(28%) of *trans*-1,2-dichlorocyclohexane were obtained. Thus it appears the presence of calcium carbonate has no effect on the course of the reaction.

F. (**Isopropyl Alcohol**).—Treatment of isopropyl alcohol with phosphorus pentachloride under the conditions described in Part A gave 12.5 g. (20%) of isopropyl chloride, b.p. 31–34.5°, n^{25}_{D} 1.3752, d^{25}_{4} 0.847 (lit.[28] b.p. 34.8°, n^{15}_{D} 1.3811, d^{15}_{4} 0.868). Propylene chloride could not be isolated from the residue by careful fractionation, and the infrared spectrum of this residue indicated that propylene chloride was not present.

G. (***n*-Octanol**).—Treatment of *n*-octanol with phosphorus pentachloride under the conditions described in part A gave 88 g. (75%) of *n*-octyl chloride, b.p. 83–87° (33 mm.), n^{25}_{D} 1.4285, d^{25}_{4} 0.881 (lit.[29] n^{20}_{D} 1.4306, d^{20}_{4} 0.875). 1,2-Dichlorooöctane could not be isolated from the residue by careful fractionation.

H. (**2-Octanol**).—Treatment of *dl*-2-octanol with phosphorus pentachloride under the same conditions as described in part A, except in one-fifth quantities, gave 12 g. (51%) of 2-chlorooöctane, b.p. 55–60° (14 mm.), n^{25}_{D} 1.4253, d^{25}_{4} 0.871 (lit.[30] n^{20}_{D} 1.4295, d^{20} 0.865) and 1.9 g. (7%) of dichlorooöctane, b.p. 84–86° (14 mm.), n^{25}_{D} 1.4496, d^{25}_{4} 1.007, M_{D} 48.90 (calcd. 48.83).

When the reaction was repeated using (+)2-octanol, $[\alpha]^{26}_{\mathrm{D}}$ 9.10° (*l* 1 dm., neat), 10 g. (45%) of (−)2-chlorooctane, b.p. 64–68° (17 mm.), n^{25}_{D} 1.4255, d^{25}_{4} 0.872, $[\alpha]^{27}_{\mathrm{D}}$ −32.6° (*l* 1 dm., neat) and 1.9 g. (7%) of dichlorooöctane, b.p. 88–88.5° (16 mm.), n^{25}_{D} 1.4500, d^{25}_{4} 1.010, $[\alpha]^{27}_{\mathrm{D}}$ −0.33° (*l* 1 dm., neat) were isolated. (−)2-Octanol, $[\alpha]^{26}_{\mathrm{D}}$ −9.23° (*l* 1 dm., neat), gave 12 g. (50%) of (+)2-chlorooöctane, b.p. 63° (17 mm.), n^{25}_{D} 1.4254, d^{25}_{4} 0.866, $[\alpha]^{27}_{\mathrm{D}}$ 34.1° (*l* 1 dm., neat) and 1.9 g. (7%) of dichlorooctane which had b.p. 87.5–87.8° (17 mm.), n^{25}_{D} 1.4492, d^{25}_{4} 1.009, $[\alpha]^{27}_{\mathrm{D}}$ 0.18° (*l* 1 dm., neat).

Conversion of Dichlorodimethylcyclohexane to 1,1-Dimethylcyclohexane.—Treatment of 17.4 g. (0.1 mole) of dichlorodimethylcyclohexane (obtained by procedure A above) with zinc dust and alcohol[31] gave 8 g. (76%) of di**methylcyclohexene**, b.p. 114–116°; n^{25}_{D} 1.4400, d^{25}_{4} 0.797, M_{D} 36.4 (calcd. 36.5).

Anal. Calcd. for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 86.84; H, 12.61.

