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Thermolysis of Sulfonyl Azides Bearing Nucleophilic Neighboring Groups. A Search for Anchimeric Assistance

Samuel P. McManus* and Maurice R. Smith

Department of Chemistry, The University of Alabama in Huntsville, Huntsville, Alabama 35899

Rudolph A. Abramovitch* and Mercy N. Offor†

Department of Chemistry and Geology, Clemson University, Clemson, South Carolina 29631

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In a search for anchimeric assistance by n- or π-donor neighboring groups in sulfonyl azide decompositions, 25 sulfonyl azides have been prepared and thermolyzed in 1-chloronaphthalene. First-order rate constants at 135 and 165 °C were determined by measuring the volume of nitrogen gas evolved. Rate constants at other temperatures were determined for some of the azides and, in all cases, activation parameters were computed. The structures examined were $Ar(CH_2)_nSO_2N_3$ ($n = 0$–4), $ArXCH_2CH_2SO_2N_3$ (X = O, S, SO_2, NH, and NEt), $PhCH{=}CHSO_2N_3$, and $o\text{-}PhSC_6H_4SO_2N_3$. *n*-Pentanesulfonyl azide was also thermolyzed for comparison. The average activation parameters for the group are $\Delta H^{\ddagger} = 33.3$ kcal/mol, $\Delta S^{\ddagger} = 1.9$ eu, and $\Delta G^{\ddagger} = 32.5$ kcal/mol. Although the activation enthalpy and entropy values varied over a 6 kcal/mol and 14 eu range, respectively, the absolute variations in $\Delta G^{\ddagger}$ at 150 °C were small (±0.3 kcal/mol). Also, no azide has a $\Delta G^{\ddagger}$(150 °C) that is more than three standard deviations from the mean. Hammett plots for the series of arylethanesulfonyl azides and (aryloxy)ethanesulfonyl azides revealed no significant reactivity differences within these series. Therefore, despite product studies that reveal neighboring group participation by some of these neighboring groups, no compelling evidence for anchimeric assistance was found.

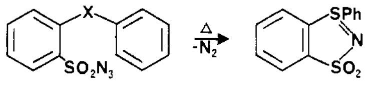
The thermal decomposition of sulfonyl azides in the absence of metals, metal compounds, nucleophiles, or olefins is believed to give singlet nitrene intermediates and nitrogen:

$$RSO_2N_3 \xrightarrow{\Delta} RSO_2\ddot{N}{:} + N_2$$

Evidence for this has come mainly from trapping experiments, kinetic studies, and the nature of the products formed.[1] Thus, the rate of nitrogen evolution from benzenesulfonyl azide derivatives at 127–135 °C is independent of the solvent polarity,[2,3] is first order,[3-5] and shows a negligible substituent effect ($\rho = -0.1$).[4,5]

A radical side reaction accompanies the normal decomposition of some sulfonyl azides under certain conditions, causing a departure from first-order kinetics.[4,6,7] This side reaction may be stopped by the use of radical scavengers.[4,6]

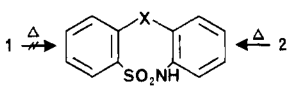
Sulfonylnitrenes have been trapped with a variety of nucleophiles including an intramolecular trapping by the *o*-thio group in 1 to give heterocycle 3.[8] This could either be a Lewis acid–base type reaction between an intermediate sulfonylnitrene and the electron pair donor or an assisted reaction of the adjacent nucleophile with the sulfonyl azide in the rate-determining or prior step. In the case of 1, it was suggested that, since the required decomposition temperature was near the normal one for sulfonyl azides (~130–150 °C), anchimeric assistance[9] by sulfur was absent or that the "assisted" and unassisted decompositions are similar in energy.[8]



1, X = S
2, X = O

3

Aryl participation is also conceivable in the decomposition of 1, but the product of that route (sultam 4) is not observed, although 5 is the only intramolecular trapping product isolated from thermolysis of 2.[8] This would suggest that 3 is the major product from 1 because sulfur is more nucleophilic than the aryl group.



