ax H-3), 2.11 (dd, 1, *J* = 17, 2 Hz, eq H-3), 2.40 (dd, 1, *J* = 10, 1 Hz, H-1), 2.4–2.5 (m, 2 H-6, H-7), 3.01 (br s, 1, H-10), 6.1–6.3 (m, 2, H-8, H-9); $^{13}$C NMR δ 27.5 (Me), 31.8 (Me); MS, *m/e* (rel intensity) 204 ($M^+$, 10), 189 (7), 125 (50), 105 (7), 92 (14), 91 (24), 81 (12), 80 (base), 79 (38), 78 (17), 77 (20), 65 (9), 56 (7), 55 (13), 53 (9), 51 (7). (2,4-Dinitrophenyl)hydrzone: mp 191–192 °C.

Anal. Calcd for $C_{20}H_{24}O_4N_4$: C, 62.49; H, 6.29; N, 14.57. Found: C, 62.60; H, 6.33; N, 14.61.

**Ethenohydrobenzosuberone 7**: colorless liquid; IR C=CH 3050 (w), C=O 1703 (s) cm$^{-1}$; $^1$H NMR δ 0.9–1.1 (m, 1, H-6), 1.21 (dddd, 1, *J* = 12, 12, 3, 3 Hz, H-12a), 1.29 (dddd, 1, *J* = 12, 12, 3, 3 Hz, H-13a), 1.40–1.48 (m, 1, H-12b), 1.45–1.52 (m, 1, H-13b), 1.5–1.8 (m, 4, H-4, C-5 Hs, H-6), 1.8–2.0 (m, 1, H-4), 2.14 (ddd, 1, *J* = 11, 2, 2, Hz, H-7), 2.2–2.5 (m, 3, C-3 Hs, H-8), 2.7–2.8 (m, 1, H-11), 2.96 [br d, 1, *J* = 11 Hz (weak W-coupling with H-10), H-1], 6.04 (dd, 1, *J* = 7, 7 Hz, H-9), 6.37 [dd, 1, *J* = 7, 7 Hz (weak W-coupling with H-1), H-10]; MS, *m/e* (rel intensity) 190 ($M^+$, 26), 175 (8), 112 (10), 111 (52), 105 (8), 93 (11), 92 (20), 91 (28), 81 (11), 80 (base), 79 (37), 78 (13), 77 (17), 55 (13). (2,4-Dinitrophenyl)hydrazone: mp 176–177 °C.

Anal. Calcd for $C_{19}H_{22}O_4N_4$: C, 61.61; H, 5.99; N, 15.12. Found: C, 61.45; H, 6.03; N, 15.10.

**Ethenohydrobenzosuberone 8**: colorless liquid; IR C=CH 3040 (w), C=O 1700 (s) cm$^{-1}$; $^1$H NMR δ 1.1–1.3 (m, 3, H-6, H-12a, H-13a), 1.4–1.5 (m, 1, H-13b), 1.5–1.6 (m, 2, H-5, H-7), 1.6–1.7 (m, 1, H-4), 1.7–1.9 (m, 3, H-4, H-6, H-12b), 1.9–2.1 (m, 1, H-5), 2.15 (d, 1, *J* = 9 Hz, H-1), 2.3–2.4 (m, 1, H-8), 2.4–2.6 (m, 2, C-3 Hs), 2.7–2.8 (m, 1, H-11), 6.19 (dd, 1, *J* = 7, 7 Hz, H-9), 6.32 (dd, 1, *J* = 7, 7 Hz, H-10); MS, *m/e* (rel intensity) 190 ($M^+$, 12), 112 (20), 111 (base), 105 (24), 93 (31), 92 (58), 91 (66), 81 (13), 80 (45), 79 (44), 78 (21), 77 (32), 67 (13), 66 (11), 65 (14), 55 (20), 53 (10), 51 (10). (2,4-Dinitrophenyl)hydrazone: mp 227–228 °C.

