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THE MECHANISM OF ELECTROCLEAVAGE REACTIONS AND PHOTOREARRANGEMENTS OF SOME SULFONIUM SALT DERIVATIVES

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Abstract—Irreversible one-electron reduction potentials (E_p) measured for a series of arylmethyl substituted-alkyl sulfonium salts (aryl = phenyl and 1-naphthyl) indicate that reductive cleavage occurs by a concerted mechanism in which bond breaking is concomitant with electron acceptance. Photolysis of the 1-naphthylmethyl substituted-alkyl sulfonium salts produces 1-thiomethyl-2-substituted-alkyl naphthylenes via a 1,3-sigmatropic rearrangement along with cleavage products. An in-cage fragmentation–recombination process involving cation-radical/radical intermediates is favored as the rearrangement mechanism even though a concerted pathway may be involved to some extent. *p*-Cyanobenzylthianthrene sulfonium trifluoromethanesulfonate also underwent photochemically as well as thermally induced rearrangement of the *p*-cyanobenzyl group from sulfur to the 1- and 2-position of the thianthrene ring system. An in-cage fragmentation–recombination mechanism is also favored in this case for both photochemical and thermal processes.

INTRODUCTION

Radical and ion-radical intermediates are important in many synthetic[1] and photosynthetic processes.[2] Our interest in these open-shell structures has evolved from their intermediacy in electrocleavage and photocleavage reactions. The scope of this paper will be limited to reductive cleavage reactions and photorearrangements of some sulfonium salt derivatives.

Electrocleavage reactions can, in general, take place by either a one-step or a two-step mechanism. In a two-step mechanism, one-electron reduction produces an intermediate, e.g. ion-radical or radical, which spontaneously undergoes bond cleavage. Two examples of a reductive cleavage process by a two-step mechanism are described below.

The one-electron reduction of *p*-nitrobenzylhalides[3] (Eq. 1) and pyridinium derivatives (Eq. 2) produces molecular fragmentation via an intermediate reduced species.

(1)

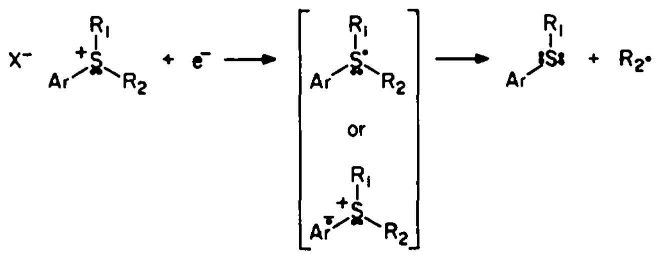
(2)

The intermediate in Eq. (1) is an anion-radical, which fragments by a heterolytic bond-breaking process to the *p*-nitrobenzyl radical and halide ion with a rate that is dependent on the nature of the leaving group, i.e. I > Br > Cl.[3] The cationic pyridinium derivative, on the other hand, is reduced via a single-electron-transfer process to an intermediate radical, which fragments by a homolytic bond-breaking mechanism to pyridine and a radical.

The two reductive cleavage processes described in Eqs (1) and (2) have in common the characteristic that the lowest unoccupied molecular orbital (LUMO) of the starting material is π^* in character. Since the reductive cleavage process involves a common intermediate, whose energy is essentially independent of the leaving group, the reduction potential for two-step reductive cleavage processes will not vary more than ~0.3–0.4 V from $E^{\circ\prime}$ for the intrinsic reduction process as long as the reducible π system remains the same.[4]

Reductive cleavage that takes place by a synchronous electron-acceptance and bond-cleavage mechanism is distinctly different from the two-step mechanism by the fact that the LUMO level of the electron acceptor is σ^* in character. In this case E_p would be expected to be extremely sensitive to the nature of the leaving group.

This paper describes the mechanism of the reductive cleavage process, i.e. one-step (σ^* LUMO) vs two-step (π^* LUMO), for a class of aryldialkylsulfonium salts. The mechanistic aspects are discussed in terms of the effect of leaving group on redox behavior, i.e. irreversible peak potentials (E_p), and variation of E_p with structural modifications such as changing the oxidation state of sulfur or forming the sulfonium ylid. In addition, photochemical rearrangements in these and a related system are described in terms of the intermediacy of ion-radical and radical species and the nature of the excited state.



