aminocyclohexanol, 38898-70-3; (±)-norephedrine, 14838-15-4; (±)-pseudoephedrine, 4125-58-0; (±)-epichlorohydrin, 61630-87-3; 1-naphthol, 90-15-3; (±)-styrene oxide, 67253-49-0; piperidine, 110-89-4; (S)-3-phenoxy-1,2-epoxypropane, 71031-03-3; (S)-3-(4-cyanophenoxy)-1,2-epoxypropane, 70987-80-3; (S)-3-(4-methoxyphenoxy)-1,2-epoxypropane, 71048-65-2.

Supplementary Material Available: Determination of absolute configuration of β-hydroxy amines (10 pages). Ordering information is given on any current masthead page.

Photochemical Conversion of Sulfonium Salts to Sulfides via a 1,3-Sigmatropic Rearrangement. Photogeneration of Brønsted Acids

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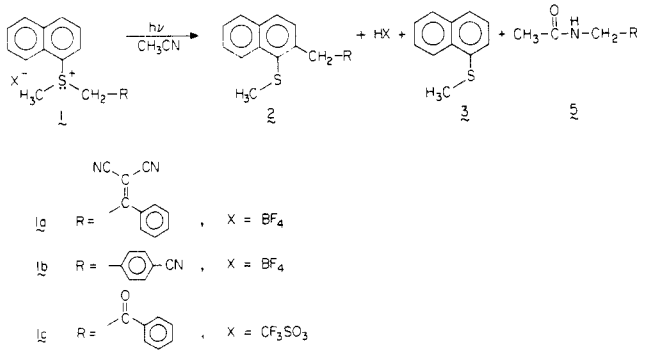
A series of 1-naphthyl methyl-substituted alkylsulfonium salts underwent 1,3-sigmatropic rearrangements to form 1-(methylthio)-2-substituted alkylnaphthalenes and the corresponding acid with quantum yields between 0.24 and 0.10. In competition with rearrangement was a bond-cleavage reaction forming 1-naphthyl methyl sulfide. The quantum yield for bond cleavage was ~0.15 for all the compounds studied.

Photolysis of triarylsulfonium and aryldialkylsulfonium salts normally provides products resulting from homolytic as well as heterolytic cleavage of carbon–sulfur bonds.[1] The product distribution is dependent on counterion[2] and solvent as well as the specific group attached to sulfur.[3]

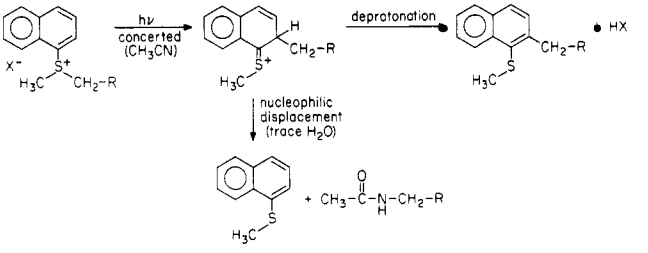
We report the novel photorearrangement of 1-naphthyl methyl-substituted alkylsulfonium salts to 1-(methylthio)-2-substituted alkylnaphthalenes and acid via a 1,3-sigmatropic rearrangement through the excited singlet electronic state of the naphthalene derivative. Products derived from sulfur–carbon bond cleavage are also observed.



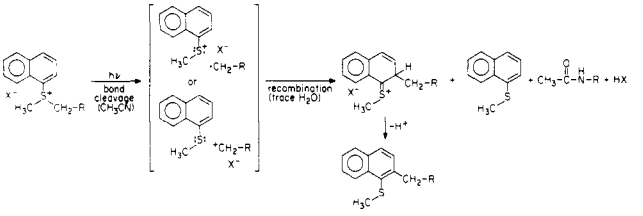
An attempt was made to elucidate the mechanism of rearrangement by means of quenching, sensitization, and product studies. The experimental observations are consistent with a photochemically allowed concerted 1,3-sigmatropic rearrangement involving four electrons or a cage bond-cleavage–recombination mechanism as shown in Schemes I and II. The naphthylene moiety in **1b** and **1c** is absorbing effectively all irradiation beyond 310 nm, whereas the naphthalene chromophore in **1a** absorbs ~63% of the light in this wavelength region and the R group the remaining 37%.

Triplet quenchers such as molecular oxygen (~10^{-3} M, E_T = 22.5 kcal/mol)[4] and 1,3-cyclohexadiene (1.0×10^{-1} M, E_T = 52.4 kcal/mol)[4] do not quench the production of **2(a–c)**, suggesting the involvement of the singlet state, whose lifetime in CH_3CN is ~1 ns. In agreement with that, attempts to sensitize the rearrangement of the naphthylsulfonium salts (E_T ~61 kcal/mol) with benzophenone (4.0×10^{-2} M, E_T = 69 kcal/mol) were unsuccessful.

