on the basis of the integrals of NMR methyl signals at δ 1.5 and 1.3, respectively. The NMR spectrum of the mixture was otherwise identical with that of authentic 3-nitro-5-methyl-2-isoxazoline.

The 3-nitro-5-methyl-2-isozazoline (**2**) was identified by independent synthesis. A mixture of 10.0 g (46.3 mmol) of 1,3-dibromobutane, 6.4 g (93 mmol) of sodium nitrite, 4.2 g (47.2 mmol) of *n*-propyl nitrite, and 60 mL of dimethyl sulfoxide was stirred for 16 h at room temperature. The resulting solution was added to 50 mL of ice water, and the product was extracted with five 20-mL portions of methylene chloride. The methylene chloride solution was washed with two 20-mL portions of water and was dried over sodium sulfate. Distillation gave 2.30 g (42%) of 3-nitro-5-methyl-2-isoxazoline: bp 92–93 °C (1.2 mm); NMR ($CDCl_3$) δ 1.5 (d, 3 H, J = 6 Hz), 3.2 (d of d, 1 H, J = 9, 16 Hz), 3.3 (d of d, 1 H, J = 10, 16 Hz), 4.8–5.4 (m, 1 H); IR 1535, 1365 cm^{-1}.

Anal. Calcd for $C_4H_6N_2O_3$: C, 36.93; H, 4.65; N, 21.53. Found: C, 37.20; H, 4.61; N, 21.45.

3-Nitro-5-(trimethylsilyl)-2-isoxazoline (4). A solution of 1.80 g (18.0 mmol) of vinyltrimethylsilane in 50 mL of methylene chloride was added to 0.96 mmol of freshly prepared tetranitroethylene by the above procedure. Preparative TLC (silica gel, 9:1 hexane–methylene chloride) gave 36.2 mg (20%) of 3-nitro-5-(trimethylsilyl)-2-isoxazoline (**4**): NMR ($CDCl_3$) δ 0.45 (s, 9 H), 3.35 (d of d, 1 H, J = 14, 16 Hz), 3.50 (d of d, 1 H, J = 12, 14 Hz), 4.72 (d of d, 1 H, J = 12, 16 Hz); IR 1535, 1365 (NO_2), 1265 (Me_3Si) cm^{-1}.

Anal. Calcd for $C_6H_{12}N_2O_3Si$: C, 38.29; H, 6.43; N, 14.88. Found: C, 38.56; H, 6.45; N, 14.78.

3-Nitroisoxazole (5). A solution of 0.6 g (23.1 mmol) of acetylene in 50 mL of methylene chloride was added to 0.96 mmol of freshly prepared tetranitroethylene by the above procedure. Preparative TLC (silica gel, 9:1 hexane–methylene chloride) gave 40.6 mg (37%) of 3-nitro-2-isoxazole (**5**): NMR ($CDCl_3$) δ 6.68 (d, 1 H, J = 2 Hz), 8.37 (d, 1 H, J = 2 Hz); IR 1545, 1360 cm^{-1}. The spectra were identical with those of a sample prepared by a reported method.[10]

3-Nitro-4,5-bis(trimethylsilyl)isoxazole (6). A solution of 1.80 g (10.6 mmol) of bis(trimethylsilyl)acetylene in 50 mL of methylene chloride was added to 0.96 mmol of freshly prepared tetranitroethylene. TLC isolation gave 60 mg (24%) of 3-nitro-4,5-bis(trimethylsilyl)isoxazole (**6**): NMR ($CDCl_3$) δ 0.50 (s, 9 H), 0.62 (s, 9 H); IR 1560, 1320 (NO_2), 1260 (Me_3Si) cm^{-1}.

Anal. Calcd for $C_9H_{18}N_2O_3Si_2$: C, 41.84; H, 7.02; N, 10.84. Found: C, 41.58; H, 7.26; N, 11.07.

3-Nitro-5-(trimethylsilyl)isoxazole (7). A solution of 1.80 g (18.4 mmol) of (trimethylsilyl)acetylene in 50 mL of methylene chloride was added to 0.96 mmol of freshly prepared tetranitroethylene by the above procedure. Preparative TLC (silica gel, 9:1 hexane–methylene chloride) gave 41.0 mg (23%) of 3-nitro-5-(trimethylsilyl)isoxazole (**7**): NMR ($CDCl_3$) δ 0.55 (s, 9 H), 6.75 (s, 1 H); IR 1560, 1320 (NO_2), 1265 (Me_2Si) cm^{-1}.