4, X = S
5, X = O

Another example where aryl participation may occur is in the decomposition of β-phenylethanesulfonyl azides. The major product of such reactions under flash vacuum pyrolytic conditions are products of cyclization.[10] While the unassisted formation of a nitrene intermediate was favored by Abramovitch and Holcomb (Scheme I),[10] no evidence was presented by exclude a weakly assisted process.

Although there has been no compelling evidence favoring an anchimeric assistance mechanism for any sulfonyl azide thermolysis, the evidence for participation in the decomposition of some other azides is substantial. Two promi-

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[†] On leave from the Department of Chemistry, University of Ibadan, Ibaden, Nigeria.

(1) Nitrene reviews: Abramovitch, R. A.; Sutherland, R. G. *Fortschr. Chem. Forsch.* **1970**, *16*, 1. Breslow, D. S. In "Nitrenes"; Lwowski, W., Ed.; Wiley-Interscience: New York, 1970. Abramovitch, R. A. In "Organic Reactive Intermediates"; McManus, S. P., Ed.; Academic Press: New York, 1973; Chapter 3. Review on carbenes with neighboring groups: Taylor, K. G. *Tetrahedron* **1982**, *38*, 2751.

(2) Horner, L.; Christmann, A. *Chem. Ber.* **1963**, *96*, 388.

(3) Leffler, J. E.; Tsuno, Y. *J. Org. Chem.* **1963**, *28*, 190.

(4) Breslow, D. S.; Sloan, M. F.; Newburg, N. R.; Renfrow, N. B. *J. Am. Chem. Soc.* **1969**, *91*, 2273.

(5) Takemoto, K.; Fujita, R.; Imoto, M. *Macromol. Chem.* **1968**, *112*, 116.

(6) McManus, S. P.; Knight, J. A.; Meehan, E. J.; Abramovitch, R. A.; Atwood, J. L., Hunter, W. E., submitted for publication.

(7) Radical-induced decomposition may also occur under some conditions; see: Abramovitch, R. A.; Holcomb, W. D. *Chem. Commun.* **1969**, 1298.

(8) Abramovitch, R. A.; Azogu, C. I.; McMaster, I. T.; Vanderpool, D. P. *J. Org. Chem.* **1978**, *43*, 1218. For other examples of intramolecular trapping by nucleophiles, see: Abramovitch, R. A.; Chellathurai, T.; Holcomb, W. D.; McMaster, I. T.; Vanderpool, D. P. *Ibid.* **1977**, *42*, 2920. Abramovitch, R. A.; Chellathurai, T.; McMaster, I. T.; Takaya, T.; Azogu, C. I.; Vanderpool, D. P. *Ibid.* **1977**, *42*, 2914. Martin, J.; Meth-Conn, O.; Suschitzky, H. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2451.

(9) Capon, B.; McManus, S. P. "Neighboring Group Participation"; Plenum Press: New York, 1976; Vol. 1, Chapter 3.

(10) Abramovitch, R. A.; Holcomb, W. D. *J. Am. Chem. Soc.* **1975**, *97*, 676.

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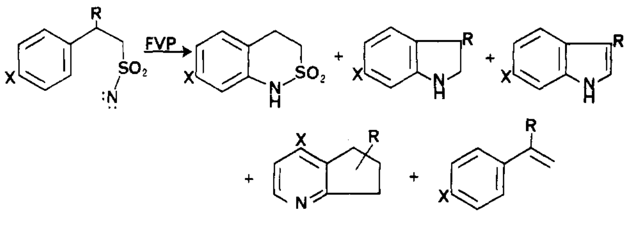
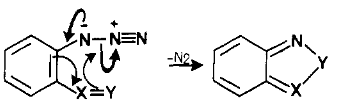
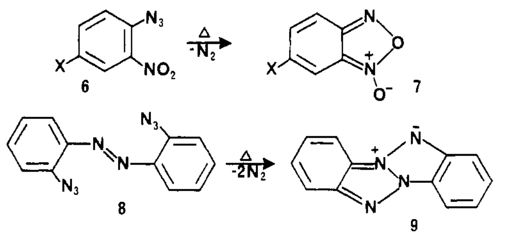
Scheme I



Scheme II

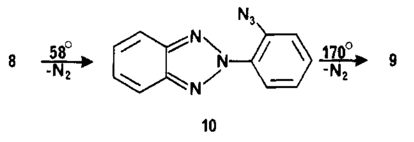


nent such examples are *o*-nitroaryl azides (**6**) and 2,2′-diazidoazobenzene (**8**).



