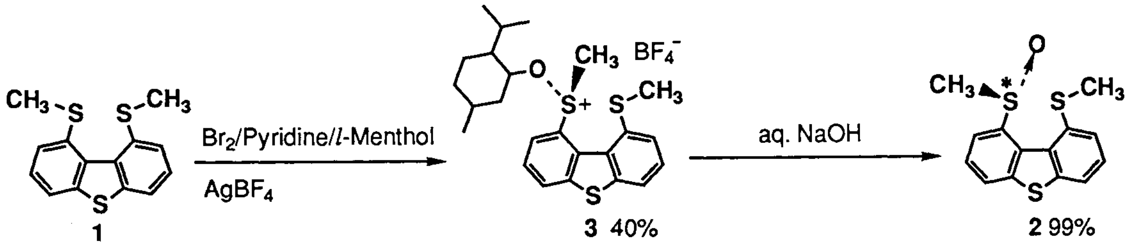
CHEMISTRY LETTERS, pp. 27-28, 1994.

Asymmetric Oxidation of 1,9-Bis(methylthio)dibenzothiophene and First Determination of Optically Active *l*-Menthoxy Sulfonium Salt by X-Ray Crystallographic Analysis

Takeshi KIMURA, Hidetaka NAKAYAMA, and Naomichi FURUKAWA*
Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

l-Menthoxy sulfonium salt of 1,9-bis(methylthio)dibenzothiophene was isolated, and the structure was first determined by X-ray crystallographic analysis.

Preparation of optically active sulfoxides by asymmetric induction has become of interest in organic synthesis.[1)] We have reported that optically active diaryl sulfoxides are prepared simply from sulfides via *l*-menthoxy sulfonium salts which are hydrolyzed in situ with aqueous NaOH with inversion of the configuration at the sulfur atom.[2,3)] In the case of asymmetric induction of diaryl sulfides, the optical yields of the sulfoxides increase as the bulkiness of the *o*-substituents at the aryl group is increased.[2)] In order to investigate the proximity effect of the bulky substituent on asymmetric oxidation, we oxidized 1,9-disubstituted dibenzothiophene with Br_2/pyridine/*l*-menthol/NaOH.[4)] This communication describes the preparation of optically pure 1-(methylsulfinyl)-9-(methylthio)dibenzothiophene (**2**) by the asymmetric oxidation of 1,9-bis(methylthio)dibenzothiophene (**1**) via *l*-menthoxy sulfonium salt (**3**) and the first determination of the configuration of **2** and **3** by X-ray crystallographic analysis.



Scheme 1.

In a typical procedure, **1** was treated with Br_2 (1.0 eq.)/pyridine in the presence of *l*-menthol (10 eq.) in CH_2Cl_2 at -20 °C under argon for 1 h. Then aqueous 2 N NaOH was added, and the solution was stirred for 12 h to give optically active **2** in 45% yield, $[\alpha]_D^{23}=-215°$ (c=0.446, $CHCl_3$). Although two equivalents of Br_2 were used in the reaction, the yield of **2** did not change and neither the corresponding bissulfoxide nor sulfone was produced. The optically active **2** was recrystallized repeatedly from CH_2Cl_2/EtOH to give optically pure **2**, $[\alpha]_D^{23}=-433°$ (c=0.406, $CHCl_3$). The enantiomeric excess of **2** was determined by 500 MHz ^{1}H-NMR spectrum using Eu(tfc)$_3$ as ee=100%. Then the structure of **2** was determined by X-ray crystallographic analysis (Fig. 1).[5)] The structure containing the *S* configuration of **2** is probably the correct choice, and its enantiomeric structure could be rejected at the 0.005 significance level by the Hamilton test.[6)]

The isolation of the *l*-menthoxy sulfonium salt was successfully performed by treatment with $AgBF_4$ to give the corresponding sulfonium salt **3** as yellow crystals in 40% yield (Scheme 1).

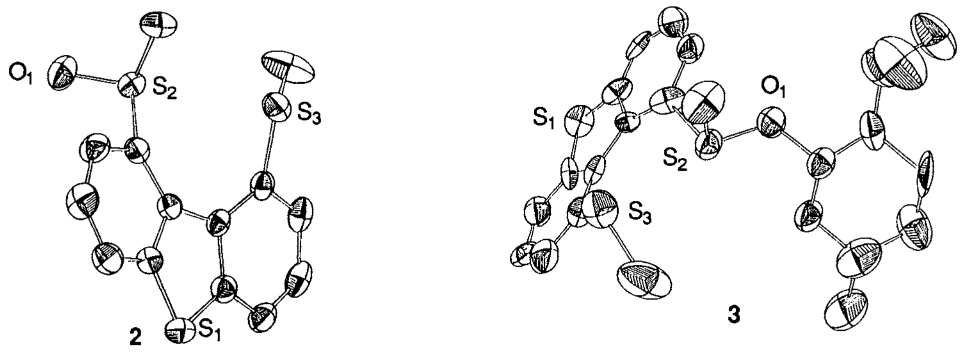


Fig. 1. ORTEP Drawings of Optically Activated **2** and **3**.

