obtained which melted at 187° after crystallization from alcohol. The analysis indicated that this was the **di-hydrazide**.

Anal. Calcd. for $C_5H_9N_5O_2S$: N, 32.6; S, 14.9. Found: N, 32.4; S, 14.8.

Seven grams of the above thiazole diester was dissolved in 50 ml. of ethanol, 5.3 g. of 85% hydrazine hydrate added and the mixture heated for 48 hours at 100° and, inadvertently, one-half hour at 140°. The solid product was filtered and washed with 50% acetic acid and with water leaving 2 g. of material melting from 352–355° (dec.). A portion was crystallized from glacial acetic acid and from water to give a pale yellow powder which darkened slightly above 300° and melted at 355° with decomposition.

Anal. Calcd. for $C_6H_5N_3O_2S$: N, 23.0; S, 17.5. Found: N, 23.1; S, 17.4.

2-(β-Styryl)-thiazolo[5,4-d]pyrimidine-5,7-diol was prepared by refluxing 0.7 g. of 2-methylthiazolo[5,4-d]pyrimidine-5,7-diol in 10 g. of benzaldehyde containing 1 g. of zinc chloride. After crystallization twice from 90% acetic acid, the product weighed 0.3 g., was cream colored, and did not melt below 360°.

Anal. Calcd. for $C_{13}H_9N_3O_2S$: N, 15.5; S, 11.8. Found: N, 15.4; S, 11.8.

2-(β-Styryl)-thiazolo[4,5-d]pyrimidine-5,7-diol was prepared similarly, 0.7 g. of 2-methylthiazolo[4,5-d]pyrimidine-5,7-diol yielding 0.3 g. of the recrystallized product, a yellow powder which melted at 329–331° with decomposition.

Anal. Calcd. for $C_{13}H_9N_3O_2S$: N, 15.5; S, 11.8. Found: N, 15.5; S, 11.9.

Acknowledgment.—We wish to thank Merck and Company, Elkton, Virginia, for a generous gift of thioformamide. We also wish to express our sincere appreciation to Dr. H. Erlenmeyer who most graciously undertook a reinvestigation of the reactions between bromobarbituric acid and certain thioamides.

CHAPEL HILL, NORTH CAROLINA RECEIVED MARCH 9, 1951

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

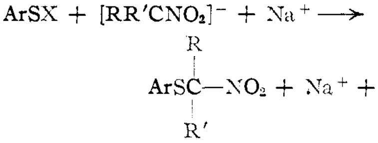
Derivatives of Sulfenic Acids. VI. The Synthesis of α-Nitro Sulfides

BY NORMAN KHARASCH AND JAMES LORNE CAMERON[1]

The reaction of sulfenyl halides with the sodium salts of nitroalkanes leads to the heretofore unreported α-nitro sulfides. A series of the new products has been prepared and evidence is given to substantiate their structures.

This paper reports the preparation of a series of α-nitro sulfides by the interaction of sulfenyl chlorides, bromides or thiocyanates with the sodium salts of nitroalkanes. The new products obtained are listed in Table I.

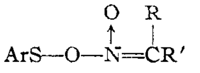
Whereas the sulfenyl halides fail to react with nitroalkanes, the sodium salts react smoothly. The reaction presumably involves a nucleophilic attack on sulfur by the nitroalkane anion.


$$\mathrm{ArSX} + [\mathrm{RR'CNO_2}]^- + \mathrm{Na}^+ \longrightarrow \mathrm{ArS}\overset{\mathrm{R}}{\underset{\mathrm{R'}}{\mathrm{C}}}\mathrm{-NO_2} + \mathrm{Na}^+ + \mathrm{X}^-$$

I

Absolute ether or benzene serve as suitable solvent for the preparations.

