+28.1° (c 1.3, absolute ethanol; 45% optically pure)) and 25 mg (0.047 mmol) of dichloro[1,2-bis(diphenylphosphino)ethane]-nickel(II)[23] in 10 mL of ether at room temperature was added a solution (2 mL, 3 mmol) of 1.5 M methyllithium in ether. Upon addition of methyllithium the orange nickel complex completely dissolved, and a clear yellow solution was formed. The solution was stirred for 2.5 h and hydrolyzed with water. The ether layer was washed with 10% hydrochloric acid and saturated sodium chloride solutions and dried over anhydrous magnesium sulfate. Removal of solvent gave 0.3 g (91%) of a liquid which was shown by NMR and GLC analyses to consist almost entirely of (4-methylcyclohexylidene)ethane (2). Purification of the liquid by bulb-to-bulb distillation [25 °C (2 torr)] afforded 0.1 g (33%) of the alkene, $[\alpha]^{25}_{Hg}$ +7.14 ± 0.4° (c 1.2, $CHCl_3$; 40.3% optically pure, with a corrected optical purity of 92%). The IR and NMR spectra of the alkene were identical with those of authentic (4-methylcyclohexylidene)ethane.

Reaction of (+)-(*S*)-(4-Methylcyclohexylidene)bromoethane (1) with Methyllithium in the Presence of $Fe(DBM)_3$. To a mixture of 0.5 g (2.63 mmol) of bromide[18] ($[\alpha]^{25}_{Hg}$ +26.4° (c 1.2, absolute ethanol; 42% optically pure)) and 30 mg (0.042 mmol) of iron(III)[24] tris(dibenzoylmethide) in 10 mL of THF at room temperature was added dropwise a solution (2 mL, 3 mmol) of 1.5 M methyllithium in ether. The initial red solution became dark green and, finally, dark brown during the addition. After the mixture was stirred for 2 h at room temperature, the reaction was quenched with water. The ether layer was washed with dilute hydrochloric acid and saturated sodium chloride and dried over anhydrous magnesium sulfate. Removal of solvent under reduced pressure gave 0.3 g (91%) of liquid which was shown by GLC and NMR analyses to consist predominantly of (4-methylcyclohexylidene)ethane. Purification by bulb-to-bulb distillation [25 °C (2 torr)] afforded 0.15 g (43%) of the alkene, $[\alpha]^{25}_{Hg}$ +6.89 ± 0.4° (c 1.3, $CHCl_3$; 39% optically pure, with a corrected optical purity of 92%). The IR and NMR spectra of the compound were identical with those of an authentic sample.

Reaction of (+)-(*S*)-(4-Methylcyclohexylidene)bromoethane (1) with Methyllithium in the Presence of $CoCl_2(Ph_3P)_2$. To a mixture of 0.5 g (2.63 mmol) of bromide[18] ($[\alpha]^{25}_{Hg}$ +27.25° (c 1.4, absolute ethanol; 43% optically pure)) and 25 mg (0.038 mmol) of bis(triphenylphosphine)dichlorocobalt(II)[25] in 5 mL of THF at −75 °C was added a solution (2 mL, 3 mmol) of 1.5 M methyllithium in ether. The mixture was stirred at −75 °C for 30 min and then allowed to warm to room temperature. The resulting dark viscous mixture was allowed to stir for 2 h at room temperature. The reaction was then quenched with water and the organic layer separated. The combined ether extracts were washed successively with water, 10% hydrochloric acid, and saturated sodium chloride. The extracts were dried over anhydrous magnesium sulfate, and the solvent was removed to give 0.4 g (100%) of a liquid which was purified by bulb-to-bulb distillation [25 °C (2 torr)]: 0.2 g (61%); $[\alpha]^{25}_{Hg}$ +6.0 ± 0.99° (c 0.5, $CHCl_3$; 34% optically pure). The corrected optical purity of the alkene was 79%. The compound was shoown by GLC and NMR analyses to be (4-methylcyclohexylidene)ethane (2).

In a separate experiment, an excess of bromide was allowed to react with methyllithium and the cobalt complex. A solution (0.5 mL, 0.75 mmol) of methyllithium in ether was added to a mixture of 0.5 g (2.63 mmol) of bromide ($[\alpha]^{25}_{Hg}$ +54.25° (c 1.0, absolute ethanol; 87% optically pure) and 25 mg (0.038 mmol) of cobalt complex in 10 mL of THF at −75 °C. After being stirred for 30 min at −75 °C, the mixture was allowed to warm to room temperature and to stir for 2 h. After the workup 0.4 g of liquid was obtained which was chromatographed on 25 g of 25% silver nitrate–silicic acid. Elution with 400 mL of pentane and removal of the solvent gave 0.2 g (40% recovery) of bromide, $[\alpha]^{25}_{Hg}$ +50.81 ± 0.5° (c 3.1, absolute ethanol; 82% optically pure). The bromide retained 94% of its original optical activity.

