The fractions after 500 ml gave 1-methyl-4,4-diphenyl-3-piperidinol (**10**), mp 162–165° (lit.[8] mp 158–159°). The infrared spectrum showed an OH stretching absorption and the nmr spectrum gave a signal (quartet) at τ 5.32, a carbinol CH of an ABX system.

Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.50; H, 7.93; N, 5.41.

Registry No.—1, 2206-30-6; 2-d_4, 13427-20-8; **2a**, 13427-21-9; **7**, 1589-60-2; **8**, 13441-17-3; **9**, 1891-24-3; **9** hydrochloride, 13427-23-1; **10**, 7507-74-6; 1-methyl-3,4-diphenyl-4-piperidinol, 13427-24-2.

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Derivatives of Azidosulfonic Acid. Halides, Amides, and Salts

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The preparation of sulfuryl azide chloride, sulfamoyl azide, and several aromatic sulfamoyl azides was achieved by the metathetical reaction of sodium azide and the related chloro derivatives. A broadly applicable synthesis of substituted sulfamoyl azides was found in the reaction of sulfuryl azide chloride and amines. Previously developed preparations of inorganic azidosulfonate salts were utilized in the synthesis of quaternary ammonium azidosulfonates. The reactions of selected products indicated that these materials have chemical properties similar in kind to those of sulfonyl azides.

A number of derivatives of azidosulfonic acid are known. Sulfuryl azide, $SO_2(N_3)_2$,[1] sulfuryl azide fluoride, FSO_2N_3,[2] pyrosulfuryl azide, $N_3SO_2OSO_2N_3$,[3] N,N-dialkylsulfamoyl azides, $R_2NSO_2N_3$,[4] and azidosulfonate salts, N_3SO_3M,[3,5–7] have been reported. We now wish to describe the preparation of additional examples of azidosulfonic acid derivatives and to suggest, from the results of a brief study of their reactions, that their chemical properties are similar to those of the sulfonyl azides.

Sulfuryl Azide Chloride

The synthesis of the explosive liquid, sulfuryl azide chloride (I), was accomplished in high yield by the reaction of sulfuryl chloride fluoride with sodium azide in the presence of a catalytic amount of dimethylformamide. The preferential replacement of fluoride by azide is in accord with previously described reactions of sulfuryl chloride fluoride and amines.[8,9] In the absence of dimethylformamide, the yields of azide I are not consistent, while an excess of the amide causes decomposition of the product.

$$ClSO_2F + NaN_3 \longrightarrow \underset{I}{ClSO_2N_3} + NaF \qquad (1a)$$

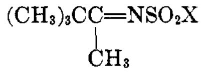
It was suggested that a trace of moisture promotes the formation of sulfuryl azide from sulfuryl chloride.[1] It has now been found that azide I can be isolated when the reaction is carried out under anhydrous conditions.

$$SO_2Cl_2 + NaN_3 \longrightarrow ClSO_2N_3 + NaCl \qquad (1b)$$

Another synthesis of sulfuryl azide fluoride[2] (eq 2) was found in the reaction of sulfuryl fluoride and lithium azide. Attempts to obtain this product from fluoride exchange reactions with azide I were unsuccessful.

$$SO_2F_2 + LiN_3 \longrightarrow FSO_2N_3 + LiF \qquad (2)$$

In a reaction which is characteristic of azides,[10] compound I and tetramethylethylene combine to form the iminosulfonyl chloride II which, upon treatment with dimethylamine, is converted to the sulfamide III.



$$(CH_3)_3C\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NSO_2X$$

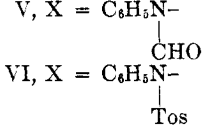
II, X = Cl
III, X = $N(CH_3)_2$

Sulfamoyl Azides

Sulfamoyl azide (IV) was isolated as a low melting, explosive solid from the reaction of sulfamoyl chloride and sodium azide (eq 3). The sulfamoyl azides V and VI were obtained from similar reactions of N-chlorosulfonylformanilide and N-chlorosulfonyl-*p*-toluenesulfonanilide.[11] Since the synthesis of aromatic sulfamoyl chlorides appears to be limited to compounds having an electronegative substituent on the nitrogen atom, the

$$XSO_2Cl + NaN_3 \longrightarrow \underset{IV-VI}{XSO_2N_3} + NaCl \qquad (3)$$

IV, X = NH_2-



$$V,\ X = C_6H_5\underset{\displaystyle CHO}{\underset{|}{N}}-$$

$$VI,\ X = C_6H_5\underset{\displaystyle Tos}{\underset{|}{N}}-$$

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[1] T. Curtius and F. Schmidt (*Ber.*, **55**, 1571 (1922)) and R. A. Abramovitch and B. A. Davis (*Chem. Rev.*, **64**, 149 (1964)) summarized the work done with sulfuryl azide.

