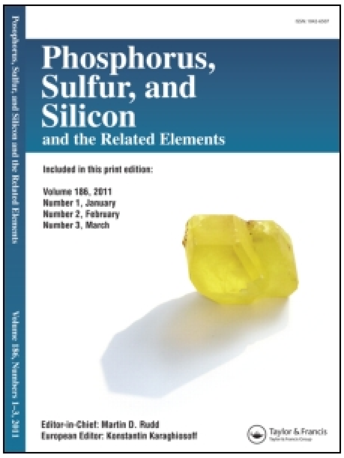

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

ANODIC OXIDATION OF 1,*n*-HALO(ALKYLTHIO)ALKANES AND 1,*n*-CHLORO(ALKYLSULFINYL)ALKANES

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To cite this Article Aced, Ahmed , Anklam, Elke , Asmus, Klaus-Dieter , Pohl, Klaus , Glass, Richard S. , Steffen, L. Kraig and Wilson, George S.(1990) 'ANODIC OXIDATION OF 1,*n*-HALO(ALKYLTHIO)ALKANES AND 1,*n*-CHLORO(ALKYLSULFINYL)ALKANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 48: 1, 53 — 62

To link to this Article: DOI: 10.1080/10426509008045882

URL: http://dx.doi.org/10.1080/10426509008045882

Phosphorus, Sulfur, and Silicon, 1990, Vol. 48 pp. 53–62
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ANODIC OXIDATION OF 1,*n*-HALO(ALKYLTHIO)ALKANES AND 1,*n*-CHLORO(ALKYLSULFINYL)ALKANES

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Anodic oxidation of 1,*n*-halo(alkylthio)alkanes [$X\text{-}(CH_2)_n\text{-}S\text{-}R$, $X = Cl, Br, I$] and 1,*n*-halo(alkylsulfinyl)alkanes [$Cl\text{-}(CH_2)_n\text{-}S(O)\text{-}R$] was studied by cyclic voltammetry in anhydrous acetonitrile and by controlled potential electrolyses. The ease of sulfur oxidation was not affected by the alkyl substituents R or the number of methylene groups *n* in compounds with $n > 2$. The oxidation of the 1,2-halo(alkylthio)ethanes ($n = 2$) occurred at slightly higher potentials. The peak potentials decreased slightly in the order $Cl > Br > I$ which is probably due to the electronegativity of the halogen atoms. The investigated anodic oxidation was shown to be a two electron irreversible process. Electrolyses in aqueous acetronitrile led to the corresponding sulfoxides and sulfones in good yields.

INTRODUCTION

The electrochemical oxidation of organic sulfides leads to the formation of sulfonium compounds, sulfoxides, sulfones and other condensed species.[1–3] In contrast to the well investigated oxidation mechanism for aromatic[4–11] and aliphatic sulfides[12–16] only little is known about the anodic oxidation of sulfoxides.[17,18] Sulfonium salts are the main products during oxidation of sulfides in dry aprotic media, while in the presence of water the formation of sulfoxides prevails. At higher potentials mainly sulfones are formed. The electrochemical oxidation of sulfides has been shown to be a preparative method for sulfoxides and sulfones,[19–21] even stereoselective oxidation of unsymmetrically substituted sulfides or thiane derivatives has been reported.[22–23] The electron transfer process, involving two electrons is irreversible for most of the sulfides and sulfoxides and passes via the sulfur radical cation as intermediate. Many aromatic and olefinic sulfides form radical cations with appreciable lifetimes when they are oxidized in nonaqueous systems.[4,8,24–26] Radical cations of simple organic sulfides are unstable because of proton loss from the α-carbon and further oxidation to yield sulfonium salts or sulfoxides, respectively, from water attack on $R_2S^{+\cdot}$. Sulfoxide radical cations $R_2SO^{\cdot+}$ are also short lived transients but could be positively identified in acid ($pH < 6$) aqueous solutions in a recent pulse radiolysis study.[27]

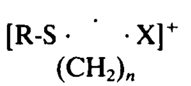
It is well known that neighbouring group participation facilitates sulfur oxidation.[28,29] Electron rich neighbouring groups aid in stabilization of the positive charge at the sulfur atom after formation of the radical cation. Such groups can be aromatic systems, amino groups or other sulfur atoms.[29–33] The oxidation potentials for 1,n-bis(alkylthio)alkanes with $n = 3,4$ are much lower than for other dithioethers or for simple sulfides.[3,12,32,34,35] It has been reported that the mesocyclic 1,5-dithiacyclooctane forms a long lived radical cation during its oxidation and even undergoes reversible oxidation.[34,36–38] Pulse radiolysis studies of 1,n-bis(alkylthio)alkanes also demonstrated that the most stable three-electron bonded radical cations (generated by intramolecular stabilization of the oxidized sulfur atom with the other sulfur in its ground state) are those of compounds with $n = 3,4$ (formation of the five- and six-membered cyclic radical cations).[35,39,40]

