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Single-Atom Peri-Bridged Naphthalenes. 2. Synthesis, Crystal Structure, and Reactions of Naphtho[1,8-*bc*]thiete Derivatives

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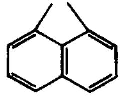
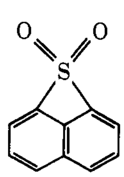
Abstract: Naphtho[1,8-*bc*]thiete (**5**) was prepared in high yield by ultraviolet irradiation of naphtho[1,8-*cd*]1,2-dithiole 1,1-dioxide (**7**). Peracid oxidation of **5** gave the corresponding sulfoxide (**6**) and sulfone (**1**); methylation of **1** gave sulfonium salt (**20**). The x-ray crystal structure of **1** shows a planar naphthalene ring with a compressed C(1)–C(8) peri-carbon distance (2.22 Å). The reactions of **5** and its derivatives with lithium aluminum hydride and other nucleophiles were studied. These reactions generally result in cleavage of the four-membered ring by attack of the nucleophile at the sulfur atom.

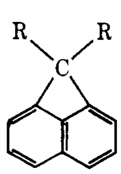


I

Single-atom peri-bridged naphthalenes (I) are compounds in which the 1- and 8-carbon atoms of a naphthalene ring are bonded to a single atom in a bridging group (Z), forming a four-membered ring. These compounds are of interest for a number of reasons, including the expected distortion of the bond lengths and angles of the naphthalene ring and the possibly enhanced tendency of the four-membered ring to undergo ring-opening reactions. The first description of this type of compound appeared in 1965, when Hoffmann and Sieber published the synthesis of naphtho[1,8-*bc*]thiete 1,1-dioxide (**1**).[1] Since that time, numerous attempts to synthesize the carbon-bridged (**2**),[2] nitrogen-bridged (**3**),[3] and oxygen-bridged (**4**)[4] analogues have been unsuccessful. The failure of many of these approaches may be attributed in part to the strain expected for compounds of this general structure. Nevertheless, an ingenious synthesis of **2** (R = H) was achieved by Bailey and Shechter[5] and we reported the efficient synthesis of naphtho[1,8-*bc*]thiete (**5**), naphtho[1,8-*bc*]thiete 1-oxide (**6**), and naphtho[1,8-*bc*]thiete 1,1-dioxide (**1**) at about the same time.[6] Herein we describe more fully the preparation of **5** and its derivatives, the x-ray crystal structure of **1**, and some interesting reactions of these sulfur-bridged naphthalenes.



1



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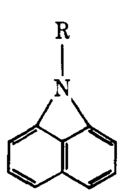

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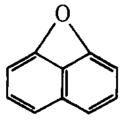

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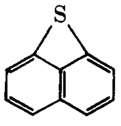

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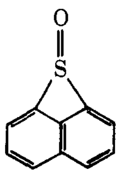
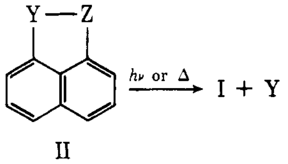


6

A compound of the general structure II, in which the peri positions of a naphthalene ring have been joined by the potential bridging group Z and a leaving group Y, might serve as a synthetic precursor to single-atom peri-bridged naphthalene I. Ideally Y should correspond to a stable fragment, such as nitrogen, sulfur dioxide, carbon dioxide, or carbon monoxide, which is capable of irreversible departure. Photolysis or pyrolysis of II might then lead to loss of Y and closure of the four-membered ring to give I. This strategy proved successful (with Y = N_2) when Z = SO_2 (**1**),[1] but failed for Z = CR_2 (**2**),[2] Z = NR (**3**),[3] or Z = O (**4**).[4] Naphtho[1,8-*bc*]thiete (**5**), in which Z = S, seemed accessible using this approach if the proper precursor II were chosen.



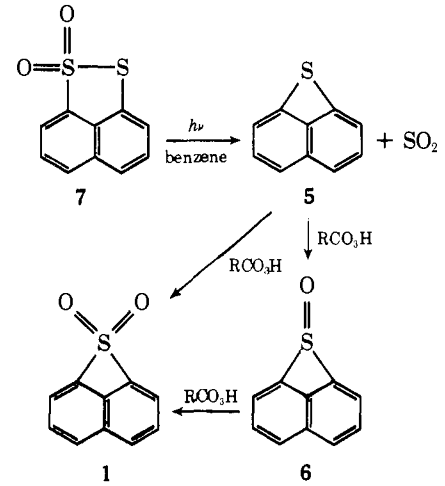
II

Results and Discussion

Synthesis of Naphtho[1,8-*bc*]thiete (**5**). Naphtho[1,8-*cd*]-1,2-dithiole 1,1-dioxide[7] (**7**, Scheme I) proved to be an excellent precursor of **5**. Ultraviolet irradiation of a dilute solution of **7** in benzene gave naphtho[1,8-*bc*]thiete (**5**) in up to 97% yield. This product could be obtained as white flakes melting at 40–42 °C. Proof of the structure of **5** is provided by its 300-MHz proton magnetic resonance and carbon-13 magnetic resonance spectra, which clearly show patterns consistent with a 1,8- (or 1,4- or 1,5-) symmetrically disubstituted naphthalene ring, and by its mass spectrum and osmometric molecular weight, which rule out a dimeric structure.

Oxidation of **5** with 1 equiv of *m*-chloroperbenzoic acid gave the corresponding sulfoxide (**6**, Scheme I), isolated as white crystals melting at 104–105 °C dec. The structure assignment is based on the infrared, nuclear magnetic resonance, and mass

Scheme I



spectra of the product. Oxidation of either sulfide **5** or sulfoxide **6** with excess peracid gave the corresponding sulfone (**1**, Scheme I), whose properties agreed well with those previously reported for **1** by Hoffmann and Sieber.[1] Besides confirming this earlier structure assignment by independent synthesis, we have further characterized **1** by its 300-MHz proton magnetic resonance and carbon-13 magnetic resonance spectra, and finally by x-ray crystallographic analysis (vide infra). The preparation of **1** by irradiation of **7**, followed by peracid oxidation of the crude product proceeds in 66% yield and surpasses the earlier synthesis in both efficiency and convenience.

