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.

Acknowledgment. Financial support for this research was provided in part by a grant from the National Cancer Institute (CA-18838). We would also like to thank Drs. J. Hutchins and J. L. Jensen for assistance with processing the kinetic data.

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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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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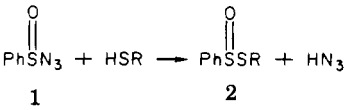
Table I. Reaction of Benzenesulfinyl Azide (1) with Thiols



1 2

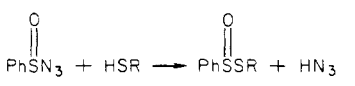
compd	R	% yield[a] thiosulfinate	% yield hydrazoic acid	melting point (reported), °C
2a	C_6H_5	93	74	68.5-69.5 (69-70)[b]
2b	$C_6H_5CH_2$	72	55	
2c	$CH_3CH_2CH_2$	81	62	
2d	$(CH_3)_2CH$	41	c	
2e	$(CH_3)_3C$	83	89	50-51 (51-53)[b]
2f	$HOCH_2CH_2$	76	100	
2g	$(CH_3)_3CCH_2$	63	d	

[a] Chromatographic yields reported. [b] Reference 7. [c] Hydrazoic acid was removed with saturated sodium bicarbonate solution. [d] Yield not obtained due to interference of minor amounts of thiol in the distillate.

in the rate of nitrogen evolution by at least an order of magnitude,[2] while thiols and amines cause a corresponding decrease in rate.[3] In neither case is the rate first order. The results with thiols and amines suggested that some intermediates might be isolated. This paper reports the results of those studies.

Results

Reaction of 1 with Thiols. Addition of a thiol to 1 at −20 °C afforded alkyl and aryl benzenethiosulfinates (2) plus hydrazoic acid (eq 1). In most cases, the vacuum



1 2 (1)

distillate from the reaction mixture contained the solvent and hydrazoic acid, as identified by its IR bands.[4] These solutions were titrated with standardized base to determine the yield of hydrazoic acid. The reaction concentrates gave crude samples of thiosulfinates as evidenced by TLC and NMR[5] and IR[6] spectroscopy. The thiosulfinate S=O band at 1100 cm^{-1} was the strongest band in the IR spectrum of each sample. Very little sulfonyl absorption was present to indicate formation of side products. The products were purified by chromatography and recrystallized when possible. The purity of chromatographed products was determined by analytical high-performance liquid chromatography (HPLC) and was always found to be greater than 95%. Results are summarized in Table I. Other results suggest that eq 1 may be an equilibrium reaction. The lowest boiling substrate, 2-propanethiol (bp 53 °C), behaved anomalously. Upon evaporation of the solvent in this case, the concentrate decomposed vigorously (typical of neat 1) and the distillate contained a great amount of unchanged thiol. Neutralization of the hydrazoic acid with sodium bicarbonate before evaporating the solvent allowed the isolation of **2d**. This also resulted in the formation of benzenesulfonamide (a decomposition product of 1 in water) as a byproduct.[2]

Chromatography of the thiosulfinates on silica gel at room temperature was always accompanied by some decomposition. Attempted purification by molecular distillation (40–45 °C, 0.02 mm) of the alkyl benzenethiosulfinates resulted in some decomposition, giving a small amount of phenyl benzenethiosulfinate (**2a**)[7] and some other decomposition products, as evidenced by comparison of retention times from HPLC. When preparative HPLC on silica gel was used, it was found that decomposition on the column was kept at a minimum when eluents giving shorter retention times were used. 2-Hydroxyethyl benzenethiosulfinate (**2f**) was the most stable thiosulfinate under these conditions, affording a sample for elemental analysis.

The purification step was carried out immediately after the reaction, since the impure thiosulfinates are quite unstable at room temperature. Significant decomposition was apparent after storing at room temperature for 30 h, with **2a** as one of the main decomposition products. Slower decomposition occurred when impure thiosulfinates were stored in a freezer at −20 °C.

Benzyl benzenethiosulfinate (**2b**) was particularly labile. It disproportionates faster than the other alkyl benzenethiosulfinates. Dibenzyl disulfide was found among the decomposition products.

The method of Block and O'Connor[8] was used to prepare two unsymmetrical thiosulfinates for comparison with the azide method. Benzyl benzenethiosulfinate (**2b**) and *n*-propyl benzenethiosulfinate (**2c**) were obtained in 56% and 63% yield, respectively, after purification by preparative layer chromatography on silica gel.

Reaction of 1 with Amines. Equimolar amounts of 1 and an amine were mixed at −20 °C in acetonitrile and the mixture was allowed to warm up slowly to room temperature and then concentrated. The distillate contained hydrazoic acid with the solvent and was analyzed as before. The concentrate was chromatographed to give the sulfinamide in greater than 95% purity. Direct recrystallization was unsuccessful and yields were not optimized. Data are summarized in Table II.