Anal. Calcd for $C_{19}H_{22}O_4N_4$: C, 61.61; H, 5.99; N, 15.12. Found: C, 61.70; H, 5.96; N, 15.15.

**Epimerization of Ketone 7.** A solution of 40 mg of ketone 7 in 8 mL of absolute ethanol was added to a 0.1 M ethanolic solution (6 mL) of sodium ethoxide under nitrogen and the mixture stirred at 22 °C until equilibrium was reached (monitored by GC analysis). After the usual workup the liquid product was shown by GC analysis to be a 1.2:1 **7**–**8** mixture.

**Acknowledgment.** F.F., L.M., F.P., and A.T. thank the Consiglio Nazionale delle Ricerche and the Ministero della Pubblica Istruzione for financial support of the work in Perugia.

**Registry No.** **1**, 592-57-4; **2**, 930-30-3; **3a**, 930-68-7; **3b**, 1073-13-8; **3c**, 4694-17-1; **4**, 1121-66-0; **5**, 56846-30-1; **5** ((2,4-dinitrophenyl)hydrazone), 117961-13-4; **6a**, 64989-29-3; **6a** ((2,4-dinitrophenyl)hydrazone), 117961-14-5; **6b**, 117961-10-1; **6b** ((2,4-dinitrophenyl)hydrazone), 117961-15-6; **6c**, 117961-11-2; **6c** ((2,4-dinitrophenyl)hydrazone), 117961-16-7; **7**, 117961-12-3; **7** ((2,4-dinitrophenyl)hydrazone), 117961-17-8; **8**, 118016-02-7; **8** ((2,4-dinitrophenyl)hydrazone), 118016-03-8.

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# Intramolecular Photochemical Rearrangement via an In-Cage Cation-Radical/Radical Pair of an Anthrylsulfonium Salt Derivative

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*Received August 26, 1988*

Since the photochemistry of triphenylsulfonium salts was reported by McEwen[1] in 1970, there has been considerable interest in the photochemical behavior of onium salts in general. This interest originates from their ability to photogenerate acid which can be used to initiate cationic polymerization as well as catalyze other chemical transformations. We have previously reported photoinduced rearrangements in a variety of sulfonium[2,3] and arsonium[4] systems. We believe the σ* character of the lowest unoccupied molecular orbital in onium salts is responsible for the observed photochemistry[5] and have found AM1 calculations[6] helpful at predicting photochemical behavior.

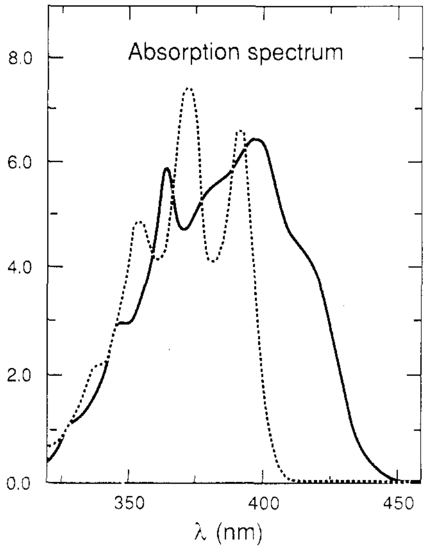

**Figure 1.** Absorption spectra of 9-(methylthio)anthracene (---) and 9-anthrylmethyl(*p*-cyanobenzyl)sulfonium hexafluorophosphate (—) in acetonitrile solvent.

We now report the photochemical behavior of 9-anthrylmethyl(*p*-cyanobenzyl)sulfonium hexafluorophosphate (**1**), which further supports the proposed in-cage radical pair mechanism.