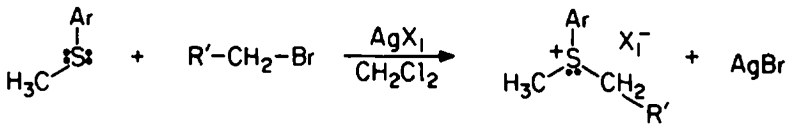
(3)

(4)

RESULTS AND DISCUSSION

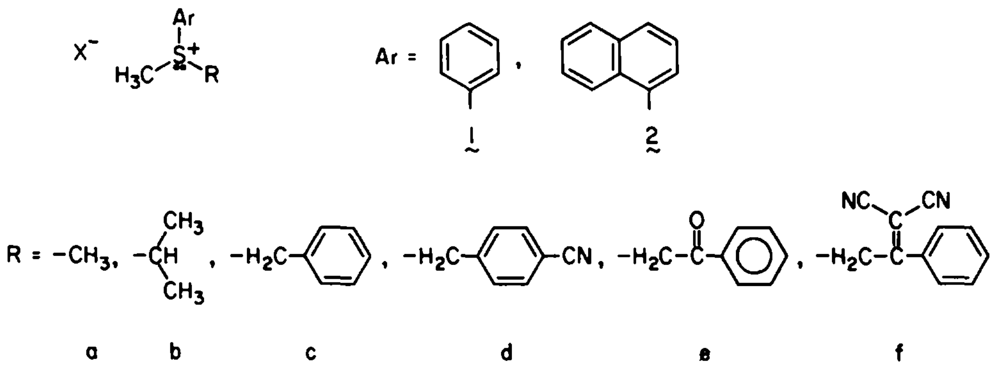
Synthesis

The sulfonium salts used throughout the study[5] were synthesized by the reaction of the arylmethyl sulfide (or thianthrene) with an alkyl halide in the presence of a silver salt. The reactions take place at room temperature in methylene chloride, and the product is readily purified by recrystallization from acetonitrile/diethyl ether at low temperature.[5]



Mechanism of reductive cleavage

Cyclic voltammetry (CV) was used to probe the electrochemical reductive cleavage of the following two series of arylmethylsulfonium salts:



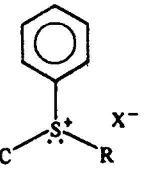
$X = CF_3SO_3, BF_4, OTs$

The reduction potentials for 1 and 2 (a–f) were all irreversible at the fastest scan rate used, i.e. 1 V s^{-1}. The peak potential E_p for the irreversible electrochemical reduction at constant scan rate, substrate concentration, and temperature was extremely sensitive to the nature of the fragmenting group.[5] Within systems 1 and 2, E_p varied by more than 1.4 and 1.3 V vs the standard calomel electrode (SCE), respectively,[5] and there was good correspondence between systems (Tables 1 and 2). The sensitivity and magnitude of shift of E_p with the electron-withdrawing nature of the leaving group suggests that the reductive cleavage occurs by a synchronous (concerted) process whereby bond breaking is concomitant with electron acceptance.[3–5]

We conclude that reductive cleavage within the series of sulfonium salts studied takes palce by a concerted process due to the σ^* nature of the LUMO level and that E_p values provide a relative measure of the energy of the LUMO of the sulfur–carbon bond being cleaved.

Molecular orbital calculations using the MOPAC package of Dewar and Thiel[6] and MNDO, which is the default Hamiltonian, showed that the LUMO level of all the compounds studied was σ^*, which is con-

Table 1. Electrochemical peak (E_p) potentials for the reduction of substituted phenylmethylsulfonium salts

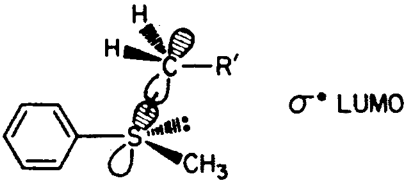


1

Compound	R	X	E_p^a Pt	E_p^a GC
1a	CH_3	CF_3SO_3	−1.64	−1.73
1b	$CH(CH_3)_2$	BF_4	−1.61	−1.63
1c	$H_2CC_6H_5$	BF_4	−1.20	−1.31
1d	$H_2CC_6H_4$—*p*-CN	BF_4	−0.95	−0.99
1e	$H_2CCOC_6H_5$	OTS	−0.73	−0.93
1f	$H_2CC(C_6H_5)$=C(CN)$_2$	BF_4	−0.23	−0.26

