(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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[17] Parham, W. E.; Edwards, L. D. *J. Org. Chem.* 1968, *33*, 4150.

Ferrocenesulfonyl Azide: Structure and Kinetics of Solution Thermolysis

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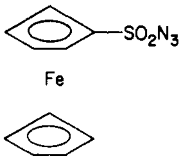
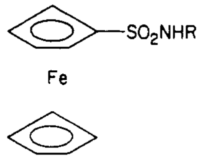
Ferrocenesulfonyl azide (**1**) undergoes thermolysis in 1-chloronaphthalene giving apparent activation parameters: $\Delta H^* = 45.1$ kcal/mol and $\Delta S^* = 36.6$ eu. Extensive structural studies were carried out in an attempt to determine if the unusual chemistry of the azide has a structural 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.

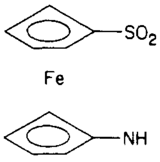
Introduction

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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[1] Abramovitch, R. A.; Kyba, E. P. In "The Chemistry of the Azide Group"; Patai, S., Ed.; Wiley-Interscience: New York, 1971; pp 221–329; Abramovitch, R. A.; Sutherland, R. G. *Fortschr. Chem. Forsch.* 1970, *16*, 1.

[2] Capon, B.; McManus, S. P. "Neighboring Group Participation"; Plenum Press: New York, 1976; Vol 1.

[3] McManus, S. P.; Smith, M. R.; Abramovitch, R. A.; Offor, M. N. *J. Org. Chem.* 1984, *49*, 683.

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0022-3263/85/1950-2742$01.50/0

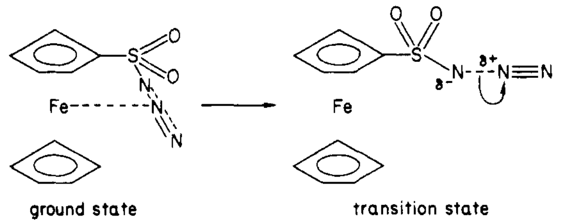
Table I. IR Absorption Bands of Sulfonyl Azides in CCl_4 (0.0005 M)

sulfonyl azide	IR absorptn, cm^{-1}		
	ν_{N_3}	$\nu_{SO_2(as)}$	$\nu_{SO_2(sym)}$
FSA	2104	1365	1185
$PhSO_2N_3$	2127	1380	1180
$PhCH_2SO_2N_3$	2127	1370	1175
$PhCH_2CH_2SO_2N_3$	2132	1360	1175
$PhCH_2CH_2CH_2SO_2N_3$	2137	1355	1183

and Sutherland[4] to propose that thermolysis of FSA leads to a metal–nitrene complex, and this suggestion found support in the results obtained from transition-metal-catalyzed decomposition of sulfonyl azides in which the main product obtained was that of hydrogen abstraction.[7] Azogu and Offor have reported[8] kinetic studies indicating that ferrocenesulfonyl azide, unlike ferrocenyl azide, does not undergo thermolysis with anchimeric assistance. Their reported activation parameters for the thermolysis of FSA, however, were disturbing; $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values were very much higher than those for the extensive series of sulfonyl azides that we have studied.[3] The present article presents our more thorough investigation of the kinetic behavior of FSA on thermolysis. Also, we report the crystal structure of FSA along with its Mössbauer and IR spectra.

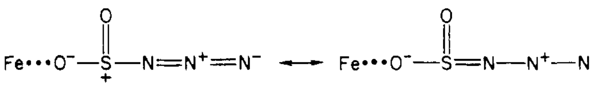
Results and Discussion

The high positive entropy of activation reported[8] for the thermolysis of FSA and confirmed below suggested the possibility that complexation between the iron atom and the azido function might be present in the ground state of the molecule but not in the transition state of the thermolysis (eq 1). To examine this possibility, we carried out a single-crystal X-ray study of 1 as well as determined its Mössbauer and infrared spectra.



