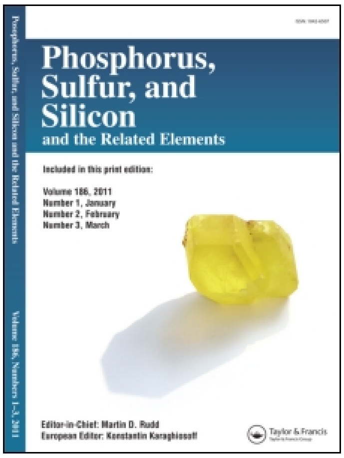

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ELECTROCHEMICAL ISOMERIZATION OF SULFINE

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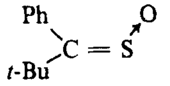
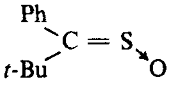
Electrochemical isomerization of 1-phenyl-2,2-dimethylpropane-1-thione *S*-oxide (phenyl-*t*-butylsulfine, *E* and *Z* form, **1a** and **1b**) was studied. Anodic isomerization of **1a** gave the two isomers of the sulfine only, but cathodic reductive isomerization of **1a** gave pivalophenone and 1-cyano-2-phenyl-3,3-dimethyl-1-butene in addition to the *E* and *Z* isomers. This is the first example of an electrochemical reaction of a sulfine.

INTRODUCTION

Sulfines represent a group of heterocumulenic compounds that contain the $>$C=S=O function. Since the CSO group is rigid and non-linear, geometrical isomerism is possible in the case of **1a** and **1b**. These isomers can be separated by column chromatography or vapor-phase chromatography (VPC). In this paper we report the electrochemical isomerization between **1a** and **1b**.[1]


1a


1b

RESULTS AND DISCUSSION

Sulfine **1a** or **1b** is stable at room temperature and does not isomerize. But these sulfines can be isomerized by cathodic reduction or by anodic oxidation. The cathodic isomerization of **1a** is shown in Figure 1. Appropriate amounts of **1a** were dissolved in acetonitrile and subjected to cathodic reduction (−1.6 vs. SCE) in the presence of tetrabutylammonium bromide as a supporting electrolyte. After 1 h, products were the other isomer, **1b**, and pivalophenone ([**1a**] = 56%, [**1b**] = 30%, pivalophenone = 15%). After 4 h, the amount of sulfine decreased ([**1a**] = 2%, [**1b**] = 4%) and main products were pivalophenone (42%) and 1-cyano-2-phenyl-3,3-dimethyl-1-butene (5%). The latter compound was the product from a reaction of pivalophenone with cyanomethyl anion ($^{-}CH_2CN$).

The anodic isomerization of **1a** is shown in Figure 2. This reaction is different from the cathodic one: only isomerization took place and no decomposition into pivalophenone was observed. After 1 h, **1b** was obtained in 20% yield and 80% of the starting material remained. The differences between cathodic and anodic isomerizations are readily explained by the involvement of radical-ion species in these reactions (Scheme 1).

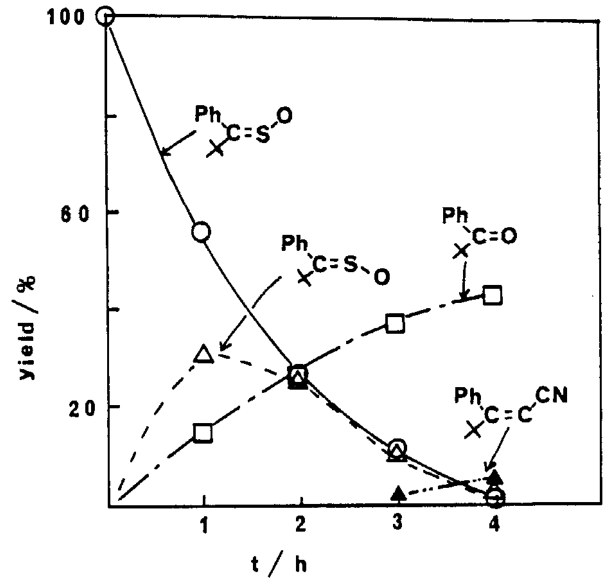


FIGURE 1 Cathodic isomerization of **1a**. (○): **1a**, (△): **1b**, (□): pivalophenone, (▲): 1-cyano-2-phenyl-3,3-dimethyl-1-butene.

