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ELECTROOXIDATIVE C-S CLEAVAGES AS A NEUTRAL DEPROTECTION FOR CARBOXYLIC ACIDS

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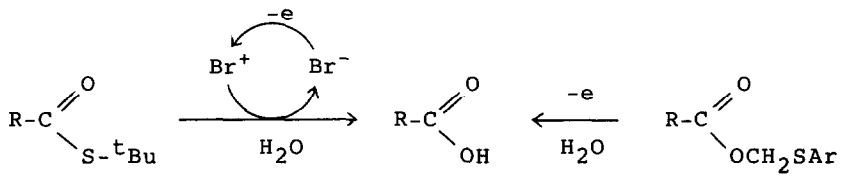
Abstract -- C-S Bond cleavages of S-t-butyl thioates (1) and 4-methoxyphenylthiomethyl esters (2) are achieved electrochemically in an indirect and direct manner, respectively, in aqueous acetonitrile, affording an efficient method for deprotection of carboxylic acids under neutral conditions.

In protecting and deprotecting carboxylic acids, a large number of substituted methyl and ethyl esters have been devised according to diversified demands for deprotecting conditions such as acidic, basic, non-hydrolytic, oxidative or reductive conditions.[1-4] Frequently required are neutral conditions in order to render the deprotections mild and selective. Electrochemical methods have great advantage in controlling redox potentials and in performing the reactions under neutral conditions.[3,4] For example, various β-halo substituted ethyl esters can be deprotected at different reduction potentials.[5] Steckhan et al. have reported the deprotection of substituted benzyl esters using triphenylamines as an electron-transferring mediator.[6,7]

Sulfur-containing methyl or ethyl esters have been known as useful protective compounds which can be converted oxidatively to carboxylic acids using metallic or other oxidants.[8-12] Although electrochemical oxidation of sulfur compounds has been proved useful in organic syntheses,[13] applications of C-S cleavages as a deprotection reaction are not thoroughly exploited.[7,14] We have communicated that S-t-butyl thioates (1) can be deprotected under neutral conditions electrochemically using bromide salts as the electrolyte.[15] Detailed aspects on the bromonium ion-mediated oxidation[16] are described here. 4-Methoxyphenylthiomethyl esters (2, Ar = *p*-anisylthiomethyl, ATM) are also found to be readily converted to carboxylic acids electrooxidatively. We describe here that these two methods by

indirect and direct electrooxidations could be applied as useful deprotections for carboxylic acids.



1 2

Bromonium-Ion Mediated Electrooxidation of Thioates **1**. Thioates (thiol esters)[17,18] could be considered as activated esters.[19,20] S-Phenyl and S-ethyl thioates are known to undergo a facile alkaline hydrolysis, whereas S-t-butyl thioates (**1**) show sluggishness toward their hydrolysis under weakly alkaline (e.g., 0.1 N NaOH) or acidic conditions (e.g., 0.1 N HCl). Thus we chose **1** as an appropriate protective ester for carboxylic acids.

Oxidation potentials of **1** were examined by cyclic voltammetry (CV) as illustrated in Figure 1; the wave was irreversible suggesting the instability of the cation radical of **1**. Table 1 lists anodic peak potentials of several thioates. The oxidation potentials observed reflect those of thiol groups since the corresponding esters possess much higher potentials. The oxidation potentials for the esters of aliphatic thiols are above 2.4 V *vs.* SCE which are too high to be oxidized directly. On the other hand, the

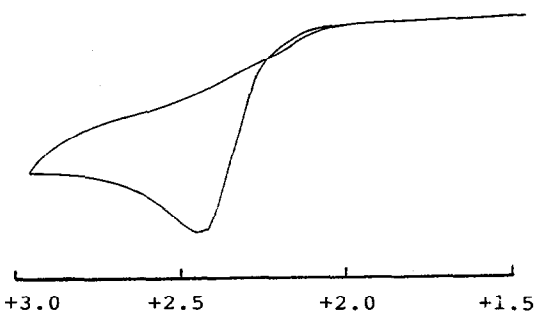


Figure 1. Cyclic voltammogram of S-t-butyl cyclohexanethioate (**1a**) in the presence of 0.1 M Bu_4NBF_4 in acetonitrile (for conditions see footnote a in Table 1).

