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) δ 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) δ 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]

Wen-Kan Xing[2] and Yoshiro Ogata*

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya 464, Japan

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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 [substance]$_{st}$ means stoichiometric concentration of that substance.

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

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]

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

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

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

Another rate equation (eq 3) was postulated by Manabe'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-

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

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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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0022-3263/82/1947-3577$01.25/0

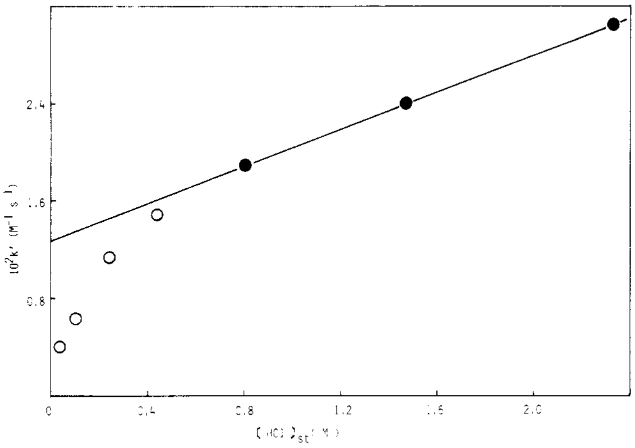

Figure 1. Plot of second-order rate constant $10^2k'$ vs. $[HCl]_{st}$ for $SnCl_2$ reduction of *o*-chloronitrobenzene in 90% EtOH at 30 °C. At low $[HCl]_{st}$, k' values deviate from the line for high $[HCl]_{st}$.

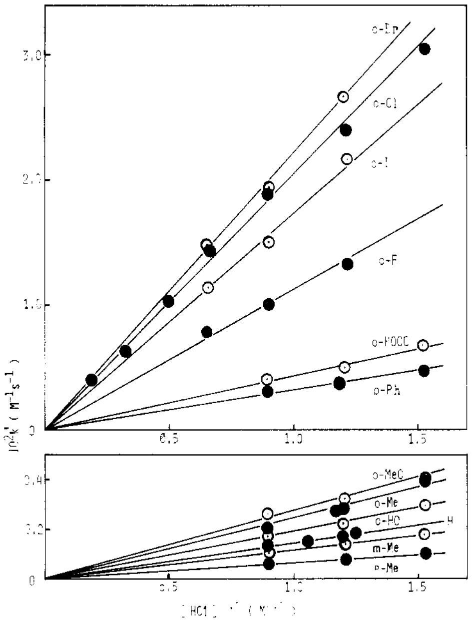

Figure 2. Plot of second-order rate constant $10^2k'$ (M^{-1} s^{-1}) vs. $[HCl]^{1/2}$ ($M^{1/2}$) for $SnCl_2$ reduction of various nitrobenzenes in 90% EtOH at 30 °C.

celerates the reduction. We report herein the kinetic data and mechanism on HCl (much in excess of the stoichiometry)-catalyzed $SnCl_2$ reduction of ortho-substituted nitrobenzenes in 90% (v/v) ethanol.

Results and Discussion

The rates were measured by iodometry of $SnCl_2$. The hydrolysis of $SnCl_2$ was measured by alkalimetry in a sodium citrate buffer.[6]

The rates were found to obey neither eq 1 nor 3 but instead a rate expression (eq 4). That is, the observed

$$v = k[ArNO_2][SnCl_2][HCl]_{st}^{0.5} \qquad (4)$$

second-order rate constant k' in the equation $v = k'[ArNO_2][SnCl_2]$, when divided by $[HCl]_{st}$, was not constant (Table I), in disagreement with eq 1, while the k' value at $[HCl]_{st} \simeq 0$ approaches zero, which disagrees with eq 3 too (Figure 1). As is obvious from Figure 2, the rate fit only eq 4, and the reaction does not occur when $[HCl]_{st}$ approaches to zero.

