(+)-batyl alcohol from a gorgonian.[14] Our observation of 1 from a marine sponge is noteworthy because alkyl ether glycerides with an OR having an odd number of carbons are rare.[8] Of further significance is that 1 along with all other chiral 1-ether glycerides known to date is of *S* configuration. Rather interesting biological activity seems to be associated with *S* ether glycerides. For example, it was recently reported that (*S*)-1-(1,3,5,7,9-dodecapentenoxy)-2,3-propanediol, a natural product from human feces,[15] displays potent mutagenic activity. Glyceride (+)-1 showed toxicity to goldfish, death in 70 min at 290 μg/mL, while (−)-1 showed no toxicity at this concentration, and (±)-1 displayed toxicity, death in 80 min at 360 μg/mL.

Experimental Section

Our general analytical, chemical, and chromatographic methods have been described previously.[16] Mass spectral data were obtained by direct inlet with an impact voltage of 20 eV and temperature programed at 100 °C for 1 min followed by a 3°/min ramp to 200 °C. Rotations were measured on an Autopol III Automatic polarimeter with a 1.0-dm cell (0.8 mL) at Stanford University. (±)-2,2-Dimethyl-1,3-dioxolane-4-methanol (**6**) was synthesized[17] and purified by distillation (bp 80–81 °C, 11 mm); commercially available compounds (Aldrich Chemical Co.) were used without further purification and included (+)-**6**, (−)-**6**, 1-tridecanol, and methanesulfonyl chloride. Bioassays were done by using the Bakus assay procedure.[3a]

(*S*)-(+)-1-Tridecoxy-2,3-propanediol (1). A red sponge (168 g, dry weight, collection No. DM-I-2) was collected from Lotuma of the Tonga Vava'u Island group. This sponge is in an undescribed genus, though it may belong to the family Plocamiidae, and it is probably closest to the genus *Tumata*.[18] Immediate extraction, with CH_2Cl_2 at room temperature, of the freshly collected sponge yielded 3.43 g of crude oil. A ^1H NMR spectrum (benzene-d_6) was obtained on the crude oil, and peaks characteristic of 1 were visible. The crude oil was partitioned between wet methanol–hexanes (1:1) to yield 1.10 g of methanol solubles; 1.0 g of this oil was flash chromatographed with a solvent gradient of ether–hexanes (1:1), followed by ether and methanol. Polar fractions 13 and 14 (0.0434 g) showing one TLC spot (R_f 0.25; ethyl acetate–hexanes (1:1)) were further purified by HPLC. Though only one HPLC peak was observed, 18 fractions were collected. Fractions 8–9 gave slightly impure 1 (10.8 mg), while fractions 10–14 yielded pure 1 (8 mg): mp 57 °C; $[\alpha]^{19.5}_D$ +2° (*c* 0.02 M, $CHCl_3$); ^1H NMR (benzene-d_6, 360 MHz) δ 3.74 (m, H_2), 3.58 (dd, J = 10.8, 4.7 Hz, H_{1a}), 3.48 (dd, J = 10.8, 5.4 Hz, H_{1b}), 3.30 (dd, J = 10.8, 5 Hz, H_{3a}), 3.26 (dd, J = 10.8, 5 Hz, H_{3b}), 3.21 (dt, J = 5.5, 5.5, 2 Hz, $H_{1'}$), 2.8 (br s, OH), 2.3 (br s, OH), 1.48 (m, $H_{2'}$), 1.31 (br s, A = 18 ± 2), 1.28 (m, $H_{3'}$), 0.92 (t, J = 5.5, $Me_{13'}$) [Spin-decoupling at δ 3.74 eliminated J = 4.7 at δ 3.58, J = 5.4 at δ 3.48, J = 5 at δ 3.30 and J = 5 at δ 3.26; spin-decoupling at δ 3.21 collapsed the multiplet at δ 1.48 to a triplet; spin-decoupling at δ 1.48 collapsed the multiplet at δ 3.21 to a broad singlet and simplified a shoulder of the δ 1.31 peak]; ^{13}C NMR (benzene-d_6, 25 MHz) δ 72.3 (t, J_R = 77.0, $C_{1'}$), 71.8 (t, J_R = 77.0, C_1), 70.7 (d, J_R = 85.5, C_2), 64.2 (t, J_R = 77.0, C_3), 31.9 (t, $C_{11'}$), 29.0 (t, A = 7–8, $C_{2'}$, C_4–$C_{10'}$), 26.0 (t, J_R = 47.0, $C_{3'}$), 22.6 (t, $C_{12'}$), 13.9 (q, $C_{13'}$) (multiplet data for entries without J_R is based upon INEPT experimental results); MS, *m/e* 256 ($M^+ - H_2O$), 225, 224 ($M^+ - H_2O$, CH_3OH).