The exact manner in which the naphthalene ring of a bridged compound of general formula I accommodates the strain imposed by the four-membered ring has not previously been determined. Hoffmann and Sieber described the ultraviolet absorption spectrum of **1** as being naphthalene-like, while the ultraviolet spectrum of 1*H*-cyclobuta[*de*]naphthalene (**2**, R = H) was interpreted by Bailey and Shechter[5] as indicating a distorted naphthalene ring. The proton and carbon-13 magnetic resonance spectra of **2**[5] (R = H) show that the protons on the bridging carbon are equivalent, implying either that the naphthalene ring of **2** is planar or else that it is undergoing a rapid interconversion of nonplanar conformations. Proton-decoupled carbon-13 magnetic resonance spectra of **2**,[5] **1**, **5**, and **6** show only six signals for the carbons of the naphthalene rings, implying the equivalence of carbons 1 and 8, 2 and 7, 3 and 6, and 4 and 5. To verify the symmetry and locate any unusual bond lengths and angles, as well as to provide the first detailed examination of how a naphthalene ring might be distorted by a single-atom peri bridge, an x-ray diffraction study of sulfone **1** was undertaken.

X-ray Crystal Structure of Naphtho[1,8-*bc*]thiete 1,1-Dioxide. The structure was solved[8] by direct methods using the program MULTAN.[9] Atomic coordinates and anisotropic thermal parameters were refined by a full-matrix least-squares analysis[10] using a weighting function $w = 1/\sigma^2$ with $\sigma = \sum^3_{n=0} a_n|F_o|^n$. The coefficients ($a_n$) were derived from a least-squares analysis of the polynomial $||F_o| - |F_c|| = \sum^3_{n=0} a_n|F_o|^n$. After convergence of the refinement, hydrogen atoms were located in a difference-Fourier synthesis. In the final cycles of refinement, the hydrogen atoms were held constant at locations in the plane of the naphthalene ring system at an initial distance of 1.0 Å from the carbon atoms and assigned the isotropic thermal parameters of the carbon atom to which they are bonded. The final conventional residual was $R_1 = 0.051$ and the weighted residual, $R_2 = [\sum w(|F_o| - k|F_c|)^2/\sum w|F_o|^2]^{1/2}$, was 0.080. The data parameter ratio was 5.7:1. Final parameters are in Tables I and II. A final listing of observed and calculated structure factors is presented.[11]

Table I. Final Atomic Fractional Coordinates[a]

Atom	$10^4 x$	$10^4 y$	$10^4 z$
S	2767 (1)	4581 (1)	9 178 (2)
O(1)	2430 (4)	5088 (2)	10 665 (5)
O(2)	3407 (4)	5127 (2)	7 986 (5)
C(1)	1157 (5)	3730 (3)	7 760 (6)
C(2)	−396 (5)	3554 (4)	6 390 (7)
C(3)	−746 (6)	2534 (4)	6 040 (7)
C(4)	328 (6)	1793 (4)	6 915 (8)
C(5)	3307 (6)	1420 (3)	9 519 (7)
C(6)	4756 (5)	1841 (3)	10 797 (6)
C(7)	5017 (5)	2843 (3)	11 054 (6)
C(8)	3714 (5)	3406 (3)	9 929 (6)
C(9)	2253 (5)	2979 (3)	8 656 (6)
C(10)	1961 (5)	2010 (3)	8 346 (6)
H(C2)	−1230	4050	5 700
H(C3)	−1890	2360	5 070
H(C4)	−30	1120	6 500
H(C5)	3200	710	9 410
H(C6)	5680	1410	11 620
H(C7)	6090	3120	11 990

[a] The estimated standard deviations in parentheses apply to the last significant digit.

A perspective view of the structure of **1** is presented in Figure 1.[12] It is observed that the sulfur atom and the naphthalene group are planar with a maximum deviation from the plane of 0.014 Å.[11] The oxygen atoms are in a plane essentially perpendicular (89°) to the naphthalene ring.

The bond lengths in **1** (Table III) are nearly identical with those of the corresponding bonds in naphthalene itself,[14] except for the C(9)-C(10) bond distance which is 1.378 Å compared to 1.41 Å in naphthalene. The main structural difference between the two molecules is in the bond angles. The bond angle at the peri-bridge [C(1)-C(9)-C(8)] is contracted to 106°, while the C(4)-C(10)-C(5) angle is extended to 132.5°,[11] resulting in distances of 2.22 and 2.61 Å between respective pairs of peri atoms. The pattern of bond angle compression and extension to accommodate the strain is the same as that reported for acenaphthylene,[15] but the distortions are greater. The angle at the peri-bridge position for acenaphthylene and tetrakis(1,8-naphthyridine)iron(II) perchlorate[16] is 113°. The bond angle C(1)-S-C(8) (75.4°) is also smaller than the C-S-C bond angle observed in thietanes (81°)[17] and benzothiophene 1,1-dioxide.[18]

The average S-C bond length in **1** is 1.82 Å, in agreement with the S-C bond distances observed in benzothiophene 1,1-dioxide.[18] The S-C bond distance observed in dibenzothiophene[19] is 1.74 (2) Å, which is not unexpected considering the partial aromatic character of the thiophene ring.

Reactions of Naphtho[1,8-*bc*]thiete and its Derivatives with Nucleophiles. Single-atom peri-bridged naphthalenes might be expected to suffer opening of the four-membered ring upon attack by nucleophiles by any of several mechanisms. Thus nucleophilic attack at the sulfur atom itself or the C(1) position or even at a C(2) proton (to give a 1,2-naphthyne) might all be envisioned. The reactions of **5**, **6**, and **1** with lithium aluminum hydride (a source of nucleophilic hydride anion) were studied in order to ascertain which of these possibilities obtained.

Treatment of a tetrahydrofuran solution of naphtho[1,8-*bc*]thiete (**5**) with excess lithium aluminum hydride followed by methylation of the base-soluble product gave methyl 1-naphthyl sulfide[20] (**8**, R = H) in 72% yield (Scheme II). To determine the mode of ring cleavage, the reaction mixture was quenched by addition of deuterium oxide. The recovered **8** was shown by its mass spectrum to contain 60% of one naphthalene-bound deuterium. The major path for this reaction thus

Table II. Thermal Parameters ($Å^2$)[a,b]