Discussion

The rate retardation first observed when 1 was decomposed in the presence of thiols[3] is readily explained by the successful isolation of thiosulfinate intermediates and hydrazoic acid. It is further confirmed by the slow rate of nitrogen evolution observed when pure thiosulfinate and hydrazoic acid were subsequently allowed to react.[3]

The successful diversion of 1 from the sulfinylnitrene route by thiols and amines, but not by water, alcohols, carboxylic acids, ketones, or sulfoxides,[3] reflects a reactivity order that might be expected for a nucleophilic substitution reaction.[9] Such selectivity can be synthetically useful.

The most useful reaction is with 2-mercaptoethanol. This demonstrates the likelihood that any functional group that does not divert the sulfinyl azide (1) could be present in a reacting thiol without competition. This is not possible if the sulfinyl chloride method is used in the presence of alcohols[10] or sulfoxides.[11] Indeed, we found that reaction of 2-mercaptoethanol with benzenesulfinyl chloride gave a mixture of products, among which the thiosulfinate (**2f**) was a minor constituent.

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(9) (a) Swain, C. G.; Scott, C. B. *J. Am. Chem. Soc.* **1953**, *75*, 141. (b) Swain, C. G.; Moseley, R. B.; Brown, D. E. *Ibid.* **1955**, *77*, 3731.
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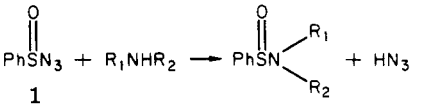
(11) Johnson, C. R.; Phillips, W. G. *J. Am. Chem. Soc.* **1969**, *91*, 682.

Table II. Reaction of Benzenesulfinyl Azide (1) with Amines



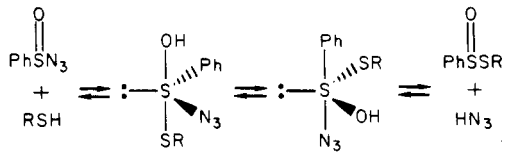
1 3

compd	R_1	R_2	% yield sulfinamide	% yield hydrazoic acid	melting point (reported), °C
3a	Ph	H	52	56	109-110 (112-114)[a]
3b	$CH_3CH_2CH_2CH_2$	H	56	47	
3c	$HOCH_2CH_2$	H	48	47	
3d	$-(CH_2)_5-$		78	65	81-82 (83)[a]

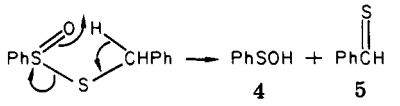
[a] Reference 14.

The observation that 2-propanethiol appears not to react under the usual conditions with benzenesulfinyl azide (1), but does in the presence of sodium bicarbonate, suggests that an equilibrium exists between reactants and products. In the usual case, hydrazoic acid (bp 37 °C) evaporates with the solvent when the reaction mixture is concentrated. However, the equilibrium may shift when removal of the thiol occurs, if its boiling point is comparable with that of hydrazoic acid. Sodium bicarbonate can selectively neutralize hydrazoic acid under the reaction conditions, because the latter is a considerably stronger acid than the thiols.

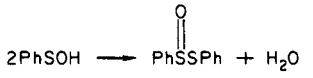
No direct evidence is available for the substitution process in this reaction, but S_N2 seems to be reasonable. However, the following tetracoordinate trigonal bipyramidal sulfurane intermediates cannot be excluded.



The unusual instability of **2b** and formation of **2a** can



2b 4 5



2a

be explained by a mechanism reported for the thermal decomposition of dialkyl thiosulfinates.[8] Thus, the major decomposition pathway for **2b** is probably a cycloelimination reaction, involving the α hydrogen in **2b**. Thiobenzaldehyde (**5**) is expected to polymerize, and benzenesulfenic acid (**4**) is expected to give **2a**.[8] Conjugation of the phenyl groups with the sulfur atoms in the transition state leading to **4** and **5** could explain the lower decomposition temperature of **2b**. The isolation of (**2b**) has been claimed before.[12]

Presumably the mechanism of the reaction of 1 with amines parallels that with thiols. The yields for the formation of the sulfinamides are satisfactory (Table II) but were not optimized. These sulfinamides were more stable than the thiosulfinates prepared in this study. This procedure may be expected to be useful with multifunctional compounds containing groups (such as hydroxyl) which are not compatible with the sulfinyl chloride method.[15]