The term $[HCl]_{st}^{0.5}$ is explicable by assuming very poor dissociation of HCl in 90% ethanol. In view of the very small acid dissociation constant ($K_a = 0.008$, $pK_a = 2.1$)[7] of HCl in ethanol (dielectric constant $\epsilon = 24.3$),[8] the dissociation constant in 90% (v/v) ethanol ($\epsilon = 32.8$–33.9 for 80% w/w ethanol)[8,9] would similarly be much smaller than that in water ($\epsilon = 78.3$–78.54).[8,9] Hence, $[Cl^-] = K_a[HCl]/[H^+] \simeq (K_a[HCl]_{st})^{1/2}$ if $[HCl]_{st}$ is much larger than $[Cl^-]$, since $[Cl^-] = [H^+]$ and $[HCl] \simeq [HCl]_{st}$. Therefore, the mechanism of eq 2 leads to the observed rate:

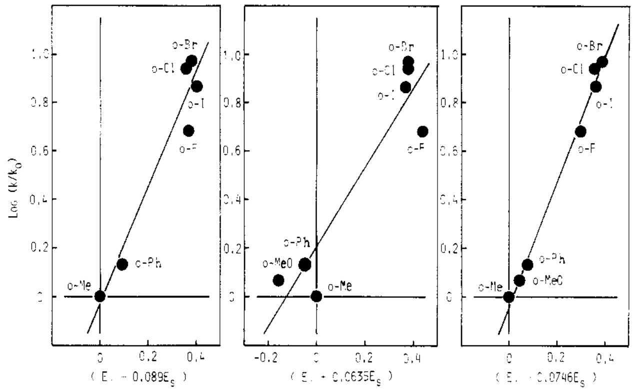

Figure 3. Taft plot for the reduction of ortho-substituted nitrobenzenes with $SnCl_2$ in 90% EtOH at 30 °C: (a) $\log (k/k'_0) = -0.0328 + 2.384(E_\sigma - 0.089E_s)$, $R = 0.9673$; $S = 0.1287$; (b) $\log (k/k_0) = 0.2052 + 1.6234(E_\sigma + 0.0635E_s)$, $R = 0.9312$, $S = 0.1958$; (c) $\log (k/k_0) = -0.0405 + 2.5595(E_\sigma - 0.0746E_s)$, $R = 0.9952$, $S = 0.0527$.

$$\begin{aligned} v = k_2K_2[ArNO_2][SnCl_2][Cl^-] &= k_2K_2K_a^{0.5}[ArNO_2] \times [SnCl_2][HCl]_{st}^{0.5} \\ &= k[ArNO_2] \times [SnCl_2][HCl]_{st}^{0.5} \end{aligned} \qquad (5)$$

In contrast, for the reduction in water, where $[Cl^-] = [HCl]_{st}$, the rate equation 1 can be applied.[3]

The effect of Cl^- was examined by addition of NaCl, which accelerated the reduction as has been reported by Goldschmidt,[3] i.e., the rate equation (eq 5) was satisfied, assuming $[NaCl]_{st}$ is equivalent to $[HCl]_{st}$.

The addition of H_2SO_4 to the reaction system exerted a small acceleration effect on the rate, suggesting a very little proton catalysis (Table II), while HCl had a large acceleration effect as shown in Figure 2 and Table I. A small acceleration with H_2SO_4 may be due to its hydrogen bonding activation of NO_2 toward nucleophilic $SnCl_3^-$.

Water has a retarding effect upon the reaction as shown in Table III. The analogous effect was also reported by Sampey.[4] This retardation may be ascribed to the hydration around $SnCl_3^-$.

