94) containing 2.55 mmol/g of $Br^-$. [l] Cross-linked poly(4-vinylpyridine) hydrobromide containing 2.72 mmol/g of $Br^-$. [m] Tetraethylammonium bromide (3.0 mmol) was used instead of resin beads. [n] Not determined.

**Table II. Epoxidation of 1-Decene by a Polymeric Reagent Electrochemically Generated and Recycled in Situ: Influence of the Amount of Water[a]**

| added water, mmol | electricity,[b] F/mol | % yield<br>epoxide[c] | <br>unchanged olefin[d] |
|---|---|---|---|
| 5 | 5.5[e] | 19 | 55 |
| 10 | 4.6[e] | 64 | 7 |
| 20 | 7.0 | 81 | 1 |
| 30 | 7.0 | 70 | 19 |
| 50 | 7.0 | 2 | 90 |

[a] Reactions were carried out with 1.0 g of dry beads of strong-base anion-exchange resin (Amberlite IRA-900) in the bromide form containing 3.01 mmol of $Br^-$, 5.0 mmol of 1-decene, 1.5 mL of DMF, and 1.0 mL of benzene. [b] Based on the olefin. [c] Determined by GLC and based on the olefin. [d] Determined by GLC. [e] Enough current to perform the reaction did not flow under the usual conditions.

The scope and limitations of the present epoxidation reaction were then examined with a range of olefins (Table I). From both terminal and internal olefins were obtained the corresponding epoxides in good yields. The capability of tolerating some functional groups is also noteworthy. No difficulty was encountered in the use of olefins containing chlorine, alkoxycarbonyl, and dialkylcarbamoyl groups, and the corresponding epoxides were obtained in satisfactory yields. However, the reaction of 11-bromo-1-undecene gave a mixture of several unidentified products, and the corresponding epoxide was not obtained in good yield. The reaction with *α,β*-unsaturated carbonyl compounds such as isophorone did not give the epoxide under similar conditions.

## Experimental Section

A Trio Model PR-653 regulated DC power supply or a Kikusui Model PAB-32-0.5 regulated DC power supply was used as a source of electric current. Infrared spectra were measured with a Hitachi Model 215 grating spectrophotometer. $^1$H NMR spectra were measured with a Varian Model T-60A spectrometer in $CCl_4$ with $Me_4Si$ as the internal standard. Analytical and preparative GLC were performed on a Shimadzu GC-4B or GC-4C gas chromatograph. Elemental analyses were performed by the Elementary Analyses Center of Kyoto University. *N,N*-Diethyl-10-undecenamide,[4] 11-chloro-1-undecene,[4] and 11-bromo-1-undecene[4] were prepared according to the literature procedures with minor modifications.

**Resins.** Amberlite IRA-900 (a macroporous strong-base anion-exchange resin which has a styrene–divinylbenzene matrix with a quaternary ammonium group), Amberlite IRA-400 (a gelular strong-base anion-exchange resin which has a styrene–divinylbenzene matrix with a quaternary ammonium group), and Amberlite IRA-94 (a macroporous weak-base anion-exchange resin which has a styrene-divinylbenzene matrix with a tertiary amino group) were supplied by Rohm and Haas Co. These resins were preconditioned and transferred into the appropriate forms by the usual method[1] and dried under vacuum. Cross-linked poly(4-vinylpyridine) hydrobromide was prepared as described previously[1] and dried under vacuum.

**Epoxidation of Olefins. General Procedure.** The electrochemical epoxidation reactions were carried out in a 5-mL, two-necked glass cell equipped with a mechanical stirrer and a calcium chloride tube. Platinum electrodes (10 × 10 × 0.5 mm) were placed in the cell parallel to each other with about 5 mm of space between them. An olefin (5.0 mmol), DMF (1.5 mL), benzene (1.0 mL), and water (20 mmol) were placed in the cell. Dry beads of Amberlite IRA-900(Br) (1.0 g) were added. The electric potential was applied between the electrodes which were dipped in the resin layer with slow stirring (30 rpm) at 30 °C. Usually the current did not flow smoothly at the initial stage of the reaction but gradually increased. After the current reached 40 mA, this current (40 mA) was maintained. The potential between the electrodes was usually 20–32 V. After 7.0 F/mol (based on the olefin) had passed, the reaction mixture was transferred into a 50-mL flask, and the appropriate GLC internal standard and benzene (30 mL) were added. The yield of the epoxide and the amount of the unchanged olefin were determined by GLC analysis of the reaction mixture. Products were isolated by preparative GLC. Spectral data, refractive indexes, and elemental analyses of some epoxides are given below. Other epoxides were identified by comparison of their $^1$H NMR and IR spectra with those of authentic materials.