Scheme I. Concerted Mechanism



Scheme II. Bond Cleavage-Recombination Mechanism



The photoproduct **2a** was isolated in 55% yield from the photolysis of **1a** in acetonitrile distilled from CaH_2 under argon. The structure of **2a** was identified unequivocally from its X-ray crystal structure. Photoproducts **2b** and **2c** were isolated in 33% yield and characterized by their ^1H NMR and mass spectra (EIMS). In separate experiments, photoproducts **2(a–c)** were shown to be stable under the reaction conditions.

A fragmentation–recombination mechanism for the formation of **2(a–c)** involving radicals (ion-radicals) or ionic intermediates is consistent with the experimental observations if it is primarily an in-cage process. A fragmentation–recombination mechanism involving long-lived

(1) Coyle, J. C. In "The Chemistry of the Sulfonium Group"; Sterling, C. J. M., Patai, S., Eds.; Wiley-Interscience: New York, 1981; Chapter 5.
(2) Ohkubo, K.; Yamabe, T. *J. Org. Chem.* **1971**, *36*, 3149.
(3) Maycock, A. L.; Berchtold, G. A. *J. Org. Chem.* **1970**, *35*, 2532.
(4) Murov, S. L. "Handbook of Photochemistry"; Dekker: New York, 1973; p 27.

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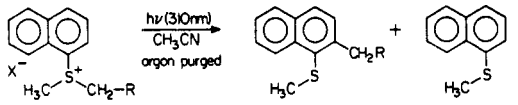
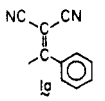
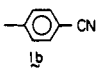
Table I. Quantum Yields[a] for Formation of Rearranged Product 2 and Photosolvolysis Product 1-Naphthyl Methyl Sulfide (3)



1 2 3

R	X	ϕ_2	ϕ_3
 1g	BF_4	0.24	0.15
 1b	BF_4	0.18	0.16
 1c	CF_3SO_3	0.10	0.14

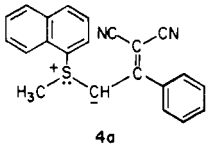
[a] Refers to the quantum yields for formation with 10^{-2} M solutions of **1a–c** in argon-purged acetonitrile. Aberchrome 540 was used to determine the photon flux of the 200-W Hg–Xe lamp used throughout these studies.[6]

ionic intermediates that can escape out of the solvent cage seems unlikely since the rearrangement, i.e., quantum yield of product formation, was not modified significantly by the presence of nucleophilic solvents such as methanol and water. The rearrangement occurred readily in methanol and in 1:2 CD_3CN–D_2O.

A reaction mechanism involving radicals and radical ions is not consistent with the lack of formation of $(RCH_2)_2$ dimers and of any product quenching due to the presence of 0.3 M benzenethiol unless it is totally an incage process. Chemically induced dynamic nuclear polarization (CIDNP) was not observed in either **1** or **2**. The fact that CIDNP was not observed in the starting material or the rearranged product is consistent with a concerted process[5] as well as with short-lived radicals produced via the singlet state.

The quantum yield for the formation of the rearranged product **2** varied from 0.24 for **2a** to 0.18 for **2b** to 0.10 for **2c**. The quantum yield for the competing carbon–sulfur bond cleavage was ~0.15 and independent of the R groups used thus far (see Table I). The carbon–sulfur bond cleavage may occur via nucleophilic displacement involving the reaction of acetonitrile on the dihydronaphthylene species in competition with deprotonation, photolysis of the sulfonium ylide, or from a "photosolvolysis" reaction.

The sulfonium ylide **4a** was not an intermediate in the formation of the rearranged product **2**, as it was thermally stable at 80 °C for 15 h and gave **3** in quantitative yield when photolyzed in acetonitrile.



4a

We speculate that the photoexcited singlet naphthylsulfonium salt may rearrange via a concerted mechanism owing to the formation of a charge-separated intermediate stabilized by the sulfonium moiety.

In summary, a series of 1-naphthylmethylalkylsulfonium salts underwent photoinduced rearrangements to form 1-(methylthio)-2-substituted alkylnaphthalenes and the corresponding acid with quantum yields between 0.24 and 0.10. Experimental observations support either a concerted, photochemically allowed, 1,3-sigmatropic rearrangement occurring through the singlet excited state of the naphthalene derivative or an incage fragmentation–recombination mechanism.

Experimental Section

Absorption spectra were run on a Perkin-Elmer Model 330 spectrophotometer equipped with a Model 3600 data station and a Model 600 printer. ^1H NMR spectra were run on a Varian EM390 (90 MHz) spectrometer. The sulfonium salts were photolyzed with an Oriel 200-W Hg–Xe lamp in combination with an Ealing 3130-Å interference filter for quantum efficiency studies. Combustion analyses were performed by the Analytical Sciences Division of the Kodak Research Laboratories.