[2] J. K. Ruff, *Inorg. Chem.*, **4**, 567 (1965).

[3] H. Lehman and W. Holznagel, *Z. Anorg. Allgem. Chem.*, **293**, 314 (1958).

[4] W. B. Hardy and F. H. Adams, U. S. Patent 2,863,866 (1958).

[5] W. Traube and A. Vockerodt, *Ber.*, **47**, 943 (1914).

[6] G. Beck, *J. Prakt. Chem.*, **156**, 237 (1940).

[7] H. Elsner and H. Ratz, German Patent 886,298 (1953).

[8] H. J. Emeleus and J. F. Wood, *J. Chem. Soc.*, 2183 (1948).

[9] H. W. Roesky and A. Hoff, *Ber.*, **98**, 2429 (1965).

[10] J. E. Franz, M. W. Dietrich, A. Henshall, and C. Osuch, *J. Org. Chem.*, **31**, 2847 (1966); F. D. Marsh, H. E. Simmons, M. E. Hermes, and A. G. Anastassiou, Abstracts of Papers, 150th National Meeting of the American Chemical Society, Sept 1965, p 62S.

[11] J. Meybeck, *Ann. Chim.* (Paris), **17**, 129 (1932); M. M. Battegay, French Patent 735,765 (1932).

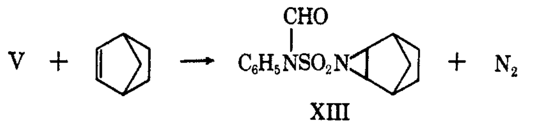
preparation of aromatic sulfamoyl azides by the azide exchange route is likewise restricted.[12]

A more general synthesis of sulfamoyl azides was found in the reaction of basic amines with sulfuryl azide chloride (I) (eq 4). Qualitative tests during a preparation of azide VII showed that the replacement of chloride occurs exclusively at first. However, prolonged contact of the sulfamoyl azide VII with aniline causes the substitution of the azide group and the formation of 1,3-diphenylsulfamide.

$$2RR'NH + ClSO_2N_3 \longrightarrow \underset{\text{VII-XII}}{RR'NSO_2N_3} + RR'NH{\cdot}HCl \qquad (4)$$

VII, R = C_6H_5; R′ = H
VIII, R = p-$CH_3C_6H_4$; R′ = H
IX, R = p-ClC_6H_4; R′ = H
X, R = C_6H_{11}; R′ = H
XI, R = n-C_4H_9; R′ = H
XII, R = R′ = n-C_4H_9

In a test of the chemical reactivity of sulfamoyl azides, photochemical and thermal initiation brought about a reaction of compound V with norbornene (eq 5). The product was identified as the *exo*-aziridine XIII.


(5)

XIII

Azidosulfonate Salts

Traube and Vockerodt reported that the reaction of hydrazinesulfonic acid and metallic nitrites afforded azidosulfonate salts which were relatively stable in neutral and basic aqueous solutions.[5] Elsner and Ratz, on the other hand, stated that sodium azidosulfonate prepared from chlorosulfonic acid and sodium azide decomposed instantly upon addition to neutral water.[7] In order to resolve this discrepancy, both procedures were repeated and the products were compared. The difference in the hydrolytic stability of the two products was confirmed and a comparison of the infrared spectra showed that each product contained sodium azidosulfonate.

The synthesis from chlorosulfonic acid must proceed by the initial formation of sodium chlorosulfonate and hydrazoic acid. The evolution of hydrogen chloride provides the driving force in the final step of the reaction (eq 6). Decomposition or loss by vaporization of part of the hydrazoic acid will result in the formation of a product which is contaminated with sodium chlorosulfonate, a hydrolytically unstable and acidic material. The hydrolytic instability of sodium azidosulfonate, prepared by this method, can be attributed to the sodium chlorosulfonate contaminant, since Traube and Vockerodt showed that azidosulfonates are immediately decomposed in acidic solutions. This was confirmed by careful neutralization of the product to give sodium azidosulfonate having normal water stability and a purity of 50–85%.

$$ClSO_3H + NaN_3 \longrightarrow ClSO_3Na + HN_3$$

$$ClSO_3Na + HN_3 \rightleftarrows N_3SO_3Na + HCl \qquad (6)$$

The known procedures for the synthesis of inorganic azidosulfonates are readily applied to the preparation of the quaternary ammonium analogues. Treatment of sodium chlorosulfonate with a soluble quaternary ammonium azide leads to the formation of the corresponding azidosulfonate. The reaction of hydrazinesulfonic acid with a quaternary ammonium nitrite gives an equivalent result (eq 7).