Recently we investigated the pulse radiolysis behavior of 1,n-halo(alkylthio)-alkanes **1–3**.[41,42]

$$R{-}S{-}(CH_2)n{-}X$$

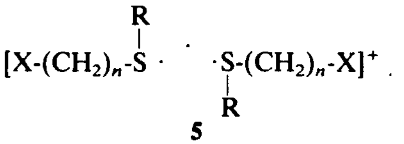
1 X = Cl, **2** X = Br, **3** X = I; *R* = alkyl

Intramolecular sulfur-iodine and sulfur-bromine three-electron bonded radical cations **4** were observed during the oxidation of compounds **2** and **3**, whereas oxidation of the chloro analogues **1** led only to the dimer sulfur–sulfur three-electron bonded radical cations **5**.



$$[R\text{-}S\cdot\ \overset{\cdot}{}\ \cdot X]^+ \quad \underset{(CH_2)_n}{}$$

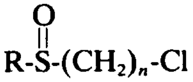
4



$$[X\text{-}(CH_2)_n\text{-}\overset{R}{\overset{|}{S}}\cdot\ \overset{\cdot}{}\ \cdot\underset{R}{\underset{|}{S}}\text{-}(CH_2)_n\text{-}X]^+$$

5

In order to compare the electrochemical behavior of 1,n-halo(alkylthio)alkanes **1–3** with their behavior in pulse radiolysis under oxidative conditions and to investigate the influence of the halogen atom and the number of methylene groups n between sulfur and iodine on the peak potentials, we studied the anodic oxidation of these compounds. The present paper is concerned with a systematic investigation of 1,n-halo(alkylthio)alkanes **1–3** and 1-chloro(alkylsulfinyl)alkanes **6**. Compounds **1–3** and **6** were synthesized according to the literature methods.[43–45] Newly prepared compounds are described in the experimental section.



$$R\text{-}\overset{O}{\overset{\|}{S}}\text{-}(CH_2)_n\text{-}Cl$$

6

RESULTS

Anodic Oxidation of 1,*n*-halo(alkylthio)alkanes **1–3** was studied by cyclic voltammetry in anhydrous acetonitrile. The 1-bromo- and 1-iodo-4-alkylthiobutanes could not be investigated due to the rapid cyclization to five membered sulfonium salts.[43,46] The oxidations of **1–3** are electrochemically irreversible at the scan rates employed of 0.05–5 V/s. The peak potentials have been determined under a standard set of conditions and are presented in Table I. Other than the peaks noted, no other oxidative processes were observed.

As can be seen from Table I, the peak potentials depend little on the halogen atom, to a limited extent on the number of methylene groups, and little on the alkyl groups R. The peak potentials of the halogen derivatives decrease in the order $Cl > Br > I$. This is demonstrated in Figure 1 showing the cyclic voltammograms of **1e**, **2b** and **3b** ($X\text{-}(CH_2)_3\text{-}S\text{-}CH_3$). The comparatively highest oxidation potentials are found for the 1,2-halo(alkylthio)ethanes **1a–1d**, and **2a** with the same halogen atom (i.e. $X = Cl$ or Br), while the compounds with $n > 2$ are oxidized at about the same, less positive potential. In the case of the iodine analogues **3**, relatively high oxidation potentials for compounds with $n = 2$ and $n = 5,6$ are observed whereas particularly low peak potentials are observed for the 1,3-iodo(alkylthio)propanes **3b–3d**. Addition of a small amount of bromide ions did not affect the oxidation potentials of e.g. 1-chloro-, 1-bromo-, or 1-iodo-3-alkylthiopropanes. For these compounds the oxidation is expected to be influenced by a strong neighbouring group effect. It has been established that the presence of trace amounts of bromide ions facilitates the oxidation at sulfur whenever neighboring group participation is in effect.[47]

In order to compare the oxidation potentials of **1–3** with those of simple sulfides ($R^1\text{-}S\text{-}R^2$) a number of the latter were electrochemically investigated under the same experimental conditions. The peak potentials for all investigated simple organic sulfides ($R^{1,2} = CH_3$, C_2H_5, C_3H_7, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$) are nearly the same and found at 1.95–2.00 V. Similar to compounds **1–3** (Table I) the nature of the alkyl groups $R^{1,2}$ does not affect the electrochemical ease of oxidation.

In order to compare the influence of the alkyl groups R and the number of methylene groups *n* on the peak potentials of the chlorinated sulfides **1** with those of the corresponding sulfoxides, we studied the anodic oxidation of 1,*n*-chloro(alkylsulfinyl)alkanes **6** under the same experimental conditions. The peak potentials obtained by cyclic voltammetry of compounds **6** in acetonitrile are listed in Table II. The 1,2-chloro(alkylsulfinyl)ethanes could not be investigated because they could not be prepared by the usual synthetic oxidation method due to the fast hydrolysis of the corresponding sulfides.[48–50] Similar to the results obtained by oxidation of 1,*n*-chloro(alkylthio)alkanes **1** with $n > 2$ all peak potentials of **6** are practically the same (2.16–2.20) regardless of the number of methylene groups (*n*) and the nature of the substituents R.