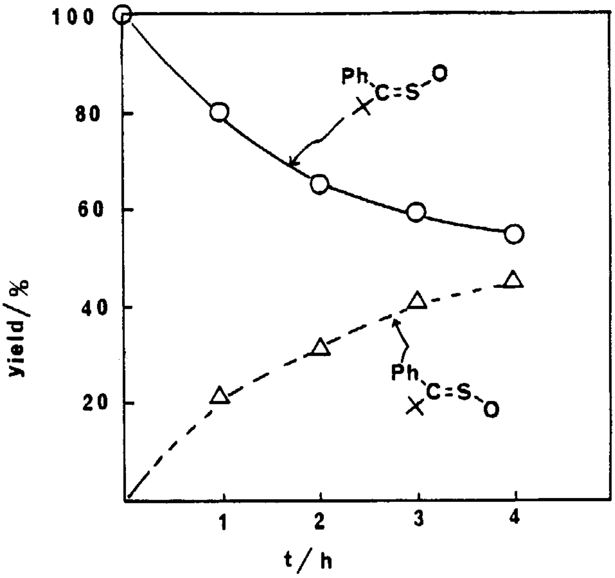
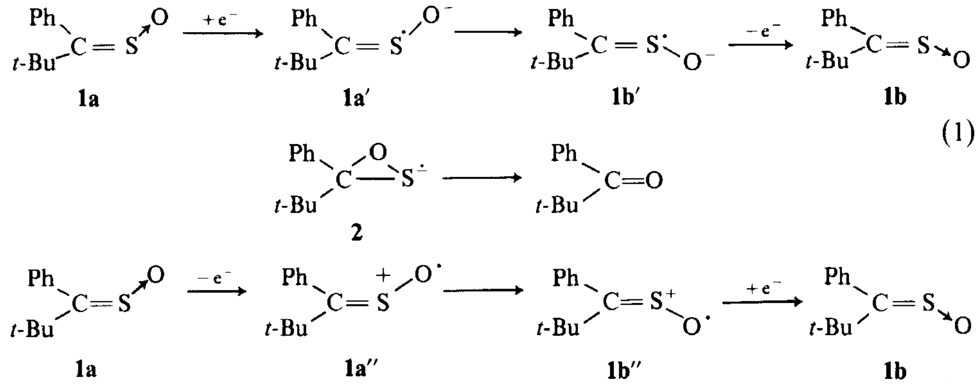


FIGURE 2 Anodic isomerization of **1b**. (○): **1a**, (△): **1b**.



SCHEME 1 Cathodic (1) and anodic (2) isomerization of sulfine.

As sulfine **1a** has S^+—O^- character, the anion radical of **1a** may be **1a′** (radical centered on sulfur and anion centered on oxygen). Then **1a′** can isomerize to **1b′** or the anion on oxygen attacks the carbon in the carbon–sulfur double bond to give **2** which decomposes into pivalophenone. On the contrary, the cation radical **1a″** has radical character on oxygen and it does not attack the carbon center in the carbon–sulfur double bond. It is known that in the reaction of free radicals with carbon–sulfur double bonds, free radicals attack on sulfur instead of carbon.[2] Cation-radical **1a″** isomerized to **1b″** but no pivalophenone was observed during the anodic isomerization.

EXPERIMENTAL

Materials. Acetonitrile was distilled three times from phosphorus pentoxide and once from potassium carbonate, then kept in a bottle filled with dry argon and capped by a silicon-rubber stopper. Tetrabutylammonium bromide was purchased from a commercial source (Nakarai Chem. Co.).

1-Phenyl-2,2-dimethylpropane-1-thione S-oxide (E form, **1a**). Thiopivalophenone (3.3 mg, 18.5 mmol) was oxidized with 30% hydrogen peroxide in acetic acid at room temperature during 20 min. The solution was neutralized with sodium bicarbonate and the product was extracted with ether. The ether layer was dried over anhydrous sodium sulfate and the solution was evaporated *in vacuo*. The white crystals thus obtained were recrystallized from hexane giving **1a** in 75% yield. Anal. found: C, 68.27; H, 7.41%. Calculated for $C_{11}H_{14}SO$; C, 68.00; H, 7.26%. m.p. 54–55°. NMR ($CDCl_3$, TMS) 1.29 (s, 9 H), 7.20–7. 73 (m, 5 H). NMR spectra of the crude material before recrystallization showed that the ratio of **1a** : **1b** = 82 : 18. The isomer **1b** was obtained by anodic isomerization followed by column chromatography on silica gel (hexane–benzene was used as eluent). Colorless oil. Anal. found: C, 68.30; H, 7.20%. NMR ($CDCl_3$, TMS) 1.40 (s, 9 H) 7.00–7.50 (m, 5 H).

Procedure. In one of the arms of an H-shaped electrolytic cell, each containing 5 cm^3 of acetonitrile and 100 mg of tetrabutylammonium bromide, was placed 35 mg of sulfine (0.18 mmol) for the cathodic or anodic reaction. Platinum electrodes were used. The reaction was run under constant voltage of + 1.6 V (vs. SCE) at room temperature. After appropriate intervals, the solution was subjected to VPC (Yanagimoto G-1800, FID, 15% BDS, 1 m, 170°C). Heptadecane was used as an internal standard.

REFERENCES AND NOTES

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2. G. Tsuchihashi, M. Yamauchi and A. Ohno, *Bull. Chem. Soc. Jpn.* **43**, 968 (1970).