Reaction of (+)-(*S*)-(4-Methylcyclohexylidene)bromoethane (2) with Methyllithium in the Presence of Silver Bromide. To a mixture of 0.75 g (3.9 mmol) of bromide[18] ($[\alpha]^{25}_{Hg}$ +26.4° (c 1.2, absolute ethanol; 42% optically pure)) and 50 mg (0.027 mmol) of silver bromide in 10 mL of ether at −75 °C was added a solution (2 mL, 3 mmol) of 1.5 M methyllithium in ether. After being stirred at −75 °C for 5 min, the mixture was allowed to warm slowly to room temperature. This resulted in the formation of a black precipitate. The mixture was stirred at room temperature for 15 h and then hydrolyzed with water. The ether extracts were washed with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solvent was removed to give 0.5 g of liquid which was chromatographed on 20 g of 25% silver nitrate–silicic acid. The bromide was recovered by elution with 400 mL of pentane. The alkene was then obtained by elution with 50 mL of anhydrous ether. From the pentane fraction was obtained 0.4 g (53%) of bromide which was further purified by bulb-to-bulb distillation (pot temperature 50–60 °C (2 torr); $[\alpha]^{25}_{Hg}$ +23.2° (c 2.9, absolute ethanol; 37% optically pure). The bromide retained 88% of its initial optical purity. The ether fraction afforded 0.15 g (41% based on methyllithium) of (4-methylcyclohexylidene)ethane which was distilled [25 °C (2 torr)] and was found to be completely racemic.

Registry No. (+)-1, 60164-94-5; (+)-2, 60164-99-0; (±)-2, 79464-57-6; methyllithium, 917-54-4; $NiCl_2$ (dpe), 38754-20-0; $Fe(DBM)_3$, 14405-49-3; $CoCl_2(Ph_3P)_2$, 14126-40-0; AgBr, 7785-23-1.

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Chemistry of Organic Chloramines. Formation of Arenesulfonamides by Derivatization of Organic Chloramines with Sodium Arenesulfinates[1]

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Organic chloramines react rapidly with sodium benzenesulfinate or sodium toluenesulfinate to form arenesulfonamides. Derivatization was carried out by three different methods, one involving derivatization of pure chloramines and two involving derivatization of the chloramines generated in situ by reaction of the amine with sodium hypochlorite. Seventeen arenesulfonamides whose amine precursors included primary and secondary aliphatic amines, aromatic amines, and amino acids were synthesized in poor to excellent yields depending on the method used. Effects of structure, stability, and water solubility of the chloramine precursors are discussed. Benzenesulfonyl chloride can be isolated from the reaction of 10^{-4} M *N*-chloropiperidine with sodium benzenesulfinate. Competing hydrolysis of the sulfonyl chloride accounts for low yields of sulfonamide for dilute solutions of chloramine.

Although haloamines are recognized byproducts of the chlorination of natural water systems, none have been specifically identified because there is currently no suitable method for their isolation and identification.[2] As a class,

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Table I. Primary Amines and Amino Acids

amine precursor of chloramine	method	sulfonamide derivative	isolated yield, %
ammonia	B	benzenesulfonamide	89[a]
allylamine	B	*p*-toluenesulfonamide	100
aniline	B	benzenesulfonamide	88
n-hexylamine	B	benzenesulfonamide	89
n-hexylamine	C	benzenesulfonamide	11
sec-butylamine	B	benzenesulfonamide	99
sec-butylamine	C	benzenesulfonamide	43
ethylenediamine	B	*N,N'*-ethylenebis(benzenesulfonamide)	81
leucine	B	benzenesulfonamide	81
glycine	B	benzenesulfonamide	70[a]

[a] Crude yield.