The application of the Taft equation[10,11] ($\log (k/k_0) = \rho_\sigma E_\sigma + \delta E_s$) to the observed k value for ortho-substituted nitrobenzenes is illustrated in Figure 3a. The following equation was obtained by introducing values of constants by the binary regression method: $\log (k/k_0) = -0.0328 +$

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Table I. Effect of [HCl] on the Rate of $SnCl_2$ Reduction of Nitrobenzenes in $EtOH-H_2O$ (90:10 v/v) at 30 °C[a]

substituent in $PhNO_2$	$[HCl]_{st}$, M	$10^2k'$, M^{-1} s^{-1}	$10^2k'/[HCl]_{st}$, M^{-2} s^{-1}	$10^2k'/[HCl]_{st}^{0.5}$, $M^{-1.5}$ s^{-1}	10^2k(av), $M^{-1.5}$ s^{-1}
none	1.5625	0.1818	0.1164	0.1454	0.1418
	1.4512	0.1660	0.1144	0.1378	
	1.1171	0.1478	0.1323	0.1398	
	0.7999	0.1290	0.1613	0.1442	
o-HO	2.3383	0.2945	0.1260	0.1926	0.1881
	1.4338	0.2197	0.1532	0.1835	
	0.7992	0.1682	0.2105	0.1881	
o-CH_3	2.3289	0.3923	0.1685	0.2571	0.2364
	1.4395	0.2800	0.1945	0.2334	
	1.3695	0.2695	0.1968	0.2303	
	0.7982	0.2008	0.2516	0.2248	
o-CH_3O	2.3309	0.4010	0.1720	0.2627	0.2741
	1.4547	0.3217	0.2212	0.2667	
	0.7982	0.2617	0.3279	0.2929	
o-C_6H_5	2.3215	0.4702	0.2025	0.3086	0.3201
	1.4018	0.3680	0.2625	0.3108	
	0.8000	0.3048	0.3810	0.3408	
o-HOOC	2.3130	0.6763	0.2924	0.4447	0.4351
	1.4558	0.4945	0.3397	0.4098	
	0.7952	0.4020	0.5055	0.4508	
o-F	1.4801	1.3263	0.8961	1.0902	1.1308
	0.8073	0.9812	1.2154	1.0931	
	0.4243	0.7877	1.8565	1.2092	
o-I	1.4791	2.1670	1.4651	1.7818	1.7324
	0.8056	1.5082	1.8652	1.6803	
	0.4297	1.1373	2.6467	1.7350	
o-Cl	2.3309	3.0513	1.3091	1.9986	2.0640
	1.4673	2.3973	1.6338	1.9791	
	0.8036	1.8847	2.3453	2.1025	
	0.4389	1.4400	3.2809	2.1736	
	0.2460	1.0305	4.1890	2.0776	
	0.1053	0.6322	5.4831	1.9482	
	0.0346	0.4037	11.6676	2.1704	
o-Br	1.4418	2.6652	1.8485	2.2195	2.2148
	0.8046	1.9360	2.4062	2.1583	
	0.4259	1.4792	3.4731	2.2666	
m-CH_3	2.3299	0.1792	0.0769	0.1174	0.1166
	1.4628	0.1387	0.0948	0.1147	
	0.8069	0.1058	0.1311	0.1178	
	0.4178	0.0775	0.1770	0.1199	
	0.2141	0.0573	0.2347	0.1238	
	0.1131	0.0442	0.3089	0.1314	
p-CH_3	2.3337	0.0992	0.0425	0.0649	0.0642
	1.4642	0.0760	0.0519	0.0628	
	0.8053	0.0583	0.0724	0.0650	
o-CN	1.4514	4.9868	3.4359	4.1393	
o-CH_3CO	1.3916	0.8665	0.6227	0.7345	
o-C_2H_5	1.3948	0.2895	0.2076	0.2451	
2,6-$(CH_3)_2$	1.5008	0.0060	0.0040	0.0049	

[a] $v = k'[ArNO_2][SnCl_2] = k[ArNO_2][SnCl_2][HCl]_{st}^{0.5}$. Initial concentrations: $[ArNO_2] = 0.05$ M, $[SnCl_2] \simeq 0.15$ M.

Table II. Effect of H_2SO_4 on the Rate of $SnCl_2$ Reduction of Nitrobenzenes Catalyzed by HCl in $EtOH-H_2O$ (90:10 v/v) at 30 °C[a]

substituent in $PhNO_2$	$[SnCl_2]$, M	$[HCl]_{st}$, M	$[H_2SO_4]$, M	$10^2k'$, M^{-1} s^{-1}
none	0.1523	1.4948	0.2319	0.1687
	0.1513	1.4948		0.1600
o-HOOC	0.1502	1.5562	0.2150	0.5317
	0.1492	1.5562		0.5125
	0.1487	1.0568	0.4300	0.4713
	0.1497	1.0568		0.4315

[a] $v = k'[ArNO_2][SnCl_2]$. Initial concentration of $[ArNO_2] = 0.05$ M.