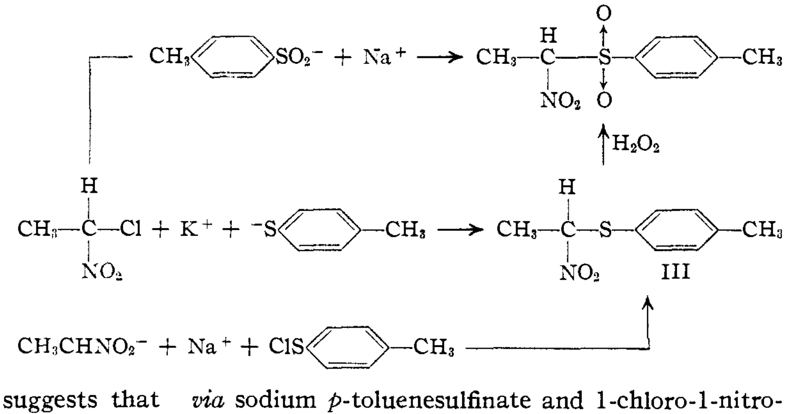
Consideration of the mode of synthesis, elementary analyses, and—in one instance—the molecular weight suggests that the products listed in Table I have either structure I or II.


$$\mathrm{ArS{-}O{-}}\overset{\mathrm{O}\atop\uparrow}{\mathrm{N}}\mathrm{{=}}\overset{\mathrm{R}}{\mathrm{C}}\mathrm{R'}$$

II

The following observations, however, strongly favor the α-nitro sulfide structures. (1) Those products which we have designated as having the formula $ArSCHR(NO_2)$ are acidic. They dissolve in 10% aqueous alkali, and acidification of the solutions with aqueous acetic acid regenerates the original compounds. Isomeric substances corresponding to structure II would not be expected to behave in this manner.

(2) As shown below, α-nitroethyl *p*-tolyl sulfone (IV) was obtained in three alternative ways: In 70% yield by oxidation of the product resulting from the reaction of *p*-toluenesulfenyl chloride and the sodium salt of nitroethane. (2) In 71% yield *via* sodium *p*-toluenesulfinate and 1-chloro-1-nitroethane and (3) in 15% over-all yield by oxidation of the mixture obtained by reaction of 1-chloro-1-nitroethane and the potassium salt of *p*-thiocresol.[2] Similarly, the product obtained from *o*-nitrobenzenesulfenyl halides and the sodium salt of 1-nitropropane was also oxidized to a new compound whose analysis corresponds to that of *o*-nitrophenyl 1-nitropropyl sulfone. Such sulfones would not be expected by oxidation of compounds of type II.



(3) On the basis of the well-known properties of

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(1) Commercial Solvents Predoctoral Fellow, 1950–1951.

(2) N. Melnikov [*J. Gen. Chem.* (*U. S. S. R.*), **7**, 1546 (1937); *C. A.*, **31**, 8504 (1937)] reported reactions of 1-halo-1-nitroalkanes with certain thiophenols, including "thiocresol," but did not isolate α-nitro sulfides under the conditions he employed. Mention is made in his work of the α-nitro sulfides as unstable intermediates.

TABLE I

Sulfenyl chloride	Sodium salt[a] of	Product, sulfide	M.p., °C.[b]	Yield, %		Carbon, %		Hydrogen, %	
				Crude	Pure	Calcd.	Found	Calcd.	Found
2,4-Dinitrobenzene-	Nitromethane	2,4-Dinitrophenyl nitromethyl, $C_7H_5O_6N_3S$	129–129.5[c]	10		32.44	32.63	1.95	1.25
	Nitroethane	2,4-Dinitrophenyl 1-nitroethyl, $C_8H_7O_6N_3S$	117–118	74[d]	50	35.18	35.26	2.58	2.76
	1-Nitropropane	2,4-Dinitrophenyl 1-nitropropyl, $C_9H_9O_6N_3S$	81.5–82.5	85	56	37.62	37.78	3.16	3.09
	2-Nitropropane	2,4-Dinitrophenyl 1-methyl-1-nitroethyl, $C_9H_9O_6N_3S$	101–101.5	40	25	37.62	37.82	3.16	3.53
2-Nitrobenzene-	Nitromethane	Nitromethyl *o*-nitrophenyl, $C_7H_6O_4N_2S$	70–71[c]	12		39.25	39.52	2.82	3.06
	Nitroethane	1-Nitroethyl *o*-nitrophenyl, $C_8H_8O_4N_2S$	57–58	56	41	42.11	42.36	3.53	3.53
	1-Nitropropane	*o*-Nitrophenyl 1-nitropropyl,[e] $C_9H_{10}O_4N_2S$	72.5–73.0	84	56[h]	44.62	44.84	4.16	4.35
	2-Nitropropane	1-Methyl-1-nitroethyl *o*-nitrophenyl,[f] $C_9H_{10}O_4N_2S$	81–82	36	25	44.62	44.81	4.16	4.10
1-Anthraquinone-	1-Nitropropane	1-Anthraquinonyl 1-nitropropyl,[g] $C_{17}H_{14}O_4NS$	158 (dec.)	64	43	62.37	62.11	4.00	4.07
p-Toluene-	Nitroethane	*Cf.* experimental details							