Atom	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$	$B^{c,d}$
S	146 (3)	41 (1)	232 (4)	9 (1)	34 (2)	3 (1)	3.86
O(1)	213 (6)	55 (2)	298 (9)	28 (3)	78 (6)	−16 (3)	4.99
O(2)	208 (6)	51 (2)	273 (9)	−14 (3)	61 (6)	21 (3)	4.82
C(1)	140 (8)	56 (3)	224 (13)	−1 (4)	58 (8)	1 (5)	4.10
C(2)	135 (8)	91 (4)	217 (13)	14 (4)	47 (8)	9 (5)	4.74
C(3)	125 (8)	101 (4)	238 (15)	−30 (5)	53 (8)	−23 (6)	4.80
C(4)	185 (9)	83 (4)	259 (14)	−51 (5)	102 (9)	−36 (6)	4.84
C(5)	216 (9)	44 (3)	259 (13)	−6 (4)	117 (9)	8 (5)	4.30
C(6)	172 (9)	55 (3)	224 (13)	16 (4)	78 (9)	21 (5)	4.23
C(7)	125 (7)	51 (3)	204 (12)	4 (4)	49 (7)	−1 (4)	3.73
C(8)	139 (8)	43 (2)	204 (11)	−6 (4)	73 (8)	−7 (4)	3.50
C(9)	131 (8)	54 (3)	174 (11)	−7 (4)	76 (8)	5 (4)	3.41
C(10)	170 (9)	58 (3)	179 (12)	−24 (4)	103 (8)	−12 (4)	3.62
H(C2)							4.50
H(C3)							4.70
H(C4)							4.60
H(C5)							4.30
H(C6)							4.10
H(C7)							3.60

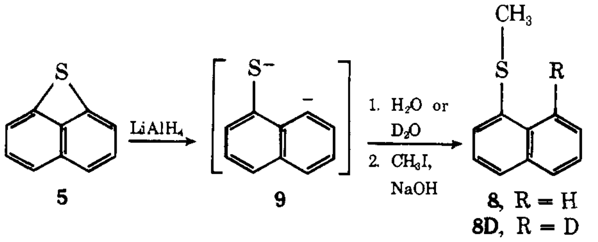
[a] The anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] The isotropic thermal parameters are in the form $\exp[-B\sin^2\theta/\lambda^2]$. [c] The isotropic equivalent of the anisotropic thermal parameters was obtained from: $B = 4.0[V^2\,det(\beta_{ij})]^{1/3}$ for the nonhydrogen atoms. [d] The isotropic thermal parameter for each hydrogen was set in refinement relative to the isotropic thermal parameter of the carbon to which it is bonded.

Table III. Interatomic Distances (Å)

Atoms	Uncorrected distance[a]	Corrected distance[b]
S-O(1)	1.432 (4)	
S-O(2)	1.437 (3)	
S-C(1)	1.821 (4)	1.827
S-C(8)	1.817 (4)	1.824
C(1)-C(2)	1.364 (6)	1.367
C(1)-C(9)	1.396 (6)	1.401
C(2)-C(3)	1.425 (8)	1.430
C(3)-C(4)	1.372 (8)	1.376
C(4)-C(10)	1.435 (7)	1.438
C(5)-C(6)	1.377 (7)	1.381
C(5)-C(10)	1.416 (7)	1.419
C(6)-C(7)	1.412 (6)	1.416
C(7)-C(8)	1.362 (6)	1.366
C(8)-C(9)	1.386 (6)	1.390
C(9)-C(10)	1.374 (6)	1.378
C(2)-H(C2)	1.006 (5)	
C(3)-H(C3)	1.004 (5)	
C(4)-H(C4)	0.996 (5)	
C(5)-H(C5)	0.990 (5)	
C(6)-H(C6)	0.999 (4)	
C(7)-H(C7)	0.996 (4)	

[a] The estimated standard deviations in parentheses apply to the last significant digit. [b] Corrected for rigid-body thermal motion with parameters determined from the anisotropic thermal parameters of the sulfur and carbon atoms.[13]

Scheme II



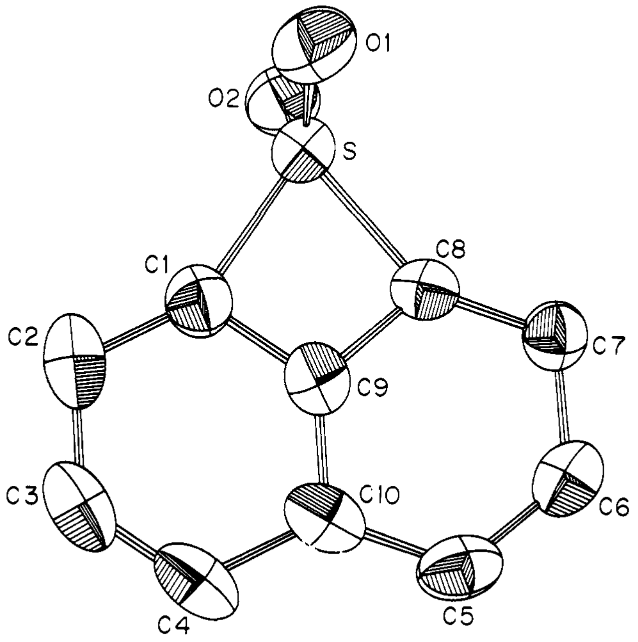
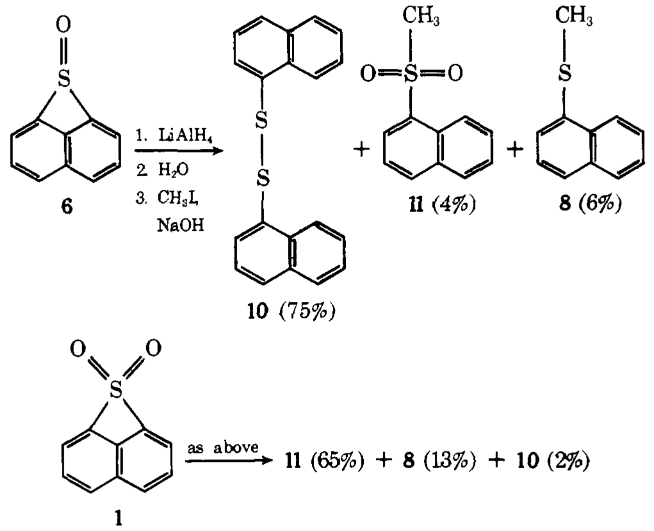


Figure 1. A perspective view of the structure of the molecule.

appears to involve attack of hydride anion at sulfur, liberating a naphthyl anion, followed by deprotonation of the resulting thiol by additional hydride to form the dianion **9**.[6] It is interesting to note by way of comparison that both thietane itself and diphenyl sulfide are inert under these conditions.[21]

