The Synthesis of Aromatic Sulfonyl Bromides from Sulfonylhydrazides

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Aromatic sulfonylhydrazides react rapidly and quantitatively with bromine in aqueous acidic media. Four equivalents of bromine are required for every hydrazyl group reacting. This reaction provides a rapid, simple, and convenient synthesis of sulfonyl bromides. Instead of bromine, a mixture of sodium bromide and sodium bromate is added to an acidic solution or suspension of an aromatic sulfonylhydrazide at room temperatures until a slight excess of bromine is present. The precipitated sulfonyl bromide may be filtered immediately and is sufficiently pure for most purposes. Generally the yields exceed 90%. Chlorination also proceeds rapidly in water to give good yields of the corresponding sulfonyl chloride. Iodine reacts slowly with sulfonylhydrazides in aqueous media at room temperatures, and no visible reaction occurs in acetic acid solution even after an hour.

Sulfonylhydrazides find application as pneumatogens[1,2] for producing expanded products—foams and sponges—from rubber and plastics. Benzenesulfonylhydrazide, *p*-toluenesulfonylhydrazide, benzene-1,3-disulfonylhydrazide, 4,4′-oxydi(benzenesulfonylhydrazide), and 3,3′-diphenylsulfonedisulfonylhydrazide are commercially available for such a purpose. In the course of our work on expanded plastics, we investigated the properties and characterization of several available sulfonylhydrazides.

Despite the economic importance of sulfonylhydrazides, suitable procedures for their determination are lacking. Several methods for the quantitative analysis of hydrazine are summarized by Audrieth and Ogg,[3] but substituted hydrazines are not considered. Aromatic hydrazines, however, have been converted quantitatively into the corresponding diazonium salts by chlorine or bromine.[4] Nevertheless, bromimetric procedures for analyzing hydrazines are subject to various limitations, and aromatic hydrazines apparently cannot be determined in this way.[5] Phenylhydrazine has been analyzed by an iodate–iodine monochloride procedure[6] and, unsatisfactorily, with potassium iodate.[7] The application of iodimetry to sulfonylhydrazides is subject to considerable uncertainty because the sulfonyl group can be reduced by iodine.[8]

Recently, Carpino[9] described a general synthesis for acid chlorides and bromides of carboxylic acids by halogenation of their hydrazides in nonaqueous media under mild conditions. Several aromatic acid chlorides, benzoyl bromide, and succinyl chloride were prepared in yields of 48–79%.

Carpino's work and a brief reference[10] to oxidative chlorination of *m*- and *p*-nitrobenzenesulfonylhydrazides suggested that oxidative bromination of sulfonylhydrazides should give good yields of the corresponding sulfonyl bromides. In particular, we believed that bromination would provide a useful and simple synthesis for sulfonyl bromides if the reaction could be carried out in aqueous media. Furthermore, transformation of thermolabile sulfonylhydrazide groups into substituents of greater stability is desirable for characterizing sulfonylhydrazides.

Previous methods for preparing sulfonyl bromides entail the bromination of aromatic sulfinic acids or their salts,[11], thiophenols,[12] and S-substituted thiuronium salts[13]; the reaction of phosphorus pentabromide with aromatic sulfonic acids or their salts[14]; the reaction of sulfuryl chloride on Grignard reagents from alkyl bromides[15]; solvolysis of aromatic sulfonic anhydrides with hydrogen bromide[16]; and photochemical sulfobromination of aliphatic hydrocarbons with sulfur dioxide and bromine.[17] Sulfonyl bromides also have been claimed from the bromination of disulfides in aqueous media[18] and of trityl aryl sulfide that solvolyzed to triphenylcarbinol and the thiophenol prior to oxidation,[19] but the sulfonyl bromides were not isolated. Gregg and Blood,[19] however, converted their reaction products into the corresponding sulfonamides to demonstrate the formation of the intermediate sulfonyl bromide. These methods are laborious and generally involve intermediates not readily available.