Table II. Secondary Amines

amine precursor of chloramine	method	sulfonamide derivative	isolated yield, %
piperidine	A	benzenesulfonamide	78
piperidine	B	benzenesulfonamide	81
piperidine	C	benzenesulfonamide	77
piperidine	B	*p*-toluenesulfonamide	90
pyrrolidine	B	*p*-toluenesulfonamide	100
morpholine	B	benzenesulfonamide	75
morpholine	B	*p*-toluenesulfonamide	96
tetrahydroisoquinoline	B	benzenesulfonamide	83[a]
tetrahydroisoquinoline	C	benzenesulfonamide	10
diisobutylamine	B	benzenesulfonamide	85
diisobutylamine	C	benzenesulfonamide	10
dimethylamine	A	*p*-toluenesulfonamide	100
dimethylamine	B	*p*-toluenesulfonamide	87
diethylamine	A	*p*-toluenesulfonamide	63
diethylamine	B	*p*-toluenesulfonamide	58

[a] Crude yield.

organic haloamines are thermally labile. While some can be prepared and isolated by distillation, their purification must be carried out at temperatures as low as possible. Some organic chloramines undergo rapid exothermic decomposition on all attempts at isolation.

For some of our studies on the organic chemistry of water chlorination, we require a method of isolating and characterizing organic chloramines formed. We report here a mild and simple method for the rapid derivatization of haloamines in good yields and for the conversion of amines to arenesulfonamides by way of their chlorination.

Results

Synthesis. The sulfonamides were generated by three different methods. The first involved generation and isolation of the pure chloramine followed by its addition to an aqueous solution of the arenesulfinate salt (method A). The second implicated generation and immediate reaction by addition of aqueous sodium hypochlorite to a solution of the amine and arenesulfinate in water (method B). Finally, the chloramine was generated in aqueous solution by reaction of the amine with hypochlorite and the mixture allowed to stir before addition of the arenesulfinate salt (method C). Both sodium benzenesulfinate and sodium toluenesulfinate were used.

The organic chloramines studied give high yields of arenesulfonamides under varying conditions depending upon the method of generation, solubility, stability, and class of each amine. Tables I and II list the amines studied and the yields of their corresponding sulfonamide derivatives.

From these tables it is apparent that methods A and B generally give better yields than method C. This is particularly evident with the amines which form relatively unstable or water-insoluble chloramines. Under the reaction conditions of method C, the primary chloramines are found to dehydrohalogenate to imines, which hydrolyze rapidly to carbonyl compounds. Gas chromatographic analysis illustrates that there is a correlation between lower yields of sulfonamide and the appearance of the hydrolyzed dehydrohalogenation product of *N*-chloro-*sec*-butylamine, i.e., 2-butanone. It has been found that the yield of 2-butanone increases on standing with a corresponding decrease in the yield of sulfonamide. When the chloramine is stirred overnight before the addition of sulfinate, a yield of only 43% is obtained. By contrast, method B, which derivatizes the chloramine as it is formed, gives a quantitative yield. Aniline, which undergoes facile ring chlorination via the Orten reaction, is intercepted at the chloramine stage. Although the product is slightly contaminated by colored oxidation products, the yield after recrystallization is still high.

The pH of the solution during reaction has a dramatic effect on the yields of the sulfonamides of some amines. Unless fresh sodium hypochlorite solution is used, the reaction solution becomes very basic during the addition of the hypochlorite, and product yields are drastically reduced. To overcome this problem, we added 1 equiv of acetic acid. In addition, the acid solubilizes the less water soluble amines such as aniline and diisobutylamine and buffers the solution against the strongly basic solution of hypochlorite. The yield is greatly improved and easily reproducible.

Solubility of several of the chloramines is responsible for some of the poor results observed when method C is used. The *N*-chloro derivatizes of *n*-hexylamine, diisobutylamine, and tetrahydroisoquinoline give low yields which are attributable to poor phase transfer. When ethanol is added as a cosolvent, no increase in yield is observed. Other cosolvents such as THF, dioxane, Me_2SO, and acetonitrile also do not improve the yield. Addition of a crown ether along with a two-solvent system also proves ineffective. None of these cosolvents produces a single phase or combination of phases suitable for the favorable interaction of the ionic sulfinate with a nonpolar chloramine.

The conditions used in method B overcome this problem. The chloramine is trapped as it is formed and before it can undergo a phase separtion. In this way the yield of sulfonamide derivative of diisobutylamine is increased from 10% to 85%, that of tetrahydroisoquinoline from 10% to 83%, and that of *n*-hexylamine from 11% to 89%.

The reaction studied was applied to the *N*-chloro amino acids glycine and leucine. The sulfonamides were prepared by method B, but it was necessary to first solubilize the solid amino acid by adding sulfuric acid dropwise until the amino acid had completely dissolved. In this case acetic acid was not added. The reaction was then continued according to the procedure mentioned, and after completion of the reaction, the mixture was strongly acidified to give the corresponding sulfonamides in good yields.

Mechanism. When very dilute solutions of *N*-chloropiperidine (I) are derivatized with sodium benzenesulfinate

(1) Taken from the M.S. thesis of K.F.B., Old Dominion University, May 1981.

