from chromatographic analysis.

Gas chromatography was performed with a 6 ft × 1/4 in. Carbowax 20 M on Chromosorb W column. The column temperature was programmed from 110 to 180 °C over a period of 9 min, and the flow rate was 30 mL/min. Under these conditions *cis*-cyclohexane-1,2-diol has a rentention time of 6.8 min. The analysis of the photolysis solution showed no peak at this retention time.

Control experiments showed that the diol survives the workup procedure and that it is not bound to or decomposed by any of the photolysis products. A limit for detectability of cis diol of 2% was established by adding an amount of cis diol corresponding to this yield to cyclohexene, and then subjecting this solution to the oxidative workup described above.

Binaphthyl, naphthol, and the cyclohexene dimers were also resolved by gas chromatography. The binaphthyl and naphthol were identified and quantified by reference to authentic samples. The cyclohexene dimers all showed molecular ions at m/e 162 in the mass spectrum.

High-pressure liquid chromatographic analysis on a C 8/10 column eluting with 28.5% H_2O/71.5% CH_3CN confirmed the identity of the binaphthyl and showed that its formation was not a consequence of thermolysis of some intermediate in the injection port of the gas chromatograph.

Survival of 1,1′-Binaphthyl in Cyclohexene Solution in the Presence of Radicals. A solution of binaphthyl (9.2×10^{-4} M) and *tert*-butyl peroxynaphthoate (1.1×10^{-2} M) in cyclohexene was prepared and deoxygenated. The solution was irradiated through Vycor glass until all of the peroxide was reacted. Gas chromatographic analysis of the reaction mixture after the irradiation showed the concentration of binaphthyl to be 9.1×10^{-4} M.

Acknowledgment. Financial support of this work by the National Science Foundation is gratefully acknowledged.

Registry No. TNB, 6962-78-3; 1-NB, 62981-86-6.

Kinetics of the Thermal Decomposition of Benzenesulfinyl Azide[1]

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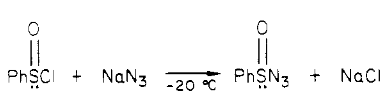
Kinetic studies show that the thermal decomposition of benzenesulfinyl azide (2) follows first-order kinetics in the presence of a variety of substrates. The typical rate constant at 20 °C was 3×10^{-3} s^{-1}. In acetonitrile, $\Delta H^{\ddagger} = 19$ kcal/mol and $\Delta S^{\ddagger} = -4$ eu. These results are consistent with a postulated dipolar sulfinylnitrene intermediate. Thermal decomposition of 2 in the presence of strong nucleophiles, however, was not first order. Thiols and amines caused significant decreases in the rate.

A limited kinetic study of the thermal decomposition of arenesulfinyl azides has been reported as part of a paper on their reactions with sulfoxides.[2] In that report, rate constants were determined only at 0 °C by using cumbersome apparatus at constant atmospheric pressure. The scope of added substrates was limited to sulfoxides. The present report describes results obtained at different temperatures and at constant volume for the reaction of benzenesulfinyl azide (2) with a wide variety of substrates.

Results

Solutions of 0.2 M benzenesulfinyl azide (2) were prepared at −20 °C (±5 °C) from benzenesulfinyl chloride (1)



1 2

$$\mathrm{PhS(=O)Cl} + \mathrm{NaN_3} \xrightarrow{-20\ ^\circ\mathrm{C}} \mathrm{PhS(=O)N_3} + \mathrm{NaCl}$$

in either 1,2-dimethoxyethane (DME) or acetonitrile. Kinetic runs were recorded as increases in pressure at constant volume and temperature by means of a pressure transducer.

Table I lists the first-order rate constants for the decomposition of 2 at 20 °C in DME alone and with 2 and 10 equiv of various added substrates. Good first-order plots were obtained to three half-lives in most cases. A nonlinear least-squares curve-fitting program was used to calculate the rate constants from eq 1, where P_∞ and P_0

$$\ln ((P_\infty - P_0)/(P_\infty - P_x)) = kt \qquad (1)$$

are the pressure related recorder response at infinite and zero time, respectively; P_x is the response at different times during the reaction. The standard deviations for each

