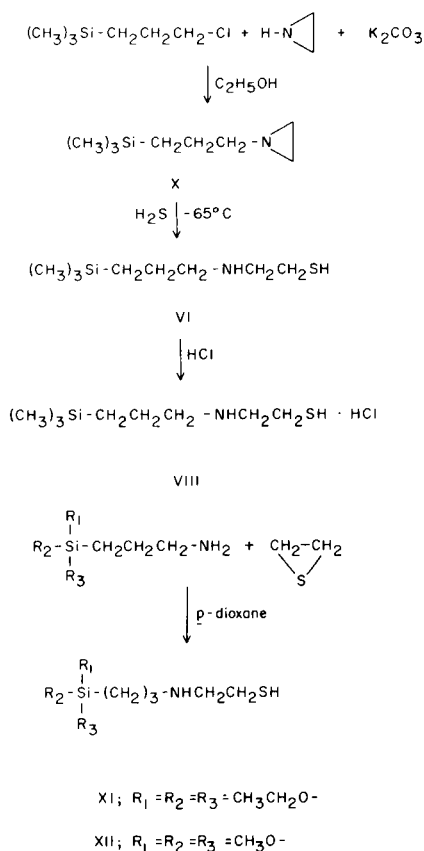


SCHEME C



The preparation of XI and XII, in yield of 54 and 68% respectively, was accomplished by treatment of a refluxing *p*-dioxane solution of the trialkoxysilicon-containing amine with ethylene sulfide. This procedure appears to be quite superior, in yield and complexity, to that reported by Bulbenko (12) who obtained XI in 24% yield.

EXPERIMENTAL

The melting points reported were determined on a Fisher-Johns apparatus and are uncorrected. The infrared spectra were determined with a Beckman IR-5 spectrophotometer. Chromatograms were obtained on an Aerograph, Model A-700 "Autoprep" gas chromatograph using a Silicon GE, 30% SE-30, acid washed column. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee. All chlorosilanes were distilled prior to use. Distillations were carried out using a 15" Vigreux column.

N-(3-Trimethylsilylpropyl)aminoethanethiosulfuric Acid (IV).

An alcoholic solution (95%, 300 ml.) of sodium hydroxide (10.0 g., 0.25 mole) was treated with 2-aminoethanethiosulfuric acid (39.3 g., 0.25 mole) dissolved in a minimum amount of water and the resulting solution was heated to reflux. γ -Chloropropyltrimethylsilane (30.1 g., 0.2 mole) was added dropwise to

the refluxing solution over 1.5 hours and refluxing was maintained for an additional 5.0 hours, at which time ethanol (250 ml.) was removed by distillation and replaced with an equal volume of water. After neutralization with glacial acetic acid, the mixture was allowed to stand overnight in the cold to give 11.6 g. (21.4%) of IV, melting at 194-197° dec. Purification by recrystallization from water afforded the pure product melting at 215-216° dec.

Anal. Calcd. for $\text{C}_8\text{H}_{21}\text{NO}_3\text{S}_2\text{Si}$: C, 35.39; H, 7.79; Si, 10.35; N, 5.16; S, 23.62. Found: C, 35.59; H, 7.77; Si, 10.56; N, 5.17; S, 23.43.

The above procedure will serve as an example for the preparation of the following compounds.

N-(Trimethylsilylmethyl)aminoethanethiosulfuric Acid (I).

Chloromethyltrimethylsilane (15.0 g., 0.12 mole), 2-aminoethanethiosulfuric acid (23.6 g., 0.15 mole), and sodium hydroxide (6.0 g., 0.15 mole) were allowed to react to give 10.1 g. (34.8%) of the pure product melting at 195-196° dec.

Anal. Calcd. for $\text{C}_6\text{H}_{17}\text{NO}_3\text{S}_2\text{Si}$: C, 29.61; H, 7.03; N, 5.76; Si, 11.53; S, 26.35. Found: C, 29.67; H, 7.03; N, 5.74; Si, 11.38; S, 26.15.

N-(Dimethylvinylsilylmethyl)aminoethanethiosulfuric Acid (II).

Chloromethyldimethylvinylsilane (20.0 g., 0.15 mole), 2-aminoethanethiosulfuric acid (39.3 g., 0.25 mole), and sodium hydroxide (10.0 g., 0.25 mole) gave, after concentrating the neutralized solution to one-half volume, 13.9 g. (36.3%) of product melting at 131-135°. Two recrystallizations from absolute ethanol gave the pure product melting at 155-156°.

Anal. Calcd. for $\text{C}_7\text{H}_{17}\text{NO}_3\text{S}_2\text{Si}$: C, 32.92; H, 6.71; Si, 10.99; N, 5.48; S, 25.11. Found: C, 33.02; H, 6.65; Si, 10.77; N, 5.50; S, 24.97.