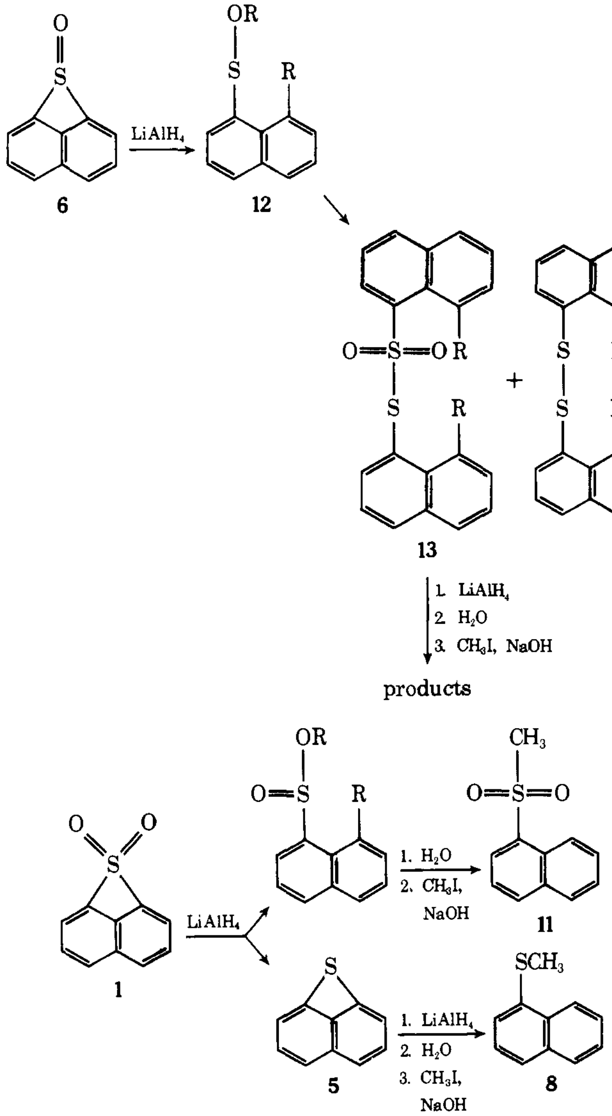
Similar reductive cleavages occurred upon exposure of **6** and **1** to lithium aluminum hydride in tetrahydrofuran (Scheme III). Reduction of **6** followed by methylation gave mostly di-1-naphthyl disulfide[22] (**10**), with smaller amounts of methyl 1-naphthyl sulfide (**8**) and methyl 1-naphthyl sulfone[23] (**11**). Reduction of **1** followed by methylation gave mostly methyl 1-naphthyl sulfone (**11**), with a smaller amount of methyl 1-naphthyl sulfide (**8**) and a trace of dl-1-naphthyl disulfide (**10**). Formation of these products probably involves an initial reductive cleavage of the four-membered ring (Scheme IV). In the case of sulfoxide **6**, a sulfenic acid (**12**) would seem to be the initial product. This might disproportionate[24] to a thiosulfonate **13**, reduction of which followed by methylation

Scheme III



Scheme IV

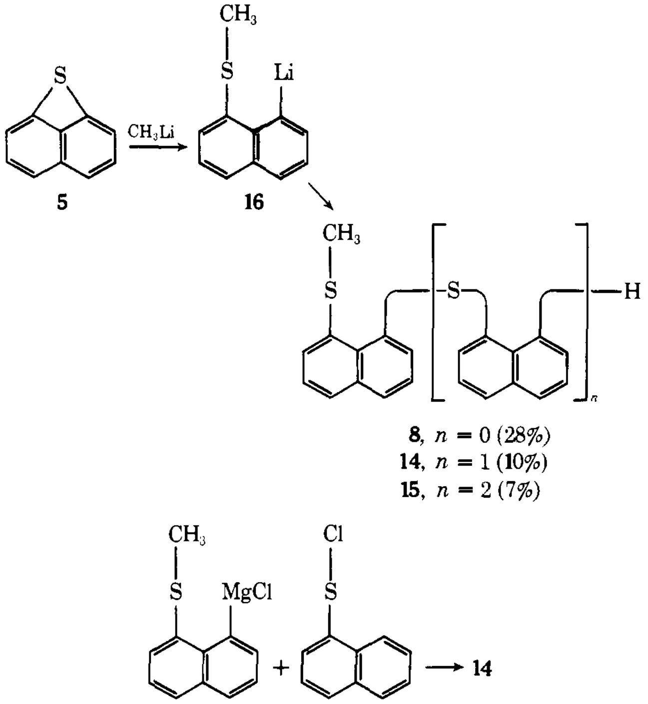
(R = H or metal)



could account for the observed products.[25] Reductive ring opening of sulfone **1** (Scheme IV) would produce a sulfinic acid, methylation of which would give methyl 1-naphthyl sulfone (**11**). The small amount of methyl 1-naphthyl sulfide (**8**) probably results from reduction of **1** to bridged sulfide **5**, followed by cleavage as before.

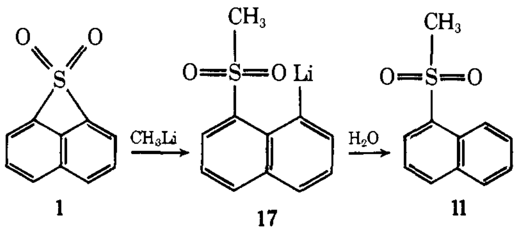
Certain other nucleophiles also react with the bridged compounds **5** and **1** to open the four-membered ring. Methyllithium reacted rapidly with **5** (Scheme V) to give not only methyl 1-naphthyl sulfide (**8**), but also methyl 8-(thionaphthyl)-1-naphthyl sulfide (**14**) and methyl 8-[8-(1-thionaphthyl)-1-thionaphthyl]-1-naphthyl sulfide (**15**). The structure assignments of **14** and **15** are based on their proton magnetic resonance and mass spectra. In addition, **14** was prepared in an independent synthesis by treating the Grignard reagent derived from methyl 8-chloro-1-naphthyl sulfide with 1-naphthalenesulfenyl chloride (Scheme V). The products **14** and **15** apparently were formed via attack on **5** by some initially formed methyl 8-lithio-1-naphthyl sulfide (**16**). A similar process has been observed in the reaction of thietane itself with *n*-butyllithium.[26]

Scheme V



In contrast to the reaction in Scheme V, treatment of sulfone **1** with methyllithium resulted only in its conversion to methyl 1-naphthyl sulfone (**11**, Scheme VI). This observation reflects the stability of **1** to attack by methyl 8-lithio-1-naphthyl sulfone (**17**) under these conditions.