(1)

Spectral Studies. Infrared spectra of FSA and of several model sulfonyl azides in carbon tetrachloride solution were measured (Table I). The azide stretching frequency for FSA (2104 cm^{-1}) is >20 cm^{-1} lower than those of the other sulfonyl azides used, which could conceivably be owing to some interaction with the iron which would have the effect of decreasing the N=N bond order. Interaction of the iron with a sulfonyl oxygen atom could have a similar effect:



$$Fe\cdots O^- - \overset{O}{\overset{\|}{\underset{+}{S}}} - N = N^+ = N^- \longleftrightarrow Fe\cdots O^- - \overset{O}{\overset{\|}{S}} = N - N^+ - N$$

To determine whether or not the bonding around the iron atom in FSA was substantially different from ferrocene, the Mössbauer spectrum of FSA was determined. At 80 K an isomer shift $\delta = +0.515 \pm 0.010\ s^{-1}$ and a quadrupole splitting of $\Delta E_Q = 2.38 \pm 0.02$ mm were observed. A comparison of these data with several literature models is given in Table II. Mössbauer spectroscopy has been shown to be particularly useful in probing electronic states of iron in ferrocenyl and ferrocenium compounds.[9–16] While the isomer shift (δ) remains about 0.5 ± 0.1 for both types of compounds, the quadrupole splitting of ferrocenium compounds drops from the normal ferrocenyl value (~2.4) to zero or near zero.[16] Hence a significantly lowered quadrupole splitting value is evidence of a ferrocenium-type structure or single electron transfer from the iron atom to some donor.[16] A smaller effect of a normal substituent is expected as shown by Nesmeyanov and coworkers,[11] who found a linear correlation between ΔE_Q and the inductive constants of ferrocene ring substituents, and concluded that the ring substituents affected the electron density near the iron atom only as they were able to affect the MO's of the sandwich compound. Assuming the substituent effect could only be transmitted through the ring by inductive polarization of the metal–ring bond, the effect should be slight, as the Mössbauer parameters reveal. A considerably different situation exists when the substituent is a carbenium ion center. Such a center requires significant stabilization from the ferrocenyl moiety, and there is evidence that iron may interact directly with this center.[13] This is a bonding interaction rather than single electron transfer. In such cases, for example entry 5 of Table II, there is a measurable increase in the quadrupole splitting value. As can be seen from the comparisons of Table II, the Mössbauer spectrum of FSA reveals none of the above "abnormalities".

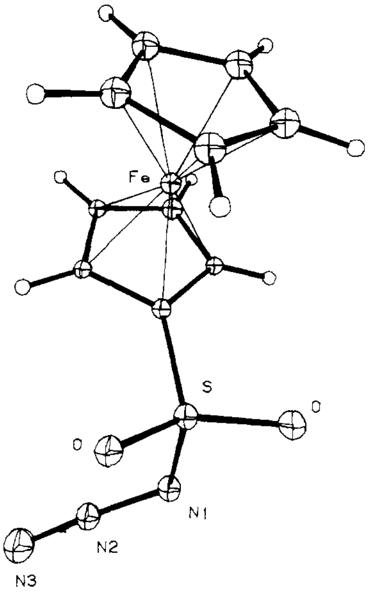


Figure 1. Molecular structure of ferrocenesulfonyl azide with the atoms represented by their 50% probability ellipsoids for thermal motion.

Single-Crystal Structure of FSA. To remove doubts about the structure of FSA, at least in the solid state, an X-ray crystallographic structure determination was per-

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[7] Abramovitch, R. A.; Knaus, G. N.; Uma, V. *J. Am. Chem. Soc.* **1969**, *91*, 7532. Abramovitch, R. A.; Knaus, G. N.; Stowe, R. W. *J. Org. Chem.* **1974**, *39*, 2513.

[8] Azogu, C. I.; Offor, M. N. *J. Organomet. Chem.* **1981**, *222*, 275.

[9] Good, M. L.; Buttone, J.; Foyt, D. *Ann. N.Y. Acad. Sci.* **1974**, *239*, 193. Dunitz, J.; Orgel, L. E.; Rich, A. *Acta Crystallogr.* **1956**, *9*, 373. Bohn, R. K.; Haaland, A. *J. Organomet. Chem.* **1966**, *5*, 470.