[a] The general method for obtaining the sodium salts is described in the experimental section for the case of the sodium salt of 1-nitropropane. The runs tabulated were made with 0.025 mole of the sodium salts and an equimolar amount of the sulfenyl chloride, except in the case of 1-anthraquinonesulfenyl chloride (*cf.* footnote *g*). [b] The melting points reported are not corrected. The melting temperatures of the crude products were generally within 3–5° of those of the pure products, except in the cases of the crude nitromethane derivatives, whose melting ranges were much wider. Thus, the crude *o*-nitrophenyl nitromethyl sulfide melted at 57–71°. [c] Purification of the nitromethyl aryl sulfides was effected by successive recrystallizations from methanol and carbon tetrachloride. Absolute ethanol and carbon tetrachloride were generally used to recrystallize the other products. [d] 2,4-Dinitrophenyl disulfide was also obtained as a side product in 15% yield in this run. Small yields of the latter disulfide, as well as of *o*-nitrophenyl disulfide, were generally observed in several of the runs tabulated. [e] Molecular weight determined by the cryoscopic method in benzene: calcd. for $C_9H_{10}O_4N_2S$, 242; found, 244. [f] In contrast to the α-nitro sulfides obtained from the primary nitroalkanes, this product was not soluble in 10% aqueous alkali. It was recovered unchanged (m.p. and mixed m.p.) after prolonged contact with the basic solution. [g] In this run 0.008 mole of the sodium salt was used for 0.002 mole of the sulfenyl chloride, and benzene was used in place of ether as solvent. Purification of the reaction residue was effected by extraction with hot benzene and recrystallization of the extracted product from carbon tetrachloride. [h] *o*-Nitrophenyl 1-nitropropyl sulfide was also obtained in 70% crude (56% pure) yield using *o*-nitrobenzenesulfenyl bromide in place of the chloride; and in 77% crude (72% pure) yield using *o*-nitrobenzenesulfenyl thiocyanate. *o*-Nitrophenyl disulfide was also obtained in 10–15% yields in these runs. [i] The microanalyses were performed by the late Dr. Gertrud Oppenheimer and by Mr. J. Swinehart, of the California Institute of Technology.

sulfenyl derivatives,[3] products of structure II would be expected to be particularly susceptible to cleavage at the sulfur to oxygen bond when subjected to the oxidative or hydrolytic conditions which were employed in carrying out the reactions mentioned above.[4]

Although the sulfenyl chlorides were usually used for preparation of the α-nitro sulfides, sulfenyl bromides and sulfenyl thiocyanates may also be employed. Thus, *o*-nitrophenyl 1-nitropropyl sulfide was obtained by the reaction of *o*-nitrobenzenesulfenyl chloride, or the corresponding sulfenyl bromide or thiocyanate, with the sodium salt of 1-nitropropane. As a matter of fact, the best yield of the pure α-nitro sulfide (72%) was obtained by using the sulfenyl thiocyanate.

It is quite likely that the relatively low yield (25%) of 2,4-dinitrophenyl 1-methyl-1-nitroethyl sulfide, obtained from the sodium salt of 2-nitropropane and 2,4-dinitrobenzenesulfenyl chloride, could be improved by further study. However, the low yield (10%) of 2,4-dinitrophenyl nitromethyl sulfide, obtained in the reaction of the sodium salt of nitromethane with 2,4-dinitrobenzenesulfenyl chloride was achieved only after considerable difficulty. The fact that this was the only case in the use of 2,4-dinitrobenzenesulfenyl chloride in which there was recovery of the sulfenyl chloride indicates that the lack of reaction may be due to some special feature of the sodium salt of nitromethane, possibly its pronounced tendency to undergo self-condensation reactions. The yield of nitromethyl *o*-nitrophenyl sulfide, obtained by reaction of *o*-nitrobenzenesulfenyl chloride with the sodium salt of nitromethane was also very low. These observations are in accord with the results of other workers who have recorded abnormalities with nitromethane which were not generally observed with the higher nitroalkanes.[5]