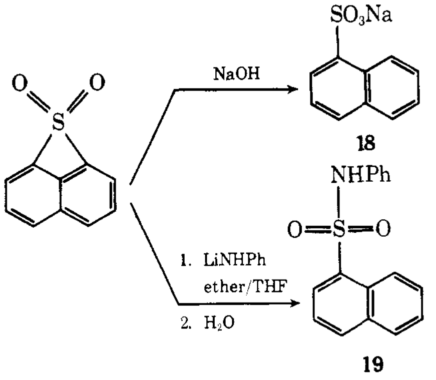
Scheme VI



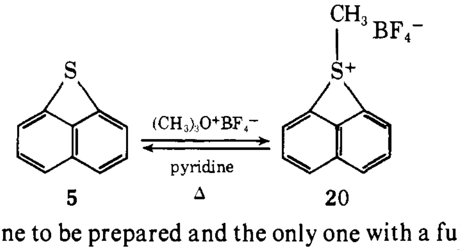
Sulfone **1** was similarly cleaved by sodium hydroxide in refluxing aqueous dioxane to give sodium 1-naphthalenesulfonate[27] (**18**, Scheme VII) and by lithium anilide in ether/tetrahydrofuran to give *N*-phenyl-1-naphthalenesulfonamide[28] (**19**).

Synthesis and Reactions of 1,8-Naphthylenemethylsulfonium Tetrafluoroborate. It was observed that naphtho[1,8-*bc*]thiete (**5**) could be methylated with trimethyloxonium tetrafluoroborate in methylene chloride (Scheme VIII) and the crude sulfonium salt **20** purified by crystallization from boiling isopropyl alcohol. Sulfonium salt **20** is the fourth sulfur-bridged

Scheme VII



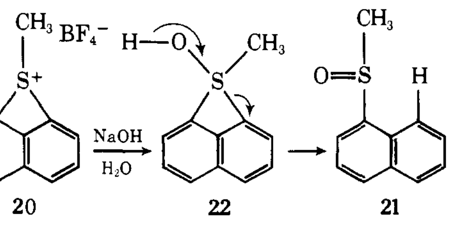
Scheme VIII



naphthalene to be prepared and the only one with a fully positively-charged bridging atom. It was characterized by its proton magnetic resonance spectrum, which showed a sharp singlet at 3.82 ppm, and by its demethylation in boiling pyridine to regenerate **5**.

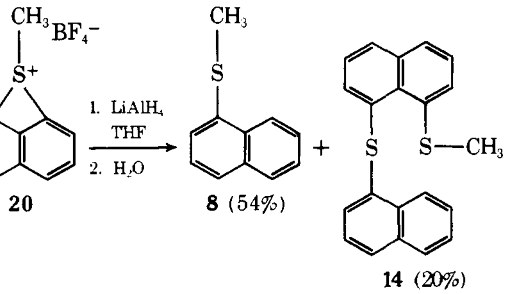
Like the other naphtho[1,8-*bc*]thiete derivatives, **20** suffered cleavage of the four-membered ring upon treatment with certain nucleophiles. Thus exposure of **20** to aqueous sodium hydroxide caused hydrolysis to methyl 1-naphthyl sulfoxide[29] (**21**, Scheme IX). A likely intermediate or transition state for this reaction is the sulfurane **22**.

Scheme IX



Reductive cleavage of **20** occurred upon treatment with lithium aluminum hydride in refluxing tetrahydrofuran (Scheme X). The products were methyl 1-naphthyl sulfide (**8**)

Scheme X



and methyl 8-(1-thionaphthyl)-1-naphthyl sulfide (**14**). Although lithium aluminum hydride has been shown to demethylate other methylsulfonium salts under these conditions,[30] the product expected from demethylation of **20** followed by reductive cleavage, 1-naphthalenethiol, was not observed. The formation of **14** might be rationalized in a variety of ways, but since we have no evidence favoring one mechanism over another, it would be premature to try to present a mechanism.

Conclusions

Naphtho[1,8-*bc*]thiete (**5**) and the corresponding sulfoxide (**6**), sulfone (**1**), and methylsulfonium salt (**20**) are easily prepared from naphtho[1,8-*cd*]1,2-dithiole 1,1-dioxide (**7**) and thus are readily available for chemical study. An in-plane distortion of the naphthalene ring in **1** is revealed by an x-ray diffraction study. We have investigated the reactions of these species with nucleophiles and found that they undergo opening of the four-membered ring via attack of the nucleophile at the sulfur atom. The ease with which carbon-sulfur bond cleavage occurs in the lithium aluminum hydride reductions indicates that relief of strain is an important driving force, since this process does not occur under comparable conditions with unstrained diaryl sulfide derivatives or thietane itself.

Experimental Section

Apparatus. Melting points were taken on a Kofler hot stage and are uncorrected. Infrared (ir) spectra were obtained on a Perkin-Elmer Model 257 or 337 grating infrared spectrophotometer and ultraviolet (uv) spectra on a Cary Model 14 spectrophotometer. Proton magnetic resonance (^{1}H NMR) spectra were recorded on a Varian Associates A-60A instrument unless otherwise noted. Chemical shifts are reported as parts per million downfield from tetramethylsilane, used as an internal standard, unless otherwise stated. Coupling constants are in hertz. Mass spectra (MS) were obtained with an Associated Electrical Industries Model MS-902 spectrometer employing electron-impact ionization. A Varian Aerograph Model 2100 gas chromatograph equipped with flame ionization detector and nitrogen as carrier gas was used for gas chromatography. Eastman 6060 silica gel sheets with fluorescent indicator were used for analytical thin-layer chromatography (TLC); Analtech precoated silica gel plates (1 mm) were used for preparative TLC. Iodine vapor or ultraviolet light was used for visualization. Woelm neutral alumina was used for column chromatography. Analyses were performed by Galbraith Laboratories or Schwartzkopf Microanalytical Laboratories.

Reagents. All solvents were reagent grade and used as received, except as noted. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately before use. "Dry ether" refers to ethyl ether (Mallinckrodt anhydrous) syringed from a freshly opened can. Benzene was distilled from and stored over sodium metal. Solvents for irradiations were degassed by bubbling nitrogen through the solution for 0.5 h prior to the start of the reaction and during the irradiation period. Organic extracts were dried by washing with saturated aqueous sodium chloride solution followed by treatment with anhydrous magnesium sulfate and were evaporated in vacuo below 30 °C.