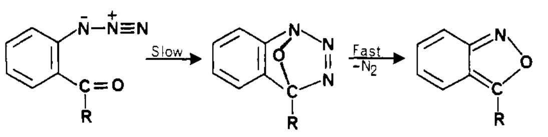
Decomposition of *o*-nitroaryl azides give furoxans (**7**) in good yield.[11] Evidence for participation comes from the lower temperature required for thermolysis (65–80 °C)[11,12] as compared to other substituted aryl azides (140–170 °C)[12] and negative entropies of activation in several solvents.[12] Kinetic involvement of the *o*-nitro group is therefore a reasonable conclusion.

The formation of the tetraazapentalene **9** from the thermolysis of **8** could suggest azo participation in decomposition of both azido groups. A closer look at the reaction, however, refutes this view. One mole of nitrogen is smoothly eliminated at a low temperature (<60 °C), suggesting participation of the azo group, and the benzotriazole **10** is formed.[13] Formation of **9**[13] requires a temperature that is about normal[11] for the decomposition of aromatic azides. Thus, participation in the first azido group decomposition, but not the second, seems to be a reasonable conclusion.



Dyall and Kemp[14] have studied some other neighboring groups in aryl azides and have proposed participation by the general class of neighboring group —X=Y in a pericyclic process as shown in Scheme II. Hall et al.,[15] who studied the pyrolysis of *o*-benzoylphenyl azides, preferred a different mechanism. Their mechanism, an intramolecular version of the well-known 1,3-dipolar addition reaction, is shown in Scheme III.

Scheme III



The present study was undertaken in search of evidence of anchimeric assistance in the thermolysis of sulfonyl azides. Of particular interest were the examples mentioned above for which product studies had revealed participation by a nucleophilic neighboring group.

Results and Discussion

Twenty-five sulfonyl azides have been prepared by standard procedures and thermolyzed in 1-chloronaphthalene at 135 and 165 °C. In some examples additional temperatures were employed in order to establish reliable activation parameters. First-order rate constants were determined by measuring the nitrogen evolved and treating the kinetic data with a least-squares program (LSKIN[16]). The rate constants and activation parameters for azides **1**, **11–13**, **14a–h**, **15a–c**, **16**, **17a–d**, and **18–22** are compiled in Table I.

Pentanesulfonyl azide (**11**) and benzenesulfonyl azide (**12**) have been included in reported kinetic studies in other solvents.[4,17] The values for these two azides in our study are consistent with data from the previous studies.[18] As mentioned above, a radical reaction that induces production of SO_2 has been previously reported upon thermolysis of alkanesulfonyl azides in mineral oil.[4] When the radical process was significant, deviation from first-order kinetics was observed.[4] Because our kinetics remained first order in all examples reported here, we do not believe this pathway to be significant for the systems studied in 1-chloronaphthalene.[19] The rates for **11** at 135 and 165 °C, which are similar to the rates reported for solvents where SO_2 production was minimal, tend to confirm that the radical pathway is not occurring to any significant degree.

The nitrogen volume measurements were made conventionally with gas burets. This experimental method is subject to certain factors that may introduce significant errors. For example, the gaseous volume is sensitive to the ambient temperature, which varies over a wide range in our laboratories. Perhaps the most significant reason for the apparent scatter in our data and the resulting variations in activation parameters is the variable contribution of a free-radical reaction that occurs in these systems.[19] Attempting to remove this as a factor by adding scavengers proved to often add new complications;[19] therefore, we

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[11] Smith, P. A. S.; Brown, B. B. *J. Am. Chem. Soc.* **1951**, *73*, 2435.