Three synthetic samples of 1 were prepared via literature methods[17,19] from 1-tridecanol and (±)-**6** to yield (±)-1 (mp 48 °C (petroleum ether)), (−)-**6** to yield (+)-1 (mp 54 °C $[\alpha]^{19.5}_D$ +2.4° (*c* 0.06 M, $CHCl_3$)) and (+)-**6** to yield (−)-1 (mp 54 °C, $[\alpha]^{19.5}_D$ −2.3° (*c* 0.05 M, $CHCl_3$)).

Acknowledgment. Support for this research was under a grant from the California Sea Grant Program, Department of Commerce, and a Sea Grant Traineeship for B. L.M. We thank the University of California Research Expeditions Program for support of our field work. We are also grateful to Jim Loo for his technical assistance with some of the spectroscopic work at UCSC and Joe Hanke (UCSC) and Steve Naylor (UCSC) for their stimulating comments. The 360-MHz NMR spectra were obtained at the Stanford Magnetic Resonance Laboratory supported by the National Science Foundation (Grant No. GR23633) and the National Institutes of Health (Grant No. RR00711).

Registry No. 1, 86803-75-0.

(14) Kind, C. A.; Bergman, W. *J. Org. Chem.* **1942**, *7*, 424.
(15) Hirai, N.; Kingston, D. G. I.; Van Tassel, R. L.; Wilkins T. D. *J. Am. Chem. Soc.* **1982**, *104*, 6149.
(16) Selover, S. J.; Crews, P.; Tagle, B.; Clardy, J. *J. Org. Chem.* **1981**, *46*, 964.
(17) Renoll, M.; Newman, M. S. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 502.
(18) We thank Prof. G. J. Bakus, Department of Biological Sciences, University of Southern California, for his taxonomic analysis of this sponge. A voucher sample has been donated to his collection, and an underwater photograph is available from P.C.
(19) Baumann, W. J.; Mangold, H. L. *J. Org. Chem.* **1964**, *29*, 3055.

Onium Ions. 27.[1a] Oxidation of Sulfoxides to Sulfones with Nitronium Salts

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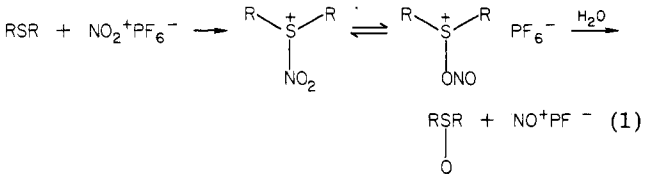
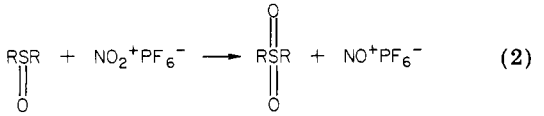
Received March 8, 1983

Recently we reported[3] a detailed study of the ambident reactivity of nitronium ion with heteroorganic (S, Se, P, As, and Sb) compounds. Sulfides, for example, reacted readily at −78 °C with nitronium hexaflourophosphate (tetrafluoroborate), affording, upon basic workup, sulfoxides (**4**) as the major products (eq 1) Even when an



(1)

excess of nitronium salt was used, the reaction did not lead to any observable amounts of sulfones. This selective oxidation of sulfides to sulfoxides led to the conclusion that the intermediate-formed *S*-nitrito onium ions prevented further oxidation by NO_2^+ and gave upon workup sulfoxides. In continuation of our work, we now investigated the reaction of sulfoxides with nitronium salts[1b] and found that sulfoxides (alkyl or aryl) on treatment with NO_2^+ are oxidized to sulfones in good to excellent yield (eq 2).