Hydrogenation of 4 g. (0.04 mole) of the above dimethylcyclohexene using 0.4 g. of 10% palladium-on-charcoal at atmospheric pressure gave 1,1-dimethylcyclohexane, b.p. 117.5–118°, n^{25}_{D} 1.4261, d^{25}_{4} 0.774 (lit.[32] b.p. 118.5–120°, n^{18}_{D} 1.4342, d^{20}_{4} 0.782). The infrared spectrum of this material was indistinguishable from the published spectrum of 1,1-dimethylcyclohexane.[33]

Reaction of 3,3-Dimethylcyclohexanol with Phosphorus Pentachloride in the Presence of Cyclopentyl Chloride.—3,3-Dimethylcyclohexanol was treated with phosphorus pentachloride under the same conditions described in part A with the exception that 41 g. (0.39 mole) of cyclopentyl chloride was added with the solvent. The products were isolated as described above, and 17 g. (42%) of recovered cyclopentyl chloride, 59 g. (51%) of 3,3-dimethylcyclohexyl chloride and 46 g. (33%) of dichlorodimethylcyclohexane were obtained. The appropriate fraction, b.p. 59–94° (79 mm.), was carefully refractionated to determine whether any *trans*-1,2-dichlorocyclopentane was present. None of these fractions had bands at 7.8 or 11.2 μ where the spectrum of *trans*-1,2-dichlorocyclopentane has strong bands.

Reaction of Cyclopentanol with Phosphorus Pentachloride in the Presence of 3,3-Dimethylcyclohexyl Chloride.—Cyclopentanol was treated with phosphorus pentachloride under the same conditions as described in part A with the exception that 45 g. (0.31 mole) of 3,3-dimethylcyclohexyl chloride was added with the solvent. From this experiment 45 g. (100%) of recovered 3,3-dimethylcyclohexyl chloride, 29 g. (36%) of cyclopentyl chloride and 10 g. (9.6%) of *trans*-1,2-dichlorocyclopentane were isolated. Distillation of the residue gave no indication of the presence of any dichlorodimethylcyclohexane which would distil at a higher temperature than any of the chlorides isolated.

Reaction of Cyclohexene and 2-Pentene with Phosphorus Pentachloride.—Treatment of 64 g. (0.78 mole) of cyclohexene with phosphorus pentachloride under the same conditions as described above for the alcohols, gave 91 g. (77%) of *trans*-1,2-dichlorocyclohexane. Under similar conditions 2-pentene was converted to 2,3-dichloropentane in 76% yield.

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[28] J. Timmermans and F. Martin, *J. chim. phys.*, **25**, 411 (1928).

[29] A. I. Vogel, *J. Chem. Soc.*, 636 (1943).

[30] R. H. Clark and H. R. L. Streight, *Trans. Roy. Soc. Can.*, **23**, 77 (1929).

[31] A. W. Crossley and N. Renouf, *J. Chem. Soc.*, 1487 (1905).

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[33] National Bureau of Standards, American Petroleum Institute Research Project 44, Washington, D. C., No. 370.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Anomalous Silico-alkylation of Acetonitrile

BY MAURICE PROBER

RECEIVED SEPTEMBER 21, 1955

The reaction of trimethylchlorosilane with acetonitrile and sodium yields trimethylisocyanosilane and a high boiling fraction which consists of two silico-alkylated compounds—a nitrile $[(CH_3)_3Si]_2CHCN$, and the unusual ketenimine, $(CH_3)_3SiCH{=}C{=}NSi(CH_3)_3$. Minor reaction products are tetramethylsilane and cyanomethyltrimethylsilane. The ketenimine is thermally stable but rearranges easily to the nitrile in the presence of water—a rearrangement not hitherto observed. Benzyl cyanide also undergoes silico-alkylation to form nitrile and ketenimine.