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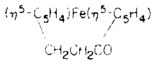
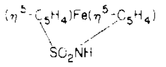
[16] Kramer, J. A.; Herbstein, F. H.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1980**, *102*, 2293.

Table II. Mössbauer Data for Ring-Substituted and/or Bridged Ferrocenes

	Mössbauer data[a]			structural data	
compd	δ,[b] mm/s	ΔE_Q, mm/s	ref	structure	ref
$(\eta^5\text{-}C_5H_5)_2Fe$	0.52	2.41	9	rings are planar and antiparallel; small rotational barrier	10
	0.53	2.40	11		
$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4SO_2N_3)$, FSA	0.52	2.38	*c*	see text	
$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CN)$	0.50	2.32	11	ferrocene structure expected	
$(\eta^5\text{-}C_5H_4CHO)_2Fe$	0.51	2.16	9	structure has eclipsed rings with trans substituents	12
$(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4CH_2^+CF_3SO_3^-)$	0.47	2.67	13	structural studies on a variety of structures similar to this suggest that Fe-CH_2^+ bonding may be present	13
 $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)$, CH_2CH_2CO	0.48	2.20	9	rings are tilted by 8.8° and twisted by 11.8°	14
 $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)$, SO_2NH	0.49	2.33	14	rings almost eclipsed and tilted 23°	14
$(\eta^5\text{-}C_5H_5)_2Fe^+I_3^-$	0.53	0.00	15	ferrocene structure expected	

[a] All Mössbauer data reported are for experiments with absorber temperatures of 77 or 80K. [b] Isomer shift is given relative to NBS standard iron foil absorber. [c] This work.

formed. The crystal data are given in the experimental section, and computed intramolecular distances and angles, final fractional coordinates and isotropic thermal parameters, and a drawing of a unit cell are included as supplementary material. A drawing of a single molecule of FSA is shown in Figure 1.

Analysis of the bond length and angle data reveals that the ferrocene structure is not too different from other known ferrocenyl structures in Table II. The rings are eclipsed with the iron atom slightly offset toward the sulfonyl azide group. The O–S–O angle is slightly wider (124°) that that in the bridged sultam **3** (118°),[14] but the S–O bond lengths are about the same. The S–N bond length in FSA is longer by 0.06 Å than that in sultam **3** indicative of the lower degree of resonance in the S–N group in FSA owing to the important resonance in the azido group. The S–N bond length in other sulfonyl azides is not known, so this finding does not eliminate the possibility of a slight interaction of the Fe with the sulfonyl group (vide supra). The N–N–N group is not perfectly linear, being deformed by about 5–7°. Roberts commented on the low calculated bending energy of this bond and its significance to 1,3-dipolar cycloaddition reactions.[17] Finally, since the azido group is oriented away from the iron atom, there is obviously no intramolecular interaction between these groups in the solid state. The position of the oxygen atoms and the slight offset of the iron toward the SO_2 group suggests a *weak* bonding interaction between the metal d orbitals and either one of the oxygens or with an empty sulfur d orbital. Between pairs of molecules, there are no interactions of less than 2.5 Å.

Kinetic Studies. In view of the inconclusive nature of the above structural studies in providing an explanation for the observed kinetic data[8] we have studied the kinetics of the thermal decomposition of **1** again.

Kinetics of thermolysis of FSA in 1-chloronaphthalene at several temperatures were determined by measuring the volume of nitrogen evolved. Initially, some difficulty in obtaining good first-order kinetics was experienced, and, in some instances, the data could not be fitted to first-order kinetic expressions at all. Since we may have had competing photolysis occurring, greater care was taken to exclude stray light. Despite this, it was observed that these reactions had a variable induction period after which reasonable first-order kinetics were generally followed. The results of the experiments which gave reasonable agreement (<10% difference between rates) in duplicate runs

