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Organic Sulfur Compounds. IX. The Reactions of *N*-Sulfinylamines with Nitrogen Tetroxide and Nitrosyl Chloride

By Michio KOBAYASHI* and Koichi HONDA

Department of Chemistry, Yokohama City University, Mutsuura-machi, Kanazawa-ku, Yokohama

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N-Sulfinylaniline reacted with nitrogen tetroxide to form the anhydrous benzenediazonium nitrate. The reactions of *N*-sulfinylaniline and several of its *p*-substituted derivatives with nitrosyl chloride also gave the anhydrous diazonium chlorides in the crystalline state. Aliphatic *N*-sulfinylamines reacted with nitrosyl chloride to form alkyl chlorides, probably by the decomposition of the initially-formed diazonium chlorides; during this reaction, no rearrangement of the alkyl group was observed.

Recent a short communication[1] which described the formation of benzenediazonium fluoroborate and hexafluoroantimonate from *N*-sulfinylaniline and, respectively, nitrosyl fluoroborate and hexafluoroantimonate prompted us to publish our similar studies of the reactions of *N*-sulfinylamines with nitrogen tetroxide or nitrosyl chloride.

Several addition reactions to *N*-sulfinylamines (I), in which a cationic part of the attacking reagent became attached to the nitrogen, and an anionoid part to the sulfur atoms, of I, have been known.[2,3]

$$\mathrm{R{-}N{=}S{=}O + ArSH \rightarrow R{-}\underset{H}{\underset{|}{N}}{-}\underset{O}{\underset{\downarrow}{S}}{-}S{-}Ar} \qquad (1)$$

(I)

$$\mathrm{R{-}N{=}S{=}O + R'MgX \rightarrow R{-}\underset{XMg}{\underset{|}{N}}{-}\underset{O}{\underset{\downarrow}{S}}{-}R'} \qquad (2)$$

On the other hand, many carbonyl compounds give condensation products with such reactive *N*-sulfinylamines as *N*-sulfinyl sulfonamides,[4] as shown below:

$$\mathrm{R{-}N{=}S{=}O + R'CHO \rightarrow R{-}N{=}CH{-}R' + SO_2} \qquad (3)$$

Analogous condensation between the nitroso compounds and *N*-sulfinylamines could take place according to the following equation:

$$\mathrm{R{-}N{=}S{=}O + X{-}NO \rightarrow R{-}N{=}N{-}X + SO_2} \qquad (4)$$

If X-NO is an ionic compound, which could dissociate to form a nitrosonium cation and an anion X^-, the above condensation would lead to the formation of the diazonium salts:

$$\mathrm{R{-}N{=}S{=}O + NO^+X^- \rightarrow [R{-}N{\equiv}N]^+X^-} \qquad (5)$$

In the case of the aliphatic *N*-sulfinylamines, the primary product, alkyldiazonium salt with a well-known low stability, would decompose to RX and nitrogen:

$$\mathrm{[R{-}N{\equiv}N]^+X^- \rightarrow RX + N_2} \qquad (6)$$

These expectations have been fully realized, as will be described in this paper.

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* To whom correspondence should be sent: Department of Chemistry, Faculty of Science, Tokyo Metropolitan University, Setagaya-ku, Tokyo.

[1] K. Bott, *Angew. Chem.*, **77**, 132 (1965).

[2] G. Kresze and H. P. Patzschke, *Chem. Ber.*, **93**, 380 (1960).

[3] a) H. Gilman and H. L. Morris, *J. Am. Chem. Soc.*, **48**, 2399 (1926); b) D. Klamann, C. Sass and M. Zelenka, *Chem. Ber.*, **92**, 1910 (1959); c) W. T. Smith, Jr., P. A. Thio and M. Grasley, *J. Org. Chem.*, **27**, 692 (1962).

[4] G. Kresze and R. Albrecht, *Angew. Chem.*, **74**, 781 (1962).