[12] L'abbé, G. *Ind. Chem. Belge* **1968**, *33*, 4051. Fagley, T. F.; Sulter, J. R.; Oglukian, R. L. *J. Am. Chem. Soc.* **1956**, *78*, 5567. Patai, S.; Gotshal, Y. *J. Chem. Soc. B* **1968**, 489.

[13] Carboni, R. A.; Castle, J. E. *J. Am. Chem. Soc.* **1962**, *84*, 2453. Also see: Montevecchi, P. C.; Spagnola, P. *J. Org. Chem.* **1982**, *47*, 1996.

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[15] Hall, J. H.; Behr, F. E.; Reed, R. L. *J. Am. Chem. Soc.* **1972**, *94*, 4952. For related studies, see: Abramovitch, R. A.; Vanderpool, D. P. *J. Chem. Soc. Chem. Commun.* **1977**, 18. Belinka, B. A., Jr.; Hassner, A.; Hendler, J. M. *J. Org. Chem.* **1981**, *46*, 631.

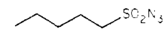
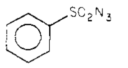
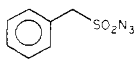
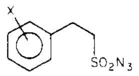
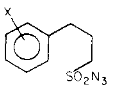
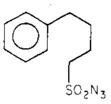
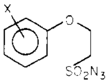
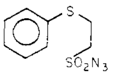
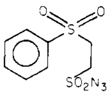
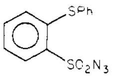
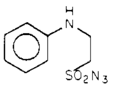
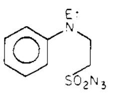
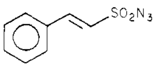
[16] DeTar, D. F. In "Computer Programs for Chemistry"; DeTar, D. F., Ed.; W. A. Benjamin: New York, 1968; pp 126–7.

[17] Balbanov, G. Pp.; Dergunox, Y. I.; Gallperin, V. G. *J. Org. Chem. U.S.S.R.* **1966**, *2*, 1797.

[18] For **12**, reported[17] $\Delta H^\ddagger = 33.9$ kcal/mol and $\Delta S^\ddagger = 5.2$ eu; for **11**, the reported[4] rate at 165 °C is 4.10×10^{-4} s^{-1}.

[19] Breslow et al.[4] found that SO_2 production at 165 °C in aromatic solvents was <5%. Also, our high correlation coefficients, obtained on calculating rate constants, and the absence of an induction period (cf. ref 6) suggest that radical processes were not significant. We decided to evaluate the extent to which the radical process may be contributing to the $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values of the decomposition of **17a** and **18**, both of which are higher than the mean of all compounds studied. Breslow and his co-workers[4] found that radical scavengers minimized the radical reaction for **11** in mineral oil. When we added diphenylamine in a kinetic run of **17a** at 150 °C, there was a slight decrease in the rate constant (from 2.05 to 1.81×10^{-4} s^{-1}), indicating that a radical reaction may be occurring to a limited extent (<~5%). Unlike the result with diphenylamine as inhibitor, hydroquinone caused an increase in the reaction rate. This reaction is under investigation.

Table I. First-Order Rate Constants and Activation Parameters for Thermolysis of Sulfonyl Azides in 1-Chloronaphthalene