Table III. Effect of H_2O on the Rate of $SnCl_2$ Reduction of Ortho-Substituted Nitrobenzenes Catalyzed by HCl in $EtOH-H_2O$ (v/v) at 30 °C[a]

ortho-substituent in $PhNO_2$	$10^2k'$, M^{-1} s^{-1}	
	90% EtOH	55% EtOH
none	0.1660	0.1107
HO	0.2197	0.1170
CH_3	0.2800	0.1605
CH_3O	0.3217	0.2123
HOOC	0.4945	0.4257
F	1.3262	0.8488
Cl	2.3973	1.6845
Br	2.6652	1.8003

[a] $v = k'[ArNO_2][SnCl_2]$. Initial concentrations: $[ArNO_2] = 0.05$ M; $[SnCl_2] \simeq 0.15$ M; $[HCl]_{st} \simeq 1.45$ M.

$2.384E_\sigma - 0.2122E_s$, where $\rho_\sigma = 2.384$, $\delta = -0.2122$, *R* (correlation coefficient) = 0.9673, *S* (standard deviation from the regression line) = 0.1287, *n* (the number of compounds used in the calculation) = 6, $I_p = 6.27$, and $I_s = 1.33$ (see footnotes in Table IV). The polar effect is more important than steric effect in view of their I_p and I_s values.

Apparently, the electron-attracting groups such as halogens accelerate the reduction as expected from the nucleophilic attack of $SnCl_3^-$, which is reported also in the case of meta- and para-substituted nitrobenzenes.[5] A

Table IV. Comparison of Taft's E_σ and the Assumptive E_σ Derived from Meta Values by means of the Recurrent Method for the Reduction of Ortho-Substituted Nitrobenzenes with $SnCl_2$ in 90% EtOH at 30 °C, Rates for Diazo Coupling with Arylhydrazones (k_a),[13] and Semicarbazone Formation Equilibria (K_{ov}) and Rates (k_{ov})[14]

ortho-substituent, X	assump E_σ	Taft's		$SnCl_2$ redn, 10^2k, $M^{-1.5}\ s^{-1}$	diazo coupl,[13] k_a, $M^{-1}\ s^{-1}$	semicarbazone[14] equilib const, $10^{-5}K_{ov}$, M^{-1}	semicarbazone[14] rate const, $10^{-7}k_{ov}$, $M^{-2}\ s^{-1}$
		E_s	E_σ				
OCH_3	0.12	0.99	−0.22	0.2741		8.2	4.75
OC_2H_5	0.10	0.90	−0.18				
F	0.34	0.49	0.41	1.1308	0.61		
Cl	0.37	0.18	0.37	2.0643	0.19	23.3	1.94
Br	0.39	0.00	0.38	2.2148	0.11		
CH_3	0.00	0.00	0.00	0.2364	0.34	7.0	1.49
I	0.35	−0.20	0.38	1.7324			
NO_2	0.71	−0.75	0.97			75	0.52
C_6H_5	0.01	−0.90	0.01	0.3201	0.04		
ρ_σ (ρ_σ)				2.5595 (1.6234)	−1.391 (−1.1889)	1.3807 (1.3113)	−0.0594 (−0.0426)
δ (δ)				−0.191 (0.1031)	1.1507 (1.1396)	−0.0793 (0.3434)	0.5335 (0.5243)
R^a (R)				0.9952 (0.9312)	0.9976 (0.9781)	0.9994 (0.9993)	0.9978 (0.9975)
S^b (S)				0.0527 (0.1958)	0.0224 (0.1342)	0.0283 (0.0316)	0.0458 (0.048)
C^c (C)				−0.0405 (0.2052)	0.078 (0.0469)	0.0011 (0.0021)	0.0019 (−0.0029)
$I_p{}^d$ (I_p)				20.30^f (5.11^f)	17.55^g (2.58^g)	19.88^f (16.82^f)	0.49^i (1.14^h)
$I_s{}^e$ (I_s)				5.05^g (0.75^i)	38.74^f (6.11^f)	2.60^g (6.05^g)	10.18^f (6.08^f)