Table III. First-Order Rate Constants and Activation Parameters for the Thermolysis of Ferrocenesulfonyl Azide in 1-Chloronaphthalene with Light Excluded

run no.	temp[a] °C	10^4k,[b] s^{-1}	ΔH,* kcal/mol	ΔS,* eu
1	119.0	0.767	45.1	36.6
2	123.5	1.42		
3	126.5	1.13		
4	130.0	2.72		
5	137.5	10.6		
6	142.5	22.0		
7	150.0	50.8		
8	154.0	64.7		
9	127.4[c]	4.12		
10	133.5[c]	5.46		
11	142.2[c]	9.78		
12	150.2[c]	33.4		
13	135.4[d]	2.38[e]	30.8	−0.42
14	150.4[d]	9.88		
15	165.3[d]	33.8		

[a] Temperatures are averaged over the run and are ±0.5 °C. [b] Rate constants are averages of duplicate runs. Duplicates agreed within ±10% in each case. [c] Oxygen excluded. [d] Oxygen excluded; with hydroquinone. [e] Single rate determination at this temperature.

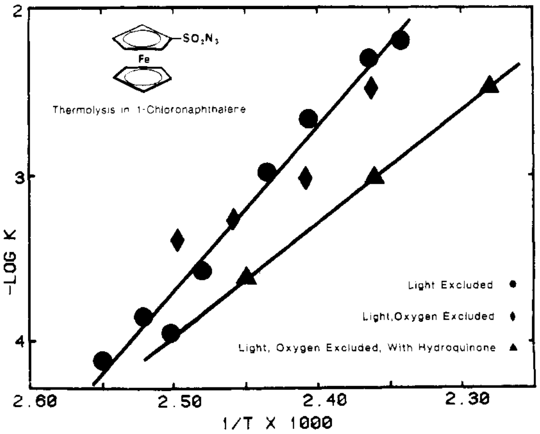


Figure 2. Arrhenius plot for FSA.

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[17] Roberts, J. D. *Chem. Ber.* **1961**, *94*, 273.

(runs 1–8) are shown in Table III, and an Arrhenius plot is shown in Figure 2. The $\Delta H^{\ddagger}$ (45.1 kcal/mol) and $\Delta S^{\ddagger}$ (36.6 eu) values[18] are considerably different from the average values (33.3 kcal/mol and 1.9 eu, respectively) obtained for other sulfonyl azides.[3]

Another possible explanation of the unusual kinetics of FSA may be that competing homolytic S–N cleavage and sulfonylnitrene formation are occurring. Breslow and his co-workers[19] studied the thermolysis of alkyl- and arylsulfonyl azides in mineral oil and in diphenyl ether and observed that, unlike arylsulfonyl azides, alkylsulfonyl azides gave poor first-order plots in mineral oil. For example, they obtained a 16–20% yield of SO_2 from *n*-pentanesulfonyl azide in mineral oil. In diphenyl ether or in the presence of radical scavengers such as hydroquinone, SO_2 production dropped to ca. 3–4% and good first-order plots were obtained. The radical process shown in eq 2–4 was postulated[19] to account for the SO_2 production.

$$R\cdot + C_5H_{11}SO_2N_3 \rightarrow C_5H_{11}SO_2\cdot + RN_3 \tag{2}$$

$$C_5H_{11}SO_2\cdot \rightarrow C_5H_{11}\cdot + SO_2 \tag{3}$$

$$C_5H_{11}\cdot + RH \rightarrow C_5H_{12} + R\cdot \tag{4}$$

Abramovitch and co-workers had already carried out product studies which supported the Breslow mechanism.[20] Thermolysis of mesitylene-2-sulfonyl azide in *n*-dodecane (1 atm) at 150 °C gave 2–4% of mixed dodecanyl azides, among other products (including SO_2). It was suggested that the solvent radical, i.e., R· in eq 2, could arise by reaction of solvent with triplet sulfonylnitrene, e.g., eq 5–8.