The oxidations of **1–3**, **6** are electrochemically irreversible at the applied scan rates between 0.02 and 0.5 V/s. In order to establish the irreversible nature of the anodic oxidation of compounds **1–3**, **6** the scan rate dependence of the anodic waves and the relation between the rotation rate of a rotating disk electrode and the current were investigated for a number of selected compounds **1–3**. The

TABLE I

Anodic oxidation of 1,*n*-halo(alkylthio)alkanes **1–3** by cyclic voltammetry. (Peak potentials (E_p) of first oxidation peak determined at a Pt electrode (1.47 cm^2), 0.2 V s^{-1} scan rate and measured in anhydrous acetonitrile (1 mM), 0.1 M TBAPF$_6$ versus Ag/AgCl in LiCl/sat. EtOH reference electrode; ferrocene (Fc) as internal standard)

Comp.	X	*n*	R	E_p	E_p vs. Fc
1a	Cl	2	CH_3	2.12	1.58
1b	Cl	2	C_2H_5	1.98	1.49
1c	Cl	2	C_3H_7	2.02	1.54
1d	Cl	2	*i*-C_3H_7	2.08	1.59
1e	Cl	3	CH_3	1.83	1.33
1f	Cl	3	C_2H_5	1.85	1.37
1g	Cl	3	C_3H_7	1.90	1.42
1h	Cl	3	*i*-C_3H_7	1.91	1.45
1i	Cl	3	*t*-C_4H_9	1.97	1.47
1j	Cl	4	CH_3	1.87	1.32
1k	Cl	4	C_2H_5	1.92	1.44
1l	Cl	4	*i*-C_3H_7	1.90	1.41
1m	Cl	4	*t*-C_4H_9	1.88	1.39
1n	Cl	5	CH_3	1.78	1.29
1o	Cl	5	C_2H_5	1.99	1.45
1p	Cl	5	*i*-C_3H_7	1.85	1.36
1q	Cl	5	*t*-C_4H_9	1.91	1.43
1r	Cl	6	CH_3	1.84	1.34
1s	Cl	6	C_2H_5	1.80	1.32
1t	Cl	6	C_3H_7	1.85	1.37
1u	Cl	6	*i*-C_3H_7	1.85	1.37
1v	Cl	6	*t*-C_4H_7	1.87	1.38
2a	Br	2	CH_3	1.98	1.49
2b	Br	3	CH_3	1.75	1.28
2c	Br	3	CH_2H_5	1.80	1.33
2d	Br	3	C_3H_7	1.88	1.33
2e	Br	3	*i*-C_3H_7	1.88	1.33
2f	Br	3	*t*-C_4H_9	1.86	1.31
2g	Br	5	C_2H_5	1.81	1.26
2h	Br	5	C_3H_7	1.85	1.36
2i	Br	5	*i*-C_3H_7	1.85	1.30
2j	Br	6	C_2H_5	1.80	1.32
2k	Br	7	C_2H_5	1.80	1.32
2l	Br	8	C_2H_5	1.82	1.32
2m	Br	10	C_2H_5	1.81	1.33
3a	I	2	CH_3	1.96	1.42
3b	I	3	CH_3	1.75	1.23
3c	I	3	C_2H_5	1.78	1.24
3d	I	3	*t*-C_4H_9	1.74	1.22
3e	I	5	C_2H_5	1.90	1.36
3f	I	6	CH_3	1.94	1.40
3g	I	6	C_2H_5	1.96	1.41

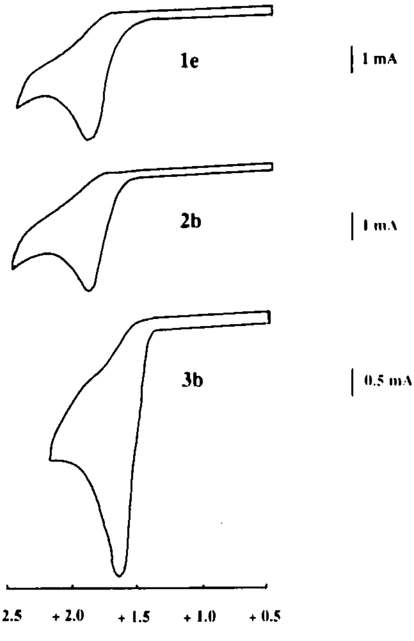


FIGURE 1 Cyclic voltamogramms of the compunds **1e, 2b, 3b** in acetonitrile (scan rate: 200 mV/s).

slopes in the plots of E_p vs lg v (scan rate) are found to be in the order of 55–65 mV per decade which is indicative of irreversible electron transfer.[51–54] Furthermore, the linear dependence of the current on the reciprocal of the square root of the rotation rate is also typical for a diffusion controlled process.[51] The anodic oxidations of compounds **1–3** are found to be diffusion controlled. The coulometric *n*-values obtained by electrolyses of a selected number of 1,*n*-halo(alkylthio)alkanes **1–3** and the diffusion coefficients calculated according to the literature [50,54] are listed in Table III. The area of the electrode was calibrated with ferrocene (taking $D = 2.4 \times 10^{-5}\ cm^2\ s^{-1}$).[54]