Table I. Kinetics of Benzenesulfinyl Azide Decomposition in the Presence of Various Substrates in DME at 20.0 °C

added substrate	mole ratio of azide to substrate[a]	average rate constants,[b] $s^{-1} \times 10^3$	number of runs
		2.62 ± 0.08	5
H_2O	1:2	2.65 ± 0.03	1
H_2O	1:10	2.88 ± 0.03	1
CH_3OH	1:2	2.50 ± 0.08	6
CH_3OH	1:10	2.70 ± 0.17	5
$CH_2{=}CHCH_2OH$	1:2	2.47 ± 0.05	2
$CH_2{=}CHCH_2OH$	1:10	2.67 ± 0.05	3
$CH_3CH_2CH_2CH_2OH$	1:2	2.47 ± 0.07	3
$CH_3CH_2CH_2CH_2OH$	1:10	2.55 ± 0.07	3
$HC{\equiv}CCH_2OH$	1:2	2.48 ± 0.03	4
$CH_2{=}CHCHOHCH_3$	1:2	3.27 ± 0.03	3
$CH_2{=}CHCH_2CO_2H$	1:2	2.37 ± 0.10	5
$CH_3C({=}O)CH_3$	1:2	2.58 ± 0.03	2
$CH_3C({=}O)CH_3$	1:10	2.57 ± 0.03	1
$CH_3S({=}O)CH_3$	1:2	2.47 ± 0.02	1

[a] Initial concentrations of the azide range between 0.2 and 0.3 M. [b] ± standard deviations.

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(1) Abstracted in part from the Masters Thesis of C.N.A., California State University, Long Beach, CA, 1978.

(2) Maricich, T. J.; Hoffman, V. L. *J. Am. Chem. Soc.* 1974, 96, 7770.

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Table II. Rate Constants for the Decomposition of Benzenesulfinyl Azide in Acetonitrile

temp, °C	$k \times 10^3$, s^{-1}	std dev $\times 10^3$
15	1.87	0.21
20	3.03	0.21
25	5.12	0.26
30	9.38	0.15
35	16.6	0.6
40	28.6	1.6

Table III. Activation Parameters for the Decomposition of Benzenesulfinyl Azide in Acetonitrile

parameter	value	corr coef
slope	-9.98×10^3	-0.997
intercept	2.83×10^1	
E_a	19.8 ± 1 kcal/mol	
A	1.9×10^{12} s^{-1}	
T_{av}	300.6 °K	
$\Delta H^{\ddagger\, a}$	19.2 ± 1 kcal/mol	
$\Delta S^{\ddagger\, a}$	-4 ± 1 eu	
$\Delta G^{\ddagger\, a}$	20.5 ± 1 kcal/mol	

[a] Calculated at the average temperature.

point on the curves and for the calculated rate constants were typically less than ±3% and at worst ±6%. The average rate constants for each substrate did not vary significantly from the average for all of the substrates ($2.62 \pm 0.22 \times 10^{-3}$ s^{-1}), the standard deviation being less than ±10%. The rate constant variations for 2 and 10 equiv of added water, methanol, allyl alcohol, 1-butanol, and acetone were less than ±5% standard deviation. No significant trend in the data was evident, such as might reflect substrate polarity differences.

The kinetics of the reaction with added thiols was no longer first-order in nitrogen evolution and the rates were at least an order of magnitude slower. Similar results were observed with primary and secondary amines. These reactions were shown to give thiosulfinates and sulfinamides, respectively, plus hydrazoic acid.[3] The results of these synthetic studies are reported in the following paper.[3]

To investigate aspects of the kinetics for the reaction with thiols, equimolar amounts of hydrazoic acid and phenyl benzenethiosulfinate in acetonitrile were monitored for gas evolution by using a pressure transducer. Evolution ceased after 60 h (50% of theory evolved) with about half of the total amount evolved in 30 h. The results did not follow first-order kinetics.

Activation parameters for the decomposition of benzenesulfinyl azide (**2**) were determined by measuring the rates of nitrogen evolution of 0.12 M solutions of **2** in acetonitrile at 15, 20, 25, 30, 35, and 40 °C. The data were treated in the same way as before for determining the rate constants. The reactions were followed for the first three half-lives. The first and last recorder readings obtained in each run were used as the trial initial zero and infinity values, respectively. The initial estimate of the rate constant was obtained by subtracting the trial initial zero value from the initial infinity value, dividing by two, and adding this to the zero value. This crude estimate of the half-life was multiplied by ln 2 to give an initial rate constant for use in the nonlinear least-squares computer program. Several iterations were required to obtain the best fit of the data points. The calculated infinity values were within 10 percent of the observed values. A typical rate plot is shown in Figure 1. Three runs were made at each temperature. The rate constants used for the calculation of the activation parameters are given in Table II.