Naphtho[1,8-*bc*]thiete (5). Naphtho[1,8-*cd*]1,2-dithiole 1,1-dioxide (**7**) was prepared in two steps from 8-amino-1-naphthalenesulfonic acid (Eastman) following the reported procedure,[7] giving yellow flakes, mp 143–144 °C (lit.[7] 148–149 °C) in 22% overall yield: uv (95% ethanol) 243 (ϵ 1.6×10^4) and 325 nm (3.6×10^3); MS *m/e* 222 (100%, M$^+$), 174 (61), 158 (91), 114 (30), and 113 (24). A solution of 0.570 g (2.57 mmol) of **7** in 225 ml of dry, degassed benzene was irradiated in a vessel equipped with a cooling jacket, condenser, magnetic stirbar, calcium sulfate drying tube, and nitrogen inlet, using a Hanovia medium-pressure 450-W light source with Pyrex filter. After 9.5 h of irradiation, analytical TLC (benzene) showed no remaining starting material and a single new product. The yellow solution was evaporated onto 0.5 g of alumina, which was placed at the head of an alumina column (25 g) and eluted with methylene chloride. The first 100 ml was collected and evaporated to give a yellow oil, 0.394 g (97% yield), which solidified upon cooling in the freezer. The solid material could be sublimed (25 °C (0.01 mm)) and recrystallized from hexane to give **5**, mp 40–42 °C. However, the crude product had proton magnetic resonance and infrared spectra and TLC behavior identical with those of pure **5** and was therefore used directly for subsequent experiments.

Anal. Calcd for $C_{10}H_6S$: C, 75.91; H, 3.82; S, 20.26. Found: C, 75.85; H, 3.74; S, 20.18.

Ir (CCl$_4$) 3050, 1922, 1780, 1657, 1615, 1474, 1442, 1337, 1315, 1206, 977, 946, 924, 857, 672, 645, 573, and 525 cm^{-1}; ^{1}H NMR

(CCl_4) 7.0-7.5 (m); MS *m/e* 158 (100%, M^+), 114 (20), and 113 (8); uv (95% ethanol) 220 (ϵ 3.2×10^4), 260 (5.0×10^3), 280 (2.8×10^3), and 290 (sh) nm (1.7×10^3); osmometric molecular weight 163 (benzene); 300-MHz ^1H NMR (Me_2SO-d_6) 7.38 (d, J = 7 Hz, $H_{4,5}$), 7.50 (d of d, J = 8, 7 Hz, $H_{3,6}$), and 7.63 (d, J = 8 Hz, $H_{2,7}$); ^{13}C NMR (Me_2SO-d_6) 140.541 ($C_{1,8}$), 133.069, 124.751, 121.928 ($C_{2,7}$, $C_{3,6}$, $C_{4,5}$), 138.595 (C_9), and 126.823 (C_{10}).

The evolution of sulfur dioxide during the irradiation was detected by bubbling nitrogen through the solution and into a trap containing aqueous sodium hydroxide. After the irradiation was complete, the basic solution was acidified with concentrated hydrochloric acid and warmed. The sulfur dioxide thus liberated was allowed to come into contact with freshly prepared zinc nitroprusside paste,[31] which in turn was exposed to ammonia vapor. A red color developed in the paste, indicating a positive test for sulfur dioxide.[31] A control test on aqueous sodium hydroxide was negative.

Naphtho[1,8-*bc*]thiete 1-Oxide (6). The benzene solution containing **5** after irradiation of 0.57 g (2.57 mmol) of **7** was treated with 0.522 g (2.57 mmol) of 85% *m*-chloroperbenzoic acid (Aldrich) in 10 ml of methylene chloride and the mixture was stirred for 15 h at 15 °C. The solvent was evaporated and the residue was dissolved in chloroform, which was washed with saturated aqueous sodium bicarbonate, dried, and evaporated. The crude product was purified by preparative TLC (benzene) and the sulfoxide was collected and sublimed (50 °C (0.01 mm)) to give 0.283 g (70% overall yield from **7**) of **6** as a white solid. Crystallization from hexane gave pure **6**, mp 105-106 °C dec.

Anal. Calcd for $C_{10}H_6SO$: C, 68.94; H, 3.47; S, 18.40. Found: C, 68.73; H, 3.31; S, 18.50.

Ir (KBr) 1467, 1442, 1080, 803, 770, 619, and 483 cm^{-1}; ^1H NMR (Me_2SO-d_6) 7.52-8.08 (m); MS *m/e* 174 (100%, M^+), 146 (8), 145 (12), and 102 (50); uv (95% ethanol) 221 (ϵ 3.0×10^4), 265 (4.8×10^3), 276 (4.5×10^3), 288 (4.6×10^3), and 319 nm (3.5×10^2); 300-MHz ^1H NMR (Me_2SO-d_6) 7.73 (t, J = 7 Hz, $H_{3,6}$), 7.80 (d, J = 7 Hz, $H_{4,5}$), and 8.04 (d, J = 8 Hz, $H_{2,7}$); ^{13}C NMR (Me_2SO-d_6) 164.745 ($C_{1,8}$), 133.192, 122.345, 129.236 ($C_{2,7}$, $C_{3,6}$, $C_{4,5}$), 151.290 (C_9), and 131.482 (C_{10}).

Naphtho[1,8-*bc*]thiete 1,1-Dioxide (1). The benzene solution containing **5** after irradiation of 0.50 g (2.25 mmol) of **7** was treated with 1.57 g (7.7 mmol) of *m*-chloroperbenzoic acid in 25 ml of methylene chloride and the reaction mixture was stirred for 15 h at 15 °C. The solvent was evaporated and the residue was dissolved in chloroform, which was washed with saturated aqueous sodium bicarbonate, dried, and evaporated. Crystallization from methyl alcohol gave 0.284 g (66% overall yield from **7**) of **1** as white needles, mp 183-184 °C (lit.[1] 184 °C); MS *m/e* 190 (93%, M^+), 174 (8), 162 (73), 161 (8), 148 (5), 134 (78), 133 (8), 126 (100), 125 (6), 114 (35), and 100 (2); 300-MHz ^1H NMR (Me_2SO-d_6) 7.81 (d of d, J = 8, 7 Hz, $H_{3,6}$), 7.88 (d, J = 7 Hz, $H_{4,5}$), and 8.13 (d, J = 8 Hz, $H_{2,7}$); ^{13}C NMR (Me_2SO-d_6) 162.477 ($C_{1,8}$), 133.888, 120.672, 130.180 ($C_{2,7}$, $C_{3,6}$, $C_{4,5}$), 138.271 (C_9), and 131.865 (C_{10}).

Sulfone **1** was also prepared from sulfoxide **6**. A solution of 0.100 g (0.57 mmol) of **6** in 11 ml of methylene chloride was stirred with 0.129 g (0.63 mmol) of 85% *m*-chloroperbenzoic acid for 12 h at 20 °C. Workup as described previously gave 0.087 g (80% yield) of **1**.

