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ELECTROCHEMISTRY OF ORGANIC SULFUR COMPOUNDS II.[1)]
ANODIC SULFOXIDATION OF PHENYL SULFIDES

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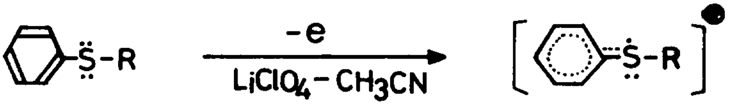
Anodic substitution of aromatic compounds is a subject of detailed investigations in recent years.[2)] Many substituted aromatic compounds indicate that substitutions on aromatic nucleous and/or benzylic position are typical reaction pathways for the oxidation process.[2)] But very few investigations on aromatic compounds having second-row elements such as sulfur[3)] and phosphorus[4)] as substituents have been reported. Phenyl sulfides are expected to suffer electrochemical oxidation to provide thiophenyl radical cations 1a-3a which would undergo somewhat different type of reactions as compared with alkylbenzenes since 1a-3a have no α C-H bond available for the substitution on benzylic position but a divalent sulfur group which could readily leave as a thiophenoxy radical. We would like to describe here a new type of aromatic oxidation process for phenyl sulfides 1-3.



1 ~ 3 1a ~ 3a

R ; CH_3, CH_2Ph, $C(Ph)_3$

Phenyl sulfides 1-3 (5×10^{-3} mols) were subjected to electrolysis in 20 ml of distilled acetonitrile containing 0.1 g of water and 1.0 g of lithium perchlorate at 30-40°C using 3 cm^2 Pt foils as electrodes without separation of electrolysis compartments. 1.5 Equivalent amounts of constant current (300 mA) was applied while terminal voltage ranges were 6-10 volt. The reaction mixtures were treated as usually and products separated by column

Table I. Products and Their Yields of Anodic Oxidation of Sulfides.[a)]

	Product / R	$\mathrm{Ph\text{-}\overset{O}{\overset{\|}{S}}\text{-}R}$	Ph-S-S-Ph [c)]	R-OH	$\mathrm{R\text{-}NHCOCH_3}$	Ph-S-R [b)]
1	$\mathrm{CH_3}$	74	0	0	0	12
2	$\mathrm{CH_2Ph}$	25	12	3	11	36
3	$\mathrm{C\begin{array}{l}\diagup Ph\\ -Ph\\ \diagdown Ph\end{array}}$	0	48	52	0	28

a) Yield based on Ph-S group. (%) (b) Recovered starting sulfide.
c) 2 x (yield of disulfide).

Table II. Bromine Oxidation of Phenyl sulfides 1-3 in 70% $\mathrm{AcOH\text{-}H_2O}$ [a)]

	Product / R	$\mathrm{Ph\text{-}\overset{O}{\overset{\|}{S}}\text{-}R}$	Ph-S-S-Ph	R-OH
1	$\mathrm{CH_3}$	85	0	0
2	$\mathrm{CH_2Ph}$	83	6	5
3	$\mathrm{C\begin{array}{l}\diagup Ph\\ -Ph\\ \diagdown Ph\end{array}}$	0	40	81

a) 0.9 Equivalent of bromine-pyridine complex was used.

chromatography and identified were listed in Table I.

Thioanisole 1 gave phenyl methyl sulfoxide as an only product. Meanwhile phenyl triphenylmethyl sulfide 3 afforded no corresponding sulfoxide but diphenyl disulfide and triphenylcarbinol nearly in same yields. Phenyl benzyl sulfide 2 produced both sulfoxide and S-R bond scission products. Since the starting sulfides were completely recovered on keeping them in the electrolytic condition without passing current, formation of the sulfoxides suggests that sulfides 1 and 2 are oxidized anordically to provide cation radicals la and 2a which then suffer ready hydrolysis. (Path 1 in Fig. 1) The mechanism of the anodic sulfoxidation resembles that of bromine oxidation of sulfides in which bromine complex 4 is hydrolyzed to afford the corresponding