(2)

Interestingly, in the case of aromatic sulfoxides, there is no ring nitration observed.[4] This approach allows an easy

(1) (a) For Part 26, see: Mertens, A.; Lammertsma, K.; Arvanaghi, M.; Olah, G. A. *J. Am. Chem. Soc.* **1983**, *105*, 5657–5670. (b) Presented in part at the 183rd American Chemical Society National Meeting, Las Vegas, NV, 1982.
(2) Present address: Celanese Research Company, 86 Morris Ave, Summit, NJ 07901.
(3) Olah, G. A.; Gupta, B. G. B.; Narang, S. C. *J. Am. Chem. Soc.* **1979**, *101*, 5317–5322.

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Table I. Oxidation of Sulfoxides Using Nitronium Tetrafluoroborate

$$RSOR' \xrightarrow{NO_2BF_4} RSO_2R'$$

R	R'	reaction conditions: temp, °C	reaction conditions: time, h	yield of sulfone,[a] %	mp or bp(torr), °C(mm): obsd	mp or bp(torr), °C(mm): lit.[b]
CH_3	CH_3	25	5[c]	78	105.6	108-10
n-C_3H_7	n-C_3H_7	25	5[c]	65	70-3(0.3)	270(760)
n-C_4H_9	n-C_4H_9	25	5[c]	67	44.1	43-5
-$(CH_2)_4$-		25	5[c]	68	80-3(0.1)	285(760)
$C_6H_5CH_2$	$C_6H_5CH_2$	mixture of products				
C_6H_5	C_6H_5	~100	2[d]	78	128.4	123-5
p-$CH_3C_6H_4$	p-$CH_3C_6H_5$	~100	2[d]	92	160.3	159[e]
p-ClC_6H_4	p-ClC_6H_4	~100	2[d]	82	148.7	145.5-48.5

[a] Isolated yield of the pure chromatographed product. [b] The Aldrich Catalog, 1979-80. [c] Products isolated by nonaqueous workup (method B); the reaction was carried out in dichloromethane. [d] Products isolated by aqueous workup (method A), the reaction was carried out in nitromethane. [e] CRC Handbook of Chemistry, 55th ed.; Cleveland, OH, 1974-75.

Table II. ^{13}C NMR Chemical Shifts of Nitratosulfonium, Nitritosulfoxonium Ions, and Their Precursors in SO_2 Solution at −60 °C[a]

	C_1	C_2	C_3	C_4	C_5
$(CH_3)_2SO$	37.9				
$(CH_3)_2S^+ONO_2BF_4^-$	35.4				
$(CH_3)_2SO_2$	42.5				
$(CH_3)_2S^+(O)ONOBF_4^-$	42.4				
$(CH_3CH_2)_2SO$	43.1	7.5			
$(CH_3CH_2)_2S^+ONO_2BF_4^-$	42.2	6.9			
$(CH_3CH_2)_2SO_2$	46.4	6.3			
$(CH_3CH_2)_2S^+(O)ONOBF_4^-$	46.3	6.1			
$(CH_3CH_2CH_2)_2SO$	51.6	17.1	13.5		
$(CH_3CH_2CH_2)_2S^+ONO_2BF_4^-$	50.0	16.7	13.0		
$(CH_3CH_2CH_2)_2SO_2$	53.8	16.0	13.3		
$(CH_3CH_2CH_2)_2S^+(O)ONOBF_4^-$	53.8	15.9	13.2		
$(C_6H_5)_2SO$	144.0	130.7	126.1	133.0	
$(C_6H_5)_2S^+ONO_2BF_4^-$	137.2	131.2	127.5	134.9	
$(C_6H_5)_2SO_2$	141.3	130.7	128.3	135.0	
$(C_6H_5)_2S^+(O)ONOBF_4^-$	141.3	130.7	128.3	135.1	
$(p$-$CH_3C_6H_4)_2SO$	143.9	131.4	126.5	140.9	21.6
$(p$-$CH_3C_6H_4)_2S^+ONO_2BF_4^-$	138.1	132.1	128.5	147.6	21.8
$(p$-$CH_3C_6H_4)_2SO_2$	146.2	131.1	128.2	138.5	21.5
$(p$-$CH_3C_6H_4)_2S^+(O)ONOBF_4^-$	146.0	131.0	128.1	138.4	21.4