Data for the crystal-structure determination were collected on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo Kα radiation and are given as supplementary material.[8]

All the sulfonium salts **1a–c** were synthesized as previously described.[7]

1-(Methylthio)-2-[2-phenyl-3,3-dicyanopropenyl]-naphthalene (2a). 1-Naphthylmethyl[2-phenyl-3,3-dicyanopropenyl]sulfonium tetrafluoroborate (**1a**) (4.0 g, 9.3 mmol) was dissolved in 75 mL of acetonitrile freshly distilled from CaH_2 under argon. The solution was placed in a Pyrex tube and purged with argon while being irradiated with a 200-W Hg–Xe lamp for 15 h. The reaction mixture was condensed and chromatographed on silica gel, with *n*-hexane used to elute **3** and 10% ethyl acetate in *n*-hexane to elute **2a**, which was obtained in 55% yield (1.74 g) after recrystallization from hexane: mp 90–92 °C; ^1H NMR (CD_3CN) δ 2.23 (s, 3 H), 4.90 (s, 2 H), 8.50 (m, 1 H, Ar), 7.30–7.90 (m, 10 H, remaining Ar). Anal. Calcd for $C_{22}H_{16}N_2S$: C, 77.6; H, 4.74; N, 8.23. Found: C, 77.6; H, 4.7; N, 8.2. The chemical structure of **2a** was confirmed from its X-ray crystal structure.

1-(Methylthio)-2-[4-cyanobenzyl]naphthalene (2b). 1-Naphthylmethyl-4-cyanobenzylsulfonium tetrafluoroborate (**1b**) (1.57 g, 4.2 mmol) was irradiated for 22 h as described for **2a**. Chromatography on silica gel as described above gave 0.40 g (33% yield) of the purified product as a colorless oil: ^1H NMR (CD_3CN) δ 2.16 (s, 3 H), 4.54 (s, 2 H), 8.62 (m, 1 H, Ar), 7.00–7.70 (m, 9 H, remaining Ar); mass spectrum (EIMS), *m/e* 289.

1-(Methylthio)-2-phenacylnaphthalene (2c). 1-Naphthylmethylphenacylsulfonium trifluoromethanesulfonate (**1c**) (1.02 g, 2.31 mmol) was irradiated for 30 h as described for **2a**. Chromatography on silica gel, as above, gave 0.22 g (33% yield) of the purified product as a colorless oil: ^1H NMR (CD_3CN) δ 2.18 (s, 3 H), 4.58 (s, 2 H), 8.62 (m, 1 H, Ar); mass spectrum (EIMS), *m/e* 292.

Photolysis and Thermal Treatment of 1-Naphthylmethyl[2-phenyl-3,3-dicyanopropenyl]sulfonium Ylide (4a). The ylide **4a** [^1H NMR ($CDCl_3$) δ 2.90 (s, 3 H,), 5.10 (s, 1 H); 1.0 g], prepared by the reaction of the sulfonium salt **1a** with 1 equiv of sodium hydride in anhydrous tetrahydrofuran, was dissolved in 50 mL of dry acetonitrile freshly distilled from CaH_2 under argon. The solution was irradiated as above for 15 h. The reaction mixture was condensed, and the ^1H NMR spectrum in CD_3CN showed that the rearranged product **2a** was not formed. 1-Naphthyl methyl sulfide was obtained in essentially quantitative yield (0.50 g, 98%) after column chromatography on silica gel. An NMR tube containing 50 mg of the ylide dissolved in 1.0 mL of CD_3CN was heated to ~80 °C for 15 h without decomposition of the starting material and formation of the rearranged product.

Quenching Experiments in Methanol, in Acetonitrile–Water, and with Benzenethiol. In a typical quenching experiment, 50 mg of 1-naphthylmethyl[2-phenyl-3,3-dicyanopropenyl]sulfonium tetrafluoroborate (**1a**) was dissolved in 3.0

(5) Kelts, L. W., private communication.
(6) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 1*, **1981**, 341.
(7) Saeva, F. D.; Morgan, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4121.
(8) The structure was solved by direct methods and refined by a full-matrix least-squares[6] method to final agreement indices $R = 0.150$ and $R_w = 0.176$. Since the structure was unambiguously determined at this point, application of anisotropic thermal parameters was not necessary.

mL of deuterated methanol (or 1:2 CD_3CN/D_2O or CD_3CN + 0.3 M benzenethiol), and the solution was degassed with argon and irradiated in a quartz cell with an Ealing 3130-Å interference filter in combination with a 200-W Hg-Xe lamp for 1 h. Product analysis (quantum yield) was determined by ^1H NMR. The rearranged product **2a** was produced in each case without significant quenching as compared to the value determined in dry acetonitrile.