Results and Discussion

When an ether solution of *N*-sulfinylaniline was added to a solution of nitrogen tetroxide in ether at −10°C, the reaction started immediately, forming a white precipitate. The filtrate of this precipitate began to form a similar precipitate at once, and even after the second filtration of the second precipitate, a substantial amount of the fresh precipitate was obtained. These precipitates were shown, by their infrared spectra in a KBr disk, to be benzenediazonium nitrate. In the dry state, this compound tends to decompose violently upon a slight shock. It was easily soluble in water, and an aqueous solution gave a coupling product with an alkaline solution of β-naphthol. The ether filtrate of the diazonium nitrate smelled strongly of sulfur dioxide. Due to the hygroscopic and explosive nature of the diazonium salt, its exact yield could not be determined as such. In a separate experiment, the first, second and third precipitate were dissolved in water immediately after the filtration, and then subjected to a coupling reaction with β-naphthol to give α-phenylazo-β-naphthol, the combined yield of which was 80% of the theoretical yield based on *N*-sulfinylaniline. Since the third filtrate gave some diazonium nitrate too, the yield of the diazonium salt was considered to be almost quantitative. The third filtrate was mixed with water and sulfate anions were precipitated as barium sulfate, which amounted to 6% of the theoretical yield based on sulfinylaniline. Therefore, most of the sulfur of sulfinylaniline was converted into sulfur dioxide, of which only a small fraction underwent oxidation to a higher oxidation state such as nitrosyl sulfate by means of excess dinitrogen tetroxide. The above result may be formulated as below:

$$C_6H_5N{=}S{=}O + N_2O_4 \rightarrow C_6H_5N_2{}^+NO_3{}^- + SO_2 \qquad (7)$$

When a solution of an equimolar nitrosyl chloride in carbon tetrachloride was added to an ether solution of sulfinylaniline cooled at −70°C, a white precipitate started to form immediately. After a few minutes this precipitate was filtered off and the filtrate was stored in a refrigerator overnight, during which time a considerable amount of the same precipitate was deposited. The infrared spectrum of this precipitate exhibited strong absorptions at 2270, 1570, 1456, 1303, 1080, and 760 cm^{-1}, just as authentic benzenediazonium chloride. The first precipitate gave α-phenylazo-β-naphthol in a 33% yield in a coupling reaction with β-naphthol.

In a similar manner, *p*-nitro-*N*-sulfinylaniline rapidly reacted with nitrosyl chloride at −70°C to form the copious precipitate of *p*-nitrobenzenediazonium chloride, which gave α-*p*-nitrophenylazo-β-naphthol upon coupling with alkaline β-naphthol.

p-Methoxy-*N*-sulfinylaniline reacted slowly with nitrosyl chloride at a low temperature. After the reaction mixture had been kept in a refrigerator for 3 days, the precipitated diazonium salt was filtered off and coupled with β-naphthol to give α-*p*-methoxyphenyl-β-naphthol in a 36% yield. The filtrate of the diazonium salt was then kept for another 3 days in a refrigerator; it thus gave the same precipitate, the yield of which was estimated to be 24% by the coupling method. The total yield of *p*-methoxybenzenediazonium chloride was over 60%. The crude diazonium salt exhibited an infrared absorption at 2225 cm^{-1} the same region as in an authentic specimen of *p*-methoxybenzenediazonium chloride.

In a similar way, *p*-chloro-*N*-sulfinylaniline reacted with nitrosyl chloride in an ether - carbon tetrachloride mixture to give a white precipitate, supposed to be *p*-chlorobenzenediazonium chloride, which coupled with β-naphthol to give α-chlorophenylazo-β-naphthol in a 44% yield based on sulfinylamine. The relative velocity of the reaction of the *p*-substituted sulfinylaniline derivatives with nitrosyl chloride, as judged from the apparent velocity of the precipitation of the diazonium salts, was:

$$p\text{-nitro} > p\text{-chloro} > \mathrm{H} > p\text{-methoxy}.$$

In every case, the filtrate of the diazonium salt smelled strongly of sulfur dioxide.

On the basis of the above results, the reaction of *N*-sulfinylanilines with nitrosyl chloride can be expressed by the following formula, which is of the same type as is seen in the reaction with nitrogen tetroxide:

$$Ar{-}N{=}S{=}O + NOCl \rightarrow ArN_2{}^+Cl^- + SO_2 \qquad (8)$$

Considering the possiblity of the equilibrium:

$$N_2O_4 \rightleftarrows NO^+NO_3{}^- \qquad (9)$$

both reactions may be regarded as starting with the electrophilic attack of nitrosonium cations on the nitrogen atom of *N*-sulfinylanilines.