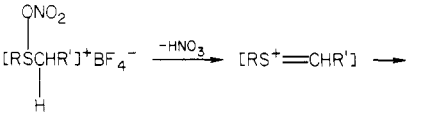
[a] All the ^{13}C NMR chemical shifts are referenced from external Me_4Si.

conversion of sulfides to sulfones in two carefully controlled steps. In contrast, the oxidation of sulfides using conventional oxidizing agents often results in a mixture of products.[5]

In a typical experiment, phenyl sulfoxide (10 mmol) was added to a solution of NO_2BF_4 (12 mmol) in nitromethane, and the mixture was heated under reflux for 2–3 h. Usual workup of the reaction mixture gave a 78% yield of diphenyl sulfone (**5f**). The reaction can also be carried out at ambient temperature, in which case, however, a longer reaction time is required for the completion of the reaction. The progress of the reaction was easily monitored by TLC. It was also found that the reaction took place readily with dichloromethane or acetonitrile as solvent.

The method seems to be general and readily applicable to aliphatic as well as aromatic sulfoxides. The oxidations proceeded extremely smoothly even at low temperatures in the case of aliphatic sulfoxides (between −15 °C and room temperature).

It is necessary to carry out the reactions under well-controlled conditions particularly in the case of aliphatic sulfoxides in order to suppress Pummerer or fragmentation reactions (eq 3). Nonaqueous workup was found to be



6

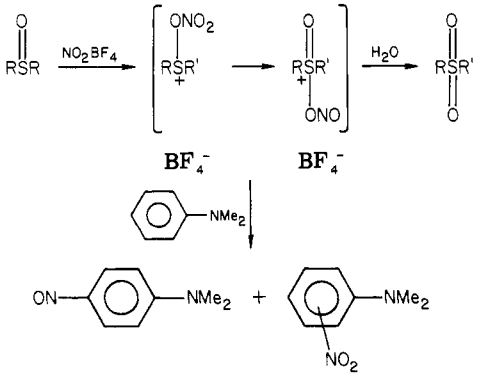
cleavage and Pummerer products (3)

very useful to obtain higher yields of the products. Product separation generally is by column chromatography using a hexane/chloroform solvent mixture as the eluent. Aromatic sulfoxides in general required higher temperatures to complete the reactions. Reaction of dibenzyl sulfoxide resulted in a mixture of products even under mild conditions (between −78 and 0 °C). The results are tabulated in Table I.

The probable mechanistic course of the oxidation of sulfides is outlines in Scheme I. In order to substantiate

(4) Marziano, N. C.; Maccarone, E.; Cimino, G. M.; Passerini, R. C. *J. Org. Chem.* **1974**, *39*, 1098–1101, and references cited therein.
(5) (a) Plesnicar, B.; Russell, G. A. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 797–798. (b) Tolstikov, G. A.; Ozhemilev, V. M.; Novitskaya, N. M.; Yuriev, V. P.; Rantyukova, R. G. *J. Gen. Chem. (USSR)*. **1971**, *41*, 1896. (c) Ogata, Y.; Suyama, S. *Chem. Ind. (London)* **1971**, 707–708.