It was also found that 1-anthraquinonesulfenyl chloride readily reacts with the sodium salt of 1-nitropropane to yield the corresponding α-nitro sulfide. Triphenylmethanesulfenyl chloride, however, upon treatment with the sodium salt of 1-nitropropane, failed to yield the α-nitro sulfide and was recovered largely unchanged.

Although it was not a major objective of this

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(3) N. Kharasch, S. J. Potempa and H. L. Wehrmeister, *Chem. Revs.*, **39**, 269 (1946).

(4) It will be noted that the α-nitro sulfides (structure I) may exist in optically active forms, whereas compounds of structure II should not. Attempts to resolve suitable derivatives are in progress. The preliminary results of our current studies of the ultraviolet absorption spectra of selected examples of the new products show precise similarities between the curves of the latter and the nitroalkanes themselves.

(5) (a) W. R. Dunstan and T. S. Dymond, *J. Chem. Soc.*, **59**, 410 (1891); (b) W. R. Dunstan and E. Goulding, *ibid.*, **77**, 1262 (1900); (c) M. Lecco, *Ber.*, **9**, 705 (1876); (d) H. S. Fry and J. F. Treon, *Rec. trav. chim.*, **55**, 1007 (1936).

study to seek a method for the characterization of nitroalkanes, the results of the present work do suggest a useful extension of already known procedures[6] for the qualitative identification of primary and secondary nitroalkanes.

Experimental

Starting Materials.—The commercially available nitroalkanes were kept over "Drierite," then fractionated. The following fractions were used: nitromethane (101.5–102°); nitroethane (113.5–114°); 1-nitropropane (130–131°); 2-nitropropane (120–120.5°). The sodium methoxide used in preparing the sodium salts of the nitroalkanes was the C.P. reagent of the Fischer Scientific Company. All of the solvents used in the syntheses of the α-nitro sulfides were also C.P. 2-Chloro-2-nitropropane (b.p. 132–133°) was obtained from the Matheson Company (Paragon Division). 1-Chloro-1-nitroethane (b.p. 125–126°) was the Commercial Solvents product.

The following compounds were prepared according to methods described in the references cited. 2,4-Dinitrobenzenesulfenyl chloride,[7] 2-nitrobenzenesulfenyl chloride,[8] 2-nitrobenzenesulfenyl bromide,[9] 2-nitrobenzenesulfenyl thiocyanate,[10] 1-anthraquinonesulfenyl chloride,[11] triphenylmethanesulfenyl chloride,[12] 1-bromo-1-nitroethane,[13] 2,4-dinitrothiophenol,[14] 2-nitrothiophenol,[15] sodium *p*-toluenesulfinate dihydrate[16] and *p*-toluenesulfenyl chloride.[17]

2,4-Dinitrophenyl 1-Nitropropyl Sulfide.—The preparation of this sulfide served as a model for preparing the other compounds of Table I. Pertinent comments to the other sulfides are given in footnotes to the table. To a stirred solution of 1.35 g. (0.025 mole) of sodium methoxide in 25 ml. of absolute alcohol there was added dropwise 4.45 ml. (0.050 mole) of 1-nitropropane during one minute. A white precipitate of the sodium salt was formed immediately. After shaking three minutes, 25 ml. of absolute ether was added. The finely divided salt was collected by suction filtration, washed on the filter plate with 25 ml. of ether and added to a stirred suspension of 5.86 g. (0.025 mole) of 2,4-dinitrobenzenesulfenyl chloride in 75 ml. of ether at −5°, contained in a three-necked flask fitted with a mechanical stirrer, an external temperature-control-bath and a reflux condenser. The cooling bath was removed, and the mixture stirred for 30 minutes at room temperature, then at reflux for 30 minutes. The condenser was adjusted for distillation, the ether was removed and the orange residue washed with 150 ml. of water and collected. The dried product (6.61 g., m.p. 75–77°) was extracted with 22 ml. of boiling methanol, leaving an undissolved residue of 0.50 g. of crude 2,4-dinitrophenyl disulfide, decomposing *ca.* 250°. Refrigeration of the methanolic solution yielded 4.99 g. of yellow crystals melting at 79–81° (85%). Recrystallization from 25 ml. of carbon tetrachloride gave 4.00 g. (56%) of pure 2,4-dinitrophenyl 1-nitropropyl sulfide, m.p. 81.5–82.5°. Analyses are given in Table I.