compd no.	sulfonyl azide	10^5k(135 °C),[a] s^{-1}	10^4k(165 °C),[a] s^{-1}	$10^5k(t)$,[a] s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$(150 °C),[b] kcal/mol
11		2.38	4.57		34.5	3.4	33.1
12		4.98	9.85		34.5	5.7	32.1
13		4.65	5.66	4.76 (140.0) 11.8 (150.0)	30.2	−5.6	32.6
14							
	a, X = H	3.83	3.64	0.445 (114.0) 3.97 (140.0) 10.8 (150.0)	28.0	−11.2	32.7
	b, X = 4-Me	2.51	4.76		33.8	2.6	32.7
	c, X = 4-Cl	1.72	3.84	3.99 (135.4)[c,d]	31.3	−3.5	32.8
	d, X = 4-MeO	2.31	4.93	18.7 (150.4)[c]	35.6	7.2	32.6
	e, X = 2,6-Me_2	1.83	5.21	0.564 (114.0) 3.41 (140.0)	29.3	−8.2	32.8
	f, X = 2,6-Cl_2	2.39	5.41		36.1	8.2	32.6
	g, X = 3,5-Me_2	2.88	5.15	3.99 (135.4)[c,e]	31.7	−2.1	32.6
	h, X = 3,5-$(MeO)_2$	4.87[f]	6.83[g]		30.7	−3.8	32.2
15							
	a, X = H	2.52	4.76		34.0	3.0	32.7
	b, X = 2-Cl	2.92	4.96		32.7	0.0	32.7
	c, X = 2,4,6-Me_3	2.70	4.31		32.0	−1.7	32.7
16		2.09	5.32		37.5	11.0	32.8
17							
	a, X = H	3.08	7.39	21.0 (150.2)[c]	36.9	10.8	32.3
	b, X = 4-Cl	3.82	7.27		34.1	4.1	32.4
	c, X = 4-MeO	3.70	7.15		34.2	4.4	32.3
	d, X = 3-CF_3	3.84	6.13		32.0	−1.0	32.4
18		4.27	7.01	0.158 (115.0) 4.16 (135.5)[c]	39.8	17.7	32.3
19		4.36	7.01	5.06 (135.3)[c]	31.4	−2.2	32.3
1		9.41	15.3	1.12 (113.5)[c] 29.3 (147.6)[c]	31.2	−1.2	31.7
20		2.66	5.64		35.3	6.5	32.5
21		7.47	9.39		29.1	−6.6	31.9
22		5.83	13.0		35.9	9.5	31.9

[a] Unless otherwise stated, temperatures are ±1.0 °C. Rate constants are the average of two runs that agree within ±10%. [b] Calculated using the relationship $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$. [c] Temperature was controlled to ±0.2 °C. [d] Single run made along side **14g**. [e] Single run made along side **14c**. [f] Temperature was 135.4 ± 0.2 °C. [g] Temperature was 165.2 ± 0.2 °C.

accepted the apparent poor precision since it did not prevent us from achieving our primary objective. We did, however, often employ several temperatures in order to minimize the errors. With use of all the data, the computed mean values of the activation parameters are $\Delta H^{*} = 33.3 \pm 2.9$ kcal/mol and $\Delta S^{*} = 1.9 \pm 6.8$ eu. The ΔG^{*} at the midpoint temperature is less affected by errors and is the best value to use in comparing reactivity of these compounds. For the series, ΔG^{*}(150 °C) = 32.5 ± 0.3 kcal/mol. The similarity of the free energies of activation

