perature of acetone. After 9 hr., a weight loss of 22.65% was observed (calcd. for full conversion of I to II, 21.50%). The resulting orange solid was collected and recrystallized from carbon tetrachloride. The m.p. was 88–89°.

Anal. Calcd. for $C_6H_3(NO_2)_2SeCl$: Cl, 12.58. Found: Cl, 13.42.

2,4-Dinitrophenyl selenium trichloride (I) *from 2,4-dinitrobenzeneselenenyl chloride.* The orange monochloride (0.3330 g.) was placed in an atmosphere of dry chlorine for 3 days at room temperature. A weight gain of 7.80% was noted, and a somewhat amorphous material resulted. Recrystallization from carbon tetrachloride gave an orange product, which lost chlorine typically at 80–85°, and turned to an orange melt at 100°.

Anal. Calcd. for $C_6H_3N_2O_4SeCl_3$: Cl, 30.15. Found: Cl, 30.54.

Acetonyl 2,4-dinitrophenyl selenide. 2,4-Dinitrophenyl selenium trichloride (3.52 g., 0.01 mole) was added to 10 ml. of acetone. The mixture was refluxed for 5 min., filtered, cooled, and the yellow product collected and recrystallized from absolute ethanol. The product melted at 116–118°.

Anal. Calcd. for $C_9H_8N_2O_5Se$: N, 9.54. Found: N, 9.94.

Ethyl 2,4-dinitrobenzeneselenate. Into 10 ml. of absolute ethanol 3.52 g. (0.01 mole) of I was added. Addition of 1 ml. of dry pyridine caused formation of an orange color. The volume of the solution was reduced to one third on the steam bath and the remaining solution cooled, causing deposits of orange needles, which were collected and washed with a few ml. of absolute alcohol. After recrystallizing from absolute alcohol, the product melted at 128–129°, which corresponds exactly to the literature value[4] for the ethyl ester.

2,4-Dinitrobenzene selenenalide. Into 15 ml. of dry ether was added 3.52 g. (0.01 mole) of 2,4-dinitrophenyl selenium trichloride. One g. of dry aniline was then added slowly, whereupon a deep red color was noted. The volume was reduced by one fifth and the residue taken up in 50 ml. of 95% ethanol. This was treated with decolorizing charcoal, the mixture was reduced to about two thirds of the original volume and the remaining solution was cooled. The red-orange crystals were collected, washed, and dried; m.p. 187–189°.

Anal. Calcd. for $C_{12}H_9N_3O_4Se$: N, 12.41. Found: N, 12.59.

2-Chlorocyclohexyl, 2,4-dinitrophenyl selenide. Into 10 ml. of dry cyclohexene, was added 3.52 g. of 2,4-dinitrophenyl selenium trichloride (0.01 mole). The reaction mixture became warm and turned a deeper yellow color. It was let stand for one hour and then, by using a stream of dry air, the solvent was removed. The residue was taken up in 10 ml. of 95% ethanol, filtered, and the filtrate cooled, yielding, 1.10 g. of yellow needles, m.p. 114–115°.

Anal. Calcd. for $C_{12}H_{12}N_2O_4ClSe$: N, 7.74. Found: N, 7.47.

The x-ray powder patterns of the selenide and corresponding sulfide were practically identical, indicating similar space distribution of the substituents and size of unit cells; *Cf.* ref. 9.

4-Dimethylaminophenyl 2,4-dinitrophenyl selenide. This was prepared from reaction of I (3.5 g.) and dimethylaniline (2 ml.) dissolved in dry benzene (10 ml.) at room temperature. The solution was concentrated and the crude deep red product recrystallized from hot methanol, giving bright red needles, m.p. 194–196°.

Anal. Calcd. for $C_{14}H_{13}N_2O_4Se$: N, 11.28. Found: N, 10.88.

Spectra. The ultraviolet and infrared absorption spectra of the several pairs of sulfur and selenium compounds encountered in this work are recorded in a catalog of spectra being prepared for publication from this laboratory. The ultraviolet spectra of I and II are defined by the following absorption coefficients, at the wave lengths stated.

2,4-Dinitrobenzenesulfenyl chloride, in ethylene chloride solution; 4180 Å (max.)/2.4 × 10^3; 3660 Å (min.)/3.5 × 10^3; 3190 Å (max.)/8.9 × 10^3; 2930 Å (min.)/6.4 × 10^3; 2640 Å (max.)/10 × 10^3.