$$ArSO_2N_3 \rightarrow ArSO_2\ddot{N}: + N_2 \tag{5}$$

$$Ar = \text{mesityl}$$

$$ArSO_2\ddot{N}: \xrightarrow{ISC} ArSO_2\underset{\cdot}{\dot{N}}: \tag{6}$$

$$ArSO_2\underset{\cdot}{\dot{N}}: + RH \rightarrow ArSO_2NH\cdot + R\cdot \tag{7}$$

$$R\cdot + ArSO_2N_3 \rightarrow RN_3 + ArSO_2\cdot \tag{8}$$

$$ArSO_2\cdot \rightarrow Ar\cdot + SO_2$$

is also supported by the isolation of mesitylene-2-sulfonamide (1–3%). The $ArSO_2NHR$ observed could then arise by two mechanisms: coupling of $ArSO_2\dot{N}H$ and R· and direct insertion of singlet $ArSO_2N$ into R–H. Thus it was suggested that the original source of radical in eq 2 could be the triplet nitrene. Considerable support for eq 2, 3, and 8 comes from a study of the rate of formation and desulfonation of alkyl- and arylsulfonyl radicals.[21,22] On the other hand, Breslow and co-workers[19] found the arylsulfonyl azides did not liberate appreciable amounts of SO_2, even in aliphatic solvents. Our more detailed kinetic studies revealed ferrocenesulfonyl azide to be an atypical aromatic sulfonyl azide.

When FSA was thermolyzed in the absence of light and oxygen (runs 9–12, Table IV), the logarithms of the first-order rate constants at four temperatures fell roughly on the correlation line from the first set of data (runs 1–8), but curvature appeared to be present for the four points alone (see Figure 3). When hydroquinone was added as a free radical scavenger and oxygen was excluded (runs 13–15, Table III and Figure 2), the thermolysis rates were appreciably lower. Also, the activation parameters for these runs were near normal for unassisted decomposition to form the sulfonylnitrene.[3] It is also obvious from an extension of the Arrhenius plot of runs 14 and 15 that the rates at the lower temperatures appear to correlate with those derived in the absence of hydroquinone. This is in agreement with an observation of Breslow et al.[19] that SO_2 production dropped with decreasing temperature. Considering our kinetic results and the fact that ferrocene is a significant product of the thermolysis of FSA in benzene or cyclohexene,[4] we conclude that FSA undergoes the normal unassisted loss of N_2 to form a sulfonylnitrene in competition with a free radical chain mechanism which yields SO_2. Furthermore, the free radical pathway is more prominent at higher thermolysis temperatures. With use of the precedents cited, eq 9–17 adequately explain our results.

$$FcSO_2N_3 \rightarrow FcSO_2\ddot{N}: + N_2 \tag{9}$$

$$Fc = \text{ferrocenyl}$$

$$FcSO_2\ddot{N}: \xrightarrow{ISC} FcSO_2\underset{\cdot}{\dot{N}}: \tag{10}$$

$$FcSO_2\underset{\cdot}{\dot{N}}: + ArH \rightarrow FcSO_2NH\cdot + Ar\cdot \tag{11}$$

$$FcSO_2\ddot{N}: + ArH \rightarrow FcSO_2NHAr \tag{12}$$

$$FcSO_2NH\cdot + ArH \rightarrow \mathbf{2} + Ar\cdot \tag{13}$$

$$FcSO_2NH\cdot + Ar\cdot \rightarrow FcSO_2NHAr \tag{14}$$

$$Ar\cdot + FcSO_2N_3 \rightarrow ArN_3 + FcSO_2\cdot \tag{15}$$

$$FcSO_2\cdot \rightarrow SO_2 + Fc\cdot \xrightarrow{ArH} FcH \tag{16}$$

$$FcSO_2\cdot + ArH \rightarrow Ar\cdot + FcSO_2H \tag{17}$$

$$FcSO_2H \rightarrow FcH + SO_2$$

Conclusions

The results indicate that there is nothing particularly special about the structure of ferrocenesulfonyl azide, at least in the solid state, and that the earlier reported activation parameters for its thermal decomposition in solution are in error, this being caused by competing homolytic and singlet sulfonylnitrene pathways. When the radicals formed are scavanged, normal[3] activation parameters are observed. Therefore, if the previously proposed metal–nitrene complex is an intermediate, it is formed after the rate-determining step for nitrogen loss.

Experimental Section

Kinetics. Rate determinations were made with protection from light on duplicate samples at several temperatures (±0.5 °C) using the modified experimental procedure previously described.[3] Several early runs had radical or light-assisted components; thus, a satisfactory first-order rate constant could not be computed. The data for runs for which rate constants could be computed are shown in Table III.