(2) See discussions in: Jolley, R. L.; Cumming, R. B.; Brungs, W. A., Eds.; "Water Chlorination: Environmental Impact and Health Effects"; Ann Arbor Scientific: Ann Arbor, MI, 1980; Vol. 3.

(II), the yields of sulfonamide are considerably reduced. For instance, when a solution of I (1×10^{-4} M) and II (1×10^{-3} M) is allowed to react, the yield of sulfonamide that can be isolated is only 8%. No sulfonamide is obtained when a 10^{-5} M solution of the chloramine is reacted with 10^{-3} M sulfinate.

These results might be expected if the reaction were a very slow second-order process. However, this is not the case. The reaction of I (9.0×10^{-5} M) with II (5.0×10^{-5} M) can be monitored for the presence of active chlorine by quenching the reaction in a solution of KI buffered to pH 4 and determining the amount of iodine formed. When a reaction is carried out at 20 °C, about half the theoretical amount of chloramine is found to be reacted in 2 min. The reaction is too fast to determine the order of the reaction or a good rate constant by simple kinetic techniques.

When a tenfold excess of sulfinate is used, this fast reaction is accelerated enough that a sulfonyl chloride product is formed rapidly. Benzenesulfonyl chloride can be isolated in high yield from the reaction solution of I (10^{-4} M) and II (10^{-3} M) if after 0.5 min of reaction the solution is acidified and extracted rapidly with chloroform.

A slower reaction appears to follow the sulfonyl chloride formation and can be detected by measuring a change in absorbance at 269 nm. When a dilute solution of I and II which is 10^{-4} M in one reagent and 10^{-3} M in the other is allowed to react, the decrease in absorbance indicates a reaction which is first order in the limiting reagent only. The measured first-order rate constant at 25 °C in 0.05 M NaCl is $(3.6 \pm 0.9) \times 10^{-3}$ s^{-1} and is the same as the rate of hydrolysis of benzenesulfonyl chloride measured under the same conditions [$(3.1 \pm 0.8) \times 10^{-3}$ s^{-1}].[3]

Discussion

The formation of arenesulfonamides by the combination of an arenesulfinic acid, an amine, and chlorine has been reported.[4-6] In these cases, however, yields were either not mentioned or were generally much lower than reported here. This may be attributed to several factors. Previous workers bubbled chlorine gas into their solutions instead of using dilute aqueous chlorine. In addition, the reactions were carried out at 40 °C, which is much higher than is needed to perform the reactions. Lastly, the amines chosen by Carter and Hey contain aromatic rings highly activated for electrophilc attack. Chlorination and oxidation of the aromatic nucleus is probably extensive under their conditions.

When a solution of sodium hypochlorite is added to an aqueous solution of an amine and a sodium arenesulfinate, the hypochlorite reacts rapidly with the amine to form a chloramine (eq 1, Scheme I). This is supported by the rate data of Morris,[7] who showed that the second-order rate constant for the reaction of amines with hypochlorite is approximately 5×10^8 M^{-1} s^{-1}. Carter and Hey have proposed a rapid reaction of an arenesulfinic acid with hypochlorous acid to form the arenesulfonyl chloride. However, Kice has shown that the reaction of hypochlorous acid with benzenesulfinic acid ($k = 1 \times 10^{-3}$ M^{-1} s^{-1}) is much lower than its reaction with an amine.[8]

Scheme I

$$R_2NH + ClO^- \rightarrow R_2NCl + HO^- \quad (1)$$

$$R_2NCl + PhSO_2^- + H_2O \rightarrow R_2NH + PhSO_2Cl + HO^- \quad (2)$$

$$PhSO_2Cl + R_2NH \rightarrow PhSO_2NR_2 + HCl \quad (3)$$

$$PhSO_2Cl + H_2O \rightarrow PhSO_3H + HCl \quad (4)$$

Once formed, the chloramine reacts rapidly with the nucleophilic arenesulfinate ion to form a sulfonyl chloride (eq 2, Scheme I) which can be isolated from a dilute reaction mixture. The products suggest a nucleophilic attack of a sulfinate on the chloramine chlorine.

Previous reports of reactions of sulfur nucleophiles with molecules containing chlorine–nitrogen or chlorine–oxygen bonds have suggested a displacement of chlorine from the oxygen or nitrogen. Thiols and thiolates, for instance, react with chloramines to form sulfenamides. The products suggest that the sulfur attacks the nitrogen center and displaces the chlorine to form a nitrogen–sulfur bond.[9] Kice has speculated that at lower pH's the benzenesulfinate ion reacts at the oxygen center of hypochlorous acid and displaces chlorine to form benzenesulfonic acid.[8] However, in neither case does the data rule out a sulfenyl chloride or sulfonyl chloride intermediate.