2,4-Dinitrophenyl selenium trichloride (in cyclohexane); 4180 Å (max.)/4.3 × 10^3; 3660 Å (min.)/2.4 × 10^3; 3235 Å (max.)/11.4 × 10^3; 2921 Å (min.)/5.0 × 10^3; 2640 Å (max.)/12.6 × 10^3; 2480 Å (min.)/11.5 × 10^3.

Acknowledgment. We are indebted to Mr. William R. Wilcox for assistance with experiments on the reactions of sulfuryl chloride with bis(2,4-dinitrophenyl) disulfide, to Dr. J. Donohue for help with the x-ray comparisons, to Dr. Adalbert Elek for microanalyses, and to the Office of Scientific Research, Air-Research and Development Command, for partial support of this study.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF SOUTHERN CALIFORNIA
LOS ANGELES 7, CALIF.

Amination of Tertiary Amines by Hydroxylamine-*O*-sulfonic Acid

HARRY H. SISLER, RICHARD A. BAFFORD,
GEORGE M. OMIETANSKI, BERNARD RUDNER,
AND RONALD J. DRAGO

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The reaction of chloramine with tertiary amines to form 1,1,1, trisubstituted hydrazinium chlorides has been clearly established.[1] It seemed desirable to us to investigate the possibility of a similar reaction with another compound of the type NH_2X where X represents an electronegative group other than chlorine. We have, therefore, investigated the reactions of hydroxylamine-*O*-sulfonic acid (NH_2OSO_3H) with a variety of tertiary amines and have found that *N*-aminating reactions of the type

$$R_3N + NH_2OSO_3H \longrightarrow [R_3NNH_2^+]\,[HSO_4^-]$$

do indeed occur. The present communication reports the results of studies of a series of these reactions. Meuwsen and Gösl have very recently reported a similar reaction with trimethylamine and pyridine.[2]

Since our results show that the reaction of tertiary amines with hydroxylamine-*O*-sulfonic takes place in basic media and that it also occurs with the sodium salt, we may postulate the following equation for the reaction

$$R_3N + H_2NOSO_2O^- \longrightarrow R_3NNH_2^+ + SO_4^=$$

The question as to whether the sulfate or hydrogen sulfate crystallizes undoubtedly depends upon solubility factors as well as the basicity of the individual nitrogen base concerned. In the case of dimethylaniline the hydrogen sulfate is obtained. In all other cases studied where crystallization occurred the sulfate was obtained.

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(1) G. Omietanski and H. Sisler, *J. Am. Chem. Soc.*, **78**, 1211 (1956).

(2) A. Meuwsen and R. Gösl, *Angew. Chem.*, 69, 754 (1957).

EXPERIMENTAL

Materials. Hydroxylamine-*O*-sulfonic acid was prepared by the reaction of hydroxylammonium sulfate and chlorosulfonic acid according to the method of Sommer, Schulz, and Nassau.[3] After preparation it was stored in a vacuum desiccator. Commercially available tertiary amines were used, in most instances, without further purification.

Procedure. The reactions were carried out by mixing a methanol, ethanol, or water solution of hydroxylamine-*O*-sulfonic acid with a methanol, ethanol, or water solution of the corresponding amine. Where necessary to initiate the reaction, the reaction mixture was heated. After reaction the mixture was allowed to stand at room temperature until the product separated. Occasionally it was necessary to add a non-polar solvent such as chloroform to precipitate the product. The procedures used do not necessarily represent conditions for optimum yields.

All the aliphatic tertiary amines studied react vigorously with solid hydroxylamine-*O*-sulfonic acid or its solution in methanol. Aromatic amines react much more slowly and these reaction mixtures were usually heated, though reaction will occur at room temperature if the reaction mixture is allowed to stand for several days.

Ammonium sulfate and considerable amounts of unidentified tarry materials are obtained as by-products in the reactions with aromatic amines. This results from the fact that hydroxylamine-*O*-sulfonic acid is an oxidizing agent, though a less active one than chloramine.

It was found that the sodium salt of hydroxylamine-*O*-sulfonic acid may also be used as an aminating agent.