The optically pure **3** was treated with aqueous 2 N NaOH solution at 0 °C for 12 h to give **2** (99%), $[\alpha]_D^{24}$=-319° (c=0.30, $CHCl_3$; optical yield: 74%). The structure of **3** was determined by X-ray crystallographic analysis as an *S* configuration at the sulfur atom (Fig. 1).7) It is apparent from these results that the hydrolysis reaction of **3** with NaOH predominantly proceeded by an elimination reaction, unlike the S_N2 type reaction observed at the sulfonium sulfur atom, since the formation of menthene was actually identified by GC-MS as a counterpart of the elimination.2,3,8) Further investigation is now in progress in this laboratory.

References

1) K. K. Andersen, W. Gaffield, N. E. Papanikolaou, J. W. Foley, and R. I. Perkins, *J. Am. Chem. Soc.*, **86**, 5637 (1964); P. Pitchen, E. Duñach, M. N. Deshmukh, and H. B. Kagan, *ibid.*, **106**, 8188 (1984); F. Di Furia, G. Modena, and R. Seraglia, *Synthesis*, **1984**, 325; N. Furukawa, T. Shibutani, and H. Fujihara, *Tetrahedron Lett.*, **28**, 5845 (1987); T. Shibutani, H. Fujihara, and N. Furukawa, *ibid.*, **32**, 2947 (1991).
2) M. Moriyama, T. Yoshimura, N. Furukawa, T. Numata, and S. Oae, *Tetrahedron*, **32**, 3003 (1976).
3) C. R. Johnson, *J. Am. Chem. Soc.*, **85**, 1020 (1963).
4) N. Furukawa, T. Kimura, Y. Horie, and S. Ogawa, *Heterocycles*, **32**, 675 (1991); N. Furukawa, T. Kimura, Y. Horie, H. Fujihara, and S. Ogawa, *Tetrahedron Lett.*, **33**, 1489 (1992).
5) Crystal data for **2**: $C_{14}H_{12}OS_3$; orthorhombic, $P2_12_12_1$, a=8.444(1), b=8.837(1), c=17.340(2) Å, V=1293.8 Å^3, z=4, D_x=1.50 g/cm^3, μ(Mo-Kα)=5.3 cm^{-1}, R=0.02461 (R_w=0.02483), 1242 with $Fo^2>3.0\sigma(Fo^2)$; When the XYZ are shifted to (1.0-X), (1.0-Y), (1.0-Z), the R value changes from R=0.02461 to R=0.02558. All calculations were performed on a VAX computer using MolEN.
6) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).
7) The optical purity of **3** was determined by ^{1}H-NMR spectrum as 98%; mp. 98-103 °C (benzene/ether); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, J=8.1 Hz, 1H), 8.22 (d, J=8.1 Hz, 1H), 7.92 (d, J=8.1 Hz, 1H), 7.91 (t, J=8.1 Hz, 1H), 7.76 (d, J=8.1 Hz, 1H), 7.64 (t, J=8.1 Hz, 1H), 4.16-4.10 (m, 1H), 4.05 (s, 3H, $SOCH_3$), 2.69 (s, 3H, SCH_3), 1.92-1.90 (m, 1H), 1.56-1.49 (m, 1H), 1.24-1.17 (m, 4H), 0.92-0.79 (m, 7H), 0.62-0.55 (m, 4H), 0.44-0.37 (m, 4H); $[\alpha]_D^{25}$=+316° (c=0.12, $CHCl_3$); Anal. Found: C, 57.98; H, 6.12%. Calcd for $C_{24}H_{31}OS_3BF_4 \cdot 1/2C_6H_6$: C, 58.16; H, 6.14%; the crystal data: monoclinic, $P2_1$, a=10.216(2), b=23.076 (7), c=12.906(2) Å, β=108.87(1)°, V=2879.1 Å^3, z=4, D_x=1.20 g/cm^3, μ(Mo-Kα)=2.8 cm^{-1}, R=0.044 (R_w=0.046), 1999 with $Fo^2>3.0\sigma(Fo^2)$; the bond length at S_2-O_1 and the distance between S_2 and S_3 atoms are 1.63 Å and 2.85 Å.
8) The results suggest that the hydrolysis reaction of **3** concomitantly proceeds via an elimination (87%) and a substitution at the sulfur atom (13%).

(Received September 20, 1993)