TABLE II

Anodic oxidation of 1,*n*-Chloro(alkylsulfinyl)-alkanes **6** by cyclic voltammetry (peak potentials (E_p) determined at a Pt electrode (1.47 cm^2), 0.2 V s^{-1} scan rate, and measured in anhydrous acetonitrile (1 mM), 0.1 M $TBAPF_6$ versus Ag/AgCl in LiCl/sat. EtOH reference electrode; ferrocene (Fc) as internal standard

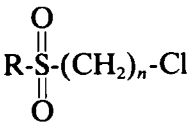
Comp.	*n*	R	E_p	E_p vs. Fc
6a	3	CH_3	2.18	1.65
6b	3	C_2H_5	2.18	1.63
6c	3	*i*-C_3H_7	2.19	1.66
6d	3	*i*-C_4H_9	2.16	1.62
6e	4	*i*-C_3H_7	2.20	1.65
6f	5	CH_3	2.16	1.62
6h	6	*i*-C_3H_7	2.20	1.66

TABLE III

Diffusion coefficients for some 1-halo-3-alkylthiopropanes determined at a Pt-rotating disc electrode (0.0314 cm^2) in acetonitrile solutions (2 mMol) with 0.1 Mol $TBAPF_6$ as supporting electrolyte versus Ag/AgCl in LiCl/sat. EtOH reference electrode

Compound	D ($cm^2 s^{-1}$)
1e	1.07×10^{-5}
1f	0.84×10^{-5}
1g	0.61×10^{-5}
2b	1.02×10^{-5}
3b	1.42×10^{-5}

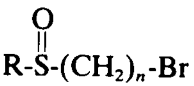
Electrolyses of **1–3** were carried out in aqueous (0.2%) acetronitrile solutions at constant voltages just beyond the first oxidation potentials (1.9 V for **1**, 1.8 V for **2** and **3**) and at the second oxidation potentials (2.2 V). Compounds **1–3** with $n = 2$ were not electrolyzed due to their fast hydrolysis in aqueous systems.[48–50] High yields (60–80% after separation) of the corresponding sulfoxides **6** and sulfones **7** could be obtained by electrolyses of the 1,*n*-chloro(alkylthio)alkanes **1**.



$$R\text{-}\overset{O}{\underset{O}{S}}\text{-}(CH_2)_n\text{-}Cl$$

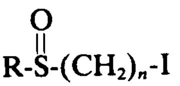
7

Electrolyses of compounds **2** and **3** at their first peak potential led to a mixture of the corresponding sulfoxides **8** and **9**, respectively and 1,*n*-hydroxy(alkylsulfinyl)alkanes **10** due to the relatively rapid hydrolysis of **2** and **3**.[45] The 1,*n*-chloro(alkylsulfinyl)alkanes **6** and 1,*n*-chloro(alkylsulfonyl)alkanes **7** were determined by GC by comparison with the corresponding synthesized compounds (which were prepared according to the literature[44]) and by NMR and MS after separation by TLC. Sulfoxides **8–10** were characterized by NMR and GC/MS from the crude samples after electrolyses; their ratios were determined by NMR- and GC-measurements and were found to be 8:2 for compounds **8** and **10** and 3:7 for sulfoxides **9** and **10**.



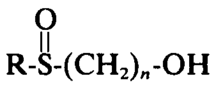
$$R\text{-}\overset{O}{S}\text{-}(CH_2)_n\text{-}Br$$

8



$$R\text{-}\overset{O}{S}\text{-}(CH_2)_n\text{-}I$$

9



$$R\text{-}\overset{O}{S}\text{-}(CH_2)_n\text{-}OH$$

10

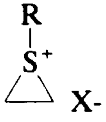
Electrolyses of the sulfoxides **6** at an applied potential of 2.2 V gave the same results as obtained for electrolyses of the sulfides **1** at the second peak potential. The corresponding 1,*n*-chloro(alkylsulfonyl)alkanes **7** were obtained in good yields of about 80% after separation.

DISCUSSION

The present results demonstrate that the anodic oxidation of 1,*n*-halo(alkylthio)alkanes **1–3** and 1,*n*-chloro(alkylsulfinyl)alkanes **6** is a two-electron irreversible process similar to the oxidation of simple organic sulfides.[12]

The ease of sulfur oxidation (sulfide or sulfoxide) is mostly not affected by the alkyl substituents R. One would expect that the oxidation potential correlates with the ionization potential. For simple dialkyl sulfides the latter varies as a function of the substituent R[−3] but the electrochemical oxidation potential does not change. The reason for this lack of correlation is still unknown. It may be probably explained by the fact that no R-S-cleavage occurs.