Table II. Properties of Some Sulfonyl Azides and Chlorides

azide no.	(% yield, mp (°C), recryst solv)	prepared from (% yield, mp (°C), recryst solv)
13	(100, 53.5-54, aq EtOH)	$PhCH_2SO_2Cl$
14a	(66, oil, bp 70 °C (0.01 mm)	$PhCH_2CH_2SO_2Cl$ (67, 30-32, ligroin)
14b	(79, 63.5-64.5, aq EtOH)	*p*-$MeC_6H_4(CH_2)_2SO_2Cl^a$ (75, 66-66.5, ligroin)
14c	(79, 68-68.5, EtOH)	*p*-$ClC_6H_4(CH_2)_2SO_2Cl^a$ (82, 74-74.5, ligroin)
14d	(58, 42-43, aq EtOH)	*p*-$MeOC_6H_4(CH_2)_2SO_2Cl^a$ (67, 41-41.5, ligroin)
14e	(87, 55.5-56, aq EtOH)	2,6-$Me_2C_6H_3(CH_2)_2SO_2Cl^b$ (85, 71.5-72.5, ligroin)
14f	(98, 59-59.5, aq EtOH)	2,6-$Cl_2C_6H_3(CH_2)_2SO_2Cl^b$ (64, 45-46, ligroin)
14g	(*d*, 49.5-50, petroleum ether)	3,5-$Me_2C_6H_3(CH_2)_2SO_2Cl^c$ (61, 48-49, petroleum ether)
14h	(79, 37.5-38, 3:1 petroleum ether-benzene)	3,5-$(MeO)_2C_6H_3(CH_2)_2SO_2Cl^e$ (68, 57-58, hexane)
16	(47, bp 125 °C (<0.001 mm))	$Ph(CH_2)_4SO_2Cl^f$ (73, 41-41.5, petroleum ether)
18	(85, oil, $n^{20}{}_D$ 1.5725)	$PhS(CH_2)_2SO_2F^g$
19	(42, 145-146, petroleum ether)	$PhSO_2(CH_2)_2SO_2Cl^h$
20[i]	(80, oil, $n^{20}{}_D$ 1.5735)	$PhNH(CH_2)_2SO_2F^g$
21[i]	(92, oil, $n^{20}{}_D$ 1.5422)	$PhNEt(CH_2)_2SO_2Cl^{g,j}$
22	(70, 31.5-33, petroleum ether)	$PhCH{=}CHSO_2Cl^f$

[a] Reference 29. [b] Reference 30. [c] Reference 24. [d] Not recorded. [e] Reference 31. [f] Reference 33. [g] Reference 22. [h] Reference 26. [i] Undergoes retro-Michael on long standing at ambient temperature. [j] Gift of Tennessee Eastman.

suggests that there is no mechanism difference within the series.

To verify the similarity of the rates, two 2-phenylethanesulfonyl azides with apparently different rates at 135 °C were thermolyzed side-by-side. Thus, at 135.4 °C the rates of decomposition of **14c** and **14g** were found to be identical. Since aryl participation in the derivatives would require that each derivative react differently on the basis of the aryl substitution pattern, a Hammett plot was constructed for the applicable derivatives of 2-phenylethanesulfonyl azide. The plot of σ vs. log k(135 °C) for **14a–d** and **14g** gave a very poor correlation ($R = 0.34$) with $\rho = -0.22$. The low correlation coefficient suggests that there is no linear free-energy relationship for the series and, therefore, no anchimeric assistance is present in the transition state for nitrogen loss.[9]

The β-phenoxyethanesulfonyl azides (**17**) could have either n participation by oxygen or π (aryl) participation. A Hammett plot of σ vs. log k (135 °C) for **17a–d** also gives a poor correlation ($R = 0.36$) and a low value of ρ (+0.05). The absence of anchimerism is indicated.[9]

Of the remaining compounds in Table I, the arylalkanesulfonyl azides **12**, **15a–c**, and **16** appear to be normal and hence deserve no special comment. A comment is needed on the remaining compounds even though their reactivity is similar to those derivatives already discussed.

2-(Phenylthio)ethanesulfonyl azide (**18**) has a stronger n donor but a weaker π donor than the analogous oxygen derivative **17a**. The similarity of the rates between **17a** and **18** suggests that no anchimeric assistance occurs.[9] This is further confirmed by data for the sulfone derivative **19**. There is very little difference in the reactivity of these systems. The mechanism of thermolysis must therefore be the same.

2-(Azidosulfonyl)phenyl phenyl sulfide (**1**), one of the key compounds of interest in these studies, reacts faster than any of the other sulfonyl azides at any temperature measured. However, $\Delta G^{\ddagger}$(150 °C) for **1** is only a little more than two standard deviations from the average value of the entire group. Although we have unequivocally established that the higher rates for the decomposition of **1** are real,[20] other explanations for the small rate differences (e.g., differences in ground-state strain or solvation between **1** and comparison models) have not been excluded. Thus, as previously put forth,[8] decomposition by both an assisted and unassisted pathway with similar transition-state barriers may be occurring simultaneously, but the evidence that anchimeric assistance is occurring is only suggestive.