The facts that the amount of precipitated diazonium salt obtained by the first filtration did not exceed certain percentages of the theoretical yield, and that the fresh precipitate began to form immediately after the filtration, suggest the existence of some kind of equilibrium between the starting materials or one of the intermediates and the diazonium salt. A similar equilibrium phenomenon has been observed in the reaction of benzalaniline with nitrosyl chloride or nitrogen tetroxide to give the diazonium salts.[5]

The following reaction mechanism may be proposed:

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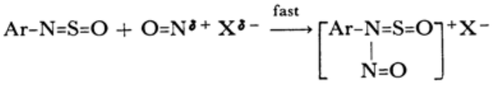
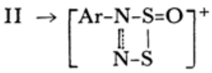
[5] J. Turcan, *Bull. soc. chim. France*, [5]**2**, 627 (1935); c. f. R. M. Scribner, *J. Org. Chem.*, **29**, 3429 (1964).



$$\mathrm{Ar{-}N{=}S{=}O} + \mathrm{O{=}N}^{\delta+}\,\mathrm{X}^{\delta-} \xrightarrow{\text{fast}} \begin{bmatrix}\mathrm{Ar{-}N{=}S{=}O}\\ \mid\\ \mathrm{N{=}O}\end{bmatrix}^{+}\mathrm{X}^{-}$$

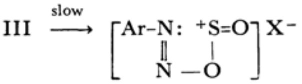
II

(10)



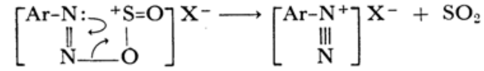
$$\mathrm{II} \rightarrow \begin{bmatrix}\mathrm{Ar{-}N{-}S{=}O}\\ \Vert\quad\mid\\ \mathrm{N{-}S}\end{bmatrix}^{+}\mathrm{X}^{-} \qquad (11)$$

III



$$\mathrm{III} \xrightarrow{\text{slow}} \begin{bmatrix}\mathrm{Ar{-}N{:}\ \ {}^{+}S{=}O}\\ \Vert\qquad\mid\\ \mathrm{N\ {-}O}\end{bmatrix}\mathrm{X}^{-} \qquad (12)$$

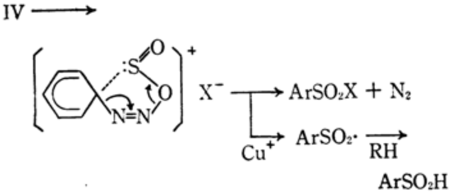
IV



$$\begin{bmatrix}\mathrm{Ar{-}N{:}\ {}^{+}S{=}O}\\ \Vert\qquad\mid\\ \mathrm{N{-}O}\end{bmatrix}\mathrm{X}^{-} \longrightarrow \begin{bmatrix}\mathrm{Ar{-}N^{+}}\\ \equiv\\ \mathrm{N}\end{bmatrix}\mathrm{X}^{-} + \mathrm{SO_2} \qquad (13)$$

V

Well-known reactions of the diazonium salts with sulfur dioxide in the presence of a copper catalyst to form the sulfinic acids or sulfonyl chlorides⁶⁾ may be attributed to the formation of IV by the reverse reaction of (13), which collapses, thus resulting in sulfonyl chloride (reaction 14) or in sulfinic acid, according to the reaction 15:

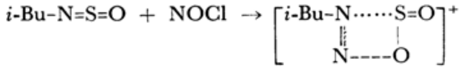


Reaction 10 seems to be very fast and irreversible, since the characteristic color of nitrosyl chloride faded almost instantly after the reactants were mixed. Only small fractions of the liberated sulfur dioxide were oxidized by nitrogen tetroxide to a higher oxidation state, suggesting that most of nitrogen tetroxide had been consumed, leaving only a small amount of it available for the oxidation when free sulfur dioxide was liberated in the reaction 13. Consequently, the reaction 10 could not be a rate determining step. Reactions 11 and 12 may form a concerted one-step process; they are probably the rate determining.

The order of the rate of the formation of the diazonium salt was *p*-nitro>*p*-chloro>unsubstituted > *p*-methoxy, as has been described above. Since the reaction 10 is a cationoid attack by nitrosonium ion, the reverse order would be expected if this reaction were the rate determining step. On the other hand, if the reaction 11 or 12, in which the adduct II rearranges to IV with a long conjugated system, is the rate determining step, the acceleration by an electron-attractive substituent is quite understandable.