The effect of a sulfonium group, i.e., dimethyl or methyl(*p*-cyanobenzyl), on the anthracene electronic behavior is to shift the short axis in-plane long wavelength $^1L_b$ electronic transition *to the red of the same transition* in anthracene (see Figure 1). There is also considerable broadening of the $^1L_b$ electronic transition relative to the long axis polarized $^1L_a$ electronic transition in **1**. We expect the lowest energy electronic transition in **1** to be $\pi \rightarrow \sigma^*$ and to be of low molecular extinction. We have assigned the ~420-nm band to this transition.

Irradiation of **1** with light of a wavelength greater than 400 nm results in a rapid bleaching of absorption in that spectral region. Five photoisomers of **1** were obtained in 56% yield (0.43 quantum yield) in addition to photosolvolysis products (44% yield, 0.34 quantum yield), which include 9-anthryl methyl sulfide and *N*-(*p*-cyanobenzyl)-acetamide derived from the reaction with acetonitrile. The 10-substituted rearrangement product is predominant, being formed in 38% overall yield.

An attempt was made to rationalize the regioselectivity in terms of spin density within the 9-anthryl methyl sulfide cation-radical and the distance between the benzylic carbon in **1** and reaction sites on the anthracene ring. The intermediate singlet cation-radical/radical pair can, in theory, couple at all sites on the anthracene ring system that has spin density. However, only carbon sites pos-

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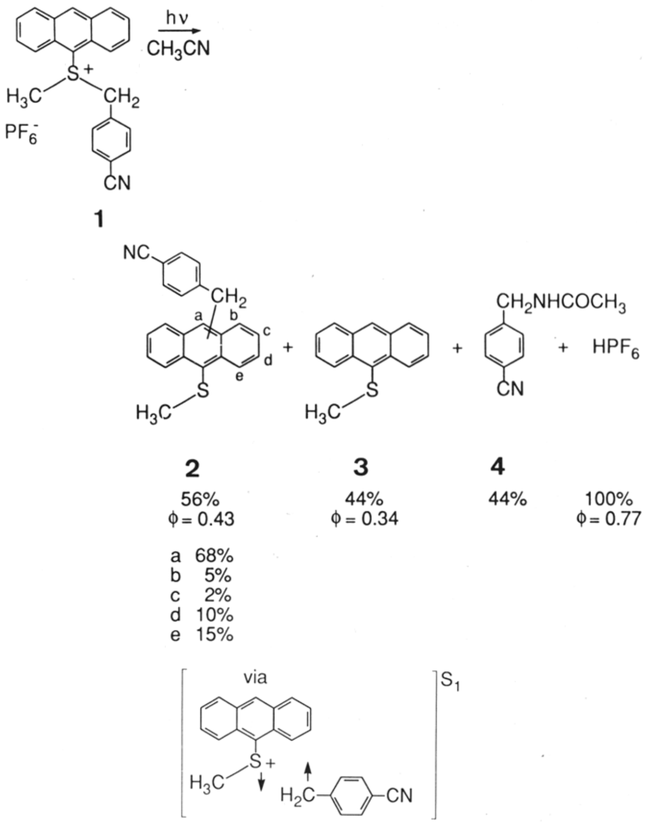
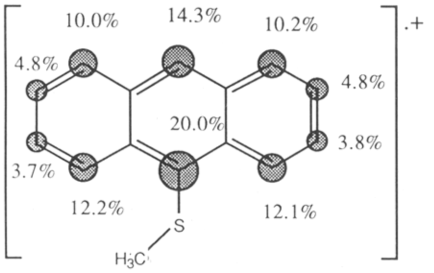
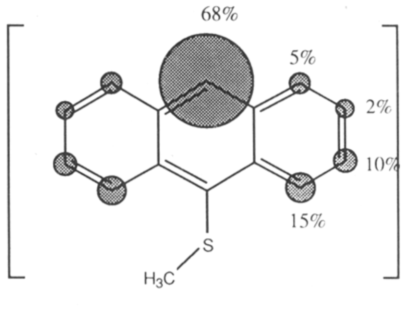


sessing a proton can yield a thermodynamically stable rearrangement product directly by deprotonation. A comparison of the spin density, i.e., probability that an electron is located on a specific atom, for the semioccupied molecular orbital (SOMO) and the product distribution for the rearrangement is provided below.