[a] Volts vs SCE in CH_3CN (50 mV s^{-1} scan rate) with 0.1 N t-butylammonium fluoroborate (TBAF) as electrolyte. Sulfonium salt concentration was 1.0×10^{-4} M. A platinum button (Pt) and a glassy-carbon (GC) electrode were used as the working electrode.

sistent with the electrochemical results. In addition, the calculations also correctly predicted the leaving-group propensities found by Beak and Sullivan.[7] In **2d**, for example, the LUMO level is localized primarily on the sulfur and the benzylic carbon. The orbital coefficients of the LUMO level predict that bond cleavage as a consequence of single-electron reduction should occur in the sequence: *p*-cyano-



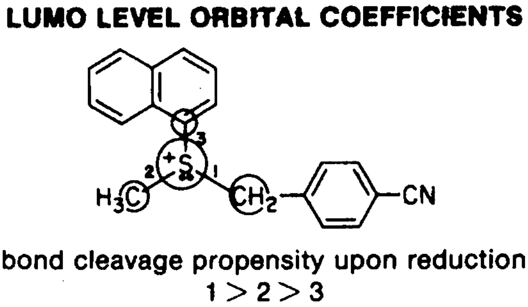
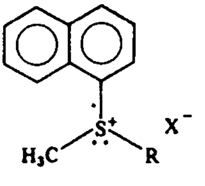


Table 2. Electrochemical peak (E_p) potentials for the reduction of some substituted 1-naphthylmethylsulfonium salts



2

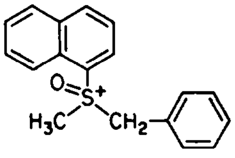
Compound	R	X	E_p^a Pt	E_p^a GC
2a	CH_3	CF_3SO_3	−1.51	−1.46
2b	$CH(CH_3)_2$	BF_4	−1.49	−1.40
2c	$H_2CC_6H_5$	BF_4	−1.23	−1.06
2d	$H_2CC_6H_4$—*p*-CN	BF_4	−0.92	−0.82
2e	$H_2CCOC_6H_5$	CF_3SO_3	−0.74	−0.80
2f	$H_2CC(C_6H_5)$=C(CN)$_2$	CF_3SO_3	−0.17	−0.15

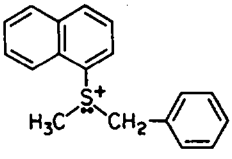
[a] Volts vs SCE in CH_3CN (50 mV s^{-1} scan rate) with 0.1 N t-butylammonium fluoroborate (TBAF) as electrolyte. Sulfonium salt concentration was 1.0×10^{-4} M. A platinum button (Pt) and a glassy-carbon (GC) electrode were used as the working electrode.

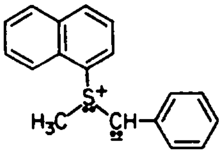
benzyl > methyl > aryl, in agreement with experiment.

Structure effects on E_p

As seen from the redox behavior of series 1 and 2, the LUMO level of the sulfonium salt can be varied over a wide range of potentials. Simple deprotonation of the sulfonium salt **2c** to the sulfonium ylid shifts E_p to more cathodic values. The corresponding transformation in **2f** shifts E_p by 1.0 V to more cathodic values. Conversion of **2c** to the oxysulfonium salt (**4**) in which the oxidation state of sulfur has been changed from +4 to +6, on the other hand, lowers the energy of the LUMO level and shifts E_p by 0.44 V to a less cathodic value. The nature of the LUMO level also has a profound effect on the photochemistry of these systems.