$$(C_6H_5CH_2)_2\overset{+}{N}(CH_3)_2\overset{-}{N_3} + ClSO_3Na$$

$$\searrow$$

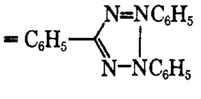
$$\underset{\text{XIV}}{(C_6H_5CH_2)_2\overset{+}{N}(CH_3)_2N_3SO_3^-} \qquad (7)$$

$$\nearrow$$

$$(C_6H_5CH_2)_2\overset{+}{N}(CH_3)_2\overset{-}{NO_2} + H_2NNHSO_3H$$

Alternatively, these products may be prepared by the exchange reaction of a quaternary ammonium salt with sodium azidosulfonate (eq 8). Variations in the hydrolytic stabilities of azidosulfonates were observed and are related to the size of the cation. Sodium azidosulfonate decomposes slowly in water at room temperature and rapidly on heating. The reaction seems to be a simple hydrolysis (eq 9). Moist tetramethylammonium azidosulfonate (XVII) is destroyed within a few hours at room temperature, while the higher molecular weight salts, XIV and XVI, can be stored several days in aqueous solutions with very little decomposition. This difference may reflect the ability of a small cation to assist hydrolysis by polarizing the azidosulfonate ion.

$$R_4\overset{+}{N}Cl^- + N_3SO_3Na \longrightarrow R_4\overset{+}{N}N_3SO_3^- + NaCl \qquad (8)$$

XV, R_4N =


XVI, R_4N = $C_6H_5N(CH_3)_2CH_2C_6H_5$
XVII, R_4N = $(CH_3)_4N$

$$N_3SO_3^- + H_2O \longrightarrow HSO_4^- + HN_3 \qquad (9)$$

The azidosulfonate salts are weak nucleophiles and are ineffective in ordinary substitution reactions. The salt XIV did not react with benzyl bromide, but did react with acetyl chloride to give acetyl azide. This conversion probably results from a direct reaction between the two reagents and does not appear to require the preliminary decomposition of the azidosulfonate to azide ion. This proposal is supported by the absence of 2-azidohexafluoroisopropyl acetate in the final product when the azidosulfonate is first treated with hexafluoroacetone and then with acetyl chloride. The ester is formed in high yield under these conditions when an azide salt is used in place of the azidosulfonate.

The negative charge on the azidosulfonate ion stabilizes the azido group. No reaction was observed between the salt XIV and cyclohexene at 150°. However, fusion of this salt with triphenylphosphine results in the evolution of nitrogen and the formation of the phosphazosulfonate salt XVIII (eq 10).

$$XIV + (C_6H_5)_3P \longrightarrow$$
$$N_2 + \underset{\text{XVIII}}{[(C_6H_5CH_2)_2N(CH_3)_2]^+[(C_6H_5)_3P{=}NSO_3]^-} \qquad (10)$$

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[12] W. Traube (*Ber.*, **24**, 360 (1891)) reported the preparation of the unstable compound, phenylsulfamoyl chloride. We were unable to repeat this work.

Spectra

The infrared spectra of the sulfamoyl azides display absorption at 4.6–4.75 (asymmetric N_3), 7.1–7.4 (asymmetric SO_2), and 8.3–8. 6 μ (asymmetric N_3 and SO_2). In some cases, the absorption in the latter region appears as a single, broad band. Infrared absorptions associated with the azidosulfonate ion appear in four characteristic regions (KBr) at 4.6–4.85, 7.8–8.2 (broad band or two bands), 9.2–9.6, and 13.2–13.8 μ.

The mass spectra of the sulfamoyl azides indicate that fragmentation at both SO_2–N bonds occurs in all of the compounds. In the aromatic derivatives, ArNH–SO_2 bond breaking gives a resonance stabilized ion, $ArNH^+$, in larger amounts than the less stable $ArNHSO_2^+$ ion. In the aliphatic compounds, fragmentation at the SO_2–N_3 bond is observed to give larger amounts of $RNHSO_2^+$ ion.

Experimental Section[13]

Sulfuryl Azide Chloride (I). From Sulfuryl Chloride Fluoride.—A mixture of 1.0 g (15 mmoles) of sodium azide, 50 μl of dimethylformamide, and 5.85 g (40 mmoles) of sulfuryl chloride fluoride[8] was stirred 18 hr at 25° in a 150-cc glass pressure flask. The flask was cooled in liquid nitrogen, opened to a high vacuum line, and allowed to warm to 25°. The vapors were passed through a −45° trap (chlorobenzene slush) into a liquid nitrogen cooled trap. The product which collected in the −45° trap amounted to 1.9 g (90%) of I, a colorless liquid: bp 116–117°; density, 1.44 g/ml; infrared bands appeared at 4.62 (N_3 asym), 7.05 (SO_2 asym), 8.40 and 8.56 (both SO_2 and N_3 sym), and 13.01 μ. The partial mass spectrum of I is given in Table I.