In contrast to the results obtained by pulse radiolysis under oxidative conditions[41,42] there is no demonstrable influence of the halogen atom on the oxidation of the sulfur atom. The oxidation potentials decrease only slightly in the order Cl > Br > I which could be related to the electronegativity of the halogen atoms. If there would be any neighbouring group participation e.g. of the chlorine atom on the oxidation of the sulfide in compounds **1** and **6** or e.g. or the bromine or iodine atom in compounds **2** or **3**, a dependence on the chain length between sulfur and halogen should be observed. The only remarkable difference was obtained in all compounds with $n = 2$ and compounds **3** with $n = 5,6$ for which the oxidation occurs at higher potentials. This is probably due to an interaction between the sulfur and halogen atom. The oxidation potentials for compounds **1a–d**, **2a** and **3a** ($n = 2$) may be high because of inductive effects (which drop off rapidly as n increases) and field effects—which could be through space interaction between the sulfur atom and the positive end of the C-X dipole and may be seen as a precursor of the corresponding thiiranium ions **11**. The latter are easily formed by hydrolysis via the strong anchimeric assistance of the sulfur atom.[48–50] The water content in the freshly distilled (over P_2O_5) acetonitrile is probably still high enough to afford hydrolysis. The relatively high oxidation potentials of the 1-iodo-5-alkylthiopentanes and 1-iodo-6-alkylthiohexanes can be explained by the fact that these compounds cyclize relatively rapidly in acetonitrile[46] to the six- and seven-membered sulfonium compounds and the oxidation potentials of these compounds were determined in presence of such sulfonium salts.



11

The electrochemical oxidation of 1,*n*-chloro(alkylthio)alkanes **1** is a good method for preparation of the corresponding sulfoxides **6** (selectively and without overoxidation) and sulfones **7** with $n > 2$ in good yields.

ACKNOWLEDGEMENT

E.A. thanks the Deutsche Forschungsgemeinschaft for financial support, Mr. J. Bitter (Max Planck Institut Mülheim, FRG) is gratefully acknowledged for recording the 400 MHz-NMR-spectra. The support provided by NATO (travel grant R685/0644) is gratefully acknowledged.

EXPERIMENTAL

General Melting points were determined with a *Mettler FP5* melting point apparatus and are uncorrected.

^{1}H- and ^{13}C-NMR spectra were obtained on a *Bruker WM 400* (400 MHz)$^{a)}$ and a Varian EM 360 (90 MHz)$^{b)}$ in CDCl$_3$-solutions with tetramethylsilane as internal reference; chemical shifts are given in δ.

Mass spectrometry was carried out with a *Finnigan MAT 44* (70 eV) mass spectrometer.

GC analyses were performed on a *Carlo Erba* (*Vega*) gas chromatograph on a 30 m OV 1701 (*Macherey–Nagel*) capillary column using He as carrier gas; a temperature program (80°C–220°C with 10°C/min) and a FID detector.

Separations by TLC were performed on silica (*Merck*) with ethyl acetate as eluent.

Compounds **1a–1d** and **5a–5i** were commercially available (Fairfield Co; Aldrich) and redistilled before use. All other 1,*n*-halo(alkylthio)alkanes **1–3**,[43,45] 1,*n*-chloro(alkylsulfinyl)alkanes **6**[44] and 1,*n*-chloro(alkylsulfonyl)alkanes **7**[44] were prepared according to the literature and redistilled or recrystallized before use. The analytical data of the newly synthesized compounds **6c–6h** and **7a**, **7c**, **7e–7h** are given in the following:

1-chloro-3-i-propylsulfinylpropane (**6c**) (oil): ^{1}H-NMR$^{a)}$: 1.26(d; 6H), 2.25(m; 2H), 2.65(m; 2H), 3.04(m; 1H), 3.65(t; 2H) ^{13}C-NMR$^{a)}$: 14.7, 25.9, 43.6, 45.6, 50.6. MS, *m/z* (relative intensity): 168 (4%; M+), 128 (26%), 126 (69%), 92 (9%), 90 (100%), 73 (26%), 63(53).

1-chloro-3-t-butylsulfinylpropane (**6d**) (oil): ^{1}H-NMR$^{a)}$: 1.13(s; 9H), 2.18(m; 2H), 2.66(m; 2H), 3.59(t; 2H). ^{13}C-NMR$^{a)}$: 22.5, 26.5, 42.3, 43.4, 52.8. MS, *m/z*(relative intensity): 182(2), 126(5), 110(5), 90(12), 69(16), 57(100).

1-chloro-4-i-propylsulfinylbutane (**6e**) (oil): ^{1}H-NMR$^{b)}$: 1.3(d; 6H), 2.1(m; 4H), 2.7(m; 2H), 3.0(m; 1H), 2.7(t; 2H). MS. *m/z*(relative intensiy): 182(−), 140(9), 104(10), 91(12), 63(25), 55(100).

1-chloro-5-methylsulfinylpentane (**6f**) (oil): ^{1}H-NMR$^{b)}$: 1.8–2.2(m; 6H), 2.5(s; 3H), 2.7(m; 2H), 3.7(t; 2H). MS, *m/z*(relative intensity): 168(1), 151(5), 78(9), 69(100), 64(61), 63(23), 55(11).