No precedent could be found in the literature for the nucleophilic displacement of hydrazoic acid from acyl or sulfonyl azides by thiols. However, some cases of displacement by amines have been reported.[16-20] Ethyl azidoformate reacts with aniline and with morpholine to give substitution products.[16] Curtius and his co-workers[17] reported on the thermal decomposition of a number of aromatic sulfonyl azides with aniline, *N*-methylaniline, and *N,N*-dimethylaniline. Reactions with aniline gave primarily the non-nitrene nucleophilic substitution products, the sulfonanilides, and hydrazoic acid or its decomposition products.[17] Cremlyn observed the substitution of hydrazoic acid from (4-acetamidobenzene)sulfonyl azide by sodium hydroxide, ammonia, and piperidine.[18] In contrast with this, a diazo transfer reaction occurred between *p*-toluenesulfonyl azide and the halomagnesium salt of aniline.[19] With benzylamine anion, *N*-benzyl-*p*-toluenesulfonamide was obtained as a byproduct.[20]

The observations that nucleophiles react with benzenesulfinyl azide (1) at a much faster rate than they do with arene sulfonyl azides is consistent with the relative reactivities found for nucleophilic attack at sulfinyl sulfur[21] vs. sulfonyl sulfur.[22]

Finally, these reactions of 1 are advantageous because they require only 1 mol of each reagent and do not require tertiary bases for removal of strong acids. Only with volatile nucleophiles (bp less than 75 °C) is a base (aqueous sodium bicarbonate) recommended as a safety precaution. This method does not require extraction with chilled 1 M H_2SO_4, like the sulfinyl chloride procedure.[8] Avoiding this step is desirable, since thiosulfinates are acid sensitive.[23]

Experimental Section

Melting points were obtained on a Thomas-Hoover melting

(12) The synthesis of **2b** has been reported[13] from the reaction of benzyl benzenethiosulfonate, $PhS(O)_2SCH_2Ph$, with triphenylphosphine in refluxing ether or benzene. We were unable to repeat those experiments.

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point apparatus and are uncorrected. Elemental analyses were performed by Robertson Laboratory, Florham Park, N.J. or Caltech Microanalytical Laboratory, California Institute of Technology, Pasadena, CA. IR spectra were obtained as a thin film on a Perkin-Elmer 237B infrared spectrometer. ^{1}H NMR spectra at 60 MHz were obtained with a Perkin-Elmer R12B or a Varian EM360A instrument using tetramethylsilane as an internal standard and deuteriochloroform as the solvent. HPLC was accomplished with a Waters Associates, Inc. Model M6000A pump equipped with an Altex 153 UV detector. Column A: "Lobar" 31.0 × 2.5 cm silica gel 60, 0.2–0.5 mm (E. Merck Co.). Column B: 30 × 1.0 cm silica gel, Lichrosorb Si60, 5 μm (Altex Inc.). A Kewaunee dry box under nitrogen atmosphere with molecular sieves as a desiccant was used. Dry solvents were obtained by the usual procedures. Thiols and amines were distilled and stored under a nitrogen atmosphere. For thin-layer chromatography, Eastman Chromatogram thin-layer plates coated with silica gel containing a fluorescent indicator were used. Deactivated silica gel especially made for dry column chromatography[24] by I. C. N. Biochemicals Co. was used. E. Merck Co., PF_{254} silica gel was used for preparative layer chromatography.

Preparation of Benzenesulfinyl Chloride. The method of Douglass and Norton[25] was used but with CH_2Cl_2 as solvent.[3]

Preparation of Benzenesulfinyl Azide (1). This procedure is reported in the preceding paper.[3]

Preparation of Thiosulfinates (2). In a typical run, the sulfinyl azide (1) solution was added directly from the cold filter to 19 mL of 0.50 M solution (0.95:1 mole ratio of thiol to 1) of the thiol in acetonitrile stirred at −20 °C. The reaction mixture was allowed to warm up slowly to room temperature (30 min, usually, and 1–2 h for sterically hindered thiols) and concentrated in vacuo. **CAUTION**: In the case of volatile thiols (bp less than 75 °C), like 2-propanethiol, the reaction mixtures should not be concentrated as usual, because some explosive concentrations of 1 may remain. In this case, the mixture was extracted with saturated aqueous sodium bicarbonate solution, dried, and concentrated in vacuo.

To the distillate containing hydrazoic acid was added 50 mL of water and this was titrated with standardized 0.1 M sodium hydroxide to a phenolphthalein end point. The residue was purified by using preparative layer or dry column chromatography on silica gel with methylene chloride as eluent, except for **2f**, where chloroform was used. The purity of the chromatographed material was checked by HPLC on Column B using methylene chloride as eluent. The purity was always found to be greater than 95%. Yields are summarized in Table I.