TABLE I

PARTIAL MASS SPECTRUM OF SULFURYL AZIDE CHLORIDE (I)

m/e	Assignment	Relative intensity, %
141	$ClSO_2N_3^+$	26
106	$SO_2N_3^+$	100
99	$ClSO_2^+$	90
83	$ClSO^+$	13
78	SO_2N^+	21
64	SO_2^+	51
48	SO^+	44
42	N_3^+	32

Caution! The mechanical shock sensitivity of I is only slightly less than that of nitroglycerin. Rapid heating may cause an explosion. Solutions of 25% by weight of I in benzene, chloroform, or methylene chloride are safe to handle under normal conditions.

Traces of chlorine must be excluded from the reaction mixture, or violent detonations will occur. Chlorine was efficiently removed by briefly contacting sulfuryl chloride fluoride with dicyclopentadiene at the melting point of the mixture.

From Sulfuryl Chloride.—To 5 g (77 mmoles) of sodium azide in a flask embedded in a polyurethan block was added 3 ml (5 g, 37 mmoles) of freshly distilled sulfuryl chloride. A calcium sulfate drying tube was set in the top of the flask which was occasionally shaken over a 3-day period. Crushed ice (20 ml) was then added and the dense product was extracted into methylene chloride. After washing with ice-cold water and drying over calcium sulfate, the extract was distilled to remove the solvent. The residue amounted to 1.4 g (27.5%) of essentially pure I. This method is too hazardous for normal laboratory procedures and should be carried out with remote handling equipment.

Sulfuryl Azide Fluoride.—A mixture of 0.25 g (5 mmoles) of lithium azide, 0.1 ml of dimethylformamide, 4.6 g of dimethyl ether, and 1.02 g (10 mmoles) of sulfuryl fluoride was stirred for 19 hr at 25° in a glass pressure flask. After cooling, volatiles distilling at −66° (chloroform slush) were removed under vacuum. The flask was warmed to room temperature and 0.2 ml of sulfuryl azide fluoride was distilled to a cooled receiver. The infrared and mass spectra of the product were identical with those reported previously.[3] Although no tests were made, the product is believed to be a hazardous chemical.

Reaction of I with Tetramethylethylene.—A mixture of 1.0 g (7.1 mmoles) of I and 0.64 g (7.6 mmoles) of tetramethylene was stirred 18 hr at 25° in a sealed, evacuated pressure flask. The unreacted starting materials were removed by distillation on a high-vacuum line. The infrared and nmr spectra indicated that the residue was 3,3-dimethyl-2-butylidenylsulfamoyl chloride (II): infrared band at 6.22 μ; nmr peaks at 152 and 307 cps in a ratio of 3:1. Attempts to purify the product resulted in decomposition. Methylene chloride (10 ml) and 0.65 g (14 mmoles) of dimethylamine were added to the crude product and stirred 3 hr. After filtration, evaporation of the solvent left 0.8 g of an oily solid which was crystallized three times from petroleum ether (bp 30–60°) (charcoal) to give 0.33 g (23%) of N,N-dimethyl-N′-(3,3-dimethyl-2-butylidenyl)sulfamide (III): mp 48–50°; infrared, 6.11 μ; nmr, 72, 141.6, and 167.5 cps in the ratio 3:1:2.

Anal. Calcd for $C_8H_{18}N_2O_2S$: C, 46.57; H, 8.80; N, 13.58. Found: C, 46.98; H, 8.89; N, 13.45.

Sulfamoyl Azide (IV).—A solution of 10 g (85 mmoles) of sulfamoyl chloride[14] in 75 ml of acetonitrile was added over a 3-hr period to a stirred mixture of 7.8 g (120 mmoles) of sodium azide in 75 ml of acetonitrile. Infrared analysis showed that the reaction was completed within 24 hr. After filtration, the solvent was removed under vacuum and the residue was distilled on a Hickman still. The colorless liquid distilling at 25–50° (0.4 μ) amounted to 6.4 g (60.6%) of IV. On standing, the oil solidified, mp 28–29°. Infrared absorptions (liquid) were observed at 2.95–3.10 (doublet), 4.72, 6.55, 7.27–7.40, and 8.50–8.65 μ. The nmr spectrum had a single broad peak at 359 cps. Sulfamoyl chloride exhibited a broad peak at 396 cps. Sulfamoyl azide has a mechanical shock sensitivity comparable with that of nitroglycerin. The partial mass spectrum of IV is given in Table II.