1-chloro-5-i-propylsulfinylpentane (**6g**) (oil): ^{1}H-NMR$^{a)}$: 1.20(d; 6H), 1.58(m; 2H), 1.78(m; 4H), 2.72(m; 2H), 3.02(m; 1H), 3.52(t; 2H). MS, *m/z*(relative intensity): 196(2), 154(10), 137(12), 69(100), 63(38), 55(11).

1-chloro-6-i-propylsulfinylhexane (**6h**) (oil): ^{1}H-NMR$^{b)}$: 1.3(d; 6H), 1.4–1.7(m; 8H), 2.6(m; 2H), 2.9(m; 1H), 3.7(t;2H). MS, *m/z*(relative intensity): 210(−), 193(3), 92(34), 89(14), 83(20), 69(38), 63(16), 61(17), 55(100).

1-chloro-3-methylsulfonylpropane (**7a**); (oil): ^{1}H(NMR$^{b)}$: 2.2(m; 2H), 2.9(s; 3H), 3.2(t; 2H), 3.7(t; 2H). MS, m/e(relative intensity): 156 (4%, M$^+$), 141 (9%), 94 (100%), 81 (67%), 80 (59%), 79 (36%), 77 (35%), 76 (13%), 65 (22%), 63 (19%), 49 (41%).

1-chloro-3-i-propylsulfonylpropane (**7c**) mp: 38.3°C ^{1}H-NMR$^{b)}$: 1.6(d; 6H), 2.3(m; 2H), 3.1(t; 2H), 3.2(m; 1H), 3.7(t; 2H). MS, *m/z*(relative intensity): 184 (1%, M$^+$), 145 (10%), 144(17%), 143 (34%), 142 (50%), 106 (15%), 79 (32%), 77 (100%), 69 (11%), 66 (18%), 63 (16%), 49 (9%).

1-chloro-4-i-propylsulfonylbutane (**7e**) (oil): ^{1}H-NMR$^{b)}$: 1.6(d; 6H), 2.1(m; 4H), 3.1(t; 2H), 3.2(m; 1H), 3.7(t; 2H). MS, *m/z*(relative intensity): 198 (<1%, M$^+$), 121 (4%), 93 (29%), 91 (86%), 63 (7%), 56 (13%), 55 (100%).

1-chloro-5-methylsulfonylpentane (**7f**) (oil): ^{1}H-NMR$^{b)}$: 1.8–2.0(m; 6H), 2.9(s; 3H), 3.1(t; 2H), 3.7(t; 2H). MS, *m/z*(relative intensity): 184(<1%, M$^+$), 105 (6%), 94 (12%), 81 (26%), 69 (100%), 68 (34%), 63 (16%), 55 (17%).

1-chloro-6-i-propylsulfonylhexane (**7g**) (oil): ^{1}H-NMR$^{b)}$: 1.6(d; 6H), 1.8–2.1(m; 8H), 3.0(t; 2H), 3.2(m; 1H), 3.7(t; 2H). MS, *m/z*(relative intensity): 226 (<1%, M$^+$), 169 (4%), 119 (9%), 83 (100%), 69 (8%), 55 (98%).

Cyclic voltammetry Electrochemical experiments were performed with a *Princeton Applied Research* (*PAR*) *Model 362*. A standard three-electrode system was used comprising a 1.47 cm^2 Pt flag working-electrode, a Pt auxiliary electrode and an Ag/AgCl (saturated LiCl in EtOH) reference electrode. The data were collected on a *Kipp & Zonen BD 90 X-Y* recorder. Voltammograms were measured in a solution of 0.1 M tetrabutylammoniumhexafluorophosphate (TBAPF$_6$ in acetonitrile freshly over P_2O_5 distilled and 1 mM of **1–3**, **6**. The performance of the reference electrode was monitored by measuring the Cr (I + /0) couple of bis(diphenyl) chromium(I) tetrafluoroborate(BCr) (−0.59 V vs. Ag/AgCl) or the Fc(I + /0) couple of ferrocene (+0.54 V vs. Ag/AgCl); $\Delta E = E^f_p(\text{Fc}) - E^f_p(\text{BCr}) = +1.13$ ($E^f_p = [E_p$ (anod.) + E_p (cath.)]/2).[51,57]

The experiments with a rotating disc electrode were carried out under the same conditions using a *Tacussel Electronique* system with a Pt-electrode (0.0314 cm^2).

Controlled potential electrolyses of 1-chloro(alkylthio)alkanes **1** (a) Samples of 0.3 mmol compounds **1**, 192 mg(1 mmol) 2,6-di-*t*-butylpyridine and 3.87 g (0.1 mol) TBAPF$_6$ were dissolved in 100 ml freshly distilled acetonitrile, adding 0.2 ml H_2O. These solutions were electrolyzed at a constant potential of 1.9 V versus Ag/AgCl in LiCl saturated ethanol reference electrode. When the current decayed to 0.1% of its initial value (≈10–12 h), 65 coulombs had passed, corresponding to an "*n*"-value of 2.0–2.2. The crude solutions were analyzed by GC and showed the corresponding sulfoxides **6** as products. About 2/3 of the acetronitrile was evaporated and 20 ml of water was added. After extraction with dichloromethane (4 × 20 ml), the organic layers were dried over anhydrous $MgSO_4$ and evaporated. The resulting residues were purified by preparative TLC. 1,*n*-Chloro(alkylsulfinyl)alkanes **6** were obtained as colorless oils in 60–70% yields.