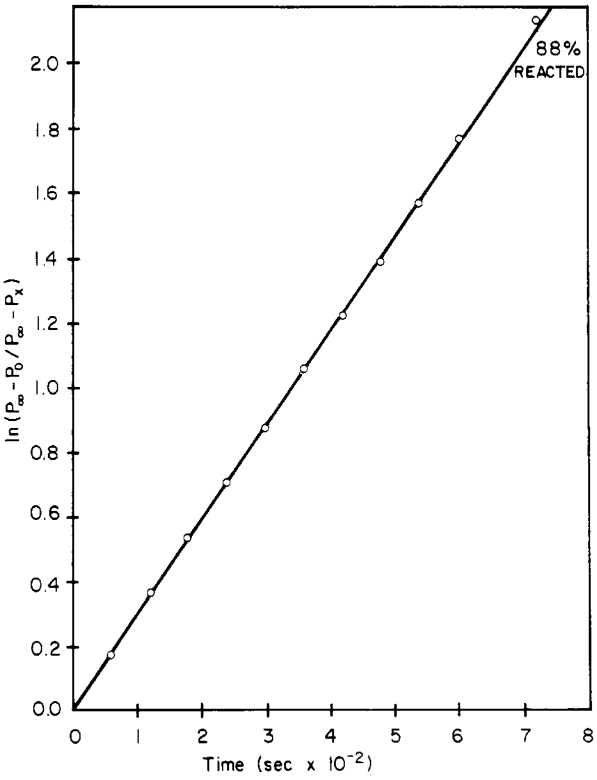


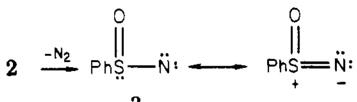
Figure 1. A typical rate plot of the decomposition of benzenesulfinyl azide in acetonitrile. Concentration about 0.11 M, 20 °C.

The activation parameters were calculated by a least-squares program and are summarized in Table III. The correlation coefficient for the best fit of ln k vs. $1/T$ was -0.997. When the Arrhenius equation was used, E_a was calculated from the slope and A (the frequency factor) was calculated from the intercept. Applying the relationships from transition-state theory to this data, the ΔH^*, ΔS^*, and ΔG^* were calculated at the average temperature of 300.6 °K.

Discussion

The results of the kinetic studies of benzenesulfinyl azide (**2**) in DME or acetonitrile with or without added substrates of low nucleophilicity strongly support a free, reactive intermediate. The small variations in rate constants with added water, methanol, allyl alcohol, 1-butanol, propargyl alcohol, 3-buten-2-ol, vinylacetic acid, acetone, and dimethyl sulfoxide rule out any complexation of the azide with these substrates before decomposition. This is dramatically illustrated by the lack of effect of different concentrations of several of the substrates.

A reasonable choice for the structure of the intermediate resulting from loss of nitrogen would be the sulfinyl nitrene (**3**). However, failure to isolate nitrene insertion products[2]



$$2 \xrightarrow{-N_2} \underset{\mathbf{3}}{PhS(=O)-\ddot{N}:} \longleftrightarrow \underset{\mathbf{4}}{Ph\overset{+}{S}(=O)=\overset{-}{N}:}$$

argues against an electrophilic nitrogen atom in the intermediate. All of the products isolated[2] support an electrophilic sulfinyl sulfur atom. Such behavior could be explained by a resonance-stabilized dipolar (nucleophilic) nitrene (**4**). Such a structure is theoretically reasonable, as well, because each atom has a full shell of electrons.

At first glance, the small negative entropy of activation (−4 eu) seems inconsistent with a fragmentation process.