TABLE II

PARTIAL MASS SPECTRUM OF SULFAMOYL AZIDE (IV)

m/e	Assignment	Relative intensity, %
122	$H_2NSO_2N_3^+$	12.0
80	$H_2NSO_2^+$	100
64	SO_2^+	11.4
48	SO^+	14.1
46	SN^+	10.8
42	N_3^+	9.8

N-Azidosulfonylformanilide (V).—A mixture of 2.2 g (10 mmoles) of N-chlorosulfonylformanilide,[11] 0.65 g (10 mmoles) of sodium azide, 50 μl of dimethylformamide, and 23 g of sulfur dioxide in a glass pressure flask was stirred 3 days at 25°. The sulfur dioxide was removed and the residue was extracted with methylene chloride. Evaporation of the extract left an oil which was induced to crystallize by cooling in Dry Ice. Recrystallization from absolute alcohol yielded 0.5 g (22%) of V, mp 79–80°.

N-Azidosulfonyl-*p*-toluenesulfonanilide (VI).—A mixture of 10 g (29 mmoles) of N-chlorosulfonyl-*p*-toluenesulfonanilide[11] and 2 g (30 mmoles) of sodium azide in 300 ml of acetonitrile was stirred 3 days at 40°. After filtration and evaporation of the solvent, the crude product was dissolved in ether and extracted with cold aqueous sodium hydroxide. The ether was dried ($MgSO_4$) and evaporated. The residue was warmed under high vacuum on a Hickman still to give, first, 2 g of *p*-toluenesulfonyl azide[15] and then 1 g (9%) of VI (sublimed) which was crystallized from ethanol, mp 117–118°.

Reaction of V with Norbornene.—A solution of 0.5 g (2.2 mmoles) of V and 0.5 g (5.3 mmoles) of norbornene in 10 ml of acetonitrile was irradiated with a low pressure mercury resonance lamp (principal line at 2537 A) for 24 hr as 54 cc (100%) of nitrogen was evolved. The mixture was treated with charcoal, filtered, and evaporated. The residual oil slowly solidified; crystallization from ethanol gave 0.25 g (39%) of a solid, mp

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(13) Proton nmr spectra were measured at 60 Mc with internal TMS. Chemical shifts are given as cycles per second downfield from the standard.

(14) R. Appel and G. Berger, *Ber.*, **91**, 1339 (1958).

(15) T. Curtius and G. Kraemer, *J. Prakt. Chem.*, **125**, 323 (1930).

118–120°, which analytical and spectroscopic data indicated was N-(N′-formyl-N′-phenylsulfamoyl)-3-azatricyclo[3.2.1.$0^{2,4}$]-octane (XIII). The infrared spectrum had strong peaks at 5.9 (C═O) and 8.6 μ (SO_2). The nmr spectrum ($DCCl_3$) was similar to that reported for 3-benzenesulfonyl-3-azatricyclo[3.2.1.$0^{2,4}$]-octane.[16] The product was also obtained in an equivalent amount by heating an acetonitrile solution of V and norbornene at 55° for 24 hr. Its nmr spectrum is given in Table III.

Anal. Calcd for $C_{14}H_{16}N_2O_3S$: C, 57.52; H, 5.52; N, 9.58; O, 16.42; S, 10.97. Found: C, 57.62; H, 5.52; N, 9.23; O, 16.42; S, 11.00.

TABLE III

NMR SPECTRUM OF COMPOUND XIII

Proton group	δ, cps
6, 7, 8	44–96
1, 5	150
2, 4	172
Benzene ring	445
CHO	549

Phenylsulfamoyl Azide (VII).—A mixture of 2.16 g (15.3 mmoles) of I, 5.7 g (61.2 mmoles) of aniline, and 65 ml of benzene was stirred 36 hr at room temperature. Filtration yielded 1.8 g of aniline hydrochloride. The filtrate was extracted with cold 2% hydrochloric acid, washed with cold water, and dried ($MgSO_4$). Occasionally, treatment with decolorizing carbon was necessary. After removal of the solvent, the crude product was distilled under high vacuum on a Hickman still to give 1.51 g (50%) of VII which usually solidified on standing, mp 48–49°. This procedure was utilized in the preparation of the sulfamoyl azides listed below.

A mixture of 0.3 g (1.5 mmoles) of VII and 0.5 g (5.4 mmoles) of aniline in 25 ml of methylene chloride was left 1 week at room temperature and then filtered. The solid was water soluble and gave a positive ferric chloride test for azide ion.[17] The filtrate was extracted with dilute hydrochloric acid and then with dilute aqueous sodium hydroxide. The basic extract was acidified to precipitate 0.23 g of a white solid, mp 112–114°, which was identified as 1,3-diphenylsulfamide[11] by its infrared spectrum.

***p*-Tolylsulfamoyl Azide (VIII).**—A mixture of 3.1 g (22 mmoles) of I and 5 g (47 mmoles) of *p*-toluidine in 130 ml of benzene for 3 days at room temperature afforded 1 g (22%) of VIII. Crystallization from *n*-hexane gave crystals, mp 41–42°.