Repetitions of the above procedure, using ten times the quantities, also led to 50–55% yields of pure 2,4-dinitrophenyl 1-nitropropyl sulfide. The order of addition of the reactants in the preparation can, if desired, be inverted without altering the course of the reaction. Thus, the suspension of the sodium salt of 1-nitropropane in ether was placed in the reaction flask, an ether solution of the sulfenyl chloride was added slowly to the cooled, stirred reaction mixture and the reaction was completed and product isolated in the manner described above. This order of addition is somewhat more convenient, for it avoids the portion-wise addition of the solid sodium salt of the nitroalkane.

Attempted Alternate Syntheses of 2,4-Dinitrophenyl 1-Nitroethyl Sulfide and *o*-Nitrophenyl 1-Methyl-1-nitroethyl Sulfide.—The attempted preparation of 2,4-dinitrophenyl 1-nitroethyl sulfide by reaction of 1-bromo-1-nitroethane with sodium 2,4-dinitrothiophenoxide in absolute alcohol solution, or with the thiophenol itself, in benzene or toluene solutions, was not successful. The major product obtained with the sodium salt was 2,4-dinitrophenyl disulfide (dec. 240–280°); while with 2,4-dinitrothiophenol most of the latter was recovered. Reaction of the fused 2,4-dinitrothiophenol with 1-bromo-1-nitroethane was suggested by the observation of Hoggarth[18] that when 2-acetamido-5-bromothiazole was fused with *p*-nitrothiophenol, the reaction to form the sulfide occurred instantaneously, whereas heating the reactants in solution was not effective. This expedient was, however, not successful in our attempted synthesis of 2,4-dinitrophenyl 1-nitroethyl sulfide.

The attempted alternate synthesis of *o*-nitrophenyl 1-methyl-1-nitroethyl sulfide by reaction of the sodium salt of *o*-nitrothiophenol and 2-chloro-2-nitropropane was also not successful. The major product obtained was *o*-nitrophenyl disulfide, m.p. 190–192°.

***o*-Nitrophenyl 1-Nitropropyl Sulfone.**—*o*-Nitrophenyl 1-nitropropyl sulfide (2.4 g.) was oxidized by 30% hydrogen peroxide (0.15 mole) in hot glacial acetic acid. Aspiration of the solvent and recrystallization of the solid residue from methanol led to 1.05 g. (37%) of the pure sulfone, m.p. 74.5–75.5°. In such oxidations, caution must be observed not to overheat solutions containing high concentrations of hydrogen peroxide during and after removal of the reaction solvent.

Anal. Calcd. for $C_9H_{10}O_6N_2S$: C, 39.41; H, 3.67. Found: C, 39.75; H, 3.78.

1-Nitroethyl *p*-Tolyl Sulfone (A).—Nitroethane (53 ml., 0.74 mole) was dropped into a stirred solution of 24.3 g. (0.45 mole) of sodium methoxide in 400 ml. of absolute alcohol. After stirring a few minutes, 400 ml. of absolute ether was added, and the finely divided sodium salt was collected on the filter plate and washed with 200 ml. of absolute ether, then added, during 20 minutes, to a stirred solution of 47.6 g. (0.30 mole) of *p*-toluenesulfenyl chloride in 500 ml. of ether at −5°. The cooling bath was removed, and the mixture stirred for 20 minutes at room temperature and then for 20 minutes at reflux temperature. The mixture was filtered to separate the sodium chloride, and the ether was removed from the filtrate by distillation at 40 mm. The residual yellow oil could not be induced to crystallize at −60°, nor by various other means. It was not soluble in water, but dissolved in 25% aqueous sodium hydroxide solution. Acidification of the latter solution with 25% acetic acid caused reprecipitation of the oily product. The weight of the oil in various runs represented yields of 80–90%, assuming that the product was 1-nitroethyl *p*-tolyl sulfide. Attempts to fractionate the oil at 2 mm. caused extensive decomposition, but distillation in a molecular still was effected without noticeable decomposition and led to good recovery (70–80%) of a nearly colorless distillate, whose analysis is given below. Reaction of the product with sodium ethoxide in ethanol and addition of ether to the reaction mixture precipitated the sodium salt of the product.