(b) Solutions as described above were electrolyzed at a constant potential of 2.2V Ag/AgCl for about 10–12 h. After the same workup procedure the corresponding 1,*n*-chloro(alkylsulfonyl)alkanes **7** were obtained as oil or white crystals in yields of about 70–80%.

Controlled potential electrolysis of 1-bromo-3-methylthiopropane (**2b**) A sample of 16.8 mg (0.1 mmol) 1-bromo-3-methylthiopropane (**2b**), 64 mg (0.3 mmol) TBAPF$_6$ 2,6-di-t-butylpyridine and 1.94 g (0.5 mol) TBAPF$_6$ was dissolved in 50 ml freshly distilled acetonitrile, 0.05 ml H_2O added, followed by electrolysis at a constant potential of 1.8 V versus Ag/AgCl in LiCl saturated ethanol reference electrode for 5 h. After using the same workup procedure as described above, an 8:2 mixture of 1-bromo-3-methylsulfinylpropane **8** and 1-hydroxy-3-methylsulfinylpropane **10** was obtained.

1-bromo-3-methylsulfinylpropane (**8**): ^{1}H-NMR$^{a)}$: 2.37(m; 2H), 2.62(s; 3H), 2.85(m; 2H), 3.58(m; 2H). ^{13}C-NMR$^{a)}$: 25, 7, 31.8, 38.5, 52.5.

1-hydroxy-3-methylsulfinylpropane (**10**): ^{1}H-NMR$^{a)}$: 2.34(m; 2H), 2.62(s; 3H), 2.93(m; 2H), 3.78(m; 2H).

Controlled potential electrolysis of 1-iodo-3-methylthiopropane (**3b**) A sample of 21.6 mg (0.1 mmol) 1-iodo-3-methylthiopropane (**3b**), 64 mg (0.3 mmol) 2,6-di-*t*-butylpyridine and 1.94 g (50 mmol) TBAF$_6$ was dissolved in 50 ml freshly distilled acetonitrile, adding 0.05 ml H_2O, and then electrolyzed at a constant potential of 1.8 V vs. Ag/AgCl for about 5 h. After workup procedure as described above a mixture of 1-iodo-3-methylsulfinylpropane (**9**) and 1-hydroxy-3-methylsulfinylpropane (**10**) (3:7) was obtained.

1-iodo-3-methylsulfinylpropane (**8**): ^{1}H-NMR$^{a)}$: 2.36(m; 2H), 2.62(s; 3H), 2.83(m; 2H), 3.34(t, 2H).

REFERENCES

1. V. D. Parker, in "*Org. Electrochem.*", (Ed. M. M. Baizer), 551 (1973).
2. J. A. Chamber in "*Encyclopedia of Electrochemistry of the Elements*" (Organic Section), (Ed. A. J. Bard and H. Lund), Dekker, New York, Vol 12, 329 (1978).
3. B. R. Coleman, R. S. Glass, W. N. Setzer, U. D. G. Prabhu and G. S. Wilson, *Adv. Chem. Ser.* **201,** 417 (1982).
4. S. Torii and K. Uneyama, *Tetrahedron Lett.*, 4513 (1972).
5. K. Uneyama and S. Torii, *J. Org. Chem.* **37,** 367 (1972).
6. D. S. Houghton and A. A. Humffray, *Electrochim. Acta* **17,** 1421 (1972).
7. H. E. Imberger and A. A. Humffray, *Electrochim. Acta* **18,** 373 (1973).
8. S. Torii, Y. Matsuyama, K. Kawasaki and K. Uneyama, *Bull. Chem. Soc. Jpn.* **46,** 2912 (1973).
9. K. Uneyama and S. Torii, *Tetrahedron Lett.*, 328 (1971).
10. F. Magno and G. Bontempelli, *J. Electroanal. Chem.* **36,** 389 (1972).
11. G. Bontempelli, F. Magno, A. Mazzochin and S. Zecchin, *J. Electroanal. Chem.* **43,** 377 (1973).