***p*-Chlorophenylsulfamoyl Azide (IX).**—A mixture of 2.7 g (19 mmoles) of I and 6.6 g (51 mmoles) of *p*-chloroaniline in 125 ml of chloroform for 3 days at room temperature yielded 1 g (22%) of IX, mp 50–52°.

Cyclohexylsulfamoyl Azide (X).—A mixture of 1.5 g (11 mmoles) of I and 2.4 g (24 mmoles) of cyclohexylamine in 25 ml of benzene for 40 hr at room temperature afforded 0.8 g (35%) of X as a clear liquid.

***n*-Butylsulfamoyl Azide (XI).**—A mixture of 1.7 g (12 mmoles) of I and 1.8 g (25 mmoles) of *n*-butylamine in 75 ml of benzene for 2.5 days at room temperature afforded 0.6 g (28%) of XI, a clear, mobile oil. Elemental analysis of this compound could not be obtained because it exploded when burned. The mass spectrum displayed the following partial cracking pattern (time of flight): m/e (ion), 178 (parent), 136 ($C_4H_9NHSO_2^+$), 135 ($C_4H_9SO_2^+$ or $CH_2NHSO_2N_3^+$), 107 ($HSO_2N_3^+$), 106 ($SO_2N_3^+$), 57 ($C_4H_9^+$), 42 (N_3^+).

Di-*n*-butylsulfamoyl Azide (XII).—A mixture of 0.72 g (5 mmoles) of I and 1.3 g (20 mmoles) of di-*n*-butylamine in 25 ml of benzene at room temperature for 19 hr yielded 0.85 g (70%) of XII, a colorless oil.[4]

Sodium Azidosulfonate.—The following is a modification of the procedure of Elsner and Ratz.[7] To a stirred mixture of 48 g (740 mmoles) of sodium azide in 450 ml of methylene chloride was added, dropwise, a solution of 93 g (800 mmoles) of chlorosulfonic acid in 75 ml of methylene chloride. After 2 days at 25–30°, the mixture was filtered in a drybox and the solid product was washed thoroughly with methylene chloride. The solid was then added in small portions to an excess of a saturated solution of barium hydroxide at 5–15° and the resulting mixture was filtered. The filtrate was treated with carbon dioxide to remove excess barium hydroxide. After filtration, the product solution was evaporated to dryness, under vacuum, as rapidly as possible at 25–40°. The residue was suspended in anhydrous acetonitrile, filtered, and dried to yield 61 g of a solid which was assayed as 73% sodium azidosulfonate (see below).

Caution! Sodium azidosulfonate is a weak explosive having a variable sensitivity to mechanical shock and heating.

Hydrolysis of Sodium Azidosulfonate.—A 2-g sample of 84% sodium azidosulfonate was refluxed 2 hr in dilute aqueous sodium hydroxide (pH 9). The final solution was acidic (pH 3). Evaporation left a white solid which was shown to be a mixture of sodium sulfate and sodium bisulfate by its infrared spectrum and by the formation of a precipitate with aqueous barium hydroxide. In other experiments carried out at room temperature, the formation of azide ion was indicated by a ferric chloride test.[17]

Dibenzyldimethylammonium Azide.[18]—Solutions of 50 g (770 mmoles) of sodium azide in 150 ml of water and 100 g (382 mmoles) of dibenzyldimethylammonium chloride in 150 ml of water were mixed and cooled in ice. The resulting precipitate was recrystallized from 225 ml of water to give 107.5 g (83%) of dibenzyldimethylammonium azide tetrahydrate, mp 63–64° (sealed capillary).

Anal. Calcd for $C_{16}H_{20}N_4 \cdot 4H_2O$: C, 56.4; H, 8.3; N, 16.5. Found: C, 56.5; H, 8.5; N, 16.8.

The product was dried to constant weight before use in the azidosulfonate preparation.

Dibenzyldimethylammonium Nitrite.—A solution of 280 g of sodium nitrite in 2800 ml of water was passed through a column of IRA-400 ion-exchange resin (Rohm and Haas Co.) and the column was rinsed with water. A solution of 100 g of dibenzyldimethylammonium chloride in 900 ml of water was passed through the column and was followed by 500 ml of water. Evaporation of the effluent yielded 90.8 g of crude hemihydrate, mp 150–151°. Crystallization from acetone gave the anhydrous salt, mp 150–151°.

Anal. Calcd for $C_{16}H_{20}N_2O_2$: C, 70.57; H, 7.40; N, 10.29. Found: C, 70.45; H, 7.78; N, 10.32.