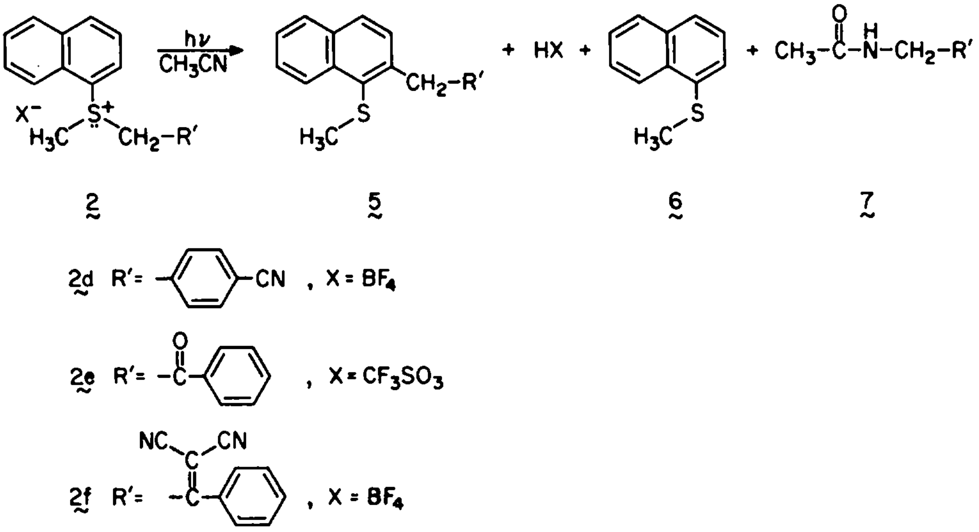


	4	2c	3
Ep (V vs SCE)	-0.79	- 1.23	-1.74

Photochemistry

Photolysis of triarylsulfonium and aryldialkylsulfonium salts normally provides products resulting from homolytic as well as heterolytic cleavage of carbon–sulfur bonds.[8] The product distribution is dependent on counterion[9] and solvent as well as the specific group attached to sulfur.[10]

We have observed that the photolysis of 1-naphthylmethyl substituted-alkyl sulfonium salts provides 1-methylthio-2-substituted-alkyl naphthalenes and acid via a 1,3-sigmatropic rearrangement.[11] Products derived from sulfur–carbon bond cleavage are also observed.[11]



2d R′ = C₆H₄–CN, X = BF_4

2e R′ = –C(=O)–C₆H₅, X = CF_3SO_3

2f R′ = –C(=C(CN)₂)–C₆H₅, X = BF_4

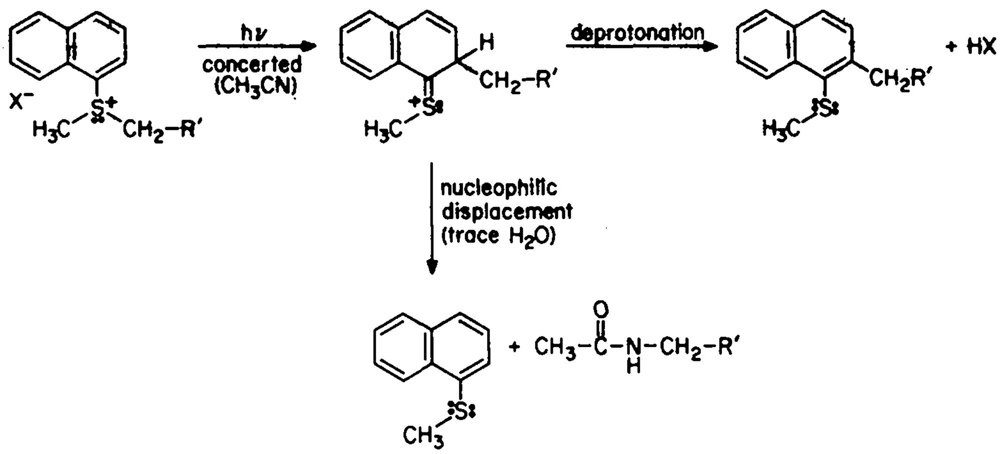
An attempt was made to elucidate the mechanism of rearrangement by means of quenching, sensitization, and product studies. The experimental observations are consistent with a photochemically allowed concerted 1,3-sigmatropic rearrangement involving four electrons or an in-cage bond-cleavage/recombination mechanism as shown below. The naphthylene moiety in **2c** and **e** is absorbing effectively all irradiation beyond 310 nm, whereas the naphthalene chromophore in **2f** absorbs ~63% of the light in this wavelength region and the R group the remaining 37% (Fig. 1).

Triplet quenchers such as molecular oxygen and 1,3-cyclohexadiene do not quench the production of **5**, 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 naphthyl sulfonium salts ($E_T \approx 61$ kcal mol^{-1}) with benzophenone ($E_T = 69$ kcal mol^{-1}) were unsuccessful.