On the other hand, since nitrogen and chlorine have similar electronegativities, chloramines exhibit characteristics of compounds containing both an electrophilic chlorine and an electrophilic nitrogen. Thus nucleophilic attack at either atom is not unexpected and different mechanisms may be explained by the inability of a bulky sulfinate nucleophile to attack a sterically hindered nitrogen.

Sulfonamide formation (eq 3, Scheme I) is dependent upon the reaction of the amine with the sulfonyl chloride.

Since only one benzenesulfonyl chloride molecule is formed for each chloramine present, the yields of benzenesulfonamide decrease dramatically at low concentrations of chloramine. Rapid solvolysis and diffusion of the amine formed leave the hydrolysis of benzesulfonyl chloride (eq 4, Scheme I) a highly competitive side reaction.

Experimental Section

General Procedure. Infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer, and NMR spectra were recorded on a Varian T-60 spectrometer and are reported in parts per million (δ) relative to the internal standard tetramethylsilane. Melting points were recorded on a Thomas-Hoover melting point apparatus and are not corrected. Ultraviolet spectra were recorded on a Cary 219 spectrophotometer. Amperometric titrations were carried out by using two platinum electrodes with a potential of 100.0 mV applied across them and an Electronic Development Corp. Model 100MV DC power supply. The current was monitored with a Fluke Model 8000A digital multimeter on the 200-μA scale and was accurate to ± 0.1 μA. Unless otherwise mentioned, all materials used were reagent grade. *tert*-Butyl hypochlorite was prepared by the method of Mintz and Walling.[10] Commerical grade sodium hypochlorite (5%, Clorox) was used as received and was standardized by iodometric titration.[11] Organic amines obtained commercially and used as received included piperidine, pyrrolidine, diisobutylamine, tetrahydroisoquinoline, ethylenediamine, L-leucine, glycine, dimethylamine, morpholine, diethylamine, and aniline. Allylamine, *sec*-butylamine, and *n*-hexylamine were distilled prior to use. Other organic reagents used as received included benzenesulfonyl chloride, *p*-toluene-

(3) Rogne has measured the hydrolysis rate constant of benzenesulfonyl chloride at 25 °C in 0.05 M KCl and found it to be 3.06×10^{-3} s^{-1}. See: Rogne, O. *J. Chem. Soc. B* **1968**, 1294.
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sulfonyl chloride, sodium benzenesulfinate, and sodium *p*-toluenesulfinate. A pH 4 buffer solution was prepared by dissolving sodium acetate trihydrate (24.3 g) in glacial acetic acid (48 g) and diluting to 100 mL with deionized water. All IR and NMR data and mixture melting points of the sulfonamides synthesized from chloramines were consistent with the sulfonamides prepared by reaction of the arenesulfonyl chloride with the amine in basic solution. Benzenesulfonyl chloride was analyzed on a Varian Model 920 gas chromatograph with a thermal-conductivity detector. A 10 ft × $^1/_4$ in. column of 10% SE-30 on acid-washed Chromosorb W was used at 170 °C with a helium flow rate of 45 mL/min. The yield of 1-(phenylsulfonyl)piperidine isolated from dilute reaction solutions was determined on a Waters Model 204 liquid chromatograph with a UV detector (0.01 AUFS). A 3.9 mm × 30 cm μ-Bondapak C-18 column was used. An eluant of 30% acetonitrile/70% H_2O (1% acetic acid) was used at a flow rate of 2 mL/min.

***N*-Chloropiperidine.** *N*-Chloropiperidine was synthesized by the method previously described.[12]

***N*-Chlorodiethylamine.** Into a sodium chloride saturated solution of 5% commerical grade sodium hypochlorite (89.4 mL) was added diethylamine (4.38 g, 60 mmol). The mixture was allowed to stir over ice and then decanted into a separatory funnel. The organic chloramine was separated and percolated with $CaCl_2$. *N*-Chlorodiethylamine was distilled at 94 °C; 3.9 g, 0.036 mol, 60% yield.[13]

***N*-Chlorodimethylamine.** Dimethylamine (2.7 g, 0.06 mol) was condensed in a test tube immersed in an ethanol–ice bath at −20 °C. The amine was added dropwise, with stirring, to a NaCl-saturated solution of 5% commercial grade sodium hypochlorite (102 mL, 0.06 mol) immersed in an ice bath. The mixture was stirred for 30 min and then decanted into a separatory funnel. The upper layer containing the organic chloramine was dried over molecular sieves, distilled at room temperature below 0.1 torr, and collected with the receiver at liquid nitrogen temperature; 2.93 g, 0.0368 mol, 61% yield.[13]