Infrared and Mössbauer Spectra. Infrared spectra of CCl_4 solutions in 0.5-mm cells were recorded by using a Perkin-Elmer 621 spectrometer. Mössbauer spectra were obtained at 80 K on an Austin Science Associates constant acceleration spectrometer by techniques previously described.[23] The samples were protected from light during the run and were unchanged during the run

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[18] The apparently linear relationship of runs 1–8 (Figure 2) is probably an artifact since oxygen may be slowing but not stopping the radical reaction. A complicating factor was noted by Breslow et al.;[19] SO_2 production increases with temperature.

[19] Breslow, D. S.; Sloan, M. F.; Newberg, N. R.; Renfrow, N. B. *J. Am. Chem. Soc.* **1969**, *91*, 2273.

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[21] Chatgilialoglu, C.; Lunazzi, L.; Ingold, K. U. *J. Org. Chem.* **1983**, *48*, 3588.

[22] A direct S–N bond homolysis, which has been previously suggested,[1] is an alternate for eq 15.

[23] Neele, A. J.; Rawlings, T. J.; McCall, E. B. *Tetrahedron* **1965**, *21*, 1299 and references cited therein.

as determined by infrared spectroscopy.

X-ray Data Collection and Structure Determination. Yellow-orange platelike crystals of ferrocenesulfonyl azide,[4] mp 42–43 °C, were obtained from petroleum ether (bp 30–60 °C). Weissenberg, oscillation and precision photographs showed the crystals to be monoclinic. Space group $P2_1/n$ was indicated by the systematic absence of reflections $0k0$ with k odd and $h0l$ with $h + l$ odd. An appropriate single crystal was mounted on a glass fiber, with the c axis of the crystal slightly inclined to the fiber axis. Final lattice parameters as determined from 12 high-angle reflections carefully centered on an Enral-Nonius CAD-4 are as follows: mol wt 291.12; $D_{\text{calcd}} = 1.699$ g cm^{-3}; space group $P2_1/n$; molecules/unit cell, 8; Mo Kα radiation ($\lambda = 0.71069$ Å); cell constants $a = 5.993$ (4) Å, $b = 35.185$ (6) Å, $c = 10.797$ (6) Å, $p = 92.28$ Å^3; cell volume = 2274.9 Å^3. Intensity data were recorded on the diffractometer in the usual manner.[12] All reflections in one independent quadrant out to $2\theta = 18°$ were measured. Two reference reflections (the 010 and the 104) were monitored every 25 reflections. Severe loss in intensity of the reference reflections (20%) occurred during the course of data collection. The intensity of each reference reflection was linear with respect to time, and the intensity data were corrected for decomposition, Lorentz, and polarization effects, but not for absorption. The MULTAN-74 system of programs was used to locate the two pairs of iron and sulfur atoms in the asymmetric unit. Difference Fourier maps phased on the positions of these atoms revealed the location of the remaining non-hydrogen atoms. The atomic coordinates and isotropic thermal parameters were refined by full-matrix least squares using the SHELX (2) system of programs. The hydrogen atoms were placed at calculated positions 1.00 Å from the bonded carbon atom. The hydrogen atoms were given fixed isotropic thermal parameters of the carbon atom to which it was bonded. In the final stages of refinement the cyclopentadienyl rings were restrained to ideal geometry and refined as rigid groups using the SHELX system. The final reliability index ($R = \sum(|F_o| - |F_c|)/|F_o|$) is 0.078.

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Registry No. FSA, 33291-37-1; $PhSO_2N_3$, 938-10-3; $PhCH_2SO_2N_3$, 20474-37-7; $PhCH_2CH_2SO_2N_3$, 54664-50-5; $PhCH_2CH_2CH_2SO_2N_3$, 80639-68-5.

Supplementary Material Available: Tables IV (intramolecular distances and angles for FSA) and V (fractional coordinates and isothermal parameters for FSA) and a drawing (Figure 3) of the unit cell (5 pages). Ordering information is given on any current masthead page.