Anal. Calcd. for $C_9H_{11}O_2NS$: C, 54.80; H, 5.62. Found: C, 56.04; H, 6.01. Calcd. for the sodium salt, $C_9H_{10}O_2NSNa$: Na, 10.5. Found: Na, 10.3.

To obtain the sulfone, 3.50 g. of the above undistilled product and 14 ml. (0.14 mole) of 30% hydrogen peroxide were dissolved in 40 ml. of glacial acetic acid, and the solution was heated to boiling during one hour and then refluxed for 30 minutes. The acetic acid was removed *in vacuo* and the residue washed with water and refrigerated to permit full crystallization. After air-drying, the crude sulfone melted at 41–43° and weighed 2.90 g. (71% yield, based on sulfide). Recrystallization from aqueous methanol raised the melting point to 47–48°. The excellent white crystals were soluble in 10% sodium hydroxide and were recovered with only minor loss by acidifying the solution with 10% acetic acid.

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(11) K. Fries, *ibid.*, **45**, 2965 (1912).

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(14) C. Willgerodt, *ibid.*, **17R**, 352 (1884). *Cf.* also R. W. Bost, P. K. Starnes and E. L. Wood, THIS JOURNAL, **73**, 1968 (1951).

(15) J. J. Blanksma, *Rec. trav. chim.*, **20**, 399 (1901); F. Mayer, *Ber.*, **42**, 3059 (1909).

(16) F. C. Whitmore and F. Hamilton, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 492.

(17) H. Lecher, *Ber.*, **58**, 409 (1925).

(18) E. Hoggarth, *J. Chem. Soc.*, 110 (1947).

Anal. Calcd. for $C_9H_{11}O_4NS$: C, 47.15; H, 4.84. Found: C, 47.36; H, 4.97.

(**B**).—To a solution of 2.74 g. (0.049 mole) of potassium hydroxide in 35 ml. of absolute ethanol, 6.21 g. (0.050 mole), of *p*-thiocresol was added. The mixture was cooled to 0° and a solution of 4.4 ml. (0.050 mole) of 1-chloro-1-nitroethane in 15 ml. of absolute ethanol at 0° was added. The mixture was set aside at 0° for 15 hours, then filtered, yielding 2.10 g. of potassium chloride. Dilution of the filtrate with 200 ml. of water precipitated 6 g. of an oil. Oxidation of the oil with hydrogen peroxide in glacial acetic acid, as above, gave a 15% yield of the same sulfone (affirmed by physical appearance, alkali solubility, melting point and mixed melting point) as resulted by oxidation of the product obtained *via* *p*-toluenesulfenyl chloride and 1-chloro-1-nitroethane. The low yield of sulfone is associated with the presence of considerable *p*-tolyl disulfide in the oily product subjected to oxidation. The disulfide was separated and its identity confirmed by melting point and mixed melting point with authentic *p*-tolyl disulfide.

(**C**).—α-Nitroethyl *p*-tolyl sulfone also resulted (71% yield) by interaction of 7.06 g. (0.033 mole) of sodium *p*-toluenesulfinate dihydrate with 2.19 ml. (0.025 mole) of 1-chloro-1-nitroethane in methanol (75 ml), at reflux temperature for three hours. The crystalline product was obtained by collecting the precipitated sodium chloride and removing excess solvent. It was identical (solubility in alkali, melting point and mixed melting point) with the sulfone obtained by methods (A) and (**B**) above.