Acknowledgment. We acknowledge the contribution of L. W. Kelts for the CIDNP investigations of the photorearrangement product and process.

Registry No. **1a**, 98088-07-4; **1b**, 90555-48-9; **1c**, 90584-13-7; **2a**, 98088-08-5; **2b**, 98088-09-6; **2c**, 98088-10-9; **3**, 10075-72-6; **4a**, 98088-13-2; **5a**, 98088-11-0; **5b**, 98088-12-1; **5c**, 1846-33-9; HBF_4, 16872-11-0; F_3CSO_3H, 1493-13-6.

Supplementary Material Available: Crystal data and structural parameters (Tables II-V), absorption curves of **1(a-c)** (Figure 1), and the X-ray crystal structure of **2a** (Figure 2) (7 pages). Ordering information is given on any current masthead page.

The Scope and Limitations of Carboxamide-Induced β-Directed Metalation of 2-Substituted Furan, Thiophene, and 1-Methylpyrrole Derivatives. Application of the Method to Syntheses of 2,3-Disubstituted Thiophenes and Furans

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The effects of change of solvent, metalating agent, reaction time, and reaction temperature on the lithiation of *N,N*-diethylthiophene-2-carboxamide and of the *N*-*tert*-butyl 2-carboxamide derivatives of furan, thiophene, and 1-methylpyrrole are explored, and optimum conditions are established for ring β-directed metalation. The tertiary carboxamido group is less effective in this context than the secondary amide function and appears to be of limited value in these heteroaromatic systems. The high metalation levels achievable with the furan and thiophene secondary amides allow high-yielding syntheses (through reaction of the lithiated intermediates with a wide range of electrophiles) of otherwise inaccessible 2,3-disubstituted derivatives. The synthetical value of this methodology appears to be limited only by the forcing conditions required for amide hydrolysis.

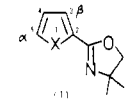
In recent papers,[1,2] we have established optimum conditions for β-directed metalation of furan, 1-methylpyrrole, and thiophene bearing the 4,4-dimethyloxazolin-2-yl substituent (**1**, X = O, NCH_3, S). Although the methodology furnishes a synthetically useful route to the otherwise inaccessible 2,3-disubstituted derivatives, there are drawbacks. In particular, the β-metallo intermediates may be contaminated with small amounts of the α (**5**) analogues or of starting material (or of both) and appear to be of only moderate nucleophilicity. Furthermore, in the 1-methylpyrrole case,[2] high β-selectivity is only achievable at the expense of a considerably lowered yield.

We have therefore continued the search for other 2-substituents as β-directing groups in metalation with a view to securing high-yielding, regioselective syntheses of 2,3-disubstituted furans, 1-protected pyrroles, and thiophenes. (A computer search of the Fine Chemicals Directory (version of October 1984 containing 47 177 compounds) for commercially available 2,3-disubstituted furans, thiophenes, and 1-H- or 1-substituted pyrroles not fused to another ring reveals only seven thiophenes, three furans, and no pyrroles, nor are there any commercially-available 3-substituted pyrroles. This may be taken as a crude measure of the inaccessibility of these deceptively simple compounds.) The results of our studies on the utility of carboxamido functionality in this connection are presented here.

Results and Discussion

(A) Tertiary Carboxamido Functionality. There is ample precedent for the use of tertiary amides as directing groups in the metalation of benzene derivatives.[3,4] Generally, lithiation adjacent to the *N,N*-diethylcarboxamido function has been achieved with *sec*-BuLi, but *n*-BuLi may be used with the more sterically congested diisopropyl analogues.

The results of an exploratory series of experiments on *N,N*-diethylthiophene-2-carboxamide (**2**) (Table I) are disappointing. Use of *sec*-BuLi in dimethoxyethane (DME) or diethyl ether gives no product from β-lithiation and only moderate selectivity for β-metalation when tetrahydrofuran (THF) is the solvent. For comparison purposes, the 2,5-disubstituted acid-amide **3** was synthesized



(1)

(3)

by the use of lithium diisopropylamide (LDA) as the metalating agent. Previous experience with the oxazolinyl

(1) Carpenter, A. J.; Chadwick, D. J. *J. Chem. Soc., Perkin Trans. 1* **1985**, 173.
(2) Chadwick, D. J.; McKnight, M. V.; Ngochindo, R. I. *J. Chem. Soc., Perkin Trans. 1* **1982**, 1343.
(3) Snieckus, V. *Heterocycles* **1980**, *14*, 1650.
(4) Beak, P.; Brown, R. A. *J. Org. Chem.* **1982**, *47*, 34.

0022-3263/85/1950-4362$01.50/0