[a] Correlation coefficient $R = [(\rho_\sigma A + \delta B)/D]^{1/2}$, where $A = n\Sigma E_\sigma(\log k/k_0) - \Sigma E_\sigma\Sigma(\log k/k_0)$, $B = n\Sigma E_s(\log k/k_0) - \Sigma E_s\Sigma(\log k/k_0)$, and $D = n\Sigma(\log k/k_0)^2 - (\Sigma \log k/k_0)^2$. [b] Standard deviation of experimental measurements from the regression line $S = [(D - \rho_\sigma A - \delta B)/n(n-3)]^{1/2}$. [c] A constant value in the equation of the regression line: $C = [\Sigma(\log k/k_0) - \rho_\sigma\Sigma E_\sigma - \delta\Sigma E_s]/n$. [d] A parameter expressing the importance of the polar effect by the binary regression method: $I_p = \rho_\sigma(nE - G/F)^{1/2}/S$, where $E = n\Sigma E_\sigma{}^2 - (\Sigma E_\sigma)^2$, $F = n\Sigma E_s{}^2 - (\Sigma E_s)^2$, and $G = (n\Sigma E_\sigma E_s - \Sigma E_\sigma\Sigma E_s)^2$. [e] A parameter expressing the importance of the steric effect by the binary regression method: $I_s = \delta(nF - G/E)^{1/2}/S$. [f] Important. [g] Less important than f. [h] Not very important. [i] Negligible.

peculiar feature of this reaction is its acceleration by bulky ortho groups as is obvious from the negative steric reaction constant δ (−0.2122). This is explained by a nucleophilic attack of $SnCl_3^-$ on the N atom of NO_2 from a direction perpendicular to the plane of NO_2. The attack is favored by a twist of the NO_2 group around its C–N bond, by a bulky orth substituent to minimize the delocalization of positive charge of the N atom to the benzene ring and to an ortho- or para-electron-releasing group, by the resonance inhibition, and also by avoidance of the steric hindrance of the ortho group. However, two methyl groups at the 2- and 6-positions exert a pronounced retarding effect due to complete shielding of NO_2 from the attacking species $SnCl_3^-$ (Table I, last line).

As is apparent from Table I, the order of the Me group effect is ortho > meta > para. this is explained by the electron-releasing power of the Me group along with its steric acceleration effect.

We found that the rate constants of reduction of ortho-substituted nitrobenzenes could approximately be correlated with Taft's E_σ values, but a rather large deviation was observed with *o*-MeO and *o*-F. A better plot was obtained when *o*-MeO was eliminated as shown in Figure 3a. If Taft's E_σ value for *o*-MeO (−0.22 or −0.24) was employed, an unsatisfactory plot ($R \simeq 0.93$, $S \simeq 0.20$) was obtained as shown in Figure 3b and Table IV, where δ (0.1031) becomes positive and ρ_σ (1.6234) is less positive. The deviation of the *o*-MeO and *o*-F groups from Taft's plot has been observed by several workers.[10,12,13]