X-ray Diffraction Study of 1. The crystals obtained from a methanol solution are monoclinic, space group $P2_1/c$, with $Z = 4$ in a cell of dimensions a = 8.806 (4), b = 13.902 (8), c = 7.382 (4) Å, β = 113.60 (4)°, and densities $D_m = 1.54$ and $D_x = 1.56$ g cm^{-3}. A suitable crystal (0.46 × 0.25 × 0.11 mm) was cut from the lath-like crystals. The diffraction intensities were measured on a Picker FACS-1 four-circle diffractometer in a θ-2θ scan mode with Fe filtered Co$K\alpha$ radiation. Each scan (1 °C/min) included a variable increment in angle above the 1.5° minimum to allow for spectral dispersion; background counts of 40-s duration were taken at both limits of each scan. Reflections equivalent to one quadrant of reciprocal space out to $2\theta = 133.00°$ were collected. Of the 819 independent reflections, a total of 789 were above the threshold value determined by the criterion $|F_o| \geq 2.33\sigma_F$. The observed structure factor (F_o) and its standard deviation are defined as $F_o = [(C - kB)/Lp]^{1/2}$, $\sigma_F = (C + k^2B)^{1/2}/(2F_oLp) + 0.02F_o$. In these expressions C and B represent total scan counts and background counts, respectively, and k is the ratio of scan time to background count time; Lp is the Lorentz-polarization correction. A secondary extinction[32] was applied. The scattering factors were those of Cromer and Mann[33] for S and C and of Stewart, Davidson, and Simpson[34] for H.

Lithium Aluminum Hydride Reduction of Naphtho[1,8-*bc*]thiete (5). A solution of 0.131 g (0.83 mmol) of **5** in 2 ml of THF was added to 0.016 g (0.42 mmol) of lithium aluminum hydride under argon at 20 °C and stirred for 0.5 h. The reaction mixture was partitioned between ether and 10% aqueous sodium hydroxide. The aqueous layer was refluxed with excess methyl iodide and extracted with ether, which was dried and evaporated to give 0.104 g (72% yield) of a mobile oil, whose infrared and proton magnetic resonance spectra and TLC behavior were identical with those of authentic methyl 1-naphthyl sulfide, (**8**).[20] The same reaction mixture, when quenched with deuterium oxide, gave 70% of a mixture of **8** and **8D**, with the following mass spectrum (molecular ion region): *m/e* 177 (5%), 176 (14), 175 (100), 174 (62), and 173 (4). Synthetic **8** showed *m/e* 176 (5%), 175 (5), 174 (100), and 173 (6). In a control experiment, 1-naphthalenethiol was treated with lithium aluminum hydride, quenched with deuterium oxide, and methylated under identical conditions. The mass spectrum indicated that no ring deuteration had occurred.

Lithium Aluminum Hydride Reduction of Naphtho[1,8-*bc*]thiete 1-Oxide (6). A solution of 0.100 g (0.57 mmol) of **6** in 3 ml of THF was added to 0.016 g (0.42 mmol) of lithium aluminum hydride under argon at 20 °C and stirred for 0.5 h. The reaction mixture was partitioned between ether and 10% aqueous sodium hydroxide. The ether layer was dried and evaporated to give 0.068 g (75% yield) of di-1-naphthyl disulfide (**10**),[22] identified by comparison of its infrared, proton magnetic resonance, and mass spectra and TLC behavior with those of authentic **10**. Methylation of the aqueous layer as described previously gave 0.010 g of yellow oil. The proton magnetic resonance spectrum showed this to be a mixture of 60% methyl 1-naphthyl sulfide (**8**) and 40% methyl 1-naphthyl sulfone (**11**).[23]

Lithium Aluminum Hydride Reduction of Naphtho[1,8-*bc*]thiete 1,1-Dioxide (1). A solution of 0.200 g (1.05 mmol) of **1** in 5 ml of THF was added to 0.040 g (1.05 mmol) of lithium aluminum hydride under argon at 20 °C and stirred for 0.5 h. The reaction mixture was partitioned between ether and 10% aqueous sodium hydroxide. Treatment of the ether layer as before gave 0.003 g (2%) of a yellow solid, whose proton magnetic resonance spectrum matched that of authentic di-1-naphthyl disulfide (**10**).[22] Treatment of the aqueous layer as described previously gave 0.163 g of a white, waxy solid. The crude product was seen by its proton magnetic resonance spectrum to be a 5:1 mixture of methyl 1-naphthyl sulfone (**11**) and methyl 1-naphthyl sulfide (**8**), respectively. Separation by preparative TLC (benzene) gave pure **11** (mp 101.5-103 °C, ethanol; lit.[23] 102-103 °C) and **8**.

Reaction of Naphtho[1,8-*bc*]thiete (5) with Methyllithium. A solution of 0.100 g (0.63 mmol) of **5** in 1 ml of dry ether was added dropwise to 0.180 g (8.2 mmol) of methyllithium (Ventron) in 5 ml of ether at 20 °C under argon. The mixture was stirred for 0.5 h, then extracted with ether, which was washed with water, dried, and evaporated to give 0.74 g of yellow oil. The crude product was separated by preparative TLC (hexane/benzene 4:1) to give three products whose structure assignments are based on their infrared, proton magnetic resonance, and mass spectra and TLC behavior: **8**: 0.032 g (28% yield); R_f 0.53; methyl 1-naphthyl sulfide; **14**: 0.010 g (10% yield); R_f 0.37; ir (CCl_4) 3067, 2930, 1501, 1433, 1381, 1360, 1315, 1200, 967, 906, and 872 cm^{-1}; ^1H NMR ($CDCl_3$) 2.51 (s, 3 H) and 7.1-7.9 (m, 13 H); MS *m/e* 332 (95%, M^+), 317 (55), 285 (23), 284 (28), and 190 (100); methyl 8-(1-thionaphthyl)-1-naphthyl sulfide; **15**: 0.007 g (7% yield); R_f 0.18; ir (CCl_4) 3075, 2931, 1500, 1432, 1419, 1381, 1355, 1323, 1314, 1198, 1149, 967, 905, and 871 cm^{-1}; ^1H NMR ($CDCl_3$) 2.45 (s, 3 H), 7.08-7.87 (m, 19 H); MS *m/e* 490 (M^+), 378, 363, 332, 317, 316, 284, and 190; methyl 8-[8-(1-thionaphthyl)-1-thionaphthyl]-1-naphthyl sulfide.

Synthesis of Methyl 8-(1-Thionaphthyl)-1-naphthyl Sulfide (14). A mixture of 0.542 g (2.78 mmol) of freshly sublimed 8-chloro-1-naphthalenethiol[3] (mp 108-110 °C, lit.[34] 106-108 °C), 40 ml of 10% aqueous sodium hydroxide, and 10 ml of methyl iodide was heated at reflux for several hours. The mixture was extracted with ether, which was dried and evaporated to give 0.598 g (100% yield) of pale yellow solid, methyl 8-chloro-1-naphthyl sulfide (mp 74-76 °C, ethanol): ir (KBr) 1537, 1420, 1300, 1181, 972, 873, 803, and 747 cm^{-1}; ^1H NMR ($CDCl_3$) 2.54 (s, 3 H), 7.25-7.82 (m, 6 H); MS *m/e* 208 (100%, M^+), 193 (25), 173 (10), 158 (23), and 149 (39).