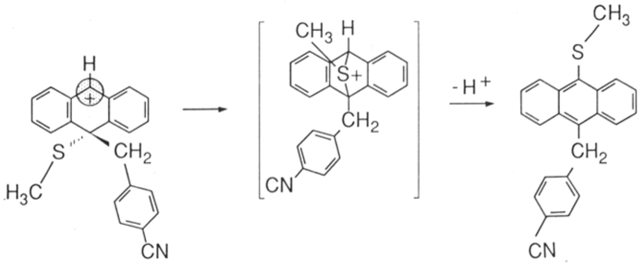


Spin Densities



Product Distribution

This comparison clearly indicates that the preponderance of 10-substituted rearrangement product is considerably more than expected from spin densities alone. It is possible that radical coupling can occur at the 9-position of anthracene to provide an intermediate that cannot readily provide product by deprotonation. It is speculated that the ipso-substituted carbocation intermediate forms a bridged sulfonium intermediate which allows migration of the methylthio group from the 9- to the 10-position of anthracene to provide the 10-substituted rearrangement product in an unexpectedly high percentage.



In summary, 9-anthrylmethyl($p$-cyanobenzyl)sulfonium hexafluorophosphate was observed to photorearrange to products consistent with a singlet in-cage ion-radical/radical pair mechanism. Rearrangement provides five regioisomeric $p$-cyanobenzyl-substituted anthryl methyl sulfides in 56% yield as well as photosolvolysis products and a quantitative yield of $HPF_6$. The major rearrangement product appears to result from migration of the methylthio group from the 9-position to the 10-position of anthracene through an ipso-substituted carbocation intermediate, as well as from $p$-cyanobenzyl radical coupling at the 10-position of 9-(methylthio)anthracene radical cation.

## Experimental Section

Absorption spectra were run on a Perkin-Elmer Model 330 spectrophotometer equipped with a Model 3600 data station and a Model 660 printer. $^1H$ NMR spectra were run on a GE Nicolet 300-MHz spectrometer. The sulfonium salts were photolyzed with an Oriel 200-W Hg–Xe lamp in combination with an Ealing 4050-Å interference filter for quantum efficiency studies. Actinometry was performed by using Aberchrome 540 to determine the flux (photons/s) of the 200-W HG–Xe lamp.[7] Combustion analyses were performed by the Analytical Sciences Division of Eastman Kodak Company.

**9-(Methylthio)anthracene (3).** A solution of 15.0 g (58 mmol) of 9-bromoanthracene in 75 mL of anhydrous tetrahydrofuran (THF) was cooled to −63 °C, and 25 mL of 2.6 M $n$-butyllithium (63 mmol) was added over 45 min. The mixture was stirred for 30 min, and a solution of dimethyl disulfide (5.50 g, 63 mmol) in 15 mL of dry THF was added over 30 min. The mixture was then quenched with 100 mL of 10% HCl. The acidic aqueous–THF layer was extracted with diethyl ether. The ether fractions were combined, washed with 10% NaOH, washed with $H_2O$, dried over $MgSO_4$, and flash evaporated to yield 12.50 g of dark yellow crystals. Recrystallization from cyclohexane yielded pale yellow crystals: mp 63–64.5 °C;[8] mass spectrum (EIMS), $m/e = 224$; $^1H$ NMR ($CD_3CN$) $\delta$ 2.40 (s, 3 H), aromatic 9.1–7.2 (m, 9 H).