Trimethyl- β -(*N*-ethylenimino)ethylsilane (IX).

The above-named compound was prepared by the method of Nametkin, Perchenko, and Grushevenko (5) in a (58%) yield, boiling at 53°/27 mm.; $n^{24} = 1.4288$. Literature reports 40-41°/18 mm., $n^{20} = 1.4300$.

N-(2-Trimethylsilylethyl)aminoethanethiosulfuric Acid (III).

Ammonium thiosulfate (10.4 g., 0.07 mole) and X (8.2 g., 0.058 mole) were placed in methanol (150 ml.) in a 250 ml. flask, equipped with thermometer, reflux condenser, and nitrogen inlet. The mixture was heated at reflux for 24 hours, and filtered hot to remove excess ammonium thiosulfate. The methanol was removed *in vacuo* to give, after recrystallization from absolute ethanol and drying, 9.0 g. (60.8%) of product melting at 172-175° dec. Three recrystallizations afforded the pure product melting at 194-195° dec.

Anal. Calcd. for $\text{C}_7\text{H}_{19}\text{NO}_3\text{S}_2\text{Si}$: C, 32.65; H, 7.44; Si, 10.91; N, 5.44; S, 24.90. Found: C, 32.63; H, 7.63; Si, 10.89; N, 5.65; S, 24.80.

Trimethyl- γ -(*N*-ethylenimino)propylsilane (X).

Ethylenimine (43.0 g., 1.0 mole), γ -chloropropyltrimethylsilane (15.1 g., 0.1 mole), and potassium carbonate (41.4 g., 0.3 mole) were placed in absolute ethanol (300 ml.) in a 500 ml. flask equipped with thermometer, reflux condenser, and nitrogen inlet. The mixture was heated at reflux for 67 hours, filtered, and the ethanol removed *in vacuo*. The last traces of inorganic materials were removed from the filtrate by treatment with anhydrous ether and subsequent filtration. Solvent removal *in vacuo* and fractionation of the residue gave 8.4 g. (53.5%) of X

boiling at 70°/21 mm., $n^{23} = 1.4322$.

Anal. Calcd. for $C_8H_{19}NSi$: C, 61.07; H, 12.17; Si, 17.86. Found: C, 60.93; H, 12.09; Si, 17.62.

N-(3-Trimethylsilylpropyl)-2-aminoethanethiol Hydrochloride (VIII).

Absolute ethanol (250 ml.) was placed in a 500 ml. flask equipped with dispersion tube, reflux condenser, and thermometer and cooled to -65° in a dry ice-acetone bath. The pre-cooled alcohol was saturated with hydrogen sulfide over a 1-hour period, at which time trimethyl- γ -(*N*-ethylenimino)propylsilane, X, (6.3 g., 0.04 mole) in 75 ml. of absolute ethanol was added in a dropwise manner over a 30-minute period. After addition was complete, the solution was stirred for 2.5 hours with hydrogen sulfide being passed through the reaction mixture. During this time the temperature rose to 25°. The ethanol was removed *in vacuo* and the residue fractionated to give 5.8 g. (75.7%) of VI boiling at 124°/0.23 mm.; $n^{19} = 1.4710$.

An ether solution (100 ml.) of VI (3.6 g., 0.19 mole) was treated with anhydrous hydrogen chloride until precipitation was complete. Filtration gave 4.3 g. (97.7%) of product, melting at 223-224° and 13.5% thiol by iodometric titration. Recrystallization from absolute ethanol or sublimation did not produce an increase in melting point.

Anal. Calcd. for $C_8H_{22}ClN_2Si$: C, 42.17; H, 9.73; Si, 12.33; N, 6.14; S, 14.07; Cl, 15.56. Found: C, 42.00; H, 9.58; Si, 12.08; N, 6.20; S, 13.49; Cl, 15.35.

The preparation of VII was conducted in the manner described above.

N-(2-Trimethylsilylethyl)-2-aminoethanethiol Hydrochloride (VII).

Trimethyl- β -(*N*-ethylenimino)ethylsilane, IX, (27.5 g., 0.19 mole) was allowed to react with hydrogen sulfide in the above manner to give 27.5 g. (81.6%) of V boiling at 108°/22 mm., $n^{21} = 1.4731$; which upon standing solidified to give a solid melting at 23-24°. Treatment with anhydrous hydrogen chloride afforded VII in 97.7% yield, melting at 233-234°, and 15.10% thiol by iodometric titration.

Anal. Calcd. for $C_7H_{20}ClN_2Si$: C, 39.32; H, 9.43; Si, 13.13; N, 6.55; S, 15.00; Cl, 16.57. Found: C, 39.55; H, 9.41; Si, 13.29; N, 6.76; Cl, 16.57.