In connection with a program on nitrile-containing organosilicon compounds, the synthesis of cyanomethyltrimethylsilane was of interest.[1] The alkylation of the nitrile carbanion is a well-known procedure[2] and the silico-alkylation of acetonitrile was attempted.

$$CH_3CN + (CH_3)_3SiCl \xrightarrow{\text{base}} (CH_3)_3SiCH_2CN \quad (A)$$

While this work was in progress the silico-alkylation of an ester carbanion was described.[3]

The silico-alkylation was carried out by the reaction of equal molar quantities of trimethylchlorosilane, sodium and acetonitrile. Sodium and acetonitrile form the desired carbanion along with other products.[4,5]

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[1] M. Prober, THIS JOURNAL, **77**, 3224 (1955).

[2] R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 599.

[3] C. R. Hance and C. R. Hauser, THIS JOURNAL, **75**, 994 (1953). The silico-alkylation of sodioacetoacetic ester has been carried out, H. Gilman and R. N. Clark, *ibid.*, **69**, 967 (1947), but the structure of the reaction product is in doubt; F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, *ibid.*, **69**, 1551 (1947).

[4] R. Holzwart, *J. prakt. Chem.*, **147**, 230 (1889).

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$$2CH_3CN + 2Na \longrightarrow CH_4 + NaCN + [CH_2CN]^-Na^+ \quad (B)$$

Sodium was chosen since it does not react with trimethylchlorosilane at room temperature and it can be removed easily after completing the reaction.

The acetonitrile was added dropwise to a stirred mixture of the other components in ether. Since the products are sensitive to hydrolysis, the reaction mixture was worked up in the absence of water.

The reaction was much more complicated than that suggested by equation (A). The following compounds were isolated, the yields being given in parentheses.

$(CH_3)_4Si$ I (6%) $(CH_3)_3SiNC$ II (27%) $(CH_3)_3SiCH_2CN$ III (2%)

$[(CH_3)_3Si]_2CHCN$ IV (7%) $(CH_3)_3SiCH{=}C{=}NSi(CH_3)_3$ V (25%)

The most volatile product, tetramethylsilane (I) may be formed by the interaction of cyanomethyltrimethylsilane (III) with sodium. Acetonitrile and benzyl cyanide react with sodium to form methane and toluene,[6] respectively, and a low yield of tetramethylsilane was obtained when cyanomethyltrimethylsilane alone reacted with sodium.

Trimethylisocyanosilane (II) may be formed by reaction of trimethylchlorosilane with the sodium cyanide produced in reaction (B). Although C.P. sodium cyanide does not react with trimethylchlorosilane in refluxing ether, the sodium cyanide of the silico-alkylation reaction is formed directly in the reaction medium and should have a much more reactive surface. The structure of the isocyanide was demonstrated by comparison of the properties with those reported for this compound prepared by reaction of trimethyliodosilane with silver cyanide.[7] When the chlorosilane is used as the starting material, better yields of the isocyanide are obtained *via* the silico-alkylation process than from the silver cyanide reaction.

The desired compound, cyanomethyltrimethylsilane (III) was formed in low yield by silico-alkylation at the α-carbon of sodio-acetonitrile. The low yield arises from the further interaction of cyanomethyltrimethylsilane with base and trimethylchlorosilane. The yield of III was doubled by halving the quantity of sodium. The structure of the nitrile was indicated by a comparison of the properties with those of cyanomethyltrimethylsilane which was prepared by treating the Grignard reagent of chloromethyltrimethylsilane with cyanogen.[1]

Unexpectedly, there was obtained a large higher boiling fraction and this arose from further silico-alkylation of $(CH_3)_3SiCH_2CN$. The analytical data were in agreement for the disilico-alkylated nitrile, IV, and infrared examination indicated nitrile absorption. However, very strong absorption at 4.93 μ was also noted. The latter band is in the cumulative double bond region, and is in good agreement with the recently reported ketenimine (C=C=N) absorption at 4.9–5.0 μ.[8] The ratio of ketenimine:nitrile in the high boiling fraction was 78:22. A cut of pure trimethylsilylketene-trimethylsilylimine (V) was obtained by careful rectification of the mixture. The ketenimine structure is in accord with the analytical and infrared data (see Fig. 1A). A possible alternative structure for the ketenimine is $[(CH_3)_3Si]_2C{=}C{=}NH$. However, this structure is ruled out since it contains an active hydrogen, =NH, and the ketenimine did not produce methane with methyl Grignard reagent, even after heating.