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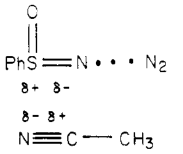
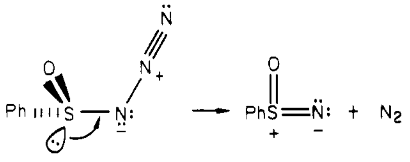
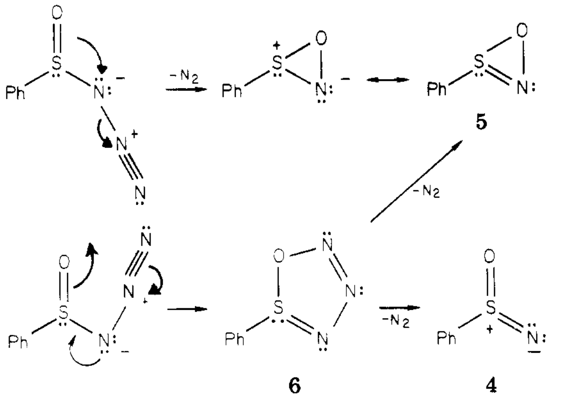
[3] Maricich, T. J.; Angeletakis, C. N. *J. Org. Chem.*, following paper in this issue.

However, comparison of this value with those for benzenesulfonyl azide (+5.2 eu)[4] and *n*-octadecyl azidoformate (+4.7 eu)[5] decomposition indicates that the transition state for the fragmentation of the sulfinyl azide (**2**) is more ordered but not dramatically so.

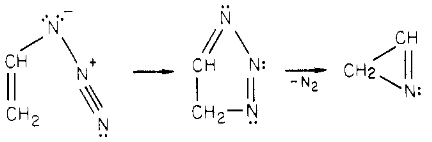
The more negative entropy of activation value for **2** may be the result of one or more of the following reasons. In contrast with the typical, uncharged nitrenes in other cases,[5,6] the dipolar sulfinylnitrene could cause greater order in the transition state in a polar solvent like acetonitrile. A better explanation might be a preferred orientation of the leaving N_2 group in the transition state relative to the sulfur lone pair. This could contribute significantly to the negative $\Delta S^{\ddagger}$ observed. Finally, the transition state could be stabilized by a cyclic interaction (or intermediate) involving the sulfinyl oxygen.



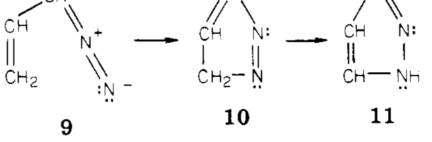




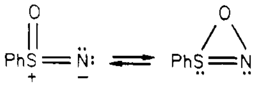
A triazoline intermediate (**7**) related to **6** has been proposed for the decomposition of vinyl azides ($\Delta S^{\ddagger}$ = −3 to +5 eu),[7] which give azirines (**8**) as final products. In a related reaction, diazoprene (**9**) cyclized to 1*H*-pyrazole (**11**) through an intermediate 3*H*-pyrazole (**10**) with similar kinetics ($\Delta S^{\ddagger}$ = −3.6 eu).[8] It is possible, that structures **4** and **5** are in equilibrium together. However, because of ring strain, **5** would probably be less stable than **4**. One might argue against **5** on the basis that similar cyclic structures would be more likely with the more electrophilic nitrenes from azidoformates and sulfonyl azides; however, those azides have positive entropies of activation. Our kinetic results cannot distinguish between these intermediates.



7 **8**



9 **10** **11**



4 **5**

The kinetics of the reaction of **2** with thiols can be explained by the isolation of thiosulfinates and hydrazoic acid, which subsequently decomposed very slowly.[3] Apparently, soft, protic nucleophiles can compete with decomposition by a facile nucleophilic substitution reaction. In an earlier report,[2] triphenylphosphine was found to accelerate the rate of decomposition of **2** significantly, resulting in the formation of phenyl disulfide, triphenylphosphine oxide, and excess nitrogen gas. A new mechanism must be responsible for these results, as well. Contrasting with our results for **2**, Shingaki and co-workers observed that benzenethiol accelerates the rate of thermal decomposition of benzenesulfonyl azide (**12**) considerably.[9] The products are benzenesulfonamide, phenyl disulfide, and nitrogen.

Conclusion

In summary, from the data in Table I, we can say that the reactions of benzenesulfinyl azide (**2**) are zero order in substrate for weaker nucleophiles and the rates are independent of the substrate structure. Thus, the rate-determining step for decomposition of **2** must give nitrogen and a reactive intermediate, which reacts with the substrates to form products. The decrease in entropy observed supports an ordered transition state leading to that intermediate. This, combined with earlier reported product studies,[2] supports a dipolar sulfinylnitrene (**4**) as the intermediate. With the better nucleophiles (thiols and amines), the reaction observed is a direct displacement of hydrazoic acid from the azide.[3]

Experimental Section

Preparation of Benzenesulfinyl Chloride (1). The method of Douglass and Norton[10] was used, but with CH_2Cl_2 as solvent. The solvent and acetyl chloride were removed under vacuum. Fresh solvent was added and removed twice. The residue was subjected to high vacuum for several hours and was purified by vacuum distillation (0.02 mm) in a modified Kontes falling-film molecular still, with refluxing water as the heat source.