Reaction with trimethylamine. A solution of 20 g. of hydroxylamine-*O*-sulfonic acid in about 75 ml. of water at 0° was added over a one hour period to a refluxing aqueous solution of 5 molar equivalents of trimethylamine. The reaction mixture was evaporated to a sirup in vacuo and was cooled. The crystals which formed were removed by filtration and repeatedly recrystallized from aqueous ethanol. They were insoluble in ether but readily soluble in water. The product decomposes from 250° to 255°.

Anal.[4] Calcd. for $[(CH_3)_3NNH_2]_2SO_4$: C, 29.26%; H, 9.00%; N, 22.75%; S, 13.00%. Found: C, 27.20, 27.41%; H, 9.16, 9.38%; N, 21.29, 21.09%; S, 13.16, 13.27%.

A portion of the salt was converted by metathesis to the hexafluorophosphate. This salt decomposes above 300°.

Anal.[4] Calcd. for $[(CH_3)_3NNH_2]PF_6$: C, 16.36%; H, 5.04%; P, 14.07%. Found: C, 16.28, 16.38%; H, 4.98, 5.14%; P, 14.01, 14.13%.

Reaction with triethylamine. A solution of 20 g. hydroxylamine-*O*-sulfonic acid in 150 ml. of ice water was added dropwise to a solution of 300 ml. of triethylamine in 300 ml. of water.

The reaction mixture was vacuum evaporated to a sirup. The sirup was heated with excess sodium hydroxide solution to drive off the excess triethylamine. The residue was neutralized with sulfuric acid and evaporated to dryness. The product was separated from the sodium sulfate by ethanol extraction. The alcoholic solution was treated with a saturated alcoholic solution of picric acid. Triethylhydrazinium picrate separated as yellow needles, m.p. 215°,[5] (reported[1] m.p. 214–215°).

Anal.[4] Calcd. for $[(C_2H_5)_3NNH_2]C_6H_2O(NO_2)_3$: C, 41.73%; H, 5.54%; N, 20.28%. Found: C, 41.76%; H, 5.61%; N, 20.31%.

Triethylhydrazinium sulfate has been obtained only as a viscous hygroscopic sirup.

Reaction with dimethylaminoethanol. To a suspension of 5.6 g. of hydroxylamine-*O*-sulfonic acid in 75 ml. of absolute ethanol was added 22 g. of dimethylaminoethanol. The mixture became hot and soon became homogeneous. When the initial reaction subsided, the mixture was gently boiled for 5 min. and placed in a refrigerator.

Addition of ether caused the solution to become cloudy, and a viscous oil separated; this oil crystallized in platelets after 3 days. This colorless, hygroscopic product weighed 5 g. (66% yield).

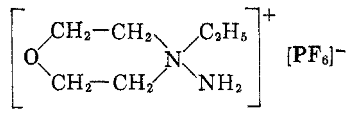
Anal.[4] Calcd. for $[HOCH_2CH_2N(CH_3)_2NH_2]_2SO_4$: C, 31.36%; H, 8.56%; N, 18.29%; S, 10.46%. Found: C, 31.00%; H, 8.50%; N, 19.25%; S, 10.69%.

The chloroplatinate salt was prepared by the method of Shriner and Fuson.[6] It melts with decomposition at 207–209°.

Anal.[4] Calcd. for $[HOCH_2CH_2N(CH_3)_2NH_2]_2[PtCl_6]$: C, 15.54%; H, 4.24%; N, 9.06%; Cl, 34.37%; Pt, 31.58%. Found: C, 16.04%; H, 4.34%; N, 8.90%; Cl, 33.20%; Pt. 31.90%.

Reaction with N-ethyl morpholine. Eastman Kodak Yellow Label *N*-ethylmorpholine was distilled through a Todd column packed with glass helices at a reflux ratio of 20:1, and the fraction distilling at 137.5° was collected. Forty grams of the purified *N*-ethylmorpholine and 50 ml. of water were heated to reflux and a solution of 8 g. of hydroxylamine-*O*-sulfonic acid in 50 ml. of ice water was added slowly and the mixture heated for 30 min. The mixture was allowed to cool and then concentrated by vacuum distillation of the solvent. The concentrated solution was treated with potassium hexafluorophosphate. The resulting solid was recrystallized twice from hot water. The product melted at 178–180° which agrees with the melting point obtained for the hexafluorophosphate obtained from the product of the *N*-ethylmorpholine-chloramine reaction.

