1153. *Silicon–Nitrogen and Silicon–Sulphur Compounds as Intermediates in the Preparation of Certain Organic Compounds.*

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A number of silanes substituted with halogens, sulphur, and nitrogen have been prepared by new methods.

THE interactions of organosilicon amines[1] and sulphides[2] with covalent inorganic halides have already proved to be extremely useful and versatile synthetic reactions. We have also found that a variety of organic compounds containing nitrogen and sulphur may be prepared by similar methods. Whilst no new class of organic compounds is reported, it is felt that these new preparative methods may on occasions prove useful.

Whereas an excess of methyl iodide reacted with diethylaminotrimethylsilane to liberate trimethyliodosilane and produce diethyldimethylammonium iodide,[3] equimolar proportions of n-butyl iodide and di-n-butylaminotrimethylsilane gave trimethyliodosilane and the tertiary amine, tri-n-butylamine.[4] The latter reaction has now been extended to give a non-symmetrical tertiary amine R_2R^1N by the interaction of n-heptyl iodide with di-n-butylaminotrimethylsilane, yielding di-n-butyl-n-heptylamine:

$$\text{n-C}_7\text{H}_{15}\text{I} + \text{Bu}^\text{n}{}_2\text{NSiMe}_3 \rightarrow \text{Bu}^\text{n}{}_2\text{N-n-C}_7\text{H}_{15} + \text{Me}_3\text{SiI} \qquad (1)$$

Neither heptafluoro-n-propyl iodide nor pentafluorobromobenzene produced fluoroalkylamines upon prolonged heating with dialkylaminotrimethyl silanes.

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[1] See E. W. Abel, D. A. Armitage, and G. R. Willey, *J.*, **1965**, **57**, and refs. therein.
[2] E. W. Abel, D. A. Armitage, and R. P. Bush, *J.*, **1964**, **5584**, and refs. therein.
[3] A. W. Jarvie and D. Lewis, *J.*, **1963**, **1073**.
[4] E. W. Abel and G. R. Willey, *J.*, **1964**, **1528**.

Reactions between aminosilanes and benzoyl chloride have been reported,[5] but only the alkylchlorosilane products were characterized. We found benzoyl chloride to react vigorously with diethylaminotrimethylsilane to give good yields of both trimethylchlorosilane and *NN*-diethylbenzamide:

$$PhCOCl + Me_3SiNEt_2 \rightarrow PhCONEt_2 + Me_3SiCl \qquad (2)$$

Benzoyl chloride has previously been reported to react with *N*-n-butylhexamethyldisilazane to form the corresponding dibenzoylamide.[6] Similarly, we find that acetyl chloride and *N*-methylhexamethyldisilazane produce trimethylchlorosilane and *N*-methyldiacetamide:

$$(Me_3Si)_2NMe + 2MeCOCl \rightarrow 2Me_3SiCl + (MeCO)_2NMe \qquad (3)$$

Ethyl chloroformate reacted vigorously with diethylaminotrimethylsilane to give *NN*-diethylethoxyformamide:

$$Me_3SiNEt_2 + ClCO{\cdot}OEt \rightarrow Me_3SiCl + Et_2NCO{\cdot}OEt \qquad (4)$$

NN-Diethylnitrosamine was produced in good yield by passing nitrosyl chloride into diethylaminotrimethylsilane:

$$Et_2NSiMe_3 + NOCl \rightarrow Me_3SiCl + Et_2N{\cdot}NO \qquad (5)$$

The reaction between aminosilanes and bromine resulted in the evolution of hydrogen bromide and a complex mixture of other products. In the case of n-butylthiotrimethylsilane, however, bromine cleaved the silicon–sulphur bond to yield di-n-butyl disulphide in excellent yield:

$$2n\text{-}BuSSiMe_3 + Br_2 \rightarrow 2Me_3SiBr + Bu^nS{\cdot}SBu^n \qquad (6)$$

Although symmetrical and unsymmetrical dialkyl sulphides have been prepared[7,8] from the reaction between alkylthiosilanes and alkyl halides, neither heptafluoropropyl iodide nor pentafluorobromobenzene reacted with silicon–sulphur compounds. As such fissions of silicon–sulphur bonds are believed[7,8] to proceed *via* a sulphonium salt, it is likely that the non-reactivity of the perfluoro-organic halides is due to these halides being polarized in the wrong direction for such ion formation. Similar reasoning may explain their lack of reaction towards the silicon–nitrogen bond also.

Sulphur dichloride and ethylthiodimethylchlorosilane were found to react to release dimethyldichlorosilane and form diethyl trisulphide in good yield:

$$2EtSSiClMe_2 + SCl_2 \rightarrow 2Me_2SiCl_2 + EtS_3Et \qquad (7)$$

A similar reaction between disulphur dichloride and ethylthiotrimethylsilane did not produce pure diethyl tetrasulphide, but a mixture of sulphides from which only a small quantity of diethyl trisulphide was obtained pure.