Table 1. Oxidation Potentials of Thioates RCOSR'[a]

RCOSR'			Peak potential[b]
R	SR'		E_{pa}, V
Cyclohexyl	S-^{t}Bu	(1a)	+ 2.43
	SEt		+ 2.64
	SPh		+ 1.98
	SC_6H_4-4-OCH_3		+ 1.48
Phenyl	S-^{t}Bu		+ 2.57
	SEt		+ 2.63
Pentyl	S-^{t}Bu	(1c)	+ 2.45

a) Cyclic voltammetry of a 0.01 M solution of **1** in acetonitrile containing 0.1 M tetrabutylammonium tetrafluoroborate was recorded at a scan rate of 200 mV/sec. b) Peak potential in V *vs.* Ag/AgCl.

peak potential of 4-methoxyphenylthioate is considerably lower, i.e., 1.48 V, and could be easily oxidized directly. However, these S-aryl thioates are not appropriate as a protecting group because of their facile hydrolysis under weakly alkaline conditions.

The problem of high oxidation potentials for S-t-butyl thioates could be overcome by using bromide or chloride salts as a supporting electrolyte. That is, when electrolytes such as LiCl, LiBr or tetrabutylammonium bromide (Bu_4NBr) were used, the electrolyses of **1** in aqueous acetonitrile (90% MeCN) proceeded smoothly and carboxylic acids were obtained in high yields (Table 2). The electrolyses with other electrolytes such as KF, LiI, $LiNO_3$, Bu_4NBF_4 and Bu_4NClO_4 resulted in much lower yields (i.e., <70%) and current efficiencies (i.e., >10 F/mol).

It is known that the electrooxidation of halide ion X^- gives rise to halonium ion X^+ (e.g., bromonium ion),[16] which can react with sulfides to yield bromosulfonium ions **3** (eq. 2).[21,22] The electrooxidation of S-aryl thioates in methanol has been reported to give a complex mixture of prod-

$$Br^- \xrightarrow{-2e} Br^+ \xrightarrow{R_2S} \underset{\mathbf{3}}{R_2\overset{+}{S}Br} \qquad (2)$$

Table 2. Yields of Carboxylic Acids Formed from the Electrolysis of 1[a]

R in 1	Electrolytes	F mol^{-1}	Yield/%[b]
Cyclohexyl (1a)	LiBr	7	87
	Bu_4NBr	7	94
	Bu_4NClO_4	13	83
Phenyl (1b)	Bu_4NBr	11	94
Pentyl (1c)	LiCl	8	96
	LiBr	8	96

a) Electrolytic conditions: **1**, 2mmol; electrolyte, 2 mmol; H_2O-MeCN (1 : 9), 25mL; in an undivided cell with platinum electrodes at a constant current of 0.1 A. b) Yields were determined by GLC of diethyl ether extract after methylation with diazomethane.

ucts due to C-S bond cleavage.[23] In contrast, the present electrolyses of S-alkyl or S-phenyl cyclohexanecarboxylates in methanol containing halide salts such as LiBr resulted in nearly quantitative formation of methyl cyclohexanecarboxylate (6-8 F/mol). The same transformation was similarly effected by controlled potential electrolyses at +1.5 or +1.0 V vs. Ag/AgCl with chlorides or bromides, respectively. Thus, it is apparent that the high yield conversion to methyl ester is based on the intermediacy of halosulfonium ion such as **3** in eq. 2.

Oxidative transformations of thioates to esters have conventionally been carried out with metallic Hg(II) or Ag(I) salts,[19] N-bromosuccinimides, and organic peracids.[24] In these oxidations, t-butyl esters are obtained in the presence of t-butanol as a result of heterolysis between the acyl carbon and the sulfur atom. In the present electrooxidation, however, we were unable to detect t-butyl esters, arguing against intervention of free acyl cation **4**. Thus, bromosulfonium intermediate **5** is probably involved in the present facile hydrolysis or alcoholysis.[25]

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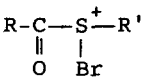


5

Direct Electrooxidation of Thiomethyl Esters **2**. We were interested in the

application of direct electrooxidative methods to thiomethyl esters as an alternative deprotective method. The deprotection of methylthiomethyl esters has been carried out using oxidants such as Hg(II),[8] H_2O_2-Mo salts[9] or via sulfonium salts and iodomethane.[9] These methods usually require excess amounts of reagents. Our point here is to utilize arylthiomethyl esters (2) which could be deprotected directly at lower oxidation potentials.