An experimental search for the appropriate ortho-substituent constants has been attempted, but there appears a difficulty in determining satisfactory E_σ values. Taft's treatment may not separate clearly steric effects from polar effects. The inductive effect of ortho substituents may be transmitted not only via chemical bonds but also through the intervening molecular cavity or medium. Since the ortho substituents exert the the resonance inhibition, the polar effect of an ortho substituent may largely be due to its inductive effect; i.e., E_σ values for ortho substituents may be appproximated to those for meta substutuents. The E_σ value, especially for an ortho substituent, depends on the solvent, the structure of aromatic molecule, and its bulkiness; hence, it may be difficlut to determine the coherent E_σ value for an ortho substituent. Tentatively, we assumed $E_\sigma{}^{o\text{-}X} \simeq E_\sigma{}^{m\text{-}X}$. This assumption gave a satisfactory plot for the reaction as shown in Figure 3c. The plot satisfies the following equation: $\log (k/k_0) = -0.0405 + 2.5595E_\sigma - 0.191E_s$, where $\rho_\sigma = 2.5595$, $\delta = -0.191$, $R = 0.9952$, and $S = 0.0527$. Here, the polar effect is more important than the steric effect on the basis of their I_p and I_s values (Table IV), similar to the case in which *o*-MeO group is eliminated (Figure 3a). A comparison of Taft's E_σ and the assumptive E_σ derived from the corresponding meta value by means of the binary regression method for the present reduction and the other reactions (i.e., rate constants for diazo coupling with arylhydrazones[13] and equilibrium and rate constants for semicarbazone formation of benzaldehydes[14]) is shown in Table IV. The cor-

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Table V. Sample Data for the Rate Constant Calculated by Eq 7 for $SnCl_2$ Reduction of Nitrobenzene in 90% (v/v) EtOH at 30 °C[a]

t, s	$a - x$, M	x, M	$3b - x$, M	$10^2k'$,[b] $M^{-1}\ s^{-1}$
0	0.1455	0.0000	0.1500	
900	0.1353	0.0102	0.1398	0.1674
1800	0.1266	0.0189	0.1311	0.1655
3600	0.1120	0.0335	0.1165	0.1655
5400	0.1000	0.0455	0.1045	0.1673
7200	0.0911	0.0544	0.0956	0.1644
9000	0.0829	0.0626	0.0874	0.1660
10800	0.0762	0.0693	0.0807	0.1662

[a] Initial concentrations: $[SnCl_2] = a = 0.1455$ M, $[PhNO_2] = b = 0.05$ M, $[HCl]_{st} = 1.4512$ M.

relation coefficient (R) and standard deviation (S) show that the meta E_σ is more appropriate than Taft's ortho E_σ for these reactions. Apparently, these results show that ortho substituents exert polar effects similar to those of meta substituents because of the steric inhibition of resonance.

Experimental Section

Materials. The inorganic and organic reagents used were all of commercial guaranteed grade and used without further purification. A 90% or 55% (v/v) ethanol solution of HCl was prepared by mixing 35% aqueous HCl or HCl gas with the appropriate amount of 99% ethanol and water, and the concentration was confirmed by alkalimetry.

Kinetics. A 90% or 55% (v/v) ethanolic solution (25 mL) containing an appropriate amount of HCl and nitro compounds (2.5 mmol) and another HCl (same amount) acidic 90% or 55% (v/v) ethanolic solution (25 mL) containing $SnCl_2$ (7.5 mmol) were placed in a thermostated bath to reach a constant temperature (30 °C). The two solutions were mixed to start the reaction, and aliquots were pipetted out at appropriate intervals of time. The concentration of $SnCl_2$ in the aliquot was determined by iodometry. For the estimation of the HCl concentration, an initial aliquot was introduced to aqueous sodium citrate and titrated with 0.5 N NaOH with phenolphthalein as an indicator to subtract the amount of HCl produced by the hydrolysis of $SnCl_2$.

The HCl-catalyzed $SnCl_2$ reduction of nitro compounds ($ArNO_2$) obeys the stoichiometric equation (eq 6).[4]

$$ArNO_2 + 3SnCl_2 + 7HCl \rightarrow ArNH_2{\cdot}HCl + 3SnCl_4 + 2H_2O \qquad (6)$$

Assuming that initial concentration of $SnCl_2$ is a and that of $ArNO_2$ is b and that the consumed concentration of $SnCl_2$ at time t is x,, we can express $[ArNO_2]$ at time t as $b - x/3$ on the basis of eq 6. Hence

$$v = -d[SnCl_2]/dt = dx/dt = k'(a - x)(b - x/3)$$

or

$$k' = \frac{6.909}{t(3b - a)} \log \frac{a(3b - x)}{3b(a - x)} \qquad (7)$$

A typical calculation of rate data for nitrobenzene is shown in Table V as an example.