Fig. 1

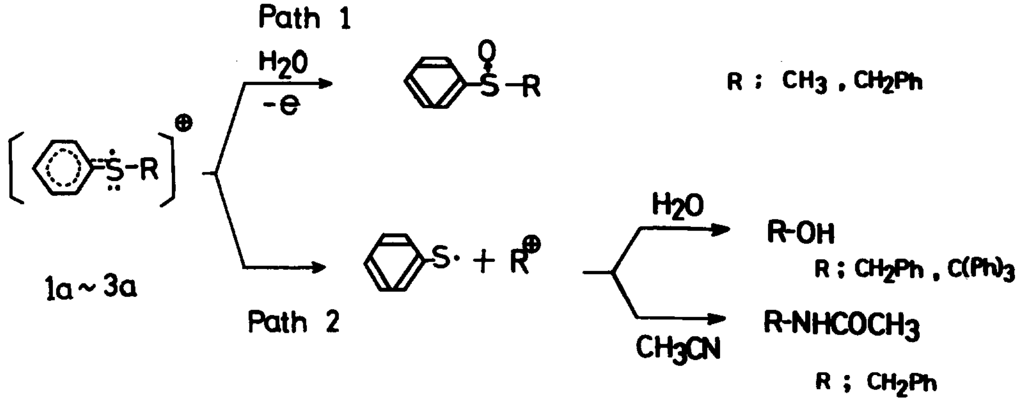
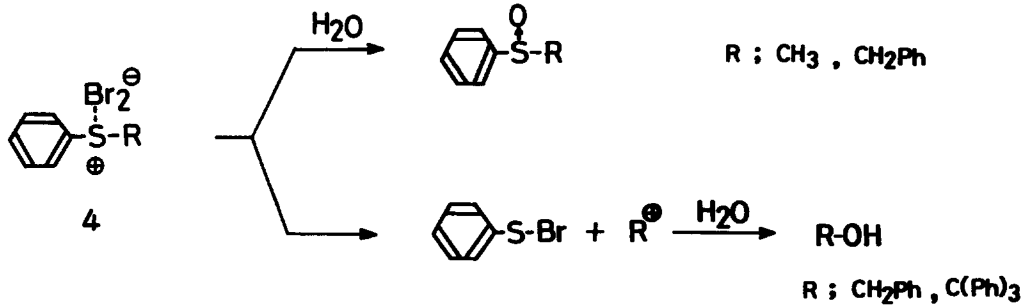


Fig. 2



sulfoxides5) (Fig. 2). In fact, reactions of sulfides 1-3 with bromine-pyridine complex in 70% aq. acetic acid afforded quite similar products for each sulfides (Table II).

Meanwhile, although sulfoxide was not obtained, formation of the cation radical 3a is assumed since oxidation potentials of thiophenyl group in 1-3 would not be much different. Probably, 3a would readily undergo S-R bond scission to afford thiophenoxy radical and corresponding cation R^+ intermediate due to the stability of the cation and the bulkyness of the substituent which would retard neucleophilic attack by water on the sulfur atom in 3a. (Fig. 1 Path 2) The predominant formation of disulfide from 3 and the formations of solvolytic products, i.e, triphenylcarbinol from 3, benzyl alcohol and benzyl acetoamide from 2, support the above hypothesis. In this sense, the fact that 1 afforded sulfoxide alone is explained by the two factors, i.e, the instability of methyl cation as a leaving group and the ready hydrolysis of 1a by water. The situation with 2 falls in the middle since benzyl group is a better leaving group than methyl, but worse than triphenylmethyl group. Thus, 2 afforded the sulfoxide and the disulfide in a 2:1 ratio.

The fact that no detectable amounts of ring substituted sulfides were obtained suggests that cation center in the radical cations 1a-3a is predominantly localized on sulfur atom. Such radical cation species were also suggested recently in the oxygen exchange reactions of sulfoxides.6)

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