Arylthiomethyl esters (2) were prepared from the base-catalyzed reaction of chloromethyl sulfide (6)[26] and carboxylic acids according the reported method (eq. 3).[27] Oxidation potentials of 2 (R = cyclohexyl) were

$$ArSCH_3 \xrightarrow{NCS} \underset{\mathbf{6}}{ArSCH_2Cl} \xrightarrow[DBU]{RCO_2H} \underset{\mathbf{2}}{ArSCH_2OC\text{-}R} \quad (3)$$

evaluated from their CV peak potentials (Table 3). Obviously, electron-donating substituents such as 4-methoxyphenyl and 1-naphthyl lowered oxidation potentials significantly. Electrolyses of these arylthiomethyl es-

Table 3. Oxidation Potentials of Thiomethyl Cyclohexanecarboxylates[a]

R' in $R'OCOC_6H_{11}$		Peak potential/V[b]	Acid/%[c]
4-MeO-$C_6H_4SCH_2$-	(**2a**)	+ 1.48	84
$C_6H_5SCH_2$-	(**2b**)	+ 1.95	59
4-NO_2-$C_6H_4SCH_2$-	(**2c**)	+ 2.24	52
1-NaphtylSCH_2-	(**2d**)	+ 1.59	48
CH_3SCH_2-	(**2e**, Ar = CH_3)	+ 2.61	70

a) For experimental conditions, see footnote a of Table 1. b) Peak potentials in V vs. Ag/AgCl. c) Yields of acids as determined by GLC as methyl esters. Electricity of 11 F/mol was passed.

ters at a constant current in aqueous acetonitrile were found to give high yields of cyclohexanecarboxylic acid; the reaction of p-anisylthiomethyl (ATM) ester (**2a**) being the most effeicient (∿ 84% yield). Several ATM esters (**2a-i**) were obtained according to eq. 3 and their electrolyses gave the corresponding carboxylic acids in good yields (Table 4).

In all cases studied, carboxylic acids were obtained in practically pure form by simple extraction of the electrolysis mixture.[28] The electrooxidative deprotection of hindered ester **2h** (R = t-butyl) resulted in

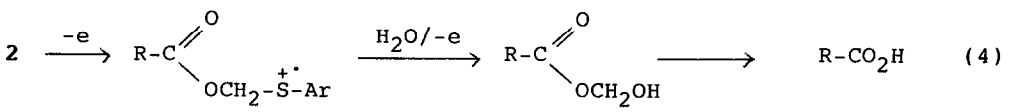
similar yield, suggesting that the hydrolysis of **2** proceeds initially via

Table 4. Yields for the Formation of ATM Esters (2) and Their Electrooxidative Deprotection to Carboxylic Acids[a]

R in 4-$MeOC_6H_4CH_2SCOR$	Ester/%[b]	Acid/%[c]
Cyclohexyl (**2a**)	85	84
Phenyl (**2f**)	92	71
Pentyl (**2g**)	82	75
t-Butyl (**2h**)	86	80
3-Cyclohexenyl (**2i**)	89	72[d]

a) Electrolytic conditions: **2**, 2mmol; electrolyte, $Bu_4N^{\oplus}F_4$, 1 mmol; in H_2O-MeCN (1:9), 25 ml; 0.1 A, 10-11 F/mol. b) Isolated yield. c) GLC yields after methylation with diazomethane. d) Controlled potential electrolysis at +1.7 V vs. Ag/AgCl.

C-S cleavage rather than C-O scission. Thus, upon electrooxidation of **2**, the resulting cation radical **7** would undergo a facile hydrolysis to give hemiacetals **8** and then carboxylic acid (eq. 4).