The stepwise formation of IV and V from $(CH_3)_3SiCH_2CN$ is indicated. When equal molar quantities of trimethylchlorosilane, sodium and cyanomethyltrimethylsilane reacted, the isocyanosilane (II) was isolated and the ketenimine and nitrile were formed in the same ratio as in the acetonitrile experiment.

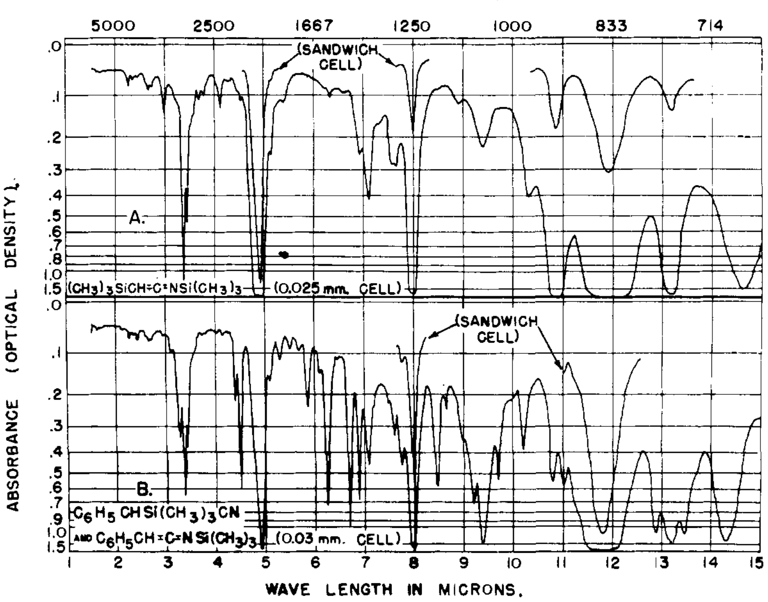

Fig. 1.—A, $(CH_3)_3SiCH{=}C{=}NSi(CH_3)_3$; B, $C_6H_5CHSi(CH_3)_3CN$ and $C_6H_5CH{=}C{=}NSi(CH_3)_3$.

The ready formation of the ketenimine is surprising since this functional group is so rare in carbon chemistry.[8–10] Sodium can react with cyanomethyltrimethylsilane to form an anion capable of resonance

$$[(CH_3)_3Si\bar{C}HC{\equiv}N] \longleftrightarrow [(CH_3)_3SiCH{=}C{=}\bar{N}]$$

The α-carbon and nitrogen are the reactive centers, with the latter somewhat more reactive. Steric and reactivity effects may be responsible for silico-alkylation taking place at the nitrogen. The bulky trimethylsilyl group renders difficult the approach of the α-carbon to another chlorosilane molecule.

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[6] M. M. Rising and G. Braun, THIS JOURNAL, **52**, 1069 (1930).

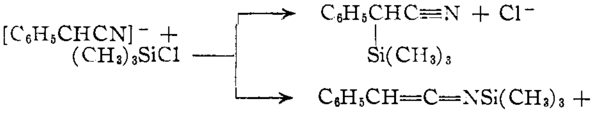
[7] J. J. McBride, Jr., and H. C. Beachell, *ibid.*, **74**, 5247 (1952); S. Sujishi, Paper 31 P, Abstracts of Meeting of the American Chemical Society, April, 1951.

[8] C. L. Stevens and J. C. French, *ibid.*, **75**, 657 (1953); **76**, 4398 (1954).

[9] H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 887 (1921).