Anal. Calcd for $C_6H_{10}N_2O_3Si$: C, 38.70; H, 5.42; N, 15.04. Found: C, 38.45; H, 5.40; N, 14.89.

Registry No. **1**, 1121-14-8; **2**, 6497-20-7; **3**, 96914-18-0; **4**, 40393-14-4; **5**, 39485-31-9; **6**, 96914-19-1; **7**, 96914-20-4; $(O_2N)_2C{=}C(NO_2)_2$, 13223-78-4; $CH_2{=}CH_2$, 74-85-1; $CH_2{=}CHCH_3$, 115-07-1; $BrCH_2CH_2CH(Br)CH_3$, 107-80-2; $CH_3CH_2CH_2NO_2$, 543-67-9; $CH_2{=}CHSiMe_3$, 754-05-2; $HC{\equiv}CH$, 74-86-2; $Me_3SiC{\equiv}CSiMe_3$, 14630-40-1; $Me_3SiC{\equiv}CH$, 1066-54-2; $(O_2N)_3CC(NO_2)_3$, 918-37-6; $(NC)_2C{=}C(CN)_2$, 670-54-2; EtOH, 64-17-5; $(O_2N)_2CHCOOEt$, 87711-32-8; anthracene, 120-12-7; 11,11,12,12-tetranitro-9,10-dihydro-9,10-ethanoanthracene, 73804-83-8; 11,11,12,12-tetracyano-9,10-dihydro-9,10-ethanoanthracene, 1625-84-9; 5,5,6,6-tetranitro-2-norbornene, 73804-86-1; cyclopentadiene, 542-92-7.

Reactions of Neopentyl Bromide with Nucleophiles by the $S_{RN}1$ Mechanism

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The photostimulated reaction of neopentyl bromide (1) with benzenethiolate ion gave neopentyl phenyl sulfide in high yields. The photostimulated reaction of 1 with benzeneselenate ion gave neopentyl phenyl selenide, dineopentyl selenide, and diphenyl selenide but in low overall yields. The photostimulated reaction of 1 with diphenylphosphide and diphenylarsenide ions gave good yields of the substitution products. These reactions are slow in the dark and the photostimulated reactions are inhibited by radical scavengers such as di-*tert*-butyl nitroxide. All these results suggest that 1 reacts with these nucleophiles by the $S_{RN}1$ mechanism of nucleophilic substitution.

Nucleophilic substitution by the $S_{RN}1$ mechanism is a well established process.[1] This mechanism has been proposed for aliphatic systems with electron-withdrawing groups,[1a,2] unactivated aromatic systems,[1b–d] vinyl halides,[3] perfluoroalkyl iodides,[4] bridgehead halides,[5] and halocyclopropanes.[6]

Except for aliphatic systems bearing electron-withdrawing groups, all the other systems have the same reactivity pattern in S_N1 or S_N2 processes in that they either react slowly or do not react at all with nucleophiles.

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Table I. Photostimulated Reaction of Neopentyl Bromide with Nucleophiles in Liquid Ammonia at -33 °C

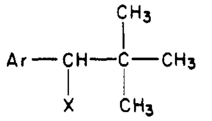
expt	1, 10^2M	nucleophile R^-	nucleophile, 10^2M	irradiation time, min	Br^-	products, % yield t-$BuCH_2R^a$
1	1.43	PhS^-	0.58	90	81	60
2	1.43	PhS^-	0.58	90^b	8	<1
3	1.43	PhS^-	0.58	$90^{b,c}$	5	<1
4	1.43	PhS^-	0.58	90^c	26	24^c
5	0.80	$PhSe^-$	0.64	90	20	9^g
6	0.80	Ph_2P^-	0.64	10	90	76^e
7	0.80	Ph_2P^-	0.64	3	44	42
8	0.80	Ph_2P^-	0.64	3^b	5.5	<1
9	0.80	Ph_2P^-	0.64	3^c	27	23
10	0.80	Ph_2P^-	0.64	$3^{b,f}$	6	<1
11	0.80	Ph_2As^-	0.64	10	90	82^e
12	0.80	Ph_2As^-	0.64	5	91	80^d
13	0.80	Ph_2As^-	0.64	5^b	14.5	4^d

[a] Yield is based on the nucleophile (R^-). [b] Dark reaction. [c] Carried out with 20 mol % of di-*tert*-butyl nitroxide. [d] Quantified by GLC. [e] Isolated. [f] Carried out with 20 mol % of *p*-dinitrobenzene. [g] Quantified by GLC together with dineopentyl selenide (<1%) and diphenyl selenide (<1%).