7 **8** (4)

Functional Compatibility in the Electrooxidation of 1 and 2. The electrooxidative C-S cleavage of S-t-butyl thioates (**1**) proceeded smoothly at +1.0 V by using bromide salts as the electrolyte. The present indirect method for oxidative deprotection of **1** is not appropriate in the presence of other functional groups such as amino, formyl or alcohols (primary and secondary) which are susceptible to the halonium ion oxidation.[16] Acid-sensitive compounds such as acetals or triphenylmethyl ethers were not stable under the electrooxidative deprotection. But, these hydrolytic changes could be suppressed by adding solid sodium bicarbonate in order to keep the solution neutral. Similar utilization of sodium bicarbonate was also effective in the direct electrooxidation of thiomethyl esters **2**. Hence, the two alternative electrooxidative deprotections of **1** and **2** can be operative under neutral conditions.

EXPERIMENTAL

^{1}H NMR spectra were recorded with a Hitachi R24B (60 MHz) and a Valian Gemini 200 (200 MHz) NMR spectrometer in CCl_4 and $CDCl_3$, respectively. IR spectra were recorded with a Hitachi 260-30 IR spectrometer. GLC analyses were performed with a Yanagimoto G180 gas chromatograph, using 25 mm x 1 m columns of PEG 20M, 10% on Chromosorb WAW; Silicone DC550, 15% on Chromosorb WAW. GC-MS analyses were carried out with a JEOL D300 mass spectrometer using a PEG 20M column.

For the constant-current electrolysis, electrodes of platinum sheets (1x3 cm^2) were inserted into a cylindrical glass vessel of 30 mL volume and set apart by 1 cm distance. The terminals were connected with a DC power supply (Takasago GPO 52-2) through a digital coulomb-amperehour meter (Hokuto Denko HF 201). A potentiostat (Hokuto Denko HA 301) and a commercially available reference electrode of Ag/AgCl (0.1 M, Yanagimoto) were also equipped for the controlled potential electrolysis.

For cyclic voltammetric measurements, a cell with nitrogen inlet was filled with 10 mL of a sample (0.01 M) solution containing Bu_4NBF_4 (0.1 M) and furnished with platinum wire electrodes and the above mentioned reference electrode. After bubbling nitrogen for 15 min, cyclic voltammograms were recorded on a polarographic analyser (Yanagimoto P 1100) at a scan rate of 200 mV/sec.

Thioates **1**. S-t-Butyl thioates were prepared in 10-50 mmol scale from carboxylic acids and dimethyl-2-propanethiol according to the Steglich's method.[17] Other thioates were prepared from the reaction of corresponding thiols and acid chlorides. The thioates thus obtained showed expected IR and NMR spectroscopic properties and their purities were checked by GLC analyses. Notably, S-alkyl and S-phenyl aliphatic thioates showed their carbonyl streching absorption at 1685-90 cm^{-1} and the corresponding benzoates at 1650-1660 cm^{-1}.

S-t-Butyl cyclohexanecarbothioate (**1a**). B.p. 109°C, 7 mm; lit.[29] b.p. 73-74°C, 0.5 mm. S-Ethyl cyclohexanecarbothioate. B.p. 91-94°C, 4 mm; lit.[30] b.p. 113-116°C, 14 mm. S-Phenyl cyclohexanecarbothioate. M.p. 33-35°C; b.p. 142-144°C, 1.1 mm; lit.[31] m.p. 33-34°C. S-4-Methoxyphenyl cyclohexanecarbothioate. B.p. 206-210°C, 4 mm. IR(film): 2950, 2875, 1700, 1240, 960 cm^{-1}; NMR (60 MHz): δ 7.05 (d, J=9 Hz, 2H), 6.67 (d, J=9Hz, 2H), 3.67 (s, 3H), 1.0-2.0 (m, 11H); MS : m/z 250 (M, 16), 140 (100), 111 (59). Calcd. for $C_{14}H_{18}O_2S$: C, 67.17; H, 7.24. Found: C, 66.78; H, 7.27.

S-t-Butyl benzothioate (**1b**). B.p. 121-122°C, 10 mm; lit.[32] b.p. 110°C, 28 mm. S-Ethyl benzothioate. B.p. 96-98°C, 1 mm; lit.[33] b.p. 134°C, 20 mm. S-t-Butyl hexanethioate (**1c**). B.p. 69°C, 1 mm; lit.[34] b.p. <80°C, 0.05 mm.

