[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Derivatives of the Methylchlorosilanes. I. Trimethylsilanol and its Simple Ethers

BY ROBERT O. SAUER

The preparation of methyl silicone[1] polymers by the hydrolysis of methylchlorosilanes has been reported.[2,3,4] However, except for a brief description[3] of an impure sample of hexamethylcyclotrisiloxane no compounds of established structure have been reported as being prepared by the hydrolysis of methylchorosilanes.

From the hydrolysis of chlorosilane, H_3SiCl, Stock[5] was able to isolate only disiloxane; no silanol was obtained due, presumably, to its instability. On the other hand, triethylsilanol and higher trialkylsilanols have been prepared and are fairly stable.[6] In view of these facts it appeared of interest to prepare the previously unreported trimethylsilanol and to study its properties. Hence, this paper is concerned primarily with the hydrolysis and alcoholysis products of trimethylchlorosilane.[7]

The hydrolytic methods commonly employed[6] to convert various higher trialkylsilyl compounds to the corresponding silanols gave appreciable yields of hexamethyldisiloxane when applied to the trimethylsilyl analogs. The isolation of trimethylsilanol (b. p. 99°) is hampered by (1) its tendency to dehydrate, forming hexamethyldisiloxane (b. p. 100°), and (2) the formation of an azeotropic mixture (b. p. 90°) with the latter compound. This behavior contrasts strongly with the stability of triethylsilanol toward both heat and acid as illustrated by the methods given for its preparation.[8] In the present work a method discovered by Kipping and Hackford[9] and applied by them to the synthesis of various higher silanols was employed to prepare the first satisfactorily pure sample of trimethylsilanol according to Eqs. 1a and 1b.

$$[(CH_3)_2SiO]_x + xCH_3MgI \longrightarrow x(CH_3)_3SiOMgI \quad (1a)$$

$$(CH_3)_3SiOMgI + H_2O \longrightarrow (CH_3)_3SiOH + MgI(OH) \quad (1b)$$

A second satisfactory procedure involves the ammonolysis of trimethylchlorosilane to hexamethyldisilazine, $(CH_3)_3SiNHSi(CH_3)_3$, and subsequent titration of the amine according to Eq. 2. This hydrolysis appears to be rapid and quantitative.

$$(CH_3)_3SiNHSi(CH_3)_3 + 2H_2O + HCl \longrightarrow NH_4Cl + 2(CH_3)_3SiOH \quad (2)$$

Trimethylsilanol is a colorless, neutral liquid with a strong camphor-like odor. It is dehydrated on prolonged refluxing at atmospheric pressure, although by rapid distillation a satisfactorily pure product may be obtained. No detectable decomposition occurs in glass for two months at room temperature, but longer storage times have resulted in some decomposition. Trimethylsilanol is dehydrated at room temperature by most desiccants. The effect of activated alumina and of potassium carbonate is illustrated in Fig. 1 which gives the refractive index of trimethylsilanol–hexamethyldisiloxane mixtures as a function of the time of contact with these materials.