LOS ANGELES, CALIFORNIA RECEIVED APRIL 6, 1950

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Preparation of Aminomethylsilicon Compounds and their Derivatives

BY JOHN E. NOLL,[1] JOHN L. SPEIER[2] AND B. F. DAUBERT

The reaction of various chloro- and bromomethylsilicon compounds with amines and ammonia to prepare aminomethylsilane derivatives is described. The quantitative removal of one methyl group from trimethylsilylmethylamines by sodium amide in ammonia to form N-methyl-(trimethylsilyl)-amine is demonstrated. Some twenty-three new silicon-containing amines are described along with their derivatives.

In continuation of the work in these laboratories aimed at a determination of the effect of organosilicon substituents on organic functional compounds, a series of amines has been prepared containing the linkages Si–C–N with alkyl, alkoxy, oxy and aryl groups on the silicon atoms and hydrogen, alkyl and aryl groups attached to the nitrogen atoms.

The most convenient method for the preparation of moderately large quantities of such amines was found to consist of treating anhydrous ammonia or amines with compounds of the formula R_3SiCH_2X, where R was any combination of alkyl, aryl, alkoxy or siloxy groups and X was chlorine or bromine. Solvents neither were necessary nor showed any advantages as a medium for the reaction. Water and alcohol were found to promote the cleavage of the halomethyl group from silicon and were therefore avoided.[3]

The reactions were generally carried out with about a 20-fold excess of ammonia or a two- to threefold excess of amine at temperatures of from 60 to 120° under pressure when necessary.

Halomethylsilanes with approximately a 20-fold excess of liquid ammonia usually formed about 50–70% primary amine, 20–30% secondary amine and a small amount of unstable material which probably was tertiary amine. Compounds of the type $(R_3SiCH_2)_3N$ were never isolated and identified as such. Repeated efforts to isolate such products led only to the production of very unstable and reactive materials which vigorously decomposed when heated and which reacted rapidly with the atmosphere to form an unstable solid of variable composition. A product thought to have been tris-(trimethylsilylmethyl)-amine was spilled upon a piece of paper and found to cause its spontaneous ignition a few seconds later.

The amines also reacted with halomethylsilanes. A two- to threefold excess of primary amine usually resulted in from 50–88% of secondary amines of the formula R_3SiCH_2NHR', with the remainder usually accounted for approximately as tertiary amines, $(R_3SiCH_2)_2NR$. Secondary amines yielded tertiary amines and probably quaternary salts. Tertiary amines reacted very sluggishly to yield quaternary salts. Ethanolamine resulted in the formation chiefly of N-methylethanolamine indicating that the halomethyl group was cleaved from the silicon.

A most interesting cleavage of a chloromethyl group occurred when chloromethyltrimethylsilane reacted with sodium amide in liquid ammonia. Cleavage and rearrangement appeared to be almost instantaneous with the formation of N-methyl-(trimethylsilyl)-amine. This product on distillation eliminated methylamine and formed N-methylhexamethyldisilazane in excellent yield. These reactions might be represented according to the equations

$$Me_3SiCH_2Cl + NaNH_2 \longrightarrow Me_3SiNHMe + NaCl$$
$$2Me_3SiNHMe \longrightarrow (Me_3Si)_2NMe + MeNH_2$$

The preparation of amines containing the linkages Si–O–Si–C–N– was effected in three different ways. First, and least successful, bis-(chloromethyl)-tetramethyldisiloxane was treated with ammonia or an amine. The difunctionality of the bis-chloromethyl compound led to the production of a mixture of products that could not be satisfactorily separated. The second method was more successful. It consisted of the hydrolysis of an alkoxysilylmethylamine in aqueous or aqueous alcoholic solution. Siloxane-methylamines were easily obtained. Methyldiethoxysilylmethylamine yielded a thermoplastic polymer, soluble in water, which reacted rapidly in air to form what appeared to be a bicarbonate salt. Triethoxysilylmethylamine yielded a white amorphous powder, which was water soluble.

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(1) Submitted in partial fulfillment of the requirements for the degree of M.Sc.

(2) Please address any communications concerning this work to Dr. John L. Speier, Mellon Institute, Pittsburgh 13, Pa.

(3) R. H. Krieble and J. R. Elliott, THIS JOURNAL, **67**, 1810 (1945).