Electrolysis of Thioates **1**. A solution of S-t-butyl thioate (**1**, 2 mmol) and Bu_4NBr (2 mmol) in 25 mL of H_2O-MeCN (1:9) was placed in a cylindrical undivided cell and electrolyzed at a constant current of 0.2 A at ambient temperature. No difference was observed

between the electrolysis under nitrogen or air. The electrooxidation was monitored by GLC analyses of aliquots and stopped after over 95% consumption of thioate (ca. 2 h). The electrolysate was poured into water and extracted with ether three times (30, 20, and 20 mL). The combined ethereal layer was washed successively with water and brine, and dried over Na_2SO_4. In order to determine the yields of carboxylic acid an aliquot was treated with diazomethane in ether and analyzed by GLC. The residue after evaporating ether was a practically pure carboxylic acid as identified spectroscopically.

Electrolyses in methanol were carried out similarly and the products were analyzed by GLC and GC-MS in comparison to authentic samples. When electrolyses of thioates (2 mmol) were conducted in the presence of 3 mmol each of 1- and 2-propanol in acetonitrile (20 mL), the product ratio was 8:2, respectively, as determined by GLC. To avoid hydrolysis of acid-sensitive substrates, the electrolyses were performed with vigorous stirring in the presence of solid sodium bicarbonate (4-5 mmol).

Arylthiomethyl Esters **2**. Aryl chloromethyl sulfides (**6**) were obtained in 80-90% by the N-chlorosuccinimde (NCS) chlorination[26] of the corresponding sulfides; 4-methoxyphenyl,[35] phenyl,[35] and 4-nitrophenyl[36] chloromethyl sulfides are known. 1-Naphthyl chloromethyl sulfide, NMR (CCl_4): δ 8.1-8.3 (m, 1H), 7.1-7.9 (m, 6H), 4.75 (s, 2H). Arylthiomethyl esters **2** was prepared according to the reported method.[27]

4-Methoxyphenylthiomethyl cyclohexanecarboxylate (**2a**). B.p. 153-156°C, 1.0 mm; IR (film): 3020, 2940, 1770 cm^{-1}; NMR (200 MHz): δ 7.41 (d, J=9 Hz, 2H), 6.85 (d, J=9 Hz, 2H), 5.30 (s, 2H), 3.80 (s, 3H), 2.25-2.38 (m, 1H), 1.20-2.00 (m, 10H); MS : m/z 280 (M, 20), 153 (10), 140 (100), 111 (90). Calcd. for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19. Founmd: C, 65.11; H, 6.82.

Phenylthiomethyl cyclohexanecarboxylate (**2b**). B.p. 163-164°C, 0.9 mm; IR (film): 2950, 2860, 1740 cm^{-1}; NMR (200 MHz): δ 7.40-7.50 (m, 2H), 7.25-7.40 (m, 3H), 5.42 (s, 2H), 2.27-2.43 (m, 1H), 1.20-1.98 (m, 10H); MS: m/z 250 (M, 10), 123 (13), 111 (100). Calcd. for $C_{14}H_{18}O_2S$: C, 67.17; H, 7.25. Found: C, 67.33; H, 7.39.

4-Nitrophenylthiomethyl cyclohexanecarboxylate (**2c**). M.p. 47-50°C; IR (KBr): 2960, 2875, 1740, 1520, 1340 cm^{-1}; NMR (200 MHz): δ 8.18 (d, J=9 Hz, 2H), 7.53 (d, J=9 Hz, 2H), 5.53 (s, 2H), 2.27-2.45 (m, 1H), 1.15-2.00 (m, 10H); MS: m/z 295 (M, 6), 168 (3), 141 (6), 111 (100). Calcd. for $C_{14}H_{17}O_4NS$: C, 56.93; H, 5.80; N, 4.74. Found: C, 56.89; H, 5.97; N, 4.71.