N-(3-Triethoxysilylpropyl)-2-aminoethanethiol (XI).

Into a 250 ml. flask equipped with thermometer, reflux condenser, and nitrogen inlet was placed 3-aminopropyltriethoxysilane (22.1 g., 0.1 mole) and 150 ml. of *p*-dioxane. Ethylene sulfide (6.0 g., 0.1 mole) was added slowly over a 30 minute period. After refluxing the mixture overnight 5.0 g. of white solid, presumed to be hydrated starting material, was removed by filtration. The *p*-dioxane was removed *in vacuo*, and the residue was fractionated giving 8.1 g. of 3-aminopropyltrimethoxysilane boiling at 69-71°/0.5 mm. and 9.5 g. (53.7%), based on recovered starting material, of XI boiling at 96°/0.1 mm., $n^{23} = 1.4500$.

Anal. Calcd. for $C_{11}H_{27}N_2Si_3O_6$: C, 46.94; H, 9.66; S, 11.39. Found: C, 46.82; H, 9.67; S, 10.28.

N-Methyl-*N*-(3-trimethoxysilylpropyl)-2-aminoethanethiol XII.

N-Methyl-3-aminopropyltrimethoxysilane (19.2 g., 0.1 mole) and ethylene sulfide (12.0 g., 0.2 mole) were allowed to react, as

described for the preparation of XI, to give 17.3 g. (68.1%) of XII boiling at 88°/0.2 mm., $n^{24} = 1.4567$.

Anal. Calcd. for $C_9H_{23}NO_3Si_3$: C, 42.65; H, 9.15; O, 18.94; Si, 11.08; N, 5.53; S, 12.65. Found: C, 42.57; H, 9.05; O, 18.84; Si, 11.33; N, 5.75; S, 12.82.

Acknowledgment.

We are grateful to Dr. W. H. Daudt of Dow-Corning for generous supplies of various organosilicons and to Mr. Anthony De Roo of Dow Chemical Company for ethylenimine and its various derivatives.

REFERENCES

- (1) This investigation was supported in part by the U. S. Army Medical Research and Development Command, Department of the Army under contract number DA-49-193-MD-2910, and the National Aeronautics and Space Administration, who provided L. H. E. with a pre-doctoral research fellowship.
- (2) S. Searles, Jr., G. E. Roelofs, M. Tamres, and R. N. McDonald, *J. Org. Chem.*, **30**, 3443 (1965); D. Rosenthal, G. Brandrup, K. H. Davis, Jr., and M. E. Wall, *ibid.*, **30**, 3689 (1965); J. R. Piper, C. R. Stringfellow, Jr., and T. P. Johnston, *J. Med. Chem.*, **9**, 563 (1966); A. F. Ferris, O. L. Salerni, B. A. Schutz, *ibid.*, **9**, 391 (1966); O. L. Salerni and R. N. Clark, *ibid.*, **9**, 778 (1966); D. L. Klayman, W. F. Gilmore, and T. R. Sweeney, *Chem. Ind. (London)*, 1632 (1965); D. L. Klayman and W. F. Gilmore, *J. Med. Chem.*, **7**, 823 (1964).
- (3) D. L. Klayman and W. F. Gilmore, *ibid.*, **7**, 823 (1964).
- (4) L. H. Sommer, D. L. Bailey, G. M. Goldberg, C. E. Buck, T. S. Bye, F. J. Evans and F. C. Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954).
- (5) J. L. Speier, J. A. Webster, and G. H. Barnes, *ibid.*, **79**, 974 (1957).
- (6) L. H. Sommer and G. A. Baughmann, *ibid.*, **83**, 3346 (1961).
- (7) L. H. Sommer, J. R. Gold, G. M. Goldberg, and N. S. Marans *ibid.*, **71**, 1509 (1949).
- (8) N. A. Nametkin, V. N. Perchenko, and I. A. Grushevenko, *Dok., Akad., Nauk SSSR*, **158**, 404 (1964).
- (9) D. L. Klayman and W. F. Gilmore, T. R. Sweeney, *Chem. Ind. (London)*, 1632 (1965).
- (10) R. D. Westland, R. A. Cooley, Jr., M. L. Mouk and J. L. Holmes, Abstracts, First International Congress of Heterocyclic Chemistry, Albuquerque, N. M., June 1967, Paper No. 74.
- (11) This does not include silylaziridines in which a silicon is attached directly to the nitrogen, *i.e.* $\equiv Si-N$. Such an investigation is presently in progress in this laboratory.
- (12) G. F. Bulbenko, French Patent 1,433,372, April 1966; *Chem. Abstr.*, **66**, 2635h (1967).

Received September 11, 1967

Hattiesburg, Mississippi 39401