Neopentyl halides show the tendency previously mentioned. Due to the fact that halogens are on a primary carbon atom neopentyl halides seldom react by the S_N1 mechanism.[7] Because of the steric hindrance of the *tert*-butyl group to backside attack, S_N2 reactions in the neopentyl system are notoriously slow[7] and rearrangement to the *tert*-amyl system is often observed.[8a] Nevertheless, substitution without rearrangement has also been observed.[8]

Evidence for a radical process in the reaction of neopentyl iodide and bromide with certain nucleophiles has been previously presented and consists of the observation of cyclization of an appropriate radical probe and of the trapping of the radical intermediate. The mechanism proposed for these reactions involves radical anions, free radicals and cage collapse of radical pairs. Experimental evidences seem to exclude the $S_{RN}1$ radical chain process.[9,10]

The $S_{RN}1$ mechanism has been proposed at a neopentyl site substituted such as to be also a benzylic carbon. These substituents are the *p*-,[11a] *m*-nitrophenyl,[11b] or 5-nitrothienyl groups.[11c]



$$Ar—\underset{X}{CH}—\overset{CH_3}{\underset{CH_3}{C}}—CH_3$$

Ar = *p* or *m*-nitrophenyl, 5-nitrothienyl

These systems are clearly different from a simple neopentyl bromide.

Taking this into account we decided to investigate the reactions of neopentyl bromide with nucleophiles with regard to the possibility that the $S_{RN}1$ mechanism will operate.

Results

Reactions with Benzenethiolate and Benzeneselenate Ions. All the reactions were carried out in liquid ammonia at -33 °C. The photostimulated reaction of neopentyl bromide (1) with benzenethiolate (2) gave 80% yield of the substitution product neopentyl phenyl sulfide (3) after 90 min of irradiation (eq 1) (Table I, experiment 1). The same reaction when carried out in the dark gave mere traces of the substitution product 3 and 8% yield of halide ions. The percentage of halide ions decreased only to a 5% yield when the dark reaction was performed in presence of 20 mol % of di-*tert*-butyl nitroxide (TBN) a well-known radical scavenger[1b] (Table I, experiments 2 and 3). A significant inhibition was observed when 20 mol % of TBN was present in the photostimulated reaction (Table I, experiment 4).

$$\underset{1}{(CH_3)_3CCH_2Br} + \underset{2}{PhS^-} \xrightarrow[NH_3]{h\nu} \underset{3}{(CH_3)_3CCH_2SPh} + Br^- \qquad (1)$$

The photostimulated reaction of 1 with benzeneselenate ion gave 20% yield of halide ion and 9% yield of substitution product neopentyl phenyl selenide. Dineopentyl selenide and diphenyl selenide were also formed in yields lower than 1% (eq 2) (Table I, experiment 5). The low yield of substitution product could be ascribed to a photodecomposition of the selenide compounds formed. It has been determined that diphenyl selenide decomposes in the presence of an excess of benzeneselenate ion under irradiation to give benzene. The reaction was explained as a photostimulated electron transfer from the nucleophile to diphenyl selenide. The radical anion thus formed decomposed to give mainly benzene (eq 3–5).[12]

$$1 + PhSe^- \xrightarrow[NH_3]{h\nu} (CH_3)_3CCH_2SePh + ((CH_3)_3CCH_2)_2Se + Ph_2Se \qquad (2)$$

$$Ph_2Se + PhSe^- \xrightarrow{h\nu} (Ph_2Se)^{-\cdot} + PhSe\cdot \qquad (3)$$

$$(Ph_2Se)^{-\cdot} \rightarrow Ph\cdot + PhSe^- \qquad (4)$$

$$Ph\cdot \rightarrow \rightarrow PhH \qquad (5)$$

Reaction with Diphenylphosphide and Diphenylarsenide Ions. The photostimulated substitution reactions of 1 with either of these nucleophiles proceeded to completion within 5–10 min of irradiation time (Table I, experiments 6, 7, 11, and 12) (eq 6). When the reactions were carried out in the absence of light the yield of substitution product (neopentyldiphenylphosphine and neopentyldiphenylarsine) decreased to 5.5% and 4% yield,