Scheme I

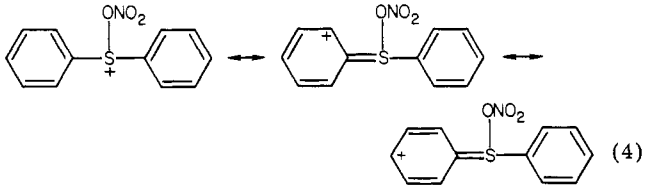


the proposed mechanism we added *N,N*-dimethylaniline to the reaction mixture and found the product mixture to contain 40% *p*-nitroso-*N,N*-dimethylaniline. The proposed intermediacy of nitratosulfonium and nitritosulfoxonium ions was further supported by ^{13}C NMR investigations of a series of these independently prepared ions as tabulated in Table II.

The nitrito onium ions were prepared, by using a similar procedure as described previously,[3] in sulfur dioxide at −78 °C, and the chemical shifts were measured at −60 °C. Thus, when dimethyl sulfoxide was treated with $NO_2^+BF_4^-$ in SO_2 at −78 °C, the proton-decoupled ^{13}C NMR spectrum showed two absorptions at δ ^{13}C (Me_4Si) 35.4 and 42.4, suggesting the formation of corresponding nitratosulfonium and nitritosulfoxonium ions, respectively. Proton-coupled ^{13}C NMR spectra further supported this, indicating that these absorptions are due to methyl groups. The peak at δ ^{13}C (Me_4Si) 35.4 slowly decreased in intensity after warming to −20 °C and disappeared after 4–5 h. When dimethyl sulfone in SO_2 was treated with nitrosonium hexafluorophosphate, it showed only one absorption in the ^{13}C NMR spectrum at δ ^{13}C (Me_4Si) 42.4. The species formed in this system was shown to be identical with the nitritosulfoxonium ion formed in the dimethyl sulfoxide system by mixing the two solutions together, which still showed a single absorption at δ ^{13}C (Me_4Si) 42.4. These data are in full agreement with the observation on the dimethyl sulfide system as described previously,[3] thus supporting the proposed mechanisms.

The ^{13}C NMR study of onium ions formed from diethyl sulfoxide, di-*n*-propyl sulfoxide, diphenyl sulfoxide, and di-*p*-tolyl sulfoxide also led to similar conclusions as in the case of dimethyl sulfoxide.

The onium ions obtained from diphenyl sulfoxide and di-*p*-tolyl sulfoxide, respectively, with NO_2^+ showed interesting ^{13}C NMR characteristics. The higher shielding of the ipso carbons and deshielding of ortho and para carbons suggest that the onium ions are stabilized by their mesomeric forms (eq 4). Such charge delocalizations have



(4)

been observed in several substituted benzyl cations,[6] protonated aryl ketones,[7] etc.

(6) Olah, G. A.; Porter, R. D.; Jeuell, C. L.; White, A. M. *J. Am. Chem. Soc.* **1972**, *94*, 2044–2052.

(7) Olah, G. A.; Grant, J. L.; Westermann, P. W. *J. Org. Chem.* **1975**, *40*, 2102–2108.

The present study further demonstrates the ambident reactivity of the nitronium ion as indicated in our previous studies.[3] Furthermore, it allows extention of the previously reported selective oxidation of sulfides to subsequent conversion to sulfones under very mild conditions. Since selective oxidation of sulfides is difficult to carry out by the majority of the known oxidizing agents,[5] this method should find its use in organic synthesis.

Experimental Section

Starting Materials. All sulfoxides used in this work were commercially available materials of at least 97% purity (Aldrich Chemical Co.). Dimethyl sulfoxide, nitromethane, and dichloromethane were purified by the usual methods.

General Procedure for the Oxidation of Sulfoxides to Sulfones Using Nitronium Tetrafluoroborate. To a solution of nitronium tetrafluoroborate (1.6 g, 12 mmol) in dry nitromethane (or dry dichloromethane) (10 mL) cooled in an ice bath under nitrogen atmosphere was slowly added a solution of the corresponding sulfoxide (10 mmol) in nitromethane (or dichloromethane) (5 mL) with continuous good stirring. The solution turned pale yellow in color. The reaction mixture was allowed to warm to room temperature while stirring was continued or in some cases heated under reflux (see Table I). The progress of the reaction was monitored by TLC (with a 1:1 mixture of hexane/chloroform as an eluant). After the completion of the reaction, the oxidized product was isolated, as described previously either by aqueous or nonaqueous workup.[3] The crude products were further purified by column chromatography using hexane as the eluant. This resulted in spectrally pure products. The products also showed the correct physical properties as summarized in Table I.