The 2-anilinoethanesulfonyl azides **20** and **21**, like some of the previously discussed compounds, are highly activated for aryl participation and also have a good n-electron pair donor. Compound **20**, however, shows completely normal behavior, while **21** is slightly more reactive than the average.[21] Since a reverse Michael addition could be occurring with this compound,[22] the results for **21** could include a contribution from the thermolysis of ethenesulfonyl azide.

The final compound to be discussed is β-styrenesulfonyl azide (**22**). Although the reactivity of **22** is about normal ($\Delta G^{\ddagger}$ at 150 °C is low by about two standard deviations), its olefinic nature could provide an alternate pathway for reaction. Alkenes are known to undergo a 1,3-dipolar cycloaddition reaction at temperatures lower than those required for sulfonyl azide thermolysis.[1,23] The products are triazolines that decomposte at temperatures lower than do the azides. This pathway seems unlikely in view of the preference of an electron-rich alkene in such reactions.[22]

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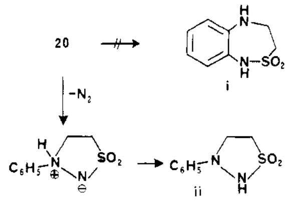
(20) A contribution from a free-radical chain reaction was eliminated by running azide **1** with and without hydroquinone. At 147.6 °C we have calculated that the radical pathway could contribute a maximum of 10% to the rate constant of **1**.

(21) After the completion of this work, an authentic sample of the sultam i, originally thought to be the major product of thermolysis of **20**, was prepared (Abramovitch, R. A.; Thompson, W. M., unpublished results, (1982). The authentic sample of i differed from the product isolated by Smith (Smith, M. R. Ph.D. Dissertation, University of Alabama, 1978) from the thermolysis of **20** in Freon 113. The probable structure of the compound isolated from the solution thermolysis of **20** and of **18** is the product of capture of the intermediate nitrene by the nucleophilic neighboring group, e.g., ii in the case of the thermolysis of **20**.



(22) Krutak, J. J.; Burpitt, R. D.; Moore, W. H.; Hyatt, J. A. *J. Org. Chem.* **1979**, *44*, 3847. Hyatt, J. A., personal communication to S.P.M., Feb 8, 1977.

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In conclusion, the kinetics and activation parameters for thermolysis of a variety of sulfonyl azides bearing reactive neighboring groups fails to reveal significant anchimeric assistance. Instead, with similarity of the rates of decomposition of these compounds is consistent with rate-limiting formation of sulfonylnitrene intermediates.

Experimental Section

General Procedures. All new compounds gave consistent IR and NMR spectra. Satisfactory elemental analysis (±0.3%) were obtained for all compounds that were purified, and mass spectral analysis was employed for key compounds. Melting points are uncorrected. Reagent-grade 1-chloronaphthalene was used.

Sulfonyl azides were prepared by reaction of the corresponding sulfonyl halides with sodium azide in aqueous acetone. The procedures recorded elsewhere for compounds **1**,[8] **11**,[4] **12**,[3] and **14g**[24] are representative. Yields and some properties of some of the azides are recorded in Table II. The details of the preparation of some azides are recorded elsewhere.[34]

Sulfonyl chlorides were generally prepared by reaction of the corresponding sulfonate salt with thionyl chloride or a similar chlorinating agent.[24-26,32] Properties of new sulfonyl chlorides are given in Table II. Some chlorides could not be prepared by this method,[26] and fluorides were used. The fluorides were prepared by a procedure now published.[21]