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respectively (Table I, experiments 8 and 13). At the same time the photostimulated reaction of 1 with diphenylphosphide ion was inhibited by TBN (Table I, experiment 9).

$$1 + Ph_2Z^- \rightarrow (CH_3)_3CCH_2ZPh_2 \tag{6}$$

$$Z = P, As$$

Discussion

The absence of rearrangement products, the important percentage of inhibition observed when the photostimulated reactions were carried out in the presence of radical scavengers, as well as the inhibition observed in the absence of light clearly indicate that in the reaction of neopentyl bromide with the nucleophiles studied, an $S_{RN}1$ process (Scheme I) is more likely than a cage collapse mechanism (Scheme II). It is likely that only the $S_{RN}1$ cycle will show inhibition since Scheme II is a nonchain mechanism. It is known that in reactions where a cage collapse mechanism has been proposed the presence of radical traps do not produce a significant effect on the overall rate of the reactions.[9]

Scheme I. $S_{RN}1$ Mechanism

Propagation Steps

$$1^{-}\cdot \rightarrow (CH_3)_3CCH_2\cdot + Br^- \tag{7}$$

$$(CH_3)_3CCH_2\cdot + Nu^- \rightarrow [(CH_3)_3CCH_2Nu]^{-}\cdot \tag{8}$$

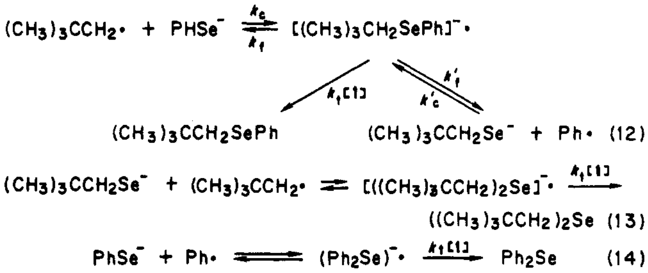
$$[(CH_3)_3CCH_2Nu]^{-}\cdot + 1 \rightarrow (CH_3)_3CCH_2Nu + 1^{-}\cdot \tag{9}$$

Scheme II. Cage Collapse Mechanism

$$1 + Nu^- \rightarrow [((CH_3)_3CCH_2Br)^{-}\cdot Nu\cdot] \tag{10}$$

$$[(CH_3)_3CCH_2\cdot\ Br^- Nu\cdot] \rightarrow (CH_3)_3CCH_2Nu + Br^- \tag{11}$$

The presence of dineopentyl selenide and diphenyl selenide in the photostimulated reaction of 1 with benzeneselenate ion could be ascribed to the frangibility of the radical anion formed in the coupling reaction, these scrambled products have been found in other systems and explained on the same grounds.[13]



The neopentyl phenyl selenide radical anion formed by coupling of neopentyl radical with benzeneselenate ion can revert to the starting radical and nucleophile, it can transfer its extra electron to give the straightforward substitution products neopentyl phenyl selenide, or it can fragment to give phenyl radicals and a new nucleophile neopentaneselenate ion (eq 12). Phenyl radicals thus formed couple with the benzeneselenate ion to give diphenyl selenide (eq 13) while neopentaneselenate ion will give dineopentyl selenide by reaction with neopentyl radicals (eq 14). These scrambled products can only be explained by the $S_{RN}1$ mechanism. The cage collapse mechanism would only give neopentyl phenyl selenide as product.

When the reaction was carried out with benzenethiolate ion the only product observed was the substitution one indicating $k'_{f_{Se}} > k'_{f_S}$.

With the nucleophiles diphenylphosphide and diphenylarsenide ions we did not see product coming from the fragmentation of the radical anion intermediate.

Experimental Section

General Methods. NMR spectra were recorded on a Varian T-60 nuclear magnetic resonance spectrometer. Mass spectral measurements were obtained with a Finningan Model 3300 mass spectrometer. Gas chromatographic analysis were performed on a Varian Aerograph Series 1400 instrument with a flame ionization detector and a column SE 30 on chromosorb P 3% (1.5 m × 3 mm). Irradiation was conducted in a reactor equipped with four 250-W UV lamps emitting maximally at 350 nm (Philips Model HPT, water refrigerated). Column chromatography was performed on MN-Silica Gel 60 (70–270 mesh ASTM) and eluted with petroleum ether in all the cases studied.