Preparation of Isobenzofuran–Aryne Cycloadducts

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A one-pot procedure is described for carrying out the sequence 1,4-elimination of acetal 1 to form isobenzofuran; the formation of 1,3-dilithioisobenzofuran; the conversion to 1,3-bis(trimethylsilyl)isobenzofuran (**5**); the generation of arynes and cycloaddition to **5**. This method allows the use of lithium tetramethylpiperidide induced dehydrohalogenation of haloaromatics to generate the arynes, a procedure which fails with unsilylated isobenzofuran due to the acidity of the 1,3-protons. The protiodesilylation of the cycloadducts occurs with surprising ease, upon treatment with either tetraalkylammonium fluoride/THF or base (potassium *tert*-butoxide or KOH) in Me_2SO, to furnish the novel unsubstituted isobenzofuran–aryne adducts. Three examples are given, utilizing benzyne, 1-naphthalyne, and 3-pyridine. Procedures for subsequent deoxygenation of the cycloadducts to anthracene, benz[*a*]anthracene, and benz[*g*]isoquinoline, respectively, are described. The cycloadduct precursor of benz[*a*]anthracene is shown to undergo highly regioselective reduction on treatment with lithium tri-*tert*-butoxyaluminohydride/triethylborane, with preferential attack occurring at the more accessible 7-position.

The cycloaddition of benzyne with furan constituted one of Wittig's proofs of the formation of this reactive intermediate,[1] generated from an *o*-dihalobenzene. Fieser[2] subsequently used the anthranilic acid route[3] to develop the same reaction on a preparative scale. These two methods of generating benzyne have been used to form adducts with various substituted furans.[4] From the viewpoint of availability of starting materials, the more general procedure for generating arynes is base-induced dehydrohalogenation.[5] A frequently observed side reaction, addition of the base to the benzyne, has been circumvented by the use of bulky lithium dialkylamide bases,[6] e.g., lithium tetramethylpiperidide (LTMP). However, application of this approach with furan failed to give cycloadduct,[6,7] although both 2,5-dimethylfuran and 1,3-diphenylisobenzofuran gave the expected products.[7] Shepard has suggested that the failure to isolate furan cycloadduct may be due to subsequent reaction of this product, and he has pointed out that phenols, which appear to be derived from cycloadducts, have occasionally been observed in these attempts. It is also of interest that the dehydrohalogenation route to some arynes has been successfully used to form cycloadducts of furan when weaker bases were employed.[8]

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[1] Wittig, G.; Pohmer, L. *Angew. Chem.* **1955**, *67*, 348.

[2] Fieser, L. F.; Haddadin, M. J. *Can. J. Chem.* **1965**, *43*, 1599.

[3] Stiles, M.; Miller, R. G. *J. Am. Chem. Soc.* **1960**, *82*, 3802.

[4] For two recent interesting examples, see: (a) Barlett, P. D.; Combs, G. L., Jr. *J. Org. Chem.* **1984**, *49*, 625. (b) LeHoullier, C. S.; Gribble, G. W. *J. Org. Chem.* **1983**, *48*, 2364. The latter illustrates the ortho dihalide approach to 2,3-naphthalyne, and use with both furan and isoindole for the preparation of polycyclic aromatics.

[5] Hoffmann, R. W. "Dehydrobenzene and Cycloalkynes"; Academic Press: New York, 1967.

[6] Olofson, R. W.; Dougherty, C. M. *J. Am. Chem. Soc.* **1973**, *95*, 582.

[7] Shepard, K. L. *Tetrahedron Lett.* **1975**, 3371.

[8] For example: (a) cyclopropabenzynes, $NaNH_2$/*tert*-butyl alcohol (5/1) (Halton, B.; Randall, C. J. *J. Am. Chem. Soc.* **1983**, *105*, 6310), this procedure involves a large excess of base and furan and has also been successfully used with bromobenzene (personal communication from Dr. Halton). (b) 3,5-dimethoxybenzyne, $NaNH_2$ (Cragg, G.M.L.; Giles, R. G. F.; Roos, G. H. P. *J. Chem. Soc., Perkin Trans. 1* **1975**, 1339.