**($p$-Cyanobenzyl)methyl-9-anthrylsulfonium Hexafluorophosphate (1).** Silver hexafluorophosphate (8.9 mmol) was added to a solution of 2.0 g (8.9 mmol) of 9-(methylthio)anthracene, 1.75 g (8.9 mmol) of $p$-cyanobenzyl bromide, and 30 mL of methylene chloride and stirred at room temperature for 3 h. The insoluble silver salts were then filtered off, and the volume was reduced to ~3 mL. The product solution was dropped slowly into diethyl ether. The product precipitated from solution, and the ether was decanted, leaving the product as a yellow gum. Recrystallization from acetonitrile–ether yielded 0.28 g of light yellow crystals: mp 132 °C dec; mass spectrum (FD), $m/e = 340$; $^1H$ NMR ($CD_3CN$) $\delta$ 3.70 (s, 3 H), 5.48 (q, 2 H), aromatic 9.1–7.27 (m, 14 H). Anal. Calcd for $C_{23}H_{18}NSPF_6$: C, 56.91; H, 3.74; N, 2.86. Found: C, 57.0; H, 3.8; N, 2.9.

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**Photolysis of 1 and Characterization of Photoproducts.** Compound 1 (200 mg) was dissolved in 50 mL of dry $CH_3CN$ previously distilled from $CaH_2$ and placed in a Pyrex glass vessel. Cyclohexane (50 mL) also was added to the glass vessel, forming two immiscible layers. Only the acetonitrile solution layer was irradiated with an Oriel 200-W Hg-Xe lamp using a Corning 0-52 cut-off filter, i.e., $h\nu > 340$ nm. The solution was continuously purged with argon during the irradiation. The cyclohexane layer (upper layer) was removed periodically and replenished with fresh cyclohexane, thus removing the nonionic photoproducts in order to eliminate secondary photochemistry. The combined cyclohexane extract was flash evaporated and subjected to silica gel chromatography using a Harrison Research chromatotron (Model 7924) to remove 3 from 2. Compound 3 and also compound 4, which remained in the acetonitrile, were characterized by $^{1}$H NMR and comparison to authentic samples that were synthesized independently. The mixture of photoisomers was subjected to careful chromatotron chromatography and was characterized by a combination of $^{1}$H NMR in $CDCl_3$ and mass spectrometry.

**$^{1}$H NMR and Mass Spectral Characterization of Photoproducts 4a–e. 9-(Methylthio)-10-(*p*-cyanobenzyl)anthracene (2a)**: $^{1}$H NMR ($CDCl_3$) $\delta$ 2.44 (s, 3 H), 5.07 (s, 2 H), 9.11 (d, 2 H, Ar), 8.18 (d, 2 H, Ar), 7.20–7.65 (m, 8 H, remaining Ar); mass spectrum (FDMS), $m/e$ = 339.

**4-(*p*-Cyanobenzyl)-9-(methylthio)anthracene (2b)**: $^{1}$H NMR ($CDCl_3$) $\delta$ 2.41 (s, 3 H), 4.63 (s, 2 H), 8.51 (s, 1 H, Ar), 8.89 (d, 2 H, Ar), 7.99 (d, 1 H, Ar), 7.20–7.65 (m, 8 H, remaining Ar); mass spectrum (FDMS), $m/e$ = 339.

**3-(*p*-Cyanobenzyl)-9-(methylthio)anthracene (2c)**: $^{1}$H NMR ($CDCl_3$) $\delta$ 2.39 (s, 3 H), 4.24 (s, 2 H), 8.48 (s, 1 H, Ar), 8.98 (d, 2 H, Ar), 7.95 (d, 2 H, Ar), 7.20–7.65 (m, 7 H, remaining Ar); mass spectrum (FDMS), $m/e$ = 339.

**2-(*p*-Cyanobenzyl)-9-(methylthio)anthracene (2d)**: $^{1}$H NMR ($CDCl_3$) $\delta$ 2.38 (s, 3 H), 4.31 (s, 2 H), 8.43 (s, 1 H, Ar), 8.96 (d, 2 H, Ar), 8.07 (d, 2 H, Ar), 7.20–7.65 (m, 7 H, remaining Ar); mass spectrum (FDMS), $m/e$ = 339.