Registry No. Nitrobenzene, 98-95-3; 2-nitrophenol, 88-75-5; 1-methyl-2-nitrobenzene, 88-72-2; 1-methoxy-2-nitrobenzene, 91-23-6; 2-nitro-1,1′-biphenyl, 86-00-0; 2-nitrobenzoic acid, 552-16-9; 1-fluoro-2-nitrobenzene, 1493-27-2; 1-iodo-2-nitrobenzene, 609-73-4; 1-chloro-2-nitrobenzene, 88-73-3; 1-bromo-2-nitrobenzene, 577-19-5; 1-methyl-3-nitrobenzene, 99-08-1; 1-methyl-4-nitrobenzene, 99-99-0; 2-nitrobenzonitrile, 612-24-8; 1-(2-nitrophenyl)ethanone, 577-59-3; 1-ethyl-2-nitrobenzene, 612-22-6; 1,3-dimethyl-2-nitrobenzene, 81-20-9; stannous chloride, 7772-99-8; ethanol, 64-17-5; 1-ethoxy-2-nitrobenzene, 610-67-3; 1,2-dinitrobenzene, 528-29-0.

Selectively Deuterated and Optically Active Cyclic Ethers

Yuhsuke Kawakami,* Tamio Asai, Kiyoshi Umeyama, and Yuya Yamashita

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464, Japan

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The high versatility and importance of optically active or selectively deuterated compounds in synthetic and mechanistic organic chemistry are well-known. We have been interested in optically active cyclic ethers, particularly the epihalohydrin type, as starting materials in the synthesis of various chiral compounds. The optically active epihalohydrins (Cl, Br, I) are versatile starting materials in synthesizing polyether-type phase-transfer catalysts (PTC), while their fluoro analogue can be transformed into a biologically interesting compound.[1-4] We reported in an earlier paper a mild and effective method for chlorine displacement in three- and four-membered cyclic ethers by potassium halide–18-crown-6 (KX–18-CR-6) systems, and, further, the reaction mechanisms of fluorination of epichlorohydrin and 3,3-bis(chloromethyl)oxetane were also elucidated, using their selectively deuterated derivatives.[5] In this paper, we report the synthesis of selectively deuterated epihalohydrins (F, Cl, Br, I) and 3,3-bis(chloromethyl-d_2)oxetane and some of our observations on the stereochemistry of each transformation. Further, the synthesis of optically active epihalohydrins, especially the optically active epifluorohydrin, from (S)-glycerol 1,2-acetonide ((S)-**2**), using mainly KX–18-CR-6 (X = F, Br, I), is reported. To our knowledge, this is the first report on the synthesis of optically active epifluorohydrin. The direct halogenation of the presynthesized optically active epichlorohydrin with the same reagents gave the racemized products.[5] The selectively deuterated or optically active compounds reported herein are expected to find a variety of uses in organic chemistry.

The synthetic schemes are relatively straightforward. Baldwin reported the synthesis of (R)- and (S)-epichlorohydrins ((R)-**18b**, (S)-**18b**) from (S)-**2**.[6] However, the yield of (S)-**18b** is variable and, moreover, dependent on reaction conditions. Since the stereochemistry of each transformation is clearly defined, we thought that the selectively deuterated epichlorohydrins (**9b**, **9e**) could be synthesized from selectively deuterated glycerol-*3,3*-d_2 1,2-acetonide (**5**). **5** was synthesized by the lithium aluminum deuteride (LAD) reduction of methyl glycerate 2,3-acetonide (**4**) and further transformed into selectively deuterated **9e** according to the Scheme I. The alteration of the order of the tosylation and chlorination steps was also attempted in order to improve the yield of the epichlorohydrin (path B). Selectively deuterated epihalohydrins other than epichlorohydrin (X = F, Br, I) were synthesized by our method through the mesylate (path C). Monodeuterated (S)-glycerol 1,2-acetonide and several of

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