Dibenzyldimethylammonium Azidosulfonate (XIV). From Chlorosulfonic Acid.—A mixture of 20 g (170 mmoles) of chlorosulfonic acid and 10 g (170 mmoles) of sodium chloride in 300 ml of methylene chloride was stirred under a nitrogen stream for 2 days until the evolution of hydrogen chloride could no longer be detected. The resulting sodium chlorosulfonate was thoroughly washed with methylene chloride in a drybox and then suspended in 200 ml of methylene chloride. Dibenzyldimethylammonium azide (40 g, 149 mmoles) in 200 ml of methylene chloride was added and the mixture was stirred overnight at 25°. Evaporation of the solvent from the entire mixture left a solid which was added, portionwise, to 200 ml of cold 3% aqueous sodium hydroxide. The mixture was filtered and the solid was washed with ice water. After drying, 30 g (59%) of XIV was isolated. Crystallization from acetonitrile gave crystals, mp 134–135°.

Anal. Calcd for $C_{16}H_{20}N_4O_3S$: C, 55.16; H, 5.79; N, 16.09; O, 13.78; S, 9.21. Found: C, 55.24; H, 5.68; N, 15.60; O, 13.87; S, 9.65.

From Hydrazinesulfonic Acid.—An ice-cold solution of 3 g (26.8 mmoles) of hydrazinesulfonic acid[19] in 50 ml of water was added dropwise to a solution of 8 g (30.6 mmoles) of dibenzyldimethylammonium chloride and 2.2 g (32 mmoles) of sodium nitrite in 120 ml of cold water. After 15 min a white solid began to separate. When the precipitation was completed, filtration yielded 5.4 g (58%) of XIV, mp 134–135°. A similar yield of XIV was obtained on mixing ice-cold aqueous solutions of equimolar amounts of hydrazinesulfonic acid and dibenzyldimethylammonium nitrite.

From Sodium Azidosulfonate. Assay Method for Soluble Azidosulfonates.—Concentrated aqueous solutions of sodium azidosulfonate and dibenzyldimethylammonium chloride were mixed and the resulting precipitate of XIV was collected, washed, and dried. The amount of product was corrected for the uncollected soluble portion of XIV (solubility, 1.0 g/100 ml at 25°) to give the assay value. Chloride and sulfate impurities did not affect the result.

Reaction of XIV and Acetyl Chloride.—A mixture of 2 g (5.5 mmoles) of XIV, 18 g of sulfur dioxide, and 0.44 g (5.6 mmoles)

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[16] J. E. Franz and C. Osuch, *Tetrahedron Letters*, No. 13, 837 (1963).

[17] F. Feigl, "Spot Tests, Inorganic Applications," Vol. I, 4th ed, Elsevier Publishing Co., Amsterdam, The Netherlands, 1954, p 268.

[18] We are indebted to Dr. N. van Gulick for this procedure.

[19] A. Meuwsen and H. Tischer, *Z. Anorg. Allgem. Chem.*, **294**, 282 (1958).

TABLE IV

ANALYSIS OF SULFAMOYL AZIDES

Sulfamoyl azide	Formula	Calcd, % C	Calcd, % H	Calcd, % N	Calcd, % S	Calcd, % O	Found, % C	Found, % H	Found, % N	Found, % S	Found, % O
V	$C_7H_6N_4SO_3$	37.2	2.65	24.8			37.4	2.65	24.8		
VI	$C_{13}H_{12}N_4S_2O_4$	44.3	3.4	15.8			44.3	3.2	14.8		
VII	$C_6H_6N_4SO_2$	36.35	3.05	28.3	16.1		36.39	2.91	28.14	15.99	
VIII	$C_7H_8N_4SO_2$	39.6	3.8	26.4	15.1		39.61	3.87	26.42	15.15	
IX	$C_6H_5N_4SO_2Cl$	31.0	2.16		13.8	13.60	30.85	2.22		13.7	13.67
X	$C_6H_{12}N_4SO_2$	35.2	5.9		15.7	15.7	35.38	5.88		15.64	15.43
XII	$C_8H_{18}N_4SO_2$	41.0	7.75		13.7	13.7	41.04	7.58		13.78	13.51

of acetyl chloride in a glass pressure flask was stirred overnight at 25°. The volatile material was pumped through a Dry Ice cooled trap in which 0.4 ml of liquid product was collected. Infrared analysis showed the product was a mixture of acetyl azide and methyl isocyanate. In another experiment, a mixture of 5.0 g (14.4 mmoles) of XIV, 3.1 g (24.6 mmoles) of hexafluoroacetone, and 29.2 g of sulfur dioxide was stirred for 3 days at 25° before 1.1 g (14.0 mmoles) of acetyl chloride was added. After stirring overnight, the mixture yielded 1.0 ml of a mixture of acetyl azide and methyl isocyanate.