[10] R. Dykstra and H. J. Backer, *C. A.*, **48**, 9900a (1954).

The terminal nitrogen does not have this steric difficulty. When the α-carbon is free of steric effects, as in $[CH_2CN]^-$, silico-alkylation takes place at the carbon atom. Secondly, the nitrogen would be the more nucleophilic center in the resonance hybrid, and silicon is readily attacked by nucleophilic reagents.[11] If the steric effects are significant then the same type of N-alkylation may occur when sterically hindered nitrile anions react with suitable alkyl halides, provided that hydrolysis conditions which destroy the ketenimine are avoided. Both carbon and nitrogen silico-alkylation take place when the benzyl cyanide anion reacts with trimethylchlorosilane (see Fig. 1B).



$$[C_6H_5CHCN]^- + (CH_3)_3SiCl \longrightarrow \begin{cases} C_6H_5\underset{\displaystyle Si(CH_3)_3}{\underset{|}{C}H}C{\equiv}N + Cl^- \\ C_6H_5CH{=}C{=}NSi(CH_3)_3 + Cl^- \end{cases}$$

The bond refraction of the keteinimine group is calculated for the first time. The known bond refractions[12,13] were subtracted from the observed molar refraction.

Compound	C=C=N bond refraction
$(C_2H_5)(C_4H_9)C{=}C{=}N(C_4H_9)$[8]	8.69
$(CH_3)_3SiCH{=}C{=}NSi(CH_3)_3$	9.82
$(C_6H_5)_2C{=}C{=}N(C_4H_9)$[8]	11.03
$(CH_3)_2C{=}C{=}N(pC_6H_4CH_3)$[8]	11.20
$(C_6H_5)_2C{=}C{=}N(CH_3)_2$[8]	12.17

The cumulative system of double bonds results in an exaltation effect since the sum of the individual bonds C=C and C=N is 7.93. This is in accord with the unusually short C=N bond length revealed by an X-ray structural analysis of a ketenimine.[14] Conjugation of the ketenimine with an aromatic system results in additional exaltation.

Ketenimines have been characterized by the addition of water and aniline. When these reagents reacted with trimethylsilylketene-trimethylsilylimine an unusual rearrangement took place.

$$(CH_3)_3SiCH{=}C{=}NSi(CH_3)_3 \xrightarrow[C_6H_5NH_2]{H_2O\text{ or}} [(CH_3)_3Si]_2CHC{\equiv}N$$

This ready rearrangement of ketenimine to nitrile has not been observed previously. The rearrangement by water takes place under very mild conditions—stirring overnight at room temperature or by exposure to atmospheric moisture. A catalyst, however, is necessary for this rearrangement. When trimethylsilylketene-trimethylsilylimine was heated overnight at 100°, no change was observed, and this ketenimine has been stored satisfactorily for over a year and a half in a desiccator.[15] Neither did the ketenimine undergo hydrogenation. This stability stands in marked contrast to the tendency toward dimerization observed with other ketenimines.[8-10]

The rearrangement results indicate that the nitrile is the stable isomer. The preponderance of the ketenimine in the reaction indicates kinetic control of the reaction products. This is another example where the unstable isomer is preferentially formed in an anionic reaction.[16]