1-Naphthylthiomethyl cyclohexanecarboxylate (**2d**). B.p. 200-204°C, 1.0 mm; IR (film): 2950, 2875, 1740 cm^{-1}; NMR (200 MHz): δ 8.40 (d, J=9 Hz, 1H), 7.75-7.90 (m, 3H), 7.40-7.63 (m, 3H), 5.43 (s, 2H), 2.18-2.40 (m, 1H), 1.14-1.93 (m, 10H); MS: m/z 300 (M, 10), 173 (20), 111 (100). Calcd. for $C_{18}H_{20}O_2S$: C, 71.97; H, 6.71. Found: C, 72.15; H, 6.78.

Methylthiomethyl cyclohexanecarboxylate (**2e**, Ar = CH_3). B.p. 146-150°C, 2.5 mm; IR (film): 2950, 2860, 1740, 1150, 1120 cm^{-1}; NMR (60 MHz): δ 4.95 (s, 2H), 2.15 (s, 3H), 1.0-2.0 (m, 11H); MS: m/z 188 (M, 20), 111 (100), 77 (20). Calcd. for $C_9H_{16}O_2S$: C, 57.41; H, 8.57. Found: C, 57.31; H, 8.50.

4-Methoxyphenylthiomethyl benzoate (2f). B.p. 172-175°C, 1.0 mm; IR (film): 2950, 2875, 1720, 1240 cm^{-1}; NMR (200 MHz): δ 8.05 (d, J=9 Hz, 2H), 7.35-7.61 (m, 5H), 6.87 (d, J=9 Hz, 2H), 5.54 (s, 2H), 3.80 (s, 3H); MS : m/z 274 (M, 53), 244 (21), 153 (12), 139 (12), 121 (7), 105 (100). Calcd. for $C_{15}H_{14}O_3S$: C, 65.67; H, 5.14. Found: C, 64.61; H, 5.15.

4-Methoxyphenylthiomethyl hexanoate (2g). B.p. 143-145°C, 1.0 mm; IR (film): 2970, 2880, 1740, 1240 cm^{-1}; NMR (200 MHz): δ 7.43 (d, J=9 Hz, 2H), 6.85 (d, J=9 Hz, 2H), 5.30 (s, 2H), 3.80 (s, 3H), 2.33 (t, J=6 Hz, 2H), 1.63 (t, J=6 Hz, 2H), 1.20-1.35 (m, 4H), 0.88 (t, J=6 Hz, 3H); MS: m/z 268 (M, 20), 139 (15), 115 (30), 99 (100). Calcd. for $C_{14}H_{20}O_3S$: C, 62.66; H, 7.51. Found: C, 62.10; H, 7.45.

4-Methoxyphenylthiomethyl 2,2-dimethylpropanoate (2h). B.p. 115-116°C, 1.0 mm; IR (film): 2960, 2850, 1740, 1130 cm^{-1}; NMR (200 MHz): δ 7.43 (d, J=9 Hz, 2H), 6.86 (d, J=9 Hz, 2H), 5.28 (s, 3H), 3.80 (s, 3H), 1.20 (s, 9H); MS : m/z 254 (M, 20), 139 (12), 101 (30), 85 (100). Calcd. for $C_{13}H_{18}O_3S$: C, 61.39; H, 7.13. Found: C, 61.10; H, 7.21.

4-Methoxyphenylthiomethyl 3-cyclohexenecarboxylate (2i). B.p. 193-194°C, 0.9 mm; IR (film): 2925, 2830, 1740, 1240, 1130 cm^{-1}; NMR (200 MHz): δ 7.42 (d, J=9 Hz, 2H), 6.86 (d, J=9 Hz, 2H), 5.68 (s, 2H), 5.32 (s, 2H), 3.80 (s, 3H), 2.50-2.70 (m, 1H), 1.93-2.30 (m, 5H), 1.60-1.80 (m, 1H); MS: m/z 278 (M, 30), 153 (12), 109 (100). Calcd. for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52. Found: C, 6361; H, 6.51.

Electrolysis of ATM esters (2). A solution of 4-methoxyphenylthiomethyl ester (2, 1 mmol) and Bu_4NBF_4 (1 mmol) dissolved in 25 mL of H_2O-MeCN (1:9) was electrolyzed at a constant current of 0.1 A as described for the above case of **1**. Aliquots were analyzed at appropriate time intervals by GLC. The electrolysis was stopped when the starting ester reached over 95% consumption, and the reaction mixture was treated as described above.

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