Alkyldiazonium salts are known to be very unstable, and they have never been isolated. In this connection, the reaction mechanism of the aliphatic *N*-sulfinylamines with nitrosyl chloride seemed to be interesting. Although the reaction of *N*-sulfinylethylamine and nitrosyl chloride failed to give any definite product attributable to the diazonium salt formation, the reactions of *N*-sulfinyl-*n*-butylamine and *N*-sulfinyl-isobutylamine with nitrosyl chloride gave *n*-butyl chloride and isobutyl chloride respectively. In both cases, no isomeric chloride was observed to be formed.

These butyl chlorides are considered to be the decomposition products of the intermediate butyldiazonium chlorides. The above results definitely exclude the formation of a free butyl cation during the decomposition, since the *n*-butyl carbonium ion is known to rearrange readily to the *s*-butyl cation, and the isobutyl carbonium ion, to *s*-butyl and *t*-butyl cations.



$$i\text{-}\mathrm{Bu{-}N{=}S{=}O} + \mathrm{NOCl} \rightarrow \begin{bmatrix}i\text{-}\mathrm{Bu{-}N\cdots\cdots S{=}O}\\ \vdots\qquad\mid\\ \mathrm{N{-}{-}{-}{-}O}\end{bmatrix}^{+}\mathrm{Cl}^{-}$$

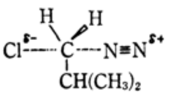
VI

(16)

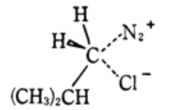
$$\mathrm{VI} \rightarrow [i\text{-}\mathrm{BuN_2}^{+}]\ \mathrm{Cl}^{-} + \mathrm{SO_2} \qquad (17)$$

VII

Therefore, the decomposition of the diazonium chloride VII to butyl chloride and nitrogen molecule must be a concerted process, in which the bond breaking between carbon and nitrogen and the bond forming between carbon and chlorine proceed simultaneously in an ion pair VII. The following two transition states, namely the S_N2 type (VIII) and the S_Ni type (IX), are conceivable for the last reaction:



VIII



IX

Since the bond between carbon and the positively charged $N_2{}^+$ group is considered to be very weak, the nucleophilic assistance by the chloride ion in the splitting of this bond can not be important in any way. The rapid collapse of the tightly-bound ion pair VIII will result in the formation of either the inverted or the retained product, or both, depending on the location of the chloride ion in this ion pair intermediate.

In the reaction of the aliphatic amines with nitrous acid to give the alcohols, the rearrangement of the alkyl groups has been reported,⁷⁾

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6) H. Meerwein, G. Dittmar, R. Göllner, K. Hafner, F. Mensch and O. Steinfort, *Chem. Ber.*, **90**, 841 (1957).

7) V. Meyer, J. Barbieri and F. Forster, *Ber.*, **10**, 130 (1877); This problem has been discussed in great detail in lit. 9 and many examples are cited in that paper.

while their reactions with nitrosyl chloride to form the alkyl chlorides are accompanied by no such rearrangement,[8] just as in our case. The proposed explanation for the above difference was that the former reaction consisted of the reaction of the free alkyl carbonium ion, separated from the counter ion by a water molecule, whereas the latter reaction occurred within the ion pair in the early stage along the reaction coordinate.[9] Probably the same explanation is applicable in the present case.

Experimental

Materials.—Sulfinylaniline was prepared from aniline hydrochloride and thionyl chloride.[10] B. p. 88°C/12 mmHg. *p*-Nitro-*N*-sulfinylaniline[11] was prepared by refluxing *p*-nitroaniline with thionyl chloride in benzene. M. p. 70°C.

p-Methoxy-*N*-sulfinylaniline, b. p. 146.5°C/25 mmHg (lit.[12] b. p. 132°C/15 mmHg), and *p*-chloro-*N*-sulfinylaniline, b. p. 136°C/40 mmHg (lit.[13] b. p. 237°C), were prepared in a similar way. *N*-Sulfinylethylamine[14] was prepared as follows: To 15 g. of ethylamine cooled in ice water, there was added a solution of 46.5 g. of *N*-sulfinylaniline in 50 ml. of ether over a 30 min. period; the mixture was kept overnight at room temperature. After repeated fractional distillations, a fraction boiling 73—74°C was retained (6.5 g.).