Experimental

Reaction of Acetonitrile, Trimethylchlorosilane and Sodium.—Acetonitrile, 164.0 g. (4.00 moles), was added to a stirred solution of 434.4 g. (4.00 moles) of trimethylchlorosilane in 1.5 l. of dry ether containing 92.0 g. (4.00 moles) of sodium. The reaction became very vigorous, and it was necessary to cool the flask. The reaction mixture was then stirred overnight at room temperature. The salts were filtered off, and the solution rectified, yielding (a) 29.1 g. of trimethylchlorosilane; (b) 34.8 g. of acetonitrile; (c) 105.8 g. of trimethylisocyanosilane, b.p. 54–55° at 87 mm., 118–119° at 760 mm., $n^{20}D$ 1.3916; m.p. 12.0–12.5°, infrared absorption curve similar to that reported; lit. b.p. 117.8°, $n^{23}D$ 1.3891, m.p. 10.5–11.5°[7]; (d) 8.9 g. of cyanomethyltrimethylsilane, b.p. 82–84° at 53 mm., $n^{20}D$ 1.4201; this fraction and neighboring cuts were free of ketenimine absorption; reported[1] b.p. 84–85° at 53 mm., $n^{20}D$ 1.4203, identical infrared absorption curves from both methods; (e) 117.9 g. of bis-(trimethylsilyl)-acetonitrile and trimethylsilylketene-trimethylsilylimine, b.p. 125–127° at 44 mm., $n^{20}D$ varied from 1.4552 to 1.4573, ketenimine: nitrile ratio established by comparison of infrared absorption with pure components; (f) 9.3 g. of residue.

A silicon analysis of the ether-insoluble salt indicated that less than 3 g. of a sodium salt of a silicon containing nitrile was present in the precipitate.

Anal. Calcd. for C_4H_9NSi ($(CH_3)_3SiNC$): C, 48.58; H, 9.12; N, 14.08; mol. wt., 99.5. Found: C, 48.9; H, 9.4; N, 14.0, 14.4; mol. wt., 95, 99.

Anal. Calcd. for $C_5H_{11}NSi$ ($(CH_3)_3SiCH_2CN$): C, 53.04; H, 9.79; N, 12.37. Found: C, 53.4; H, 10.1; N, 12.4, 12.5.

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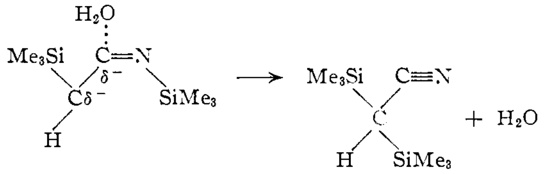
[11] H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 86 (1953).

[12] A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 531 (1952).

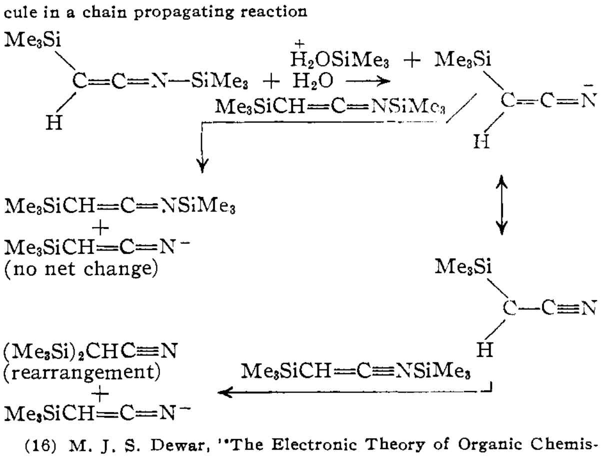
[13] A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, **58**, 177 (1954).

[14] P. J. Wheatley, *Acta Cryst.*, **7**, 68 (1954).

[15] Possible mechanisms of the rearrangement are (1) attack by the base on the central carbon atom resulting in a polar molecule which undergoes an intramolecular nucleophilic attack resulting in rearrangement



(2) attack by the base on the Si-N bond, followed by nucleophilic displacement by the anion on the Si-N bond of another ketenimine molecule in a chain propagating reaction



[16] M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, London, 1949, p. 103.

Anal. Calcd. for $C_8H_{19}NSi_2$($[(CH_3)_3Si]_2CHCN$ and $(CH_3)_3SiCH{=}C{=}NSi(CH_3)_3$): C, 51.83; H, 10.32; N, 7.55. Found: C, 51.7, 51.8; H, 10.2, 10.6; N, 7.2, 7.1.