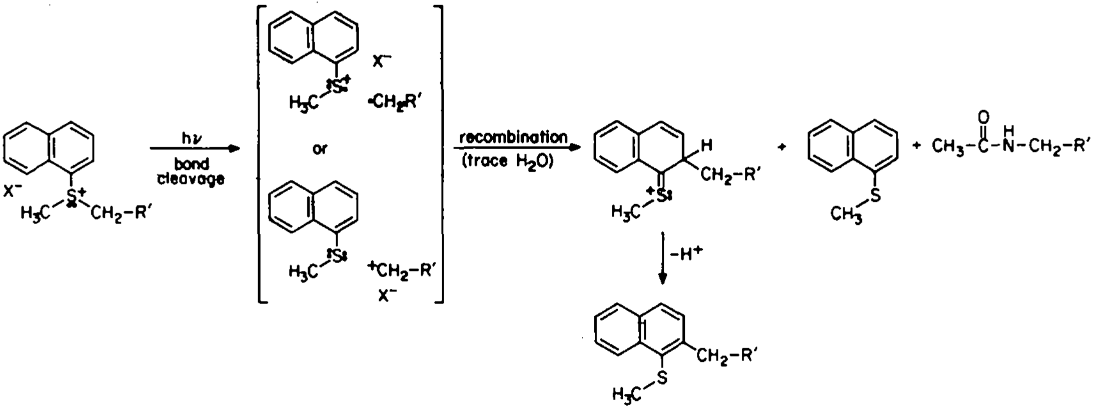
The photoproduct **5f** was isolated in 55% yield from the photolysis of **2f** in acetonitrile distilled from CaH_2 under argon. The structure of **4f** was identified unequivocally from its X-ray crystal structure. Photoproducts **5e** and **c** were isolated in 33% yield and characterized by their ^{1}H-NMR and mass spectra (EIMS). In separate experiments, photoproducts **5c**, **e** and **f** were shown to be stable under the reaction conditions.

A fragmentation–recombination mechanism for the formation of **5** 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 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 nucleo-

CONCERTED MECHANISM



BOND CLEAVAGE - RECOMBINATION MECHANISM



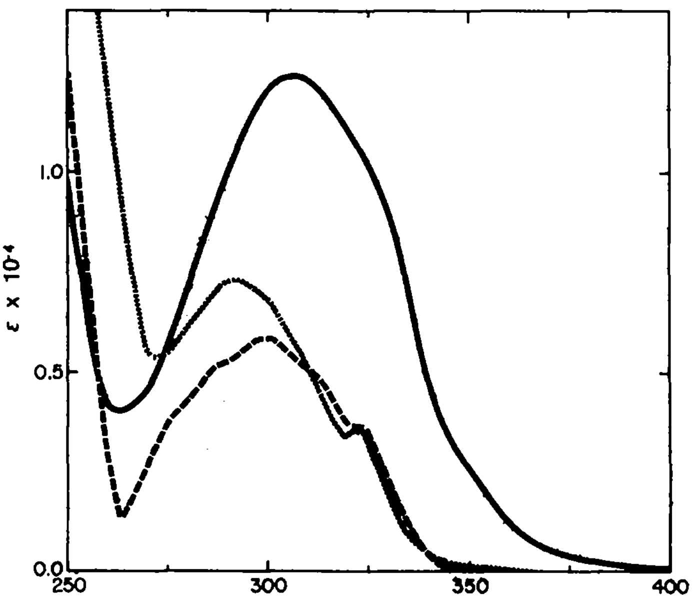


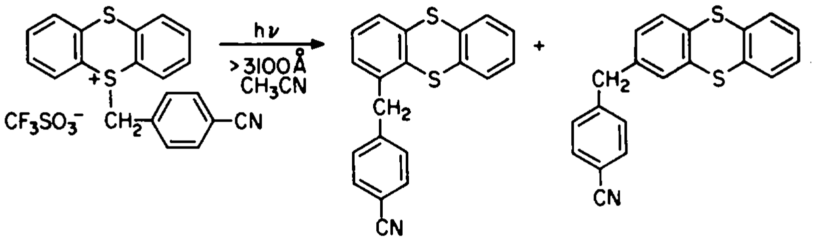
Fig. 1. Absorption spectra of **2d** (----), **2e** (····), and **2f** (——) in acetonitrile.

philic 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 in-cage process. Chemically induced dynamic nuclear polarization (CIDNP) was not observed in either **2** or **5**. The fact that CIDNP was not observed in the starting material or the rearranged product is consistent with both a concerted process[12] and short-lived radicals produced via the singlet state.

The quantum yield for the formation of the rearranged product **5** varied from 0.24 for **5f** to 0.18 for **5e** to 0.10 for **5c**. The quantum yield for the competing carbon–sulfur bond cleavage was ~0.15 and independent of the R groups used thus far. 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 ylid, or from a "photosolvolysis" reaction.