Study of Intermediate Onium Ions by NMR Spectroscopy. In all NMR studies, freshly purified[8] nitronium and nitrosonium hexafluorophosphate or tetrafluoroborate were used. The solutions were prepared at −78 °C, cooling in a dry ice–acetone bath. In a typical experiment, dimethyl sulfoxide (0.2 g) was dissolved in SO_2 (2 mL) and carefully added in a ^{13}C NMR tube with good stirring to a solution of nitronium salt (0.7 g) in SO_2 (2 mL) taken up in a ^{13}C NMR tube. Onium ions from sulfones were obtained by a similar procedure using nitrosonium salt.

^{13}C NMR studies were performed on a Varian FT-80 NMR spectrometer equipped with a heteronuclear decoupler, variable-temperature probe, and 32K memory capacity computer. The spectrometer was operated in the routine Fourier transform mode. The total number of transients for suitable S/N for individual absorption varied from 1000 to 3000. The radio frequency used was 20.1 M Hz with the resonances referenced from external Me_4Si.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

Registry No. $(CH_3)_2SO$, 67-68-5; $(n\text{-}C_3H_7)_2SO$, 4253-91-2; $(n\text{-}C_4H_9)_2SO$, 2168-93-6; $(C_6H_5CH_2)_2SO$, 621-08-9; $(C_6H_5)_2SO$, 945-51-7; $(p\text{-}CH_3C_6H_4)_2SO$, 1774-35-2; $(p\text{-}ClC_6H_4)_2SO$, 3085-42-5; $(CH_3)_2SO_2$, 67-71-0; $(n\text{-}C_3H_7)_2SO_2$, 598-03-8; $(n\text{-}C_4H_9)_2SO_2$, 598-04-9; $(C_6H_5CH_2)_2SO_2$, 620-32-6; $(C_6H_5)_2SO_2$, 127-63-9; $(p\text{-}CH_3C_6H_4)_2SO_2$, 599-66-6; $(p\text{-}ClC_6H_4)_2SO_2$, 80-07-9; $NO_2^+BF_4^-$, 13826-86-3; $(CH_3)_2S^+ONO_2BF_4^-$, 86854-67-3; $(CH_3)_2S^+(O)ONOBF_4^-$, 86854-69-5; $(CH_3CH_2)_2SO$, 70-29-1; $(CH_3CH_2)_2S^+ONO_2BF_4^-$, 86854-71-9; $(CH_3CH_2)_2SO_2$, 597-35-3; $(CH_3CH_2)_2S^+(O)ONOBF_4^-$, 86854-73-1; $(CH_3CH_2CH_2)_2S^+ONO_2BF_4^-$, 86854-75-3; $(CH_3CH_2CH_2)_2S^+(O)ONOBF_4^-$, 86854-77-5; $(C_6H_5)_2S^+ONO_2BF_4^-$, 86854-79-7; $(C_6H_5)_2S^+(O)ONOBF_4^-$, 86854-81-1; $(p\text{-}CH_3C_6H_4)_2S^+ONO_2BF_4^-$, 86854-83-3; $(p\text{-}CH_3C_6H_4)_2S^+(O)ONOBF_4^-$, 86854-85-5; tetrahydrothiophene 1-oxide, 1600-44-8; tetrahydrothiophene 1,1-dioxide, 126-33-0; *N,N*-dimethylaniline, 121-69-7; *p*-nitroso-*N,N*-dimethylaniline, 138-89-6.

(8) Yoshida, T.; Ridd, J. H. *ACS Symp. Ser.* **1976**, *22*, 103–113.