The tetramethylsilane was isolated in another run starting with two molar quantities of the reactants and using a Dry Ice trap to reduce loss of volatile products. Rectification of the ether solution gave 11.4 g. of tetramethylsilane, b.p. 25–26, n^{20}_D 1.3594; reported b.p. 26.5°,[17] n^{23}_D 1.3580.[18]

Pure trimethylsilylketene-trimethylsilylimine was obtained by rectifying IV through a 20-plate column, b.p. 117° at 30 mm., n^{20}_D 1.4573, d^{20}_4 0.822.

Anal. Calcd. for $C_8H_{19}NSi_2$: C, 51.83; H, 10.32; Si, 30.30. Found: C, 51.5; H, 10.6; Si, 30.3.

Reaction of Cyanomethyltrimethylsilane (III) and Sodium.—Sodium (1.15 g., 0.050 mole) was added to a solution of 5.65 g. (0.050 mole) of cyanomethyltrimethylsilane in ether and the mixture refluxed for four hours. The volatile reaction products were then transferred under vacuum to a liquid nitrogen trap. The tetramethylsilane, 0.1 g., was obtained by rectifying the ether solution through a Podbielniak column. The solid reaction product reacted with water, and the aqueous solution contained 0.652 g. (0.0128 mole) of sodium cyanide.

Hydrolysis of Trimethylisocyanosilane (II).[7]—Trimethylisocyanosilane, 9.9 g. (0.1 mole) was added to 50 ml. of water. The water became hot, and 7.2 g. of hexamethyldisiloxane was recovered, b.p. 100–101°, n^{20}_D 1.3780; reported[19] b.p. 100.5° n^{20}_D 1.3774. Infrared absorption indicated a trace of trimethylsilanol.

Reaction of Cyanomethyltrimethylsilane (III), Trimethylchlorosilane and Sodium.—Sodium (4.14 g., 0.18 mole) was added slowly to a stirred solution of 20.4 g. (0.18 mole) of cyanomethyltrimethyltrimethylsilane and 19.6 g. (0.18 mole) of trimethylchlorosilane in 200 ml. of dry ether. The reaction was much less vigorous than the acetonitrile experiment. The mixture was stirred overnight at room temperature followed by refluxing for eight hours. The reaction mixture was centrifuged, the solid washed with dry ether and the solution rectified. There was obtained 1.2 g. of trimethylisocyanosilane, 8.3 g. of cyanomethyltrimethylsilane (infrared absorption free of ketenimine and identical with that of starting material) and 9.4 g. of a 76:24 mixture of trimethylsilylketene-trimethylsilylimine: bis-(trimethylsilyl)-acetonitrile.

Determination of Active Hydrogen in Trimethylsilylketene-trimethylsilylimine (IV).—A solution of 0.16 g. (0.000696 mole) of trimethylsilylketene-trimethylsilylimine in 4 ml. of di-*n*-butyl ether was added to 5 ml. of a 2 *M* methylmagnesium iodide solution in di-*n*-butyl ether in an active hydrogen Grignard apparatus. The solution was stirred at room temperature for 0.5 hour but no gas was evolved. The solution was then heated at 95–98° for 0.5 hour, but the amount of gas formed was less than that produced in a blank run. Infrared analysis of the solution indicated that two-thirds of the original ketenimine was still present. There was no $C\equiv N$ absorption.

Reaction of Benzyl Cyanide, Sodamide and Trimethylchlorosilane.—Benzyl cyanide (123 g., 1.05 moles) and 39.0 g. (1.00 mole) of commercial sodamide in 500 ml. of ether were refluxed for 1.75 hours. This slurry was added to 217.0 g. (2.00 moles) of trimethylchlorosilane in 150 ml. of ether and the mixture stirred at room temperature for two hours. The salts were filtered off, and the ether solution rectified, yielding 69.0 g. of benzyl cyanide, 26.1 g. of liquid (b.p. 135–145° at 12 mm.), and 31.2 g. of a very viscous residue. The higher boiling distillate was refractionated, and 60% boiled at 126–129° at 7 mm., n^{20}_D varied from 1.5167 to 1.5220.