Method A. A solution of sodium arenesulfinate (46 mmol) in water (60 mL) was cooled in an Erlenmeyer flask to below 10 °C. Freshly distilled organic chloramine (32 mmol) was added dropwise over 0.5 h. The product mixture was stirred overnight at room temperature and filtered through a tared filter funnel. The pure product was dried in a vacuum desiccator. The high purity of the sulfonamides obtained in this manner was confirmed by their melting points and mixture melting points with material prepared by reaction of the arenesulfonyl chloride with the amine and by comparison of IR and NMR spectra with those of authentic material. Sulfonamides obtained in this manner were 1-(phenylsulfonyl)piperidine, *N,N*-dimethyl-*p*-toluenesulfonamide, and *N,N*-diethyl-*p*-toluenesulfonamide. Physical constants for these compounds are given under method B below. Yields of pure products are given in Table II.

Method B. Amine (40 mmol) and sodium benzenesulfinate (9.86 g, 60 mmol) were dissolved in water (50–100 mL), and the solution was stirred in an Erlenmeyer flask immersed in an ice bath. A standardized solution of sodium hypochlorite (50 mmol) was added dropwise over 1 h. The resulting slurry was stirred overnight at ambient temperature. Product solutions derived from reaction of primary amines or amino acids were acidified before being vacuum filtered through a tared filter funnel. Solutions from reactions of secondary amines were filtered without prior acidification. The sulfonamide product was dried in a vacuum desiccator. The purity of the sulfonamide was determined as in method A. Yields of pure products are listed in Tables I and II.

Benzenesulfonamides obtained in this manner and requiring no further purification included the following (mp, lit. mp): 1-(phenylsulfonyl)piperidine (90–92, 92 °C[14]), 1-(phenylsulfonyl)morpholine (117–118, 118 °C[15]), 1,2,3,4-tetrahydro-2-(phenylsulfonyl)isoquinoline (153–155, 154 °C[16]).

p-Toluenesulfonamides were prepared by use of the same molar ratios of reactants and 100 mL of water as the reaction solvent. Those obtained pure by this method included the following (mp, lit. mp): 1-(*p*-tolylsulfonyl)piperidine (96–98, 98 °C[17]), 1-(*p*-tolylsulfonyl)morpholine (146–147, 147 °C[18]), 1-(*p*-tolylsulfonyl)pyrrolidine (122–123, 123 °C[19]), *N,N*-dimethyl-*p*-toluenesulfonamide (79–81, 79 °C[15]), *N,N*-diethyl-*p*-toluenesulfonamide (58–60, 60 °C[20]).

Sulfonamides synthesized by the methods just described, but which required recrystallization, included the following (mp, lit. mp): benzenesulfonamide (151–153 (from ethanol), 151 °C[21]), *N*-phenylsulfonylglycine (165–168 (from water), 165–166 °C[22]).

N,N'-Ethylenebis(benzenesulfonamide) was synthesized by use of ethylenediamine (1.14 g, 25 mol), sodium benzenesulfinate (16.4 g, 100 mmol), and NaOCl (100 mmol) in the usual manner. The product mixture was acidified before being filtered. The product after recrystallization from ethanol had a melting point of 166–168 °C (lit.[23] mp 168 °C).

Despite reports of a solid compound,[24] the benzenesulfonamide of *n*-hexylamine obtained either by method B or by reaction of the amine with benzenesulfonyl chloride could not be crystallized under any conditions. IR and NMR spectra of compounds obtained by both methods are identical.

Modified Method B. A solution of amine (20 mmol), acetic acid (20 mmol), and sodium arenesulfinate (40 mmol) in water (50–100 mL) was chilled below 10 °C in an Erlenmeyer flask by immersion in an ice bath. Standardized sodium hypochlorite solution (30 mmol) was added dropwise over 1 h. The resulting mixture was stirred overnight at room temperature. Reaction mixtures involving primary amines and amino acids were strongly acidified before workup. The product was obtained by filtration by use of a tared filter funnel and was dried in a vacuum desiccator. Purity was determined as in method A. Yields of pure products obtained by this method are listed in Tables I and II.