The Grignard reagent from methyl 8-chloro-1-naphthyl sulfide was prepared as follows.[36] Metallic potassium, 0.135 g (3.46 mmol), and 0.182 g (1.92 mmol) of anhydrous magnesium chloride (Alfa) were refluxed in 5 ml of THF under argon for 2 h. Methyl 8-chloro-1-naphthyl sulfide (0.200 g, 0.96 mmol) was added and the mixture was maintained at reflux for 3 h. Naphthalene 1-sulfenyl chloride was prepared from 0.205 g (1.28 mmol) of 1-naphthalenethiol and 0.189 g (1.41 mmol) of *N*-chlorosuccinimide in 2 ml of benzene. The sulfenyl chloride was not characterized; the filtered benzene solution was added to the Grignard reagent at 20 °C and the mixture was refluxed overnight. The reaction mixture was quenched with water and extracted with ether, which was washed with water, dried, and evaporated. Preparative TLC as described previously gave 0.060 g (19% yield) of **14** as a yellow solid, mp 126–128 °C (hexane): high resolution MS *m/e* 332.0696 ($C_{21}H_{16}S_2$ requires 332.0694); the infrared, proton magnetic resonance, and TLC behavior of synthetic methyl 8-(1-thionaphthyl)-1-naphthyl sulfide were identical with those of **14** from the reaction of naphtho[1,8-*bc*]thiete with methyllithium.

Reaction of Naphtho[1,8-*bc*]thiete 1,1-Dioxide (1) with Methyllithium. Methyllithium (9.10 mmol) in 5 ml of ether was stirred at 20 °C under argon. A slurry of 0.190 g (1 mmol) of sulfone **1** in dry ether was washed into the reaction vessel (20 ml of ether total). After 0.5 h, the reaction mixture was quenched with ice and extracted with ether, which was washed with water, dried, and evaporated to give 0.197 g (96% yield) of methyl 1-naphthyl sulfone (**11**) as a white solid, crystallized from ethanol to give pure **11**, mp and mmp 101–102 °C (lit.[23] 102–103 °C).

Hydrolysis of Naphtho[1,8-*bc*]thiete 1,1-Dioxide (1). A solution of 0.190 g (1 mmol) of **1** and 0.080 g (2 mmol) of sodium hydroxide in 10% aqueous dioxane was refluxed for 1 h. After evaporation of the solvents, the infrared spectrum indicated complete conversion to sodium naphthalene sulfonate (*18*).[27] Crystallization from water gave 0.161 g (70% yield) of white flakes which did not melt below 300 °C and whose infrared spectrum exactly matched that of authentic **17**.

Reaction of Naphtho[1,8-*bc*]thiete 1,1-Dioxide (1) with Lithium Anilide. A solution of 0.300 ml (3.2 mmol) of freshly distilled aniline in 5 ml of dry ether was treated with 2.0 mmol of *n*-butyllithium (Ventron) in 2 ml of ether at room temperature under argon. A solution of 0.190 g (1.0 mml) of naphtho[1,8-*bc*]thiete 1,1-dioxide (**1**) in 7 ml of THF was added dropwise. After 10 min, the reaction mixture was partitioned between ether and 5% aqueous hydrochloric acid. The ether layer was washed with water, dried, and evaporated to give 0.238 g (84% yield) of solid product whose infrared spectrum matched that of authentic *N*-phenyl-1-naphthylsulfonamide (**19**). Crystallization from ethanol/water gave 0.175 g of pure **19**, mp and mmp 156–157 °C (lit.[28] 157 °C).

Methylation of Naphtho[1,8-*bc*]thiete (5) with Trimethyloxonium Tetrafluoroborate. The sulfide **5** from irradiation of 0.57 g (2.57 mmol) of **7** was treated with 0.5 g (3.38 mmol) of trimethyloxonium tetrafluoroborate (Cationics) in 25 ml of methylene chloride under argon with stirring at room temperature. After 12 h, the solvent was evaporated and the residue crystallized from boiling isopropyl alcohol, giving 0.430 g (64% overall yield from **7**) of **20**. Recrystallization from methylene chloride/ether gave white needles, mp 146–147 °C: ^1H NMR (Me_2SO-d_6) 3.82 (s, 3 H) and 7.83–8.28 (m, 6 H).

Reaction of Methyl Sulfonium Salt 20 with Pyridine. A solution of 0.050 g (0.192 mmol) of **20** in 5 ml of pyridine was heated to boiling for 1 h. The reaction mixture was diluted with ether, which was washed with aqueous hydrochloric acid and saturated aqueous sodium bicarbonate, dried, and evaporated to give 0.014 g (45% yield) of naphtho[1,8-*bc*]thiete (**5**), as indicated by the proton magnetic resonance spectrum.

Hydrolysis of Sulfonium Salt 20. Sulfonium salt **20** (0.10 g, 0.38 mmol) was shaken briefly in a separatory funnel with 40 ml of aqueous sodium hydroxide and 40 ml of methylene chloride. The organic phase was washed with water, dried, and evaporated to give 0.063 g (86% yield) of crude methyl 1-naphthyl sulfoxide (**21**).[29] Crystallization from hexane gave white needles, mp and mmp 66–67 °C (lit.[29] 64–64.5 °C).

Lithium Aluminum Hydride Reduction of Sulfonium Salt 20. Freshly prepared sulfonium salt **20**, 0.260 g (1 mmol), was stirred with 5 ml of THF under argon at 20 °C. Lithium aluminum hydride (0.038 g, 1 mmol) was added all at once. The reaction mixture was refluxed for 0.5 h, cooled, and partitioned between ether and 10% aqueous sodium hydroxide. Methylation of the aqueous layer as previously described gave no methylated product. The ether layer was washed with water, dried, and evaporated. Separation by preparative TLC (4:1 hexane/benzene) gave 0.094 g (54% yield) of methyl-1-naphthyl sulfide (**8**) and 0.034 g (20% yield) of methyl 8-(1-thionaphthyl)-1-naphthyl sulfide (**14**), both characterized as previously described.

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Supplementary Material Available: a complete listing of structure factor amplitudes, deviation of atoms from planes in molecules, and bond angles (6 pages). Ordering information is given on any current masthead page.

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