Anal.[4] Calcd. for



C, 26.05%; H, 5.47%; N, 10.14%; F, 41.28%. Found: C, 25.46%; H, 5.44%; N, 10.25%; F, 41.01%.

Reaction with dimethylaniline. To a suspension of 5.6 g. of hydroxylamine-*O*-sulfonic acid in 75 ml. of absolute ethanol was added 30 g. dimethylaniline. There was no exothermic reaction. The mixture was heated to boiling for 10 min. during which time the mixture darkened. When the mixture stood overnight in a refrigerator, pink platelets separated. These platelets were filtered, washed with a small amount of absolute ethanol, and recrystallized from an ethanol-diethyl ether mixture. The product melted at 142–144°. Yield: 4.5 g. (38.5%). The analytical data below indicate that the hydrogen sulfate salt crystallizes in this instance.

Anal.[4] Calcd. for $[C_6H_5N(CH_3)_2NH_2]HSO_4$: C, 41.05%; H, 5.98%; N, 11.98%; S, 13.68%. Found: C, 41.01%; H, 5.80%; N, 12.72%; S, 13.72%.

The chloroplatinate salt was prepared. It melts at 156–157° (reported 156.7°,[1] 158–159°[7]).

Anal Calcd. for $[C_6H_5N(CH_3)_2NH_2]_2[PtCl_6]$: C, 28.16%; H, 3.84%; N, 8.21%; Pt, 28.61%. Found: C, 28.04%; H, 3.66%; N, 8.09%; Pt, 27.96%.

Reaction with benzylidene-bis(N,N-dimethylaniline). To a mixture of 6.6 g. benzylidene-bis(*N*,*N*-dimethylaniline, 50 ml. of methanol, and 50 ml. of a saturated solution of sodium hydroxide in methanol was added 5.6 g. of hydroxylamine-*O*-sulfonic acid dissolved in 25 g. methanol. There was a vigorous reaction. The reaction mixture was heated for 30 min. and filtered and washed with methanol. The combined fil-

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[3] F. Sommer, O. Schulz, M. Nassau, *Z. anorg. allgem. Chem.*, **147**, 142 (1925).

[4] Microanalysis by the Clark Microanalytical Laboratory, Urbana, Ill.

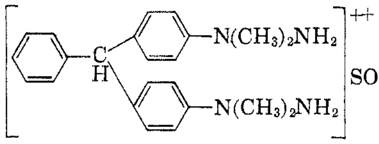
[5] All melting points are uncorrected.

[6] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th Edition, John Wiley and Sons, Inc., 1956, p. 230.

[7] B. K. Singh, *J. Chem. Soc.*, **105**, 1986 (1914).

trates were evaporated to dryness and the residue shaken with a 50/50 (by volume) mixture of water and ether. The aqueous layer was treated with Norit, and evaporated to dryness. The residue was taken up in isopropyl alcohol and reprecipitated with ethyl acetate. Weight of product: 2 g. (24% yield) m.p. (after recrystallization) 193–194°.

Anal.[4] Calcd. for



C, 60.24%; H, 6.59%; N, 12.22%; S, 6.99%. Found: C, 56.69%; H, 6.20%; N, 11.76%; S, 6.97%.

The chloroplatinate salt was prepared.

Anal.[4] Calcd. for $[C_{23}H_{30}N_4PtCl_6]$: C, 35.85%; H, 3.92%; N, 7.27%; Cl, 27.61%; Pt, 25.33%. Found: C, 36.27%; H, 4.17%; N, 7.01%; Cl, 24.19%; Pt, 25.24%.

Reaction of sodium hydroxylamine-O-sulfonate with dimethylaniline. To a methanolic solution of 5.6 g. hydroxylamine-*O*-sulfonic acid was added 6.2 g. sodium carbonate monohydrate. Carbon dioxide was immediately evolved. Dimethylaniline (6 g.) was added to the suspension of the sodium salt. The mixture was heated for 30 min. and filtered hot to remove inorganic salts. Addition of chloroform to the methanolic solution caused gradual precipitation of a dark colored product. Recrystallization of the dark material from ethanol–diethyl ether acidified with sulfuric acid produced 4.5 g. of pink platelets identical to those obtained by reaction of the free acid with the amine (38.5% yield).