In this manner the following sulfonamides were obtained [sulfonamide (mp, lit. mp)]: *N-sec*-butylbenzenesulfonamide (70–72, 72 °C[25]), *N*-allyl-*p*-toluenesulfonamide (62–64, 64–65 °C[14]), *N*-(phenylsulfonyl)leucine (118–120, 119–120 °C[26]). Other sulfonamides obtained by this method which required recrystallization included the following (mp, lit. mp): *N*-phenylbenzenesulfonamide (108–110 (from ethanol/water), 108.5–109 °C[14]), *N,N*-diisobutylbenzenesulfonamide (54–55, 55–56 °C[14]).

Method C. To a solution of amine (40 mmol) in water (50 mL) cooled in an ice bath below 10 °C was added a standardized solution of sodium hypochlorite (50 mmol) dropwise over 1 h. The reaction mixture was allowed to stir an additional hour before sodium benzenesulfinate (60 mmol) in water (50 mL) was added rapidly below 10 °C. The product mixture was stirred overnight at room temperature and filtered. The pure product was dried in a vacuum desiccator. The purity of the sulfonamides was determined as in method A. Yields of pure products are listed in Tables I and II.

Sulfonamides prepared in this manner included *N-sec*-butylbenzenesulfonamide, 1-(phenylsulfonyl)piperidine, 1,2,3,4-tetrahydro-2-(phenylsulfonyl)isoquinoline, *N,N*-diisobutylbenzenesulfonamide, and *N*-hexylbenzenesulfonamide. Physical constants for these compounds are given under method B.

Kinetics of the Primary Reaction of *N*-Chloropiperidine and Sodium Benzenesulfinate. Working solutions of *N*-chloropiperidine (1.81×10^{-4} M) and sodium benzenesulfinate (9.96×10^{-5} M) in deionized water were freshly prepared prior to use. The solutions were incubated at 20.0 ± 0.2 °C in a constant-temperature bath for at least 0.5 h. Aliquots (10 mL) of

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Table III

[chloramine], M	[sulfinate], M	ΔA
1.0×10^{-4}	9.9×10^{-4}	0.034
2.0×10^{-4}	9.6×10^{-4}	0.068
1.0×10^{-4}	1.9×10^{-3}	0.036
1.0×10^{-3}	1.0×10^{-4}	0.037
1.0×10^{-3}	2.0×10^{-4}	0.072

each solution were mixed and allowed to react. After an appropriate time the reaction solution was rapidly washed into a solution (10 mL) of KI (0.5 g) in deionized water containing 1 mL of a pH buffer solution. The resulting solution was diluted up to approximately 75 mL with deionized water, and the amount of iodine formed was determined by amperometric titration with 8.10×10^{-4} N sodium thiosulfate. Typical readings taken included the following [reaction time (volume of titrant)]: 0 min (3.13 mL), 0.5 min (2.82 mL), 1 min (2.52 mL), 1.5 min (2.37 mL), 2 min (2.35 mL), 2.5 min (2.44 mL), 3 min (2.20 mL), 5 min (2.17 mL), 6 h (1.85 mL). Scatter in the readings from multiple runs made it impossible to obtain a good rate constant.

Isolation of Benzenesulfonyl Chloride. A solution (500 mL) of *N*-chloropiperidine (1.0×10^{-4} M) in deionized water was mixed for 0.5 min in a separatory funnel with a solution (500 mL) of sodium benzenesulfinate (1.1×10^{-3} M). Concentrated sulfuric acid (30 mL) was added, and the solution was rapidly extracted with chloroform (1×100 mL and then 1×50 mL). The extract was dried over sodium sulfate, filtered, and concentrated on a rotary evaporator in a tared flask. The residue (22 mg) gave an IR spectrum and VPC retention time identical to those of benzenesulfonyl chloride. VPC indicated the presence of a small amount (<10%) of residual chloroform.

Yield of 1-(Phenylsulfonyl)piperidine at Low Concentrations of *N*-Chloropiperidine. An aqueous solution (500 mL) of sodium benzenesulfinate (2.0×10^{-3} M) was mixed with an aqueous solution (500 mL) of either 2.0×10^{-4} or 2.0×10^{-5} M *N*-chloropiperidine. The resulting solutions were allowed to react 2.5 and 15 h, respectively. They were then extracted with chloroform (4×50 mL). The extracts of the separate reactions were each dried over sodium sulfate, filtered, and concentrated on a rotary evaporator. The residue of the reaction of 10^{-4} M chloramine was diluted with acetonitrile to 100 mL in a volumetric flask. The residue from the reaction of 10^{-5} M chloramine was diluted with acetonitrile to 10 mL in a volumetric flask. Each sample was analyzed by HPLC, and peak heights were compared with equivalent injections of 1.0×10^{-3} M 1-(phenylsulfonyl)-piperidine in acetonitrile. A yield of 8% was obtained in the reaction of 10^{-4} M chloramine, and no product was detected for the reaction of 10^{-5} M chloramine.