Preparation of Benzenesulfinyl Azide (2). In a typical reaction, 1.30 g (0.02 mol) of sodium azide was added to 12 mL of anhydrous acetonitrile in a 3-neck round bottom flask equipped with a drying tube and with constant nitrogen pressure. The flask was thermostated at −20 °C (±5 °C) by using a 2-propanol/dry ice bath. After 5 min 1.61 g (0.01 mol) of benzenesulfinyl chloride dissolved in 10 mL of acetonitrile was added quickly. The mixture was left stirring for 1 h[11] at that temperature and then was filtered

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[4] Balabanov, G. P.; Dergunov, Y. I.; Gal'perin, V. A. *J. Org. Chem. USSR* **1966**, *2*, 1797.

[5] Breslow, D. S.; Prosser, T. J.; Marcantonio, A. F.; Genge, C. A. *J. Am. Chem. Soc.* **1967**, *89*, 2384.

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

[7] L'Abbe, G.; Mathys, G. *J. Org. Chem.* **1974**, *39*, 1778.

[8] Ledwith, A.; Parry, D. *J. Chem. Soc., B* **1967**, 41.

[9] (a) Takebayashi, M.; Shingaki, T. *Sci. Rept., Osaka Univ.* **1959**, *8*, 43; *Chem. Abstr.* **1960**, *54*, 17303f. (b) Shingaki, T. *Sci. Rept., Coll. Gen. Educ., Osaka Univ.* **1963**, *11*, 81; *Chem. Abstr.* **1964**, *60*, 6734a and reference cited therein.

[10] Douglass, I. B.; Norton, R. V. *J. Org. Chem.* **1968**, *33*, 2104.

[11] Previously,[2] 3-h reaction times were used; however, greater amounts of the disproportionation/decomposition products benzenesulfonyl azide and phenyl disulfide were obtained at the longer preparation times. Furthermore, a much simpler apparatus than previously reported[2] can be used, as long as atmospheric contamination is avoided.

with nitrogen pressure through a low-temperature filter containing filter aid. **CAUTION**: Concentrated (neat) samples of 2 are explosive above 0 °C.[2]

Reaction of Phenyl Benzenethiosulfinate with Hydrazoic Acid. A solution of hydrazoic acid in acetonitrile was prepared as follows: 1.30 g (0.02 mol) of sodium azide was suspended in 115 mL of acetonitrile at room temperature. Hydrogen chloride gas was bubbled through the solution. When the reaction was complete, the solution was filtered through a sintered glass funnel with some sodium azide and filter aid. The molarity of this solution was determined by titration with standardized 0.1 M sodium hydroxide to a phenolphthalein end point. The solution was diluted with acetonitrile to the desired value.

A 0.50-mL aliquot of this 0.20 M solution of hydrazoic acid was mixed with 1.00 mL of a 0.10 M solution of phenyl benzenethiosulfinate[12] in acetonitrile. The apparatus for the kinetics measurements of the decomposition of sulfinyl azide was used for the measurement of the rate of gas evolution.

Kinetics of Benzenesulfinyl Azide (2) Decomposition. Kinetics experiments were carried out on two different pressure transducer systems. The results reported in Table I were obtained with a variable resistance transducer, which was less sensitive than the variable reluctance transducer used during the temperature studies. In the first case, larger samples (2.0 mL) of azide solutions (0.2–0.3 M, depending upon amount of added substrates) were used in a larger reaction tube (45 mL, 58.5 mL for entire apparatus). Also, longer azide preparation times (3 h) were used in the first case. No substantive changes in the values of the rate constants were observed by modifying the system; but smaller sample sizes, more continuous rate curves, and better precision were obtained with the new system. The latter system is described in detail.