The sulfonium ylid of **2f** was shown not to be an intermediate in the formation of the rearranged product (**5**), as it was thermally stable at 80° for 15 h and gave **6** in quantitative yield when photolyzed in acetonitrile.



8 **9** **10**

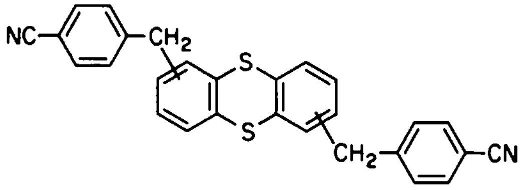
$\phi_{3130\,Å} = 0.06$ $\phi_{3130\,Å} = 0.009$

In a related study, thianthrene-*p*-cyanobenzylsulfonium triflate (**8**) underwent facile photo- and thermal rearrangement in which the *p*-cyanobenzyl group migrated from sulfur to the aryl ring. Compound **8** also participated in a variety of thermally initiated reactions.

The formation of **10** along with **9**, as a result of photolysis of **8**, is consistent with the formation of a thianthrene cation-radical/*p*-cyanobenzyl radical pair, and recombination of the radicals at either sulfur reversibly or at the 1- or 2-position of thianthrene. The product distribution, however, does not reflect the spin densities of the thianthrene cation-radical. Most of the spin density is on sulfur and the position α to sulfur. Extremely low and comparable spin density exists on positions 1 and 2.[6]

Extended photolysis times produced small quantities (1%) of *p*-tolunitrile, presumably from hydrogen atom abstraction by the *p*-cyanobenzyl radical. When the photolysis was run in the presence of 1.0 M benzenethiol as a hydrogen atom source to quench radicals, both rearrangement products were formed in the same ratio as in the absence of the thiol but with a greatly reduced efficiency, owing to the involvement of ground-state chemistry. It appears that the radicals produced react faster, i.e. react in-cage, to form product than diffusion out of cage. Consistent with this theory was the lack of detection of CIDNP effects.[12]

Thermolysis of **8**, as a solid, produces thianthrene cation-radical, as indicated by the appearance of its electronic absorption, and presumably *p*-cyanobenzyl radical at 136°. The solid-state thermal behavior of **8** was investigated by mass spectral analysis. Compound **8** provides species with the same *m/e* as the photoproducts within the probe of the mass spectrometer. The mass spectral study also indicates that as many as two *p*-cyanobenzyl groups become attached to the thianthrene moiety, both to carbon. This information supports the fragmentation–recombination mechanism for the thermal as well as the photoinduced rearrangement.