***N*-Sulfinyl-*n*-butylamine.**—To an ice-cooled solution of 25 g. of *n*-butylamine in a mixture of 55 g. of dry pyridine and 50 ml. of ether, a solution of 41 g. of thionyl chloride in ether was slowly added; the reaction mixture was then stirred for 30 min., filtered, and vacuum-distilled to give 17 g. of sulfinyl-*n*-butylamine, b. p. 47°C/50 mmHg (lit.[15] 38°C/10 mmHg). *N*-Sulfinyl-isobutylamine was prepared from 25 g. of isobutylamine in a similar way. B. p. 44°C/60 mmHg; the yield was 26.8 g. (65%). Nitrogen tetroxide was obtained by the pyrolysis, at 260°C, of nitrogen pentoxide.[16] Nitrosyl chloride was generated from sodium nitrite and concentrated hydrochloric acid; dried by passing it over sodium nitrite, hydrated potassium chloride and calcium chloride successively,and finally purified by fractional distillation.[17]

The Reaction of *N*-Sulfinylaniline and Nitrogen Tetroxide.—i) A solution of 1 g. of nitrogen tetroxide in ether was cooled to −10°C. When a solution of 1 g. of sulfinylaniline in ether was added to this solution, drop by drop, a white precipitate began to form at once. As soon as this precipitate had been filtered off, a new precipitate started to form in the filtrate; from the second filtrate, third white crystalline precipitate was obtained. The infrared spectra of the first and second precipitates in the KBr disk completely coincided with that of the authentic benzenediazonium nitrate prepared by the diazotation of aniline nitrate with isoamyl nitrite.[18] When a minute crystal of the product was crushed on a porous plate, it exploded violently. The filtrate of the diazonium salt smelled strongly of sulfur dioxide. ii) In a similar way, 1.5 g. of sulfinylaniline and 1.3 g. of nitrogen tetroxide were mixed in ether and the successively-precipitating diazonium nitrate was taken off by filtration up to the third crop. The combined yield was estimated by coupling with β-naphthol to be 80% (α-phenylazo-β-naphthol, m. p. 206°C; 2.2 g.; identified by infrared spectrum). The filtrate of the third precipitate was mixed with water, and the ether was evaporated at room temperature. To the remaining solution the diluted hydrochloric acid was added and sulfur dioxide was expelled by warming the solution on a water bath. The addition of 0.1 N barium chloride to the above solution while it was hot gave 0.148 g. of barium sulfate, in 6% yield based on sulfinylaniline.

The Reaction of Sulfinylaniline with Nitrosyl Chloride.—When 1.0 g. of nitrosyl chloride (15 mmol.) in 8 ml. of carbon tetrachloride was added to a solution of 2.2 g. of sulfinylaniline (16 mmol.) in 10 ml. of ether, a white precipitate appeared immediately. After a few min., this precipitate was filtered through a fritted glass funnel, whereupon a new precipitate started to fill the filtrate. The first precipitate was dissolved in water and coupled with β-naphthol to give 1.2 g. of α-phenylazo-β-naphthol (33%).

The Reaction of *p*-Nitro-*N*-sulfinylaniline with Nitrosyl Chloride.—The reaction between 2.6 g. of *p*-nitrosulfinylaniline and 0.8 g. of nitrosyl chloride was carried out at −70°C in a similar way. The immediately-formed white precipitate was filtered off after a few minutes. Its infrared spectrum in a KBr disk was superimposable upon that of *p*-nitrobenzenediazonium chloride prepared by the diazotation of *p*-nitroaniline hydrochloride with isoamyl nitrite in acetic acid.[19] The coupling of the first precipitate with β-naphthol gave 1.5 g. of α-*p*-nitrophenylazo-β-naphthol (40%).

The Reaction of *p*-Methoxy-*N*-sulfinylaniline with Nitrosyl Chloride.—When 2.5 g. of *p*-methoxysulfinylaniline and 1.0 g. of nitrosyl chloride were treated at −70°C as above, the rate of the precipitation of the diazonium salt was much slower than the precipitation rates of the other diazonium salts described in this paper. After it had been stored for 3 days in a refrigerator, the reaction mixture was filtered off, and the precipitated diazonium chloride was dissolved

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8) P. A. S. Smith, D. R. Baer and S. N. Ege, *J. Am. Chem. Soc.*, **76**, 4564 (1954).