General characteristics of the hydrazinium sulfates. The quaternized hydrazinium sulfates are colorless crystalline compounds, very soluble in water and generally insoluble in organic solvents. Those prepared from aminoalcohols are very hygroscopic and difficult to crystallize. The products from *N*-(2-hydroxyethyl) pyrrolidine and triethanolamine resisted all attempts at crystallization and were obtained only as viscous oils.

It was shown that hydroxylamine-*O*-sulfonic acid also reacts with *N*,*N*-diethyl cyclohexylamine, 3-dimethylamino propylamine, tri-*n*-heptylamine, *N*,*N*-dimethyl dodecylamine, but the hydrazinium salts were not isolated.

Department of Chemistry
University of Florida
Gainesville, Fla.

Washington Research Center
W. R. Grace and Company
Clarksville, Md.

Department of Chemistry
The Ohio State University
Columbus, Ohio

New Simple Preparation of Hexaphenylcyclotrisiloxane

Toshio Takiguchi

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Hexaphenylcyclotrisiloxane (1) has usually been prepared by the method of Burkhard[1] which involves condensation of diphenylsilanediol in the presence of hydrochloric acid as a catalyst.

In separate papers the author has reported two methods[2] for the preparation of I directly from diphenyldichlorosilane. It is found now that I can be obtained easily from the reaction of diphenyldichlorosilane with ammonium thiocyanate dissolved in acetone.

Stoichiometry supports the following equation:

$$(C_6H_5)_2SiCl_2 + 2NH_4CNS + H_2O \longrightarrow {}^1/_3[(C_6H_5)_2SiO]_3 + 2NH_4Cl + 2HCNS$$

Although the details of reaction mechanism are not yet clear, the acidity of by-products including ammonium chloride would cause the formation of trimer in good yields.

EXPERIMENTAL

Reagents. Ammonium thiocyanate was purified by recrystallization from methanol followed by drying in vacuum. Highest purity diphenyldichlorosilane was received from the Shin-etsu Chemical Industrial Company. Reagent grade acetone was used without further purification.

Preparation of trimer. In a 2 liter, 3-necked flask equipped with reflux condenser and dropping funnel in which 150 g. of diphenyldichlorosilane dissolved in 200 ml. of acetone had been placed, was placed 95 g. of powdered ammonium thiocyanate and 1000 ml. of acetone. When ammonium thiocyanate was dissolved by heating on a water bath, addition of silane solution portionwise immediately precipitated ammonium chloride as a fine white powder. After the addition was complete, the mixture was heated 10 min. further under reflux. After cooling, the product was filtered rapidly under suction and the precipitate was washed with a small amount of fresh acetone; 62 g. (99%) of ammonium chloride was obtained after drying. The filtrate then was transferred to a separate flask and was refluxed gently for about 1 hr. after the addition of 20 ml. of distilled water. The yellowish transparent product was transferred in a clean crystallizing dish and was concentrated to about 100 ml. on a water bath; a yellowish crystalline mass mixed with oily product having a pungent odor was obtained upon cooling. The crystalline mass was rinsed several times with a small amount of methanol and was recrystallized from ethanol-benzene (1:1); crude trimer was obtained as white shiny platelets melting at 187–188°. Further purification was effected by recrystallization from purified ethyl acetate; 108 g. (92%) of pure trimer was obtained as elongated hexagonal plates melting at 189.6°.

Anal. Calcd. for $C_{36}H_{30}Si_3O_3$: Si, 14.16; C, 72.68; H, 5.09; mol. wt., 594. Found: Si, 14.1; C, 72.5; H, 4.9; mol. wt., 588 (benzene), 579 (camphor).

The x-ray powder pattern data were in complete agreement with those given by Hyde and coworkers.[3]

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Department of Applied Chemistry
Kiryu College of Technology
Gunma University, Kiryu, Japan

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(1) C. A. Burkhard, *J. Am. Chem. Soc.*, **67**, 2173 (1945).

(2a) From oxygenation in acetone upon standing: *J. Org. Chem.*, **23**, 1216 (1958); *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*), **61**, 478 (1958).

(2b) From the reaction of diphenyldichlorosilane with formamide: *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*), **62**, 148 (1959).

(3) J. F. Hyde, L. K. Frevel, H. S. Nutting, P. S. Petrie, and M. A. Purcell, *J. Am. Chem. Soc.*, **69**, 488 (1947).