Preparation of Sulfinamides (3). The same procedure as for thiosulfinates was used, except that the molar ratio of sulfinyl azide to amine was one to one. Chloroform was used as eluent for preparative chromatography, except for **3c** where acetonitrile was used. Yields are summarized in Table II.

Spectral and Analytical Data of Thiosulfinates and Sulfinamides. Elemental analyses were obtained for those samples that were sufficiently stable to silica gel for good chromatographic separations.

Benzyl benzenethiosulfinate (2b) is a colorless oil: IR 1490, 1470, 1440, 1095 (S=O) cm^{-1}; NMR δ (4.20, 4.40 (AB q, 2, J = 13 Hz), 7.40 (m, 10).

n-Propyl benzenethiosulfinate (2c)[5] is a colorless oil: IR 1475, 1440, 1095 (S=O) cm^{-1}; NMR δ 1.06 (t, 3, J = 7 Hz), 1.75 (sextet, 2, J = 7 Hz), 3.10, 3.13 (diastereotopic t, 2, J = 7 Hz), 7.50 (m, 5).

Isopropyl benzenethiosulfinate (2d) is a colorless oil: IR 1440, 1390, 1370, 1260, 1170, 1100 (S=O) cm^{-1}; NMR δ 1.40 (d, 3, J = 5 Hz), 1.55 (d, 3, J = 5 Hz), 3.70 (septet, 1, J = 5 Hz,) 7.50 (m, 5).

2-Hydroxyethyl benzenethiosulfinate (2f) is a turbid, colorless oil: IR 3350 (br), 1475, 1440, 1090, (S=O), 1050 cm^{-1}; NMR δ 3.22 (t, 2, J = 6 Hz), 3.84 (m, 2), 4.30 (br s, 1), 7.50 (m, 5). A sample of **2f** was obtained for elemental analysis by HPLC on Column A using 40% acetonitrile–methylene chloride as eluent. Anal. Calcd for $C_8H_{10}S_2O_3$: C, 47.50; H, 4.98. Found: C, 47.59, H, 5.11.

Neopentyl benzenethiosulfinate[26] **(2g)** is a colorless oil: IR 1475, 1440, 1390, 1370, 1100 (S=O) cm^{-1}; NMR δ 1.02 (s, 9), 2.99, 3.16 (AB q, 2, J = 13 Hz), 7.60 (m, 5). This was oxidized to the more stable neopentyl benzenethiosulfonate by using a method reported in the literature.[29] It was purified on Column B using 35% methylene chloride–petroleum ether (60–90 °C). Anal. Calcd for $C_{11}H_{16}S_2O_2$: C, 54.10; H, 6.56. Found: C, 54.87; H, 6.57.

***N*-Butylbenzenesulfinamide (3b)**[14] is a colorless oil: IR 3175, 1440, 1085, 1050 (S=O) cm^{-1}; NMR δ 0.8 (m, 3), 1.3 (m, 4), 2.90, 3.05 (diastereotopic t, 2, J = 7 Hz), 7.50 (m, 5).

***N*-(2-Hydroxyethyl)benzenesulfinamide (3c)** is a red oil: IR 3200 (br), 1440, 1475, 1086, 1050 (S=O) cm^{-1}; NMR δ 3.00 (m, 2), 3.60 (t, 2, J = 5 Hz), 5.80 (br, 1), 7.50 (m, 5). A sample of **3c** obtained by repeated dry column chromatography gave the following elemental analysis: calcd for $C_8H_{11}NO_2S$, C, 51.89; H, 5.95; N, 7.57; S, 17.30; found, C, 50.80; H, 6.06; N, 7.11; S, 16.39.

In general, the spectral data are consistent with that in the literature for related compounds.[6,30–34]

Acknowledgment. Financial support for this research was provided in part by a grant from the National Cancer Institute (CA-18838).

Registry No. 1, 21230-20-6; **2a**, 1208-20-4; **2b**, 16599-27-2; **2c**, 69857-02-9; **2d**, 88687-10-9; **2e**, 63752-74-9; **2f**, 88687-11-0; **2g**, 80319-00-2; **3a**, 14933-97-2; **3b**, 6829-66-9; **3c**, 88687-12-1; **3d**, 4972-31-0; benzenethiol, 108-98-5; phenylmethanethiol, 100-53-8; 1-propanethiol, 107-03-9; 2-propanethiol, 75-33-2; 2-methyl-2-propanethiol, 75-66-1; 2-mercaptoethanol, 60-24-2; 2,2-dimethyl-1-propanethiol, 1679-08-9; benzenamine, 62-53-3; 1-butanamine, 109-73-9; 2-aminoethanol, 141-43-5; piperidine, 110-89-4; hydrazoic acid, 7782-79-8.

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