**1-(*p*-Cyanobenzyl)-9-(methylthio)anthracene (2e)**: $^{1}$H NMR ($CDCl_3$) $\delta$ 1.95 (s, 3 H), 5.26 (s, 2 H), 8.49 (s, 1 H, Ar), 8.76 (d, 1 H, Ar), 8.06 (d, 2 H, Ar), 7.20–7.65 (m, 8 H, remaining Ar); mass spectrum, $m/e$ = 339.

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# A Study of the Scope of the [4 + 2] Cycloaddition Reactions of Unactivated 1,3-Oxazin-6-ones

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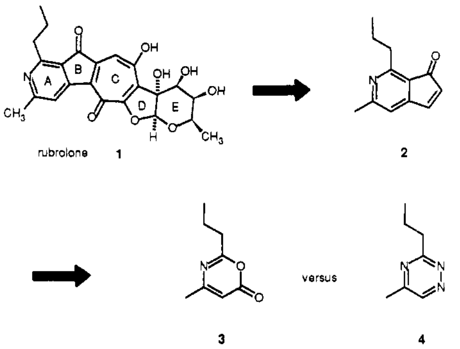
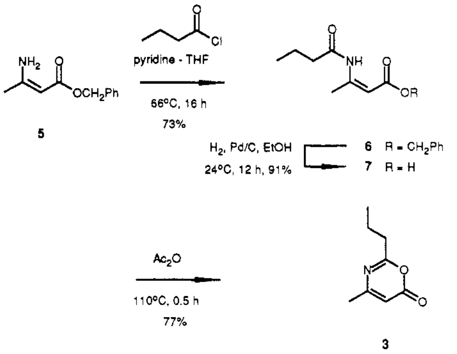
Rubrolone (1),[2] a red tropoloalkaloid[3] isolated from *Streptomyces enchinoruber* and unambiguously identified in a single-crystal X-ray structure determination, bears the unique tautomeric azaleno[2,3-*c*]pyridine-2,5,13-trione aglycon characteristic of a class of structurally related agents.[2] In a continued exploration of the inverse electron demand Diels–Alder reaction of heterocyclic azadienes[4] and in efforts to define the relative and complementary scope of the 1,2,4-triazine[4,5] versus 1,3-oxazin-6-one[6] → pyridine Diels–Alder reactions applicable to the total synthesis of rubrolone, we have examined the potential for unactivated 1,3-oxazin-6-one participation in inverse electron demand Diels–Alder reactions. Herein we detail the preparation of 4-methyl-2-propyl-1,3-oxazin-6-one (3), the scope of its participation in [4 + 2] cycloaddition reactions, and its potential for rubrolone AB ring construction (Scheme I).

**Scheme I**



The preparation of 3 is summarized in eq 1 and is based on the 1,3-oxazin-6-one synthesis introduced by Barker[7] and subsequently improved and developed by Steglich.[6] Acylation of benzyl 3-aminocrotonate employing butyryl chloride followed by clean catalytic hydrogenolysis of the benzyl ester and subsequent dehydration ($Ac_2O$, 110 °C, 0.5 h) provided 3. As noted in the work of Steglich,



(1)

attempts to promote the ester hydrolysis of 6 (3.0 equiv of LiOH, 3:1 THF–$H_2O$, 23 °C) served to preferentially deacylate the activated amide and provided 5. Additional mild dehydrating agents including dicyclohexylcarbodiimide (DCC), 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDCI), and bis(2-oxo-3-oxazolidinyl)phosphinic chloride were successful in promoting the closure of 7 to provide 3 but were found to suffer from isolation procedures that hydrolyze the moisture-sensitive 1,3-oxazin-6-one 3.

The results of the investigation of the scope of the participation of 3 in [4 + 2] cycloaddition reactions are summarized in Table I. Nucleophilic, electron-rich acetylenes (ynamines; Table I, entries 1 and 2) participate in a well-defined regiospecific [4 + 2] cycloaddition reaction

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