12. P. T. Cottrell and C. K. Mann, *J. Electrochem. Soc.* **116,** 1499 (1969).
13. M. M. Nicholson, *J. Am. Chem. Soc.* **76,** 2539 (1954).
14. I. Radoi and G. Mara, *Bull. Stiint-Teh, Inst. Politeh "Traian Vuia" Timisoara. Ser. Chim.* **29,** 59 (1984); CA 103(4): 29100 p.
15. G. Mara, M. Nemes and I. Radoi, *Rev. Chim.* **38,** 408 (1987).
16. J. Yoshida, H. Sofuhu and N. Kawabata, *Bull. Chem. Soc. Jpn.* **56,** 1243 (1983).
17. G. Bontempelli, F. Magno, G. A. Mazzochin and R. Seeber, *J. Electroanal. Chem.* **55,** 109 (1974).
18. D. Cibris and D. Pouli, *J. Electroanal. Chem.* **69,** 423 (1976).
19. F. Fichter and P. Sjöstedt, *Chem. Ber.* **44,** 3422 (1911).
20. C. Thibault and P. Mathieu, Ger. Offen. DE 1922721, 3. May 1979. CA 72(10): 5289 r.
21. C. Thibault and P. Mathieu, US 3,808,112, 30. Apr. 1974. CA 81(2): 9180p.
22. M. Kimura, N. Kuriki, M. Inaishi and Y. Sawaki, *Tetrahedron Lett.* 4665 (1984).
23. T. Komori and T. Nonaka, *J. Am. Chem. Soc.* **87,** 2647 (1984).
24. A. Zweig, A. H. Maurer and B. G. Roberts, *J. Org. Chem.* **32,** 1322 (1967).
25. A. Zweig and R. E. Lehnsen, *J. Am. Chem. Soc.* **87,** 2647 (1965).
26. J. R. Gilmore and J. M. Mellor, *Tetrahedron Lett.* 3977 (1971).
27. K. Kishore and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2,* in press.
28. O. Hammerich and V. D. Parker, *Sulfur Reports* **1,** 317 (1981).
29. R. S. Glass, M. Hojjatie, A. Petsom, G. S. Wilson, M. Göbl, S. Mahling, and K.-D. Asmus, *Phosphorus Sulfur* **23,** 143 (1985).
30. J. T. Doi, P. K. Bharadwaj and W. K. Musker, *J. Org. Chem.* **52,** 2581 (1987).
31. W. K. Musker, *Acc. Chem. Res.* **13,** 200 (1980).
32. W. K. Musker, T. L. Wolford and P. B. Roush, *J. Am. Chem. Soc.* **100,** 6416 (1978).
33. K.-D. Asmus, *Acc. Chem. Res.* **12,** 436 (1979).
34. G. S. Wilson, D. D. Swanson, J. T. Klug, R. S. Glass, M. D. Ryan and W. K. Musker, *J. Am. Chem. Soc.* **101,** 1040 (1979).
35. A. Aced, E. Anklam, K.-D. Asmus and K. Kishore, unpublished results.
36. T. G. Brown, A. S. Hirschon and W. K. Musker, *J. Phys. Chem.* **85,** 3767 (1981).
37. W. K. Musker and T. L. Wolford, *J. Am. Chem. Soc.* **98,** 3055 (1976).
38. M. D. Ryan, D. D. Swanson, R. S. Glass and G. S. Wilson, *J. Phys. Chem.* **85,** 1069 (1981).
39. K.-D. Asmus, D. Bahnemann, C.-H. Fischer and D. Veltwisch, *J. Am. Chem. Soc.* **101,** 5322 (1979).
40. E. Anklam, K.-D. Asmus and H. Mohan, *J. Phys. Org. Chem.* in press.
41. E. Anklam, H. Mohan and K.-D. Asmus, *J. Chem. Soc., Chem. Commun.* 629 (1987).
42. E. Anklam, H. Mohan and K.-D. Asmus, *J. Chem. Soc., Perkin Trans. 2,* 1297 (1988).
43. E. Anklam, *Synthesis* 841 (1987).
44. E. Anklam, *Synth. Commun.* **19,** 1583 (1989).
45. D. C. Palmer and E. C. Taylor, *J. Org. Chem.* **51,** 846 (1986).
46. E. Anklam, G. Aced and Y. Mao, *Phosphorus Sulfur* **40,** 99 (1988).
47. R. S. Glass, A. Petsom, M. Hojjatie, B. R. Coleman, J. R. Duchek, J. Klug and G. S. Wilson, *J. Am. Chem. Soc.* **110,** 4772 (1988).
48. Y.-C. Yang, J. R. Ward and T. Luteran, *J. Org. Chem.* **51,** 2756 (1986).
49. Y.-C. Yang, L. L. Szafraniec, W. T. Beadry and J. R. Ward, *J. Org. Chem.* **52,** 1637 (1987).
50. E. Anklam, Y. Mao and A. Aced, unpublished results.
51. R. J. Klingler and J. K. Kochi, *J. Am. Chem. Soc.* **102,** 4790 (1980).
52. W. H. Reinmuth, *Anal. Chem.* **32,** 1861 (1960).
53. R. S. Nicholson, I. Shain, *Anal. Chem.* **36,** 706 (1964).
54. D. Pletcher, *Chem. Soc. Rev.* **4,** 471 (1975).
55. R. N. Adams, in "*Electrochemistry at Solid Electrodes*", Marcel Dekker: New York (1969).
56. G. Gritzner and J. Kuta, *Pure & Appl. Chem.* **54** (1982) (1527).
57. R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem.* **19** (1980) 2854.