2-Azidohexafluoroisopropyl Acetate.—A mixture of 1.0 g (15.4 mmoles) of sodium azide, 7.2 g of sulfur dioxide, and 2.5 g (15 mmoles) of hexafluoroacetone was stirred overnight at room temperature in a 150-cc glass pressure vessel. The flask was cooled in Dry Ice and 1.1 g (15.4 mmoles) of acetyl chloride was added. The mixture was stirred overnight at room temperature. The flask was opened to a high-vacuum line and 3.6 g (95.3%) of the ester was isolated by trap to trap distillation, bp 115–116°. The mass spectrum displayed a parent peak at *m/e* 251 (calcd 251) and infrared absorption at 1800 and 2165 cm^{-1}.

Anal. Calcd for $C_5H_3F_6O_2N_3$: C, 23.92; H, 1.20; F, 45.4; N, 16.74. Found: C, 24.32; H, 1.17; F, 41.7; N, 16.52.

Dibenzyldimethylammonium Triphenylphosphazosulfonate (XVIII).—A solid mixture of 10 g (28.8 mmoles) of XIV and 8 g (30.5 mmoles) of triphenylphosphine was slowly heated to 100°. Gas evolution began at 68°. After 2 hr, 660 cc (93%) of gas was collected in a gas buret. The solid product was crystallized from acetonitrile to give 6.8 g of XVIII, mp 211–213°. Infrared absorption (KBr) appeared at 6.82 (m), 7.02 (m), 8.70 (s, br), 8.98 (m), 9.88 (s), 10.02 (m), and 12.6–14.7 μ (m).

Anal. Calcd for $C_{34}H_{35}N_2O_3PS \cdot {}^1/_2CH_3CN$; C, 69.70; H, 6.10; N, 5.85; P, 5.13; S, 5.03. Found: C, 70.39; H, 6.11; N, 6.05; P, 5.07; S, 5.13.

2,3,5-Triphenyl-2H-tetrazolium Azidosulfonate (XV).—Aqueous solutions of 12.0 g (35.8 mmoles) of 2,3,5-triphenyl-2H-tetrazolium chloride in 50 ml of water and 5 g (27.6 mmoles assay) of sodium azidosulfonate in 25 ml of water were mixed and cooled in ice water. The resulting precipitate of XV was filtered out, washed, and dried. The 9.6 g (83%) of product was crystallized from ethanol (charcoal) to yield 7.3 g of white plates, mp 156–158°.

Anal. Calcd for $C_{19}H_{15}N_7O_3S$: C, 54.15; H, 3.59; N, 23.27; S, 7.62. Found: C, 54.30; H, 3.70; N, 23.42; S, 7.55.

Benzyldimethylphenylammonium Azidosulfonate (XVI).—A mixture of 61 g (250 mmoles assay) of sodium azidosulfonate and 40 g (160 mmoles) of benzyldimethylphenylammonium chloride in 750 ml of acetonitrile was stirred 5 hr at room temperature and then filtered. The filtrate yielded 55.9 g of crude XVI. A 3-g portion in 20 ml of ethanol was added to 200 ml of ether to give 2.5 g of a white powder, mp 74–75°. The product evolved nitrogen when fused with triphenylphosphine.

Anal. Calcd for $C_{15}H_{18}N_4O_3S$: C, 54.04; H, 5.43; N, 16.75; O, 14.36; S, 9.59. Found: C, 54.15; H, 5.41; N, 16.41; O, 14.50; S, 9.65.

Tetramethylammonium Azidosulfonate (XVII).—A mixture of 36 g (170 mmoles assay) of sodium azidosulfonate and 13 g (120 mmoles) of tetramethylammonium chloride in 600 ml of acetonitrile was stirred overnight under dry nitrogen at 25°. The mixture was filtered and the filtrate was evaporated to give 18 g of crude XVII. Crystallization from acetonitrile in a drybox yielded a white solid, mp 151–154°, which slowly decomposed on exposure to atmospheric moisture. The product evolved nitrogen when fused with triphenylphosphine.

Anal. Calcd for $C_4H_{12}N_4O_3S$: C, 24.47; H, 6.16; N, 28.55; O, 24.45; S, 16.34. Found: C, 25.33; H, 6.49; N, 26.66; O, 24.20; S, 15.86.

Registry No.—I, 13449-15-5; II, 13444-28-5; III, 13444-29-6; IV, 13449-16-6; V, 13449-17-7; VI, 13449-18-8; VII, 13449-19-9; VIII, 13449-20-2; IX, 13479-10-2; X, 13449-21-3; XI, 13449-22-4; XII, 13479-11-3; XIII, 13444-30-9; XIV, 13449-23-5; XV, 13449-28-0; XVI, 13449-24-6; XVII, 13449-25-7; XVIII, 13444-31-0; dibenzyldimethylammonium azide, 13449-26-8; dibenzyldimethylammonium nitrite, 13444-32-1; 2-azidohexafluoroisopropyl acetate, 13449-27-9.