9) R. Huisgen and C. Ruchardt, *Ann.*, **601**, 1 (1956). See also H. Zollinger, "Azo and Diazo Chemistry, Aliphatic and Aromatic Compounds," translated by H. E. Nursten, Interscience Publishers, N. Y. (1961), p. 123.

10) A. Michaelis and R. Herz, *Ber.*, **23**, 3480 (1890); A. Michaelis, ibid., **24**, 745 (1891).

11) G. Kresze and H. Smalla, *Chem. Ber.*, **92**, 1042 (1959).

12) O. Wichterle and J. Rocek, *Chem. Listy*, **47**, 1768 (1953); Ref. 11.

13) A. Michaelis and C. Hümme, *Ber.*, **24**, 754 (1891).

14) W. K. Glass and A. D. E. Pullin, *Trans. Faraday Soc.*, **57**, 546 (1961).

15) G. Zinner, *Chem. Ber.*, **91**, 971 (1958); Ref. 3b.

16) L. Hackspill and J. Besson, *Bull. soc. chim. France*, [5] **16**, 479 (1949).

17) W. A. Harrison, E. R. H. Jones, G. D. Meakins and P. A. Wilkinson, *J. Chem. Soc.*, **1964**, 3213; L. J. Beckham, W. A. Fessler and M. A. Kise, *Chem. Revs.*, **48**, 319 (1951).

18) E. Knoevenagel, *Ber.*, **23**, 2994 (1890).

19) A. Hantzsch and R. Jochem, ibid., **34**, 3338 (1901).

in water and subjected to a coupling reaction with β-naphtol to give 1.0 g. of α-*p*-methoxyphenylazo-β-naphthol (the total yield was 2.5 g.). Infrared absorption of this diazonium salt exhibited N≡N absorption at 2225 cm^{-1} in a KBr disk and coincided with that of the authentic specimen prepared from *p*-anisidine hydrochloride and isoamyl nitrite.[19]

The Reaction of *p*-Chloro-*N*-sulfinylaniline with Nitrosyl Chloride.—After a reaction mixture of 2.8 g. of *p*-chlorosulfinylaniline and 1.0 g. of nitrosyl chloride, treated as above at −70°C, was kept for a week in a refrigerator, the white precipitate was taken up by suction. Coupling with β-naphthol gave 1.7 g. of α-*p*-chlorophenylazo-β-naphthol in 44% yield. All the azo-β-naphthols described above were identified by means of their infrared spectrum.

The Reaction of *N*-Sulfinyl-*n*-butylamine with Nitrosyl Chloride.—To a solution of 8.5 g. of nitrosyl chloride in 20 ml. of ether, cooled at −70°C, there was added, drop by drop, a solution of 15.5 g. of sulfinyl-*n*-butylamine in 20 ml. of ether. The evolution of gas started immediately, accompanied by the copious formation of the white precipitate. When the reaction mixture was allowed to warm to room temperature, gas evolved vigorously from the precipitate, which turned into a spongy mass which floated over the surface and finally settled at bottom as a black oil. The reaction mixture smelled strongly of sulfur dioxide. The upper layer was separated, washed with water, dried over magnesium sulfate, and fractionally distilled to give 2 g. of a colorless liquid, b. p. 77.5°C, which was identified as *n*-butyl chloride by its infrared spectrum. No *s*-butyl chloride was detected. The yield was 20% of the theoretical.

The Reaction of *N*-Sulfinyl-isobutylamine with Nitrosyl Chloride.—The reaction of 9.0 g. of sulfinyl-isobutylamine with 16.5 g. of nitrosyl chloride was carried out in a way similar to that used for the *n*-butyl derivative. The white crystals which formed at −70°C decomposed at room temperature with the evolution of gas and gave white leaflet crystals and an oil layer, both insoluble in ether. This leaflet (0.5 g.), m. p. 157—159°C, was readily soluble in water and identified as isobutylamine hydrochloride by its infrared spectrum and by a Kjeldahl nitrogen determination (Found: N, 11.4%; Calcd. for $C_4H_9NH_3Cl$: 12.5%). The ether layer was washed with water and fractionally distilled to give 1.5 g. of isobutyl chloride, which was identified by means of its infrared spectrum and boiling point. No indication of the presence of *s*-butyl chloride or *t*-butyl chloride was observed by infrared spectroscopy or the gas liquid chromatography.