Materials. Neopentyl bromide was synthesized by the reaction of neopentyl alcohol (Aldrich) with Ph_3PBr_2 in dimethyl formamide (DMF).[14] Neopentyl bromide and DMF were vacuum distillated and separated by solubilization of DMF in cold water. Traces of DMF (1–2%) were present in the neopentyl bromide employed. Diphenylphosphide and diphenylarsenide ions were prepared from the reaction of triphenylphosphine (Fluka) and triphenylarsine (Aldrich) with 2 equiv of sodium metal in liquid ammonia. The sodium amide formed was neutralized with *tert*-butyl alcohol. Benzenethiolate and benzeneselenate ions were prepared in liquid ammonia from diphenyl disulfide and diphenyl diselenide and 2 equiv of sodium metal. Di-*tert*-butyl nitroxide was kindly provided by Professor James F. Wolfe.

Photostimulated Reaction of Neopentyl Bromide with Nucleophiles. The photostimulated reaction with diphenylphosphide ion is representative. Into a three-necked, 500-mL round-bottom flask equipped with a cold finger condenser charged with solid CO_2 and ethanol, a nitrogen inlet, and a magnetic stirrer were distilled 250 mL of ammonia. Triphenylphosphine (1.59 mmol) and sodium metal (3.2 mmol) were added to form the nucleophile and then *tert*-butyl alcohol (1.6 mmol) was added. Neopentyl bromide (2 mmol) was added to the reaction flask under light stimulation. After the corresponding irradiation time the reaction was quenched by the addition of ammonium nitrate. Ammonia was allowed to evaporate. Water (50 mL) was added to the residue and the mixture extracted with diethyl ether. In the water layer bromide ion was determined potentiometrically.

The ether extract was analyzed by GLC and the substitution product quantified as the oxide derivative by the internal standard method.

In those were the substitution proceeded to a 100% yield the only product isolated was the corresponding substitution one identified as neopentyldiphenylphosphine oxide. This compound was recrystallized from cyclohexane: mp 164–165 °C (lit.[15] mp 165 °C); ^{1}HNMR δ 1.09 (9 H, s), 2.20 (1 H, s), 2.4 (1 H, s), 7.2–7.94 (10 H, m) [lit.[15] δ 1.17 (9 H, s), 2.33 (2 H, s), 7.28–7.93 (10 H, m)]; MS, *m/e* (relative intensity) 273 (0.4), 272 (28.7), 216 (44.8), 215 (100), 202 (1.4), 201 (35.5), 183 (4.6), 155 (1.1), 154 (1.4), 78 (3.4), 77 (16.6), 51 (8.6), 50 (1.1), 47 (13.4). Similar to that reported.[16]

Neopentyl Diphenyl Arsine. Liquid was isolated by column chromatography: MS, *m/e* (relative intensity) 300 (6.4), 229 (10.5), 227 (14.5), 154 (15.1), 153 (12.8), 152 (59.3), 151 (10.3), 91 (11.6), 77 (9.3), 71 (80.2), 65 (4.7), 57 (11.6), 55 (11.6), 51 (14.0), 43 (100), 41 (28.5), 39 (11.6), 29 (19.8), 27 (9.3); ^{1}HNMR δ 1.0 (9 H, s), 2.03 (2 H, s), 6.97–7.55 (10 H, m).

Neopentyl Phenyl Sulfide. Liquid was isolated by column chromatography: MS, *m/e* (relative intensity) 180 (3.1), 153 (6.3), 151 (2.6), 149 (10.9), 137 (8.4), 135 (14.1), 124 (15.6), 123 (23.4), 110 (31.3), 109 (53.1), 99 (11.5), 95 (13.5), 91 (12.5), 85 (9.4), 83 (15.6), 81 (19.3), 77 (26.6), 71 (51), 69 (28), 65 (22.9), 57 (100), 55

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(17.7), 51 (11.5), 45 (11.5), 43 (44.8), 41 (31.3), 39 (12.5), 32 (9.9), 29 (24.0), 27 (50.5); ^{1}H NMR δ 1.0 (9 H, s), 2.78 (2 H, s), 6.98–7.47 (5 H, m). Identical with that reported.[17]

Neopentyl Phenyl Selenide. Liquid was isolated by column chromatography: MS, *m/e* (relative intensity) 230 (2.3), 228 (9.1), 226 (4.6), 224 (2.3), 160 (4.6), 159 (4.6), 157 (18.2), 155 (13.6), 154 (13.6), 151 (4.6), 97 (4.6), 91 (9.1), 78 (22.7), 77 (36.4), 71 (72.7), 69 (18.2), 57 (18.2), 55 (15.9), 51 (9.1), 43 (100), 41 (22.7), 39 (4.6), 29 (9.1), 27 (4.6); ^{1}H NMR δ 1.0 (9 H, s), 3.09 (2 H, s), 7.08–7.6 (5 H, m).