Anal. Calcd. for $C_{11}H_{15}NSi$($C_6H_5CH[Si(CH_3)_3]CN$ and $C_6H_5CH{=}C{=}NSi(CH_3)_3$): C, 69.77; H, 7.99; N, 7.40. Found: C, 69.8; H, 8.3; N, 7.6, 7.5.

Rearrangement of Trimethylsilylketene-trimethylsilylimine (V) by Water.—Trimethylsilylketene-trimethylsilylimine, 7.0 g., and 25 ml. of water were stirred at room temperature overnight. The organic layer was dried and rectified, yielding 0.9 g. of hexamethyldisiloxane, and 3.0 g. of bis-(trimethylsilyl)-acetonitrile, b.p. 96–98° at 10 mm., n^{20}_D 1.4497. There was no trace of ketenimine in any of the fractions. The $C\equiv N$ absorption for this nitrile appears at 4.51 μ, 2217 ± 5 cm.$^{-1}$. This is outside the range of saturated nitriles, 2250 ± 10 cm.$^{-1}$, and in the range of conjugated nitriles, 2225 ± 8 cm.$^{-1}$.[20] There is some suggestion from previous work that an alpha $(CH_3)_3Si$ group shifts the $C\equiv N$ absorption to lower frequencies.[1]

Anal. Calcd. for $[(CH_3)_3Si]_2CHCN$: C, 51.83; H, 10.32. Found: C, 51.6; H, 10.5.

When a sample of the ketenimine was left in a loosely stoppered bottle for several days at room temperature it was completely converted to the nitrile.

Rearrangement of Trimethylsilylketene-trimethylsilylimine (V) by Aniline.—Trimethylsilylketene-trimethylsilylimine, 11.5 g. (0.05 mole), and aniline, 4.66 g. (0.05 mole) were heated at 100–110° for 6 hours. The reaction product boiled at 58–63° at 1.5 mm., and showed strong nitrile but no ketenimine absorption. The residue weighed 0.3 g., indicating essentially no addition of aniline. The distillate was rectified, and there was isolated 5.1 g. of pure bis-(trimethylsilyl)-acetonitrile. The low recovery is caused by the difficulty in separation due to close boiling points.

Attempted Thermal Rearrangement of Trimethylsilylketene-trimethylsilylimine (V).—A 0.3-ml. sample of the ketenimine was sealed in a glass tube taking precautions to maintain a dry atmosphere. The sealed tube was heated at 100–105° for 24 hours. The infrared curve and refractive index were identical with those of the starting material.

Attempted Hydrogenation of Trimethylsilylketene-trimethylsilylimine (V).—The ketenimine (9.3 g., 0.05 mole) and 1.0 g. of a 5% platinum on charcoal catalyst (Baker and Company) were shaken overnight at room temperature under hydrogen at 1300 p.s.i. There was a negligible pressure drop. The temperature was then raised to 85° for 7 hours, but no pressure drop was noted. The infrared curve of the reaction product was identical with that of the starting material.

Hydrolysis of Trimethylsilylketene-trimethylsilylimine (V) by Base.—Trimethylsilylketene - trimethylsilylimine, 11.5 g. (0.05 mole), and 75 ml. of 5% sodium hydroxide were refluxed overnight. Ammonia was evolved slowly. The organic layer, 6.3 g., consisted of hexamethyldisiloxane (78% of theory). The aqueous layer contained 3.75 g. of sodium acetate (91% of theory).

Acknowledgment.—I am indebted to Dr. G. D. Cooper for helpful discussion concerning reaction mechanisms, to Mr. F. O. Guenther for the determination of active hydrogen, to Mr. E. M. Hadsell for much of the distillation data, and to the Analytical Unit for the infrared and analytical data.

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