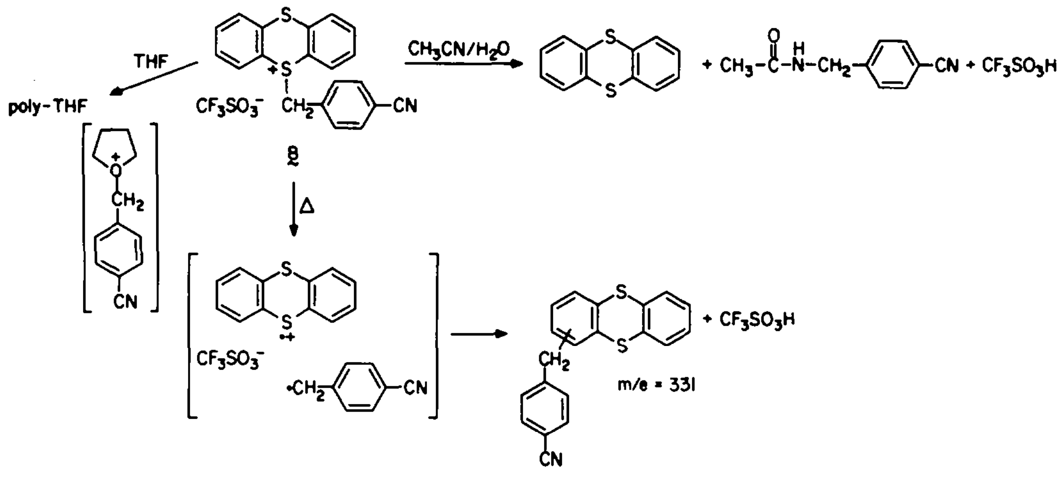
m/e = 446

The thermal chemistry appears to be governed by the fact that the sulfur–benzylic carbon bond is extremely weak and can be readily cleaved both heterolytically and homolytically. The sulfonium salt (**8**) reacts with relatively weak nucleophiles in the dark, e.g. acetonitrile and tetrahydrofuran (THF). In acetonitrile solvent (1.0×10^{-2} M) at 36°, **8** gives thianthrene (**11**) and *p*-cyanobenzylacetamide (**7**) in 58% yield in 18 h. In THF, on the other hand, **8** produces poly-THF with $\bar{M}_n = 52{,}000$, presumably through a benzyloxonium salt. The molecular weight distribution $\bar{M}_w/\bar{M}_n$ for the poly-THF was 1.96.

Photochemical excitation to the σ^* LUMO level and thermal treatment of **8** appear to produce the same intermediates, i.e. cation-radical/radical pair, which allow the observed rearrangement of a *p*-cyanobenzyl group from sulfur to the aromatic ring.

SUMMARY

The reductive cleavage and photochemical behavior of the sulfonium salts studied appear to be a direct consequence of the σ^* character of the LUMO.



Reductive cleavage is a concerted electron-acceptance/bond-cleavage process, whereas photorearrangement appears to be a 1,3-sigmatropic rearrangement via an in-cage fragmentation–recombination process involving cation-radical/radical intermediates from the singlet excited state. Some degree of concertedness cannot be ruled out at this time. The thianthrene sulfonium salt **8** gives the same products from both photochemical excitation and thermal treatment, owing to the σ^* nature of the excited singlet state and the stability of the cation-radical/radical intermediates.

EXPERIMENTAL

Absorption spectra were run on a Perkin–Elmer model 330 spectrophotometer equipped with a model 3600 data station and a model 600 printer. ^{1}H-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.[11] Combustion analyses and mass spectrometry were done by the Analytical Sciences Division of the Kodak Research Laboratories.

Materials. The sulfonium salts, **1** and **2(a–f)**, were synthesized as described.[5]

1-*Naphthylbenzylmethylsulfonium ylid* (**3**). 1-Naphthylbenzylmethylsulfonium tetrafluoroborate (**2c**) (5.0 mmol) dissolved in 50 ml of anhyd THF (freshly distilled from benzophenone ketyl) was added to 20 ml of THF containing 5.0 mmol of NaH. The mixture was stirred at room temp for 15 min and then filtered into a 200 ml round-bottom flask. The THF was flash evaporated at reduced pressure, and the resulting pale yellow solid was extracted with three 50 ml portions of cyclohexane. Evaporation of the cyclohexane gave a pale yellow solid: *m/e* 264; ^{1}H-NMR (CD_3CN): δ 5.10 (s, 1H), 2.92 (s, 3H), 7.0–8.4 (12H, Ar).

1-*Naphthylbenzylmethyloxysulfonium trifluoromethanesulfonate* (**4**). 1-Naphthylbenzylsulfoxide (10 mmol) and methyl iodide (10 mmol) were dissolved in 50 ml of dry CH_2Cl_2. To this soln was added solid silver trifluoromethanesulfonate (10 mmol), and the mixture was stirred for 15 h. The silver iodide was filtered off, and the resulting colorless soln was flash evaporated. Recrystallization from acetonitrile/diethyl ether gave 8.2 mmol of the purified product as colorless crystals: m.p. 115–116°; *m/e* 281; ^{1}H-NMR (CD_3CN): δ 4.10 (s, 3H), 5.30 (q, 2H, $\Delta\nu_{AB} = 18$ Hz), 7.0–8.5 (12H, Ar).

p-Cyanobenzylthianthrenesulfonium trifluoromethanesulfonate (**8**). Thianthrene (10 mmol) and *p*-cyanobenzyl bromide (10 mmol) were dissolved in 50 ml of CH_2Cl_2. To this mixture was added solid silver trifluoromethanesulfonate (10 mmol), and the mixture was stirred at room temp for 3 h. The mixture was filtered (to remove AgBr) into 200 ml of anhyd ether. The crude product that precipitated was collected by suction filtration. Recrystallization from acetonitrile/diethyl ether at ~8° gave the purified product (7.0 mmol) in 70% yield. m.p. 136° (dec); *m/e* 332; ^{1}H-NMR (CD_3CN): δ 4.90 (s, 2H), 7.10–7.90 (12H, Ar).

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