Dineopentyl Selenide. Liquid was isolated by column chromatography: MS, *m/e* (relative intensity) 222 (2.0), 220 (2.0), 85 (7.3), 83 (4.2), 71 (100), 69 (8.3), 67 (3.1), 57 (24.5), 55 (12.0), 53 (4.2), 51 (26), 43 (67.7), 41 (14.6), 39 (4.7), 29 (9.4), 27 (4.2); ^{1}H NMR δ 1.0 (18 H, s), 3.0 (4 H, s).

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Registry No. $(CH_3)_3CCH_2Br$, 630-17-1; NaSPh, 930-69-8; NaSePh, 23974-72-3; Ph_2PNa, 4376-01-6; Ph_2AsNa, 41006-64-8; $(CH_3)_3CCH_2P(O)Ph_2$, 3740-04-3; $Ph_2AsCH_2C(CH_3)_3$, 96503-14-9; $(CH_3)_3CCH_2SPh$, 7210-80-2; $PhSeCH_2C(CH_3)_3$, 96503-15-0; $((CH_3)_3CCH_2)_2Se$, 96532-35-3.

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Ferrocenesulfonyl Azide: Structure and Kinetics of Solution Thermolysis

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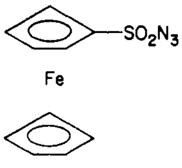
Ferrocenesulfonyl azide (**1**) undergoes thermolysis in 1-chloronaphthalene giving apparent activation parameters: $\Delta H^{*} = 45.1$ kcal/mol and $\Delta S^{*} = 36.6$ eu. Extensive structural studies were carried out in an attempt to determine if the unusual chemistry of the azide has a structural basis. Infrared and Mössbauer spectra are reported which suggest a normal structure. A single-crystal structure determination by X-ray crystallographic methods suggests no configurational basis for the thermolytic behavior. The unusual behavior is attributed to a competing reaction by radical and singlet sulfonylnitrene pathways. Thermolysis in the presence of hydroquinone minimizes the radical contribution to the rate and normal activation parameters are observed: $\Delta H^{*} = 30.8$ kcal/mol and $\Delta S^{*} = -0.42$ eu.

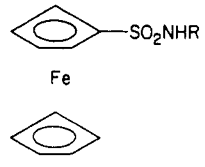
Introduction

Sulfonyl azides undergo thermolysis and photolysis to give intermediate sulfonylnitrenes that may provide useful products on further reaction.[1] When a reactive neighboring n or π donor is present, its participation[2] could, in principle, give products different from those formed in the absence of the neighboring group. Kinetic studies[3] of the thermolysis of sulfonyl azides bearing reactive neighboring groups showed that such azides undergo thermolysis without significant anchimeric assistance.[2] Thus, when a neighboring group participates in these reactions, it does so after rate-determining formation of the intermediate sulfonylnitrene.

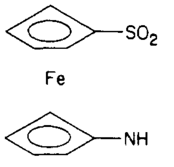
Ferrocenesulfonyl azide (FSA) behaves differently from other sulfonyl azides. While photolysis of sulfonyl azides in hydrocarbon solvents (RH) typically is accompanied by much tar formation, FSA in cyclohexane or benzene is decomposed smoothly by 350-nm light to give ferrocene, ferrocenesulfonamide (**2**), and [2]ferrocenophanethiazine 1,1-dioxide (**3**).[4] The yield of **3** is dependent on solvent, being 13.3% in cyclohexane, 67% in benzene, and zero in dimethyl sulfoxide (Me_2SO) or Me_2SO/benzene.



1=FSA



2, R=H
4, R=alkyl or aryl



3

The bridged compound **3** is not a product of thermolysis of FSA; instead, the main products are ferrocene and the sulfonamides **2** and **4** formed from reaction of the nitrene or nitrenoid with solvent. Normally, sulfonyl azides give the inter- or intramolecular substitution products as the main products of thermolysis in aromatic solvents, with hydrogen abstraction as an important side reaction.[5] With FSA, however, hydrogen abstraction is the major reaction.[4] Similarities between this reaction and copper-catalyzed[6] decomposition of sulfonyl azides led Abramovitch, Azogu,

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