Acetyl chloride was converted into *S*-n-butyl thioacetate by the action of n-butylthiotrimethylsilane:

$$MeCOCl + Me_3SiSBu^n \rightarrow Me_3SiCl + MeCOSBu^n \qquad (8)$$

Similarly, ethylchloroformate reacted with ethylthiotrimethylsilane to produce *OS*-diethylmonothiocarbonate:

$$EtSSiMe_3 + EtOCOCl \rightarrow EtO{\cdot}CO{\cdot}SEt + Me_3SiCl \qquad (9)$$

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[5] H. H. Anderson, *J. Amer. Chem. Soc.*, 1962, **74**, 1421.
[6] K. Ruhlman, *Ber.*, 1961, **94**, 2311.
[7] E. W. Abel, *J.*, 1960, 4406.
[8] E. W. Abel, D. A. Armitage, and R. P. Bush, *J.*, 1964, 2455.

Hexamethylcyclotrisilthiane and benzoyl chloride reacted (equation 10), to produce a good yield of dimethyldichlorosilane. The yield of dibenzoyl sulphide was, however, only 29%.

$$6PhCOCl + (Me_2SiS)_3 \rightarrow 3(PhCO)_2S + 3Me_2SiCl_2 \qquad (10)$$

EXPERIMENTAL

All reactions were conducted under anhydrous conditions, and the organosilicon halides formed in each case were characterised by boiling point and refractive index. Sulphur dichloride was distilled shortly before use from a mixture containing 10% of phosphorus trichloride in order to inhibit disproportionation to sulphur monochloride and chlorine during distillation. Nitrosyl chloride was taken from a Matheson Company lecture cylinder without further purification. The following organosilicon compounds were prepared by the reported methods: *N*-methylhexamethyldisilazane,[9] diethylaminotrimethylsilane,[10] di-n-butylaminotrimethylsilane,[10] alkylthiotrimethylsilanes,[7] and hexamethylcyclotrisilthiane.[11] Ethylthiodimethylchlorosilane was prepared from lead ethyl mercaptide and dimethyldichlorosilane. The colourless liquid product had b. p. 145°, n_D^{20} 1·4662 (Found: C, 31·0; H, 7·0. Calc. for $C_4H_{11}SSiCl$: C, 31·1; H, 7·2%).

Interaction of n-Heptyl Iodide with NN-*Di-n-butylaminotrimethylsilane* (equation 1).—The iodide (7·65 g.) was heated under reflux for three days with the aminosilane (6·8 g.). Subsequent distillation gave trimethyliodosilane and n-heptyldi-n-butylamine[12] (3·0 g., 39%), b. p. 60°/0·002 mm., n_D^{20} 1·4344 (Found: C, 79·5; H, 14·8; N, 6·6. Calc. for $C_{15}H_{33}N$: C, 79·4; H, 14·7; N, 6·2%).

Interaction of Benzoyl Chloride and NN-*Diethylaminotrimethylsilane* (equation 2).—During the addition of the chloride (6·3 g.) to the aminosilane (6·5 g.) an extremely vigorous reaction took place. Subsequent distillation gave trimethylchlorosilane (82%), and *NN*-diethylbenzamide[13] (7·0 g., 89%), b. p. 85°/0·002 mm., n_D^{19} 1·5260 (Found: C, 75·0; H, 9·0; N, 8·1. Calc. for $C_{11}H_{15}NO$: C, 74·6; H, 8·5; N, 7·9%).

Interaction of Acetyl Chloride and N-*Methylhexamethyldisilazane* (equation 3).—After the addition of an excess of acetyl chloride (6·3 g.) to *N*-methylhexamethyldisilazane (4·0 g.), the mixture was heated under reflux for 1 hr. Subsequent distillation yielded a mixture of trimethylchlorosilane and acetyl chloride, followed by *N*-methyldiacetamide[14] (2·0 g., 76%), b.p. 190°, n_D^{21} 1·4522 (Found: C, 51·7; H, 8·1; N, 12·2. Calc. for $C_5H_9NO_2$: C, 52·2; H, 7·9; 12·2%).

Reaction of Ethyl Chloroformate and NN-*Diethylaminotrimethylsilane* (equation 4).—The aminosilane (8·4 g.) was added to the chloroformate (6·3 g.) slowly at 0°. A vigorous reaction took place during the addition, and subsequent distillation yielded trimethylchlorosilane (93%) and *NN*-diethylethoxyformamide[15] (6·0 g., 71%), b. p. 167°, n_D^{20} 1·4220 (Found: C, 58·0; H, 10·4; N, 10·1. Calc. for $C_7H_{15}NO_2$: C, 57·8; H, 10·4; N, 9·7%).