The kinetics system for gas pressure measurements was a CJDC-6062 variable reluctance type pressure transducer system obtained from C. J. Enterprises, P.O. Box 834, Tarzana, CA. 91356. It consists of a pressure transducer and a carrier demodulator. In this system, pressure of 0–5 psi applied to the transducer is converted to a high-level dc voltage (up to 5 V) that is fed into a recorder. The transducer pressure cavity is extremely small and the volumetric displacement with pressure is negligible. The linearity of the instrument is ±1.2% at full scale.

The kinetics apparatus was standardized periodically. The pressure diaphragm was exposed to atmospheric pressure and the recorder was zeroed with the output voltage adjustment knob being at the null position. The glass tube extending from the diaphragm was then connected to a mercury manometer, a nitrogen pressure source, and a release valve using tygon tubing. A large flask (about 2 L) was also included in the system in order to "cushion" any sudden changes of pressure that might occur. Pressure was applied gradually until a reading of about 25 cm was obtained on the manometer, at which point the recorder was adjusted to read full scale by using the output voltage adjustment knob. The pressure was released by opening the release valve slowly, obtaining readings at different pen deflections at 2–4-cm pressure increments in order to check the linearity of the response of the instrument.

The combined volume of the reaction tube and the glass tube extending from the diaphragm was determined by filling them with absolute ethanol and then measuring the volume of the liquid. Three such determinations were made and the average (12.8 mL) was used to calculate the amount of gas released using the ideal gas law.

In a typical run, 0.50 mL of acetonitrile was placed inside the reaction tube (which was connected to the kinetics apparatus), the magnetic stirrer was adjusted, and 5 min were allowed for vapor pressure stabilization. Then, quickly, 0.50 mL of an approximately 0.22 M solution of benzenesulfinyl azide in acetonitrile, which was kept at −40 °C, was transferred to the reaction tube using a blanket of nitrogen to avoid moisture contamination. The tube was stoppered, springs were put in place, and the rate of pressure change vs. time was obtained on the recorder. The reaction tube was thermostated by a water jacket kept at constant temperature (± 0.1 °C) by circulating the water through a thermostated water bath. Pressure readings were obtained at the following lengths of time after the introduction of the benzenesulfinyl azide solution into the reaction tube: 60 s at 15 and 20 °C, 30 s at 25 and 30 °C, 15 s at 35 °C, and 8 s at 40 °C. This length of time was allowed for temperature equilibration of the azide.

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Registry No. 1, 4972-29-6; 2, 21230-20-6; CH_3OH, 67-56-1; $CH_2{=}CHCH_2OH$, 107-18-6; $CH_3CH_2CH_2CH_2OH$, 71-36-3; $HC{\equiv}CCH_2OH$, 107-19-7; $CH_2{=}CHCHOHCH_3$, 598-32-3; $CH_2{=}CHCH_2CO_2H$, 625-38-7; $CH_3C({=}O)CH_3$, 67-64-1; $CH_3S({=}O)CH_3$, 67-68-5; phenyl benzenethiosulfinate, 1212-08-4; hydrazoic acid, 7782-79-8.

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[12] Backer, H. J.; Kloosterziel, H. *Recl. Trav. Chim. Pays-Bas* **1954**, *73*, 129.

Reaction of Benzenesulfinyl Azide with Thiols and Amines. Preparation of Thiosulfinates and Sulfinamides[1]

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Reaction of benzenesulfinyl azide (1) with thiols at −20 °C gave thiosulfinates and hydrazoic acid. Reaction of 1 with primary and secondary amines gave sulfinamides and hydrazoic acid. The presence of a hydroxyl group in the thiol or amine did not change the course of the reaction. Thus, a thiosulfinate and sulfinamide containing a free hydroxyl group could be prepared. Yields ranging from 41% to 93% were obtained.

Benzenesulfinyl azide (1) normally decomposes with a half-life of about 4 min at 20 °C in 1,2-dimethoxyethane (DME) or acetonitrile.[2,3] The first-order rate is not affected significantly by the added presence of saturated or unsaturated alcohols, ketones, carboxylic acids, sulfoxides, or water.[2,3] Stronger nucleophiles have a more dramatic and varied effect. Triphenylphosphine causes an increase

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[1] Abstracted in part from the Masters Thesis of C.N.A., California State University, Long Beach, CA, 1978.

[2] Maricich, T. J.; Hoffman, V. L. *J. Am. Chem. Soc.* **1974**, *96*, 7770.

[3] Maricich, T. J.; Angeletakis, C. N.; Mjanger, R. *J. Org. Chem.*, preceding paper in this issue.

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