***N,N*-Diethyl-10,11-epoxyundecanamide**: $n^{25}{}_D$ 1.4647; $^1$H NMR ($CCl_4$) $\delta$ 0.9–1.9 (m, 20 H), 1.9–2.4 (m, 3 H), 2.4–2.85 (m, 2 H), 3.24 (q, $J$ = 5 Hz, 4 H); IR (neat) 3040 (vw), 2970 (sh), 2925 (s), 2855 (m), 1640 (s), 1460 (s), 1265 (m), 1140 (m), 1095 (m), 830 (m) cm$^{-1}$. Anal. Calcd for $C_{15}H_{29}NO_2$: C, 70.54; H, 11.45; N, 5.48. Found: C, 70.41; H, 11.74; N, 5.34.

**11-Chloro-1,2-epoxyundecane**: $n^{25}{}_D$ 1.4541; $^1$H NMR ($CCl_4$) $\delta$ 1.1–2.0 (m, 16 H), 2.27 (dd, $J$ = 5, 3 Hz, 1 H), 2.45–2.85 (m, 2 H), 3.43 (t, $J$ = 6 Hz, 2 H); IR (neat) 3045 (w), 2920 (s), 2855 (s), 1470 (m), 915 (m), 830 (m), 720 (m) cm$^{-1}$. Anal. Calcd for $C_{11}H_{21}ClO$: C, 64.53; H, 10.34; Cl, 17.32. Found: C, 64.75; H, 10.39; Cl, 17.13.

**Reuse of the Resin.** The resin beads were recovered from the reaction mixture by filtration, washed with benzene (3 × 3 mL), methanol (3 × 3 mL), and ether (2 × 3 mL), and dried under vacuum. The dried resin beads were used for the electrochemical epoxidation reaction in the identical fashion to the fresh ones.

**Registry No.** 1-Decene, 872-05-9; 2-octene, 111-67-1; cyclododecene, 1501-82-2; styrene, 100-42-5; methyl 10-undecenoate, 111-81-9; *N,N*-diethyl-10-undecenamide, 4899-94-9; 11-chloro-1-undecene, 872-17-3; 1,2-epoxydecane, 2404-44-6; 1,2-epoxyoctane, 2984-50-1; 1,2-epoxydodecane, 2855-19-8; styrene oxide, 96-09-3; methyl 10,11-epoxyundecanoate, 22663-09-8; *N,N*-diethyl-10,11-epoxyundecanamide, 82430-96-4; 11-chloro-1,2-epoxyundecane, 830-14-8; isophorone, 78-59-1; Amberlite IRA-900, 9050-97-9; Amberlite IRA-400, 9002-24-8; Amberlite IRA-94, 39409-19-3; poly(vinylpyridine) HBr, 82444-38-0; tetraethylammonium bromide, 71-91-0; water, 7732-18-5.

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# Steric Acceleration by Ortho Substituents of the Stannous Chloride Reduction of Nitrobenzenes in Aqueous Ethanol[1]

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Although the reduction of aromatic nitro compounds with stannous chloride, giving aromatic amino compounds, has been used from a very early period of organic chemistry, only a few mechanistic studies[3-6] have been reported. In their pioneering work, Goldschmidt and co-workers[3] found that the HCl-catalyzed $SnCl_2$ reduction of water-soluble nitro compounds $ArNO_2$ obeyed the rate equation 1, where $[\text{substance}]_{st}$ means stoichiometric concentration of that substance.

$$v = k_1[ArNO_2][SnCl_2][Cl^-] = k_1[ArNO_2][SnCl_2][HCl]_{st} \tag{1}$$

They then postulated a mechanism involving a rate-determining deoxygenation of a nitro group by $SnCl_3^-$ followed by a rapid reduction of NO to $NH_2$ (eq 2a–c), which was verified kinetically.[3]

$$SnCl_2 + Cl^- \xrightleftharpoons{\text{fast}} SnCl_3^- \text{ (equilibrium constant } K_2) \tag{2a}$$

$$ArNO_2 + SnCl_3^- \xrightarrow[k_2]{\text{slow}} ArNO + SnOCl_3^- \tag{2b}$$

$$ArNO \xrightarrow{\text{fast}} ArNHOH \xrightarrow{\text{fast}} ArNH_2 \tag{2c}$$

Another rate equation (eq 3) was postulated by Man-

$$v = k_2[ArNO_2][SnCl_2](a[HCl]_{st} + b) \tag{3}$$

abe's kinetic study on the reduction of ortho-substituted nitrobenzenes in 90% aqueous methanol.[6] Equation 3 leads to a mechanism involving the different reduction species $SnCl_2$ as well as $SnCl_3^-$. We obtained a rate expression which is different from Manabe's and observed a peculiar ortho effect in which a bulky substituent ac-

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[1] Contribution No. 296.

[2] Honored Visiting Researcher from the Department of Applied Chemistry, Faculty of Engineering, Tianjin University, China.

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