Kinetics. A 25-mL pear-shaped flask containing a magnetic stirring bar and fitted with a connecting tube with stopcock was used to contain the sulfonyl azide (0.4 g) in 1-chloronaphthalene (15 mL). The flask was connected to a gas buret with Tygon tubing. The buret was filled with water and fitted with a leveling bulb. Temperature was provided by a well-insulated oil bath heated by a thermostated hot plate. Temperatures in the reaction vessel were controlled to ±1 °C (±0.5 °C in later runs[27]). Nitrogen evolution was followed by recording the gas volume in the buret vs. time. Reactions were generally followed 1 half-life or more, and the data were treated to the least-squares method of DeTar,[16] which calculates best fit initial and final volumes and computes first-order rate constants and correlation coefficients for the data set. Typical runs gave $R = 0.99$ or better. Runs with $R < 0.97$ were unacceptable. Duplicate runs were made in all but one exceptional case when two different compounds were compared. The duplicates were required to agree within ±10%, but ±5% was normally achieved. The reproducibility of data was limited by the initial system's[27] poor reproduction of temperatures and because of changes in ambient temperature. Activation parameters were computed by utilizing the rates at two or more temperatures and the Eyring equation.[28]

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Registry No. **1**, 64939-38-4; **11**, 814-56-2; **12**, 938-10-3; **13**, 20474-37-7; **14a**, 54664-50-5; **14b**, 54664-51-6; **14c**, 54664-52-7; **14d**, 76653-00-4; **14e**, 88106-82-5; **14f**, 88106-83-6; **14g**, 70555-51-0; **14h**, 88106-84-7; **15a**, 80639-68-5; **15b**, 88106-85-8; **15c**, 88106-86-9; **16**, 80639-69-6; **17a**, 88106-87-0; **17b**, 88106-88-1; **17c**, 88106-89-2; **17d**, 88106-90-5; **18**, 88106-91-6; **19**, 88106-92-7; **20**, 88106-93-8; **21**, 88106-94-9; **22**, 15814-22-9; i, 88107-06-6; ii, 88107-07-7; $PhCH_2SO_2Cl$, 1939-99-7; $PhCH_2CH_2SO_2Cl$, 4025-71-2; *p*-$MeC_6H_4(CH_2)_2SO_2Cl$, 88106-95-0; *p*-$ClC_6H_4(CH_2)_2SO_2Cl$, 76653-13-9; *p*-$MeOC_6)H_4(CH_2)_2SO_2Cl$, 76653-14-0; 2,6-$Me_2C_6H_3(CH_2)_2SO_2Cl$, 88106-96-1; 2,6-$Cl_2C_6H_3(CH_2)_2SO_2Cl$, 88106-97-2; 3,5-$Me_2C_6H_3(CH_2)_2SO_2Cl$, 88106-98-3; 3,5-$(MeO)_2C_6H_3(CH_2)_2SO_2Cl$, 88106-99-4; $Ph(CH_2)_3SO_2Cl$, 63014-04-0; 2-$ClC_6H_4(CH_2)_3SO_2Cl$, 88107-00-0; 2,4,6-$Me_3C_6H_2(CH_2)_3SO_2Cl$, 88107-01-1; $Ph(CH_2)_4SO_2Cl$, 88107-02-2; $PhO(CH_2)_2SO_2Cl$, 3384-01-8; *p*-$ClC_6H_4O(CH_2)_2SO_2Cl$, 88107-03-3; *p*-$MeOC_6H_4O(CH_2)_2SO_2Cl$, 3383-76-4; *m*-$CF_3C_6H_4O(CH)_2)_2SO_2Cl$, 88107-04-4; $PhS(CH_2)_2SO_2F$, 71517-42-5; $PhSO_2(CH_2)_2SO_2Cl$, 64440-81-9; $PhNH(CH_2)_2SO_2F$, 60353-00-6; $PhNEt(CH_2)_2SO_2Cl$, 88107-05-5; $PhCH{=}CHSO_2Cl$, 4091-26-3; sodium azide, 26628-22-8.

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(27) For the latter runs, an improved system was employed. It consisted of 20 × 150 mm tubes as reaction vessels without stirrers. The bath was more heavily insulated and was heated internally with the heating controlled by using a mercury switch and relay. With this system, temperatures in the reaction vessel were ±0.2 °C. For all runs with this system, the solutions were degassed and saturated with nitrogen prior to the run.

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