Experimental[20]

A. **Aromatic Sulfonylhydrazides.**—The products synthesized were prepared almost quantitatively by adding the sulfonyl chloride dissolved in ether to a slight excess of hydrazine in ether,[21] filtering the precipitate, washing out hydrazine hydrochloride with water, and recrystallizing the insoluble hydrazide from warm water or ethanol. The compounds were also prepared more conveniently in water. *p*-Methoxybenzenesulfonyl-

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(1) Pneumatogens are substances that decompose into one or more gaseous products; they are commonly called "blowing agents" in the trade for manufacturing foamed plastics.

(2)(a) R. A. Reed, *Brit. Plastics*, **33**, 468 (1960); (b) R. A. Reed "Plastics Progress 1955," P. Morgan, Ed., Iliffe and Sons Ltd., London, 1956, p. 51; (c) H. R. Lasman, "Modern Plastics Encyclopedia 1963," Plastics Catalogue Corp., New York, N. Y., p. 422.

(3) L. F. Audrieth and B. A. Ogg, "The Chemistry of Hydrazine," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 153.

(4) F. D. Chattaway, *J. Chem. Soc.*, **93**, 852 (1908).

(5) S. Siggia, "Quantitative Organic Analyses Via Functional Groups," John Wiley and Sons, Inc., New York,, N. Y., 1949, pp. 74, 111. In the third edition (1963, p. 536) analyses for hydrazine and hydrazides are discussed in greater detail, but a bromination procedure is no longer mentioned.

(6) G. F. Smith and C. S. Wilcox, *Ind. Eng. Chem.* (*Anal. Ed.*), **14**, 49 (1942).

(7) G. S. Jamieson, "Volumetric Iodate Methods," Chemical Catalog Co., New York, N. Y., 1926.

(8) T. Curtius and F. Lorenzen, *J. prakt. Chem.*, [2] **58**, 160 (1898).

(9)(a) L. A. Carpino, *J. Am. Chem. Soc.*, **79**, 96 (1957); *Chem. Ind.* (London), 123 (1956); (b) U. S. Patent 2,845,429 (1958).

(10) W. Davies, F. R. Storrie, and S. H. Tucker, *J. Chem. Soc.*, 624 (1931).

(11)(a) R. Otto and H. Ostrop, *Ann.*, **141**, 365 (1867); (b) R. Otto and O. von Gruber, *ibid.*, **142**, 92 (1867).

(12)(a) T. Zincke and W. Frohneberg, *Ber.*, **42**, 2721 (1909); (b) **43**, 837 (1910).

(13) T. B. Johnson and J. M. Sprague, *J. Am. Chem. Soc.*, **58**, 1348 (1936).

(14) T. H. Norton, *ibid.*, **19**, 835 (1897).

(15) E. Cherbuliez and O. Schnauder, *Helv. Chim. Acta*, **6**, 249 (1923).

(16) V. O. Lukashevich, *Dokl. Akad. Nauk SSSR*, **103**, 627 (1955); *Chem. Abstr.*, **50**, 5556g (1956).

(17) A. L. Fox, U. S. Patent 2,346,568 (1944).

(18) S. Siggia and R. L. Edsberg, *Ind. Eng. Chem.*, *Anal. Ed.*, **20**, 938 (1948).

(19) D. C. Gregg and C. A. Blood, *J. Org. Chem.*, **16**, 1255 (1951).

(20) Melting points are uncorrected. The analyses were carried out by the analytical group at Armstrong Cork Co.

(21) L. F. Audrieth and M. von Brauchitsch, *J. Org. Chem.*, **21**, 426 (1956).

TABLE I

SYNTHESIS AND IDENTIFICATION OF SOME AROMATIC SULFONYL BROMIDES

Sulfonylhydrazide	Bromine, meq. / Hydrazide, g.		Sulfonyl bromide							Sulfonamide, m.p., °C.	
			M.p. (b.p.), °C.		Analysis, %				Yield, %[a]		
					Sulfur		Bromine				
	Found	Calcd.	Found	Lit.	Found	Calcd.	Found	Calcd.		Found	Lit.
Benzenesulfonylhydrazide	22.8[b] 22.5[c]	23.3	Oil	(140–141[d] dec.)	...	...	...	...	98	153–154	153[e]
p-Toluenesulfonylhydrazide	21.7[f] 21.7[c]	21.5	95–96	93–94[g]	...	...	...	...	95	138–140	137[h]
p-Methoxybenzenesulfonylhydrazide	38.9[c]	19.8	29–30	...	12.9	12.8	31.9	31.9	88	112–114	112–113[i]
Benzene-1,3-disulfonylhydrazide	30.1[j]	30.1	53–54	52[k]	...	...	...	...	82	231	229[l]
4,4′-Oxydi(benzenesulfonylhydrazide)	15.9[m]	22.3	142–145	...	13.9	14.1	34.4	35.1	96	179–181	158–160[n]
3,3′-Diphenylsulfonedisulfonylhydrazide	12.9[o]	19.7	187–188	...	19.1	18.9	31.2	31.7	86	244–248	242[p]

[a] Based on crude product. [b] Porofor BSH. All Porofors (Farbenfabriken Bayer) were obtained through Nafton, Inc., New York, N. Y. [c] Materials synthesized in our laboratory. [d] Ref. 14. [e] J. Stenhouse, *Ann.*, **140,** 284 (1866). [f] A. & S. Corp., Verona, N. J. [g] Ref. 12a. [h] Ref. 22, p. 694. [i] W. B. Shober, *Am. Chem. J.*, **18,** 858 (1896). [j] Porofor B-13. [k] J. Troger and W. Meine, *J. prakt. Chem.*, [2] **68,** 313 (1903). [l] W. Koerner and G. Monselise, *Gazz. chim. ital.*, **6,** 133 (1876). [m] Celogen, Naugatuck Chemical Div., U. S. Rubber, Naugatuck, Conn. [n] Ref. 23. [o] Porofor D-33. [p] R. Otto and A. Rossing, *Ber.*, **19,** 3124 (1886).

hydrazide was obtained in 95% yield and crystallized from hot water; m.p. 108–110° dec.

Anal. Calcd. for $C_7H_{10}O_3N_2S$: C, 41.58; H, 4.95; N, 13.86. Found: C, 41.69; H, 4.98; N, 14.01.

B. **Bromimetric Analysis of Aromatic Sulfonylhydrazides.**—The bromimetric procedure used is the adaptation given by Siggia.[5] Our analytical results for a number of sulfonylhydrazides are shown in Table I.

C. **Synthesis of Aromatic Sulfonyl Bromides.**—The synthesis of p-toluenesulfonyl bromide described here in detail is typical for preparing other sulfonyl bromides. Sodium bromide (2.1 g.) and sodium bromate (6.1 g.) dissolved in 35 ml. of water was added in 10 min. to a stirred turbid solution of p-toluenesulfonylhydrazide (11.1 g., 0.06 mole) in 200 ml. of 10% hydrochloric acid at about 25°; the yellow color of bromine persisted. The evolution of nitrogen transformed the white precipitate into a thick persistent froth that was filtered immediately, washed with cold water, and dried. The product, p-toluenesulfonyl bromide (13.4 g., 95%), m.p. 94–96°, after recrystallization from low boiling petroleum ether, melted at 95–96°.[12a]

4,4′-Oxydi(benzenesulfonyl bromide) and 3,3′-diphenylsulfonedisulfonyl bromide were prepared in 50% aqueous ethanol and crystallized from benzene.

The properties and yields of the sulfonyl bromides prepared are given in Table I.

D. **Bromination of p-Toluenesulfonylhydrazide with Sodium Bromate.**—Sodium bromate (4.0 g.) in 20 ml. of water was added over a period of 15 min. to a murky solution of p-toluenesulfonylhydrazide (1.86 g.) in 30 ml. of 50% sulfuric acid. A vigorous evolution of gas ensued with an immediate precipitation of a white solid; the mixture had to be cooled to maintain a temperature of 25°. The resultant froth was filtered, washed with water, and dried giving 1.6 g. of p-toluenesulfonyl bromide, m.p. 93–95°. The clear colorless filtrate was neutralized and shown to contain p-toluenesulfonic acid by precipitation as its benzyl thiuronium salt, m.p. 179–184°, after recrystallization from ethanol; lit.[22] m.p. 181–182°.

E. **Bromination of p-Toluenesulfonylhydrazide in Carbon Tetrachloride.**—A solution of bromine in carbon tetrachloride (0.32 g. bromine/ml.) was added in small portions to a shaken slurry of p-toluenesulfonylhydrazide (11.5 g., 0.062 mole) in 100 ml. of carbon tetrachloride at 25°. A permanent bromine color was achieved when 8 ml. of the bromine solution had been added; an additional 2 ml. was then added, the slurry shaken intermittently for about 15 min., and the precipitate filtered. The filtrate and washings after evaporation left 2.2 g. of a pale yellow solid, m.p. 89–93°, identified as p-toluenesulfonyl bromide.

The cream-colored precipitate (12.0 g.) was analyzed and found to contain 17.5% ionizable bromine; on titration with bromine 17.4 meq. bromine/g. of product was required. Extraction of a 10.0-g. sample with ether left a white powder (8.8 g.).

Anal. Calcd. for $2C_7H_7SO_2N_2H_3 \cdot HBr$: ionizable bromine 17.7; equivalents of bromine required, 17.7 mequiv./g. Found: ionizable bromine, 19.5, equivalents of bromine required, 17.0 mequiv./g.

The ether-soluble product (1.0 g.) melted at 99–104° dec. and is probably impure toluenesulfonylhydrazide.

The salt (1.36 g.) insoluble in carbon tetrachloride was converted quantitatively into p-toluenesulfonyl bromide (1.4 g., m.p. 94–95°) by bromination in acidulated water.

A repetition of the experiment with 9.3 g. (0.050 mole) of p-toluenesulfonylhydrazide, but tripling the amount of bromine (9.0 g.), gave 2.6 g. of p-toluenesulfonyl bromide, m.p. 88–92° (the product soluble in carbon tetrachloride), and 10.4 g. of insoluble product. The latter was extracted with ether to leave 9.6 g. of a white powder.

Anal. Calcd. for $C_7H_7SO_2N_2H_3 \cdot HBr$: ionizable bromine, 30.0; bromine uptake, 15.7 mequiv./g. Found: ionizable bromine, 28.0; bromine uptake, 15.0 mequiv./g. of sample.

The white powder (1.34 g.) was brominated to give 1.09 g. of p-toluenesulfonyl bromide (m.p. 94–95°), corresponding to a 93% yield based on p-toluenesulfonylhydrazide hydrobromide.

Bromination in ether gave a salt showing 28.5% ionizable bromine and requiring 15.7 mequiv. of bromine/g. of sample.

F. **Chlorination of Sulfonylhydrazides.**—4,4′-Oxydi(benzenesulfonylhydrazide) (10.0 g.) dissolved in 75 ml. of 25% hydrochloric acid was chlorinated at 0° until frothing ceased. The precipitated 4,4′-oxydi(benzenesulfonyl chloride) was filtered and washed with cold water; yield, 5.1 g. (50%). On recrystallization from hot ligroin the melting point was 131–132°; lit.[23] m.p. 128–129°.

G. **Preparation of Sulfonamides.**—These derivatives were made by dissolving the corresponding sulfonyl bromide in an excess of concentrated ammonium hydroxide at 5° (warming if necessary), neutralizing the solution with hydrochloric acid, and filtering the precipitated sulfonamide. Yields were almost quantitative and purification usually was unnecessary.

4,4′-Oxydi(benzenesulfonamide) melted at 179–181°; lit.[23] m.p. 158–160°. Another synthesis from 4,4′-oxydi(benzenesulfonyl chloride) gave a product of m.p. 183–186° after recrystallization from water.

The properties of the sulfonamides are given in Table I.

H. **Amount of Gas Evolved in the Bromination of p-Toluenesulfonylhydrazides.**—Sufficient aqueous sodium bromide–sodium bromate solution was added to 1.86 g. of p-toluenesulfonylhydrazide suspended in 35 ml. of 20% hydrochloric acid at 10° to give

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[22] N. Cheronis and J. Entrikin, "Semi-micro Qualitative Organic Analysis," Interscience Publishers, Inc., New York, N. Y., 1958, p. 697.

[23] C. M. Suter, *J. Am. Chem. Soc.*, **53,** 1112 (1931).

a permanent yellow color, and the gas evolved (270 ml.) was collected over water at 24° (753 mm.) After corrections for vapor pressure of water, displacement of gas by the brominating solution (15.5 ml.), and standard conditions, this amounted to 225 ml. compared to a theoretical value of 224 ml. The precipitated *p*-toluenesulfonyl bromide was filtered, washed, and dried; the yield was 2.25 g. (96%).

Discussion

Synthetic and commercially available sulfonylhydrazides (Table I) were brominated in hydrochloric acid solution. The hydrazides of benzene- and toluenesulfonic acids and benzene-1,3-disulfonic acid gave results conforming to the stoichiometry given in this equation.

$$\mathrm{ArSO_2NHNH_2 + 2Br_2 \longrightarrow ArSO_2Br + N_2 + 3HBr}$$

Four equivalents of bromine reacted with each hydrazyl group. The other sulfonylhydrazides deviated from this stoichiometry, but we have not examined the analytical aspects of the reaction in sufficient detail to clarify the observed discrepancy. The low bromine values for 4,4′-oxydi(benzenesulfonylhydrazide) and 3,3′-diphenylsulfonedisulfonylhydrazide are in marked contrast to high yields of the corresponding sulfonyl bromides obtained.

The high bromine equivalent found for 4-methoxybenzenesulfonylhydrazide at first was attributed to formation of 4-methoxy-3,5-dibromobenzenesulfonyl bromide as a consequence of bromination on the ring. Attempts to prepare the dibromobenzenesulfonyl bromide, however, were unsuccessful; only the 4-methoxybenzenesulfonyl bromide was obtained in high yield even when a large excess of bromine was used and reaction times extended to one hour. Furthermore, it was shown that 4-methoxybenzenesulfonyl halides are unaffected by bromine under conditions of our experiments. Thus, we conclude that the apparent paradox is a consequence of the large excess of bromine present and of reactions at some stage after potassium iodide had been added to the brominating solution.[5] An attempt is being made to clarify the source of discrepancy.

Despite the anomalies found, our preliminary results indicate that, in absence of other groups sensitive to bromine, bromimetry offers some promise for determining hydrazyl groups in sulfonylhydrazides. The procedure can be adapted to measure the volume of nitrogen evolved, thus circumventing spurious results introduced by ring bromination or other reactions with bromine when unknown sulfonylhydrazides are examined.

The interesting observation has been made that sulfonylhydrazides undergo oxidative bromination with bromates in acidic solutions. Two-thirds of the sulfonylhydrazide is converted into the corresponding sulfonyl bromide.

$$\begin{aligned}&\mathrm{3\ \mathit{p}\text{-}CH_3C_6H_4SO_2NHNH_2 + 2NaBrO_3 + H_2SO_4 \longrightarrow}\\&\qquad\mathrm{2\ \mathit{p}\text{-}CH_3C_6H_4SO_2Br + \mathit{p}\text{-}CH_3C_6H_4SO_3Na +}\\&\qquad\qquad\mathrm{3N_2 + NaHSO_4 + 5H_2O}\end{aligned}$$

Reaction is vigorous and a voluminous amount of nitrogen is evolved. The toluenesulfonyl bromide is obtained as a highly pure, white powder in a 67% yield, conforming to the equation given. Under similar conditions, chlorates have no effect and the sulfonylhydrazide can be recovered completely even after a two-hour reaction period. If sufficient bromide is present, however, the sulfonylhydrazide is converted quantitatively to the sulfonyl bromide. Apparently chlorates are unable to oxidize sulfonylhydrazides; bromination is a consequence of the oxidation of bromide anions to bromine followed by an immediate reaction with the hydrazide.

The possibility of converting the thermolabile hydrazosulfonyl group into more stable substituents is of considerable importance for investigating pneumatogens bearing such groups. While the brominations can be carried out in aqueous media with bromine or other brominating agents, the procedure we have discovered is particularly convenient when aqueous solutions of sodium bromide–sodium bromate are used as a source of bromine. Many variants are possible but the following equation summarizes the reaction taking place.

$$\begin{aligned}&\mathrm{3RSO_2NHNH_2 + 2NaBrO_3 + NaBr + 3HCl \longrightarrow}\\&\qquad\mathrm{3RSO_2Br + 3N_2 + 3NaCl + 6H_2O}\end{aligned}$$

When the reaction is carried out by adding a sodium bromide–sodium bromate solution to an acidic solution or slurry of the sulfonylhydrazide at room temperatures, an immediate reaction occurs with evolution of nitrogen and precipitation of the hydrophobic sulfonyl bromide. Some cooling is necessary but the reaction is easily controlled. The product can be filtered or extracted with organic solvents as soon as an excess of bromine is indicated—preferably after removing excess bromine with a small amount of sodium bisulfite. It may be advantageous, when the solubility of the sulfonylhydrazide in water is low, to brominate in aqueous organic solutions, *e.g.*, acetic acid, ethanol, etc. Generally the yield exceeds 90% and further purification is unnecessary.

The aromatic sulfonyl bromides are white (if they bear no chromophoric groups) stable substances insoluble in water, readily crystallized from organic solvents, and melt in a range convenient for identification. Benzenesulfonyl bromide, however, is a liquid. In contrast to sulfonyl chlorides, sulfonyl bromides have not been studied extensively and information on them is rather meager.[24] For the most part their reactions resemble those shown by the analogous sulfonyl chlorides; *e.g.*, they can be converted easily into sulfonamides and other derivatives.

Although bromination occurs readily in aqueous organic solvents, *e.g.*, 50% acetic acid, the sulfonylhydrazide generally is not converted completely to the sulfonyl bromide in organic solvents. Thus, when bromination is carried out in glacial acetic acid with bromine at room temperatures, only one mole equivalent of bromine is taken up rapidly; further reaction is not apparent. When such a clear reaction mixture containing an excess of bromine is diluted with water, the theoretical amount of bromine is taken up and the sulfonyl bromide precipitates.

Bromination in carbon tetrachloride is slow at 0° but rapid at room temperatures; only a fraction of bromine required to convert the sulfonylhydrazide to the sulfonyl bromide is consumed. The insoluble sulfonylhydrazide hydrobromide is resistant to further bromination. When a slight excess of bromine (manifest by permanent color) is added to a suspension of *p*-toluenesulfonylhydrazide at room temperatures, a small

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(24) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 513.

amount of *p*-toluenesulfonyl bromide is formed along with a considerable quantity of the insoluble 2:1 salt, bis(*p*-toluenesulfonylhydrazide) hydrobromide. This salt reacts slowly with bromine since, if it is in

$$7\ p\text{-}CH_3C_6H_4SO_2NHNH_2 + 2Br_2 \longrightarrow p\text{-}CH_3C_6H_4SO_2Br + 3(2\ p\text{-}CH_3C_6H_4SO_2N_2H_3\cdot HBr) + N_2$$

contact with a large excess of bromine, the 1:1 salt, *p*-toluenesulfonylhydrazide hydrobromide, forms. When the 2:1 salt is digested in ether partial reversion to the

$$4\ p\text{-}CH_3C_6H_4SO_2N_2H_3 + 2Br_2 \longrightarrow p\text{-}CH_3C_6H_4SO_2Br + 3\ p\text{-}CH_3C_6H_4SO_2N_2H_3\cdot HBr + N_2$$

1:1 salt occurs. The 1:1 salt also has been prepared by bromination in ether.

The identity of the salts follows from the stoichiometry of their formation, analysis for ionizable bromine, bromimetric analysis for the hydrazyl group, and quantitative isolation of the sulfonyl bromide when the salts are brominated in aqueous solution. Hydrazide perbromides, analogous to those isolated by Carpino[9a] when benzoylhydrazide reacted with bromine in nitromethane saturated with hydrogen bromide, were not observed in our experiments.

Our results with bromine in nonaqueous media are in contrast to the experiences of Carpino[9] with hydrazides of carboxylic acids and of Davies, Storrie, and Tucker[10] with nitrobenzenesulfonylhydrazides. They found that chlorination occurred easily and the salts, undoubtedly formed, reacted readily. Thus, *m*- and *p*-nitrobenzenesulfonylhydrazides were converted into the corresponding sulfonyl chlorides in yields of 82 and 88%, respectively, by chlorination at 0° in petroleum ether or chloroform.

It is of considerable interest to note that brominations in water carried out in presence of chloride ions does not lead to serious contamination with sulfonyl chloride as one might expect. Even under conditions believed to be favorable for the formation of sulfonyl chlorides, *i.e.*, adding slowly an aqueous solution of sodium bromide–sodium bromate (mole ratio, 1:2) to a solution of *p*-toluenesulfonylhydrazide in 25% hydrochloric acid saturated with sodium chloride, the sulfonyl halides consisted primarly of the bromide. The mixture of halides (about 95% yield) contained 25.95% bromine and 5.25% chlorine corresponding to 69 and 31 mole % of the respective sulfonyl halides. No attempt was made to ascertain whether chlorine was a consequence of exchange between the sulfonyl bromide and chloride anions or whether the chlorine was incorporated during the transient oxidative phase. The amount of sulfonylhydrazide converted to sulfonyl bromide is essentially the same as that found when sodium bromate is used as the brominative oxidant; the provocative relationship is probably fortuitous. Formation of a sulfonyl chloride is obviated by carrying out the reaction in sulfuric acid solution.

These observations preclude the possibility that cationic species such as $ArSO_2N_2^+$ or $ArSO_2^+$ are important in these brominations. The mechanistic picture, however, is obscure and undoubtedly complex. Higginson[25] has discussed the oxidation of hydrazine and the nature of the intermediates involved.

Chlorination of sulfonylhydrazides has been carried out in nonpolar organic solvents[10]; the reaction with chlorine is rapid in water to give good yields of the sulfonyl chloride. No attempts were made to find conditions suitable for high yields.

The reaction of iodine with sulfonylhydrazide was examined cursorily. In aqueous acidic solution iodine is decolorized slowly at room temperature and rapidly on warming; in acetic acid no perceptible reaction was observed. Others,[8] much earlier, have noted that iodine reacts sluggishly with sulfonylhydrazides to give 1,2-disulfonylhydrazines among other reaction products. Sodium iodide reacts with aromatic sulfonyl halides[26] leading to sodium sulfinate, disulfones, and other products. Thus in presence of iodides or iodine a variety of products containing sulfur in various oxidative states may be produced.

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[25] W. C. E. Higginson, "Recent Aspects of the Inorganic Chemistry of Nitrogen," Spec. Publ. no. 10, The Chemical Society, London, 1957, p. 95.

[26] (a) E. Gebauer-Fulnegg, E. Riesz, and S. Ilse, *Monatsh.*, **49**, 41 (1928); (b) E. Gebauer-Fulnegg and F. Riesenfeld, *ibid.*, **47**, 185 (1926).

Oxidation of N,N-Disubstituted Ketohydrazones by Lead Tetraacetate. Carbon–Nitrogen Bond Cleavage[1]

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N,N-Disubstituted ketohydrazones are oxidized with lead tetraacetate to effect carbon–nitrogen cleavage of primary or secondary alkyl groups. A monosubstituted hydrazone intermediate has been demonstrated and an azoacetate and a carbonyl compound are isolated products.

It recently has been shown that azoacetates are produced in good yields when ketohydrazones are added to a solution of lead tetraacetate[3]

$$R_1R_2C{=}N{-}NH{-}R_3 + Pb(OAc)_4 \longrightarrow R_1R_2C(OAc){-}N{=}N{-}R_3 + Pb(OAc)_2 + HOAc$$

It was initially anticipated that N,N-disubstituted ketohydrazones would fail to react with this oxidizing agent.[4] However, benzophenone dimethylhydrazone, benzophenone methylphenylhydrazone, and other simi-

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[2] From the M.A. thesis of Elisabeth Cerda, Western Michigan University, 1961. Presented in part at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

[3] D. C. Iffland, L. Salisbury, and W. R. Schafer, *J. Am. Chem. Soc.*, **83**, 747 (1961).

[4] Although ketoximes react with lead tetraacetate to yield nitrosoacetates, oxime O-alkyl ethers may be recovered from reaction mixtures containing lead tetraacetate. *Cf.* ref. 3, footnote 9.