Kinetics of the Secondary Reaction of *N*-Chloropiperidine and Sodium Benzenesulfinate. Hydrolysis of Benzenesulfonyl Chloride. Stock solutions of *N*-chloropiperidine and sodium benzenesulfinate were prepared so that when 0.100 mL of a solution of one reagent was micropipetted into 2.90 mL of a solution of the other in a cuvette, the solutions indicated in Table III were obtained. The absorbance (at 269 nm) was read 12 s after mixing (A_I) and 132 s after mixing (A_F). From these $\Delta A = A_I - A_F$ was calculated.

The change in absorbance with time was measured for a solution of 1.0×10^{-4} M *N*-chloropiperidine and sodium benzenesulfinate in 0.05 M NaCl at 25 °C. A plot of log (absorbance at time t − absorbance at t_∞) vs. time gave a straight line of slope $(-3.6 \pm 0.9) \times 10^{-3}$ s^{-1}.

The rate of hydrolysis of benzenesulfonyl chloride at 25 °C in 0.05 M aqueous NaCl was determined spectrophotometrically at 269 nm as described above by using solutions prepared by the method of Rogne.[3] Instead of acetone, acetonitrile was used to disperse the benzenesulfonyl chloride. A rate of hydrolysis of $(3.14 \pm 0.8) \times 10^{-3}$ s^{-1} was obtained.

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Registry No. Ammonia, 7664-41-7; allyl amine, 107-11-9; aniline, 62-53-3; *n*-hexylamine, 111-26-2; *sec*-butylamine, 13952-84-6; ethylenediamine, 107-15-3; leucine, 61-90-5; glycine, 56-40-6; piperidine, 110-89-4; pyrrolidine, 123-75-1; morpholine, 110-91-8; tetrahydroisoquinoline, 91-21-4; diisobutylamine, 110-96-3; dimethylamine, 124-40-3; diethylamine, 109-89-7; sodium benzenesulfinate, 873-55-2; sodium *p*-toluenesulfinate, 824-79-3; *N*-chloropiperidine, 2156-71-0; 1-(phenylsulfonyl)piperidine, 5033-23-8; *N,N*-dimethyl-*p*-toluenesulfonamide, 599-69-9; *N,N*-diethyl-*p*-toluenesulfonamide, 649-15-0; 1-(phenylsulfonyl)morpholine, 5033-21-6; 1,2,3,4-tetrahydro-2-(phenylsulfonyl)isoquinoline, 79409-51-1; 1-(*p*-tolylsulfonyl)piperidine, 4703-22-4; 1-(*p*-tolylsulfonyl)morpholine, 6339-26-0; 1-(*p*-tolylsulfonyl)pyrrolidine, 6435-78-5; benzenesulfonamide, 98-10-2; *N*-phenylsulfonylglycine, 5398-96-9; *N,N'*-ethylenebis(benzenesulfonamide), 4392-52-3; *N*-*sec*-butylbenzenesulfonamide, 23705-41-1; *N*-allyl-*p*-toluenesulfonamide, 50487-71-3; *N*-(phenylsulfonyl)leucine, 68305-76-0; *N*-phenylbenzenesulfonamide, 1678-25-7; *N,N*-diisobutylbenzenesulfonamide, 41178-58-9; *N*-hexylbenzenesulfonamide, 7250-80-8.

Synthesis and Reactions of Perfluorobutanesulfonyl Hypohalites

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Two new hypohalites, perfluoro-*n*-butanesulfonyl hypochlorite and hypobromite, are reported. The hypochlorite is prepared by the low-temperature reaction of ClF with the acid $C_4F_9SO_2OH$. The hypobromite is prepared by reaction of the hypochlorite with bromine. The new compounds contain very electrophilic halogen atoms and exhibit reactions similar to the analogous trifluoromethanesulfonates, CF_3SO_2OX (X = Cl, Br). The new hypohalites exhibit somewhat greater stability than the trifluoromethanesulfonates but form analogous decomposition products. Characterization of the new compounds is given along with several reactions with olefins and halides to yield a variety of new esters.

The synthetic utility of the halogen derivatives of several strong oxyacids has now been well established.[1] The primary reaction for these halogen derivatives involves electrophilic addition across an olefinic bond which gives rise to a variety of esters and ethers. Interestingly, the additions appear to stereospecific and cis in many cases.[2] An additional important reaction type is exhibited by four

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