Interaction of Nitrosyl chloride with NN-*Diethylaminotrimethylsilane* (equation 5).—Nitrosyl chloride (8·5 g., excess), was passed into the aminosilane (8·07 g.) in dry light petroleum (40 c.c., b. p. 100—120°). An exothermic reaction took place and subsequent distillation produced trimethylchlorosilane, solvent, and finally *NN*-diethylnitrosamine[16] (3·5 g., 62%) b. p. 172°, n_D^{20} 1·4366 (Found: C, 47·0; H, 9·7; N, 27·5; Calc. for $C_4H_{10}N_2O$: C, 47·0; H, 9·9; N, 27·4%).

Interaction of Bromine with n-Butylthiotrimethylsilane (equation 6).—Bromine (7·36 g.) was slowly added to the thiosilane (14·8 g.), giving a vigorous reaction, and immediate decolouration of the bromine. Subsequent distillation gave trimethylbromosilane (84%) and di-n-butyl disulphide[17] (7·2 g., 88%) b. p. 53°/0·001 mm., n_D^{19} 1·4931 (Found: C, 53·7; H, 9·8. Calc. for $C_8H_{18}S_2$: C, 53·9; H, 10·2%).

Interaction of Sulphur Dichloride and Ethylthiodimethylchlorosilane (equation 7).—Sulphur dichloride (2·38 g.) was added to ethylthiodimethylchlorosilane (7·15 g.) at −78°, and the mixture allowed to warm to room temperature. During subsequent heating (*ca.* 100°) dimethyldichlorosilane (85%) was slowly distilled from the mixture. Vacuum distillation of the residual oil

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[11] T. Nomura, M. Yokoi, and K. Yamasaki, *J. Amer. Chem. Soc.*, 1955, **77**, 4484.

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[14] I. M. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London 1943, Vol. 2, p. 611.

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[16] E. Schmidt and R. Schumacker, *Ber.*, 1921, **54**, 1418.

[17] H. Gilman, L. E. Smith, and H. H. Parker, *J. Amer. Chem. Soc.*, 1925, **47**, 859.

yielded diethyl trisulphide[18] (3·1 g., 87%), b. p. 82°/10 mm., n_D^{20} 1·5640 (Found: C, 31·5; H, 6·4. Calc. for $C_4H_{10}S_3$: C, 31·4; H, 6·5%).

Interaction of Disulphur Dichloride and Ethylthiotrimethylsilane.—Disulphur dichloride (4·03 g., 1 mol.) was added to the thiosilane (8·0 g., 2 mol.) at −78°. A vigorous reaction took place even at low temperature, and after warming to room temperature slowly, the mixture was carefully heated to remove trimethylchlorosilane (89%). Subsequent vacuum distillation of the residue yielded diethyl trisulphide (2·25 g.), b. p. 33°/0·1 mm., n_D^{20} 1·5645, together with higher-boiling fractions which had higher refractive indices. These appeared, from physical properties and analyses, to be mixtures of the tri- and tetra-sulphides, but no tetrasulphide could be obtained free from trisulphide contamination. A brown-black tar remained after distillation.

Interaction of Acetyl Chloride and n-Butylthiotrimethylsilane (equation 8).—The thiosilane (5·0 g., 1 mol.) and acetyl chloride (slight excess) were heated under reflux for 15 hr. Subsequent distillation yielded a mixture of acetyl chloride and trimethylchlorosilane, together with *S*-n-butylmonothioacetate[19] (2·9 g., 60%), b. p. 160°, n_D^{25} 1·4572 (Found: C, 53·8; H, 8·6. Calc. for $C_6H_{12}OS$: C, 54·5; H, 9·15%).

Interaction of Ethyl Chloroformate and Ethylthiotrimethylsilane (equation 9).—The thiosilane (6·0 g.) and ethyl chloroformate (4·86 g.) were heated together for 3 hr., during which time trimethylchlorosilane (72%) distilled from the mixture. Subsequent distillation gave *OS*-diethyl monothiocarbonate[20] (3·9 g., 65%), b. p. 154°, n_D^{26} 1·4467 (Found: C, 44·8; H, 7·45. Calc. for $C_5H_{10}O_2S$: C, 44·8; H, 7·5%).

Interaction of Benzoyl Chloride with Hexamethylcyclotrisilthiane (equation 10).—Upon heating, the chloride (26·5 g.) and silthiane (8·48 g.) reacted rapidly, evolving dimethyldichlorosilane (85%), which was distilled from the reaction vessel. Recrystallisation of the residue from methylene chloride gave pale yellow crystals of dibenzoyl sulphide[21] (6·5 g., 29%), m. p. 48—49° (Found: C, 69·9; H, 4·6. Calc. for $C_{14}H_{10}O_2S$. C, 69·4; H, 4·2%).

The authors are grateful to Midland Silicones Ltd., for a generous supply of alkylchlorosilanes, and to D.S.I.R. for a Research Award (to D.A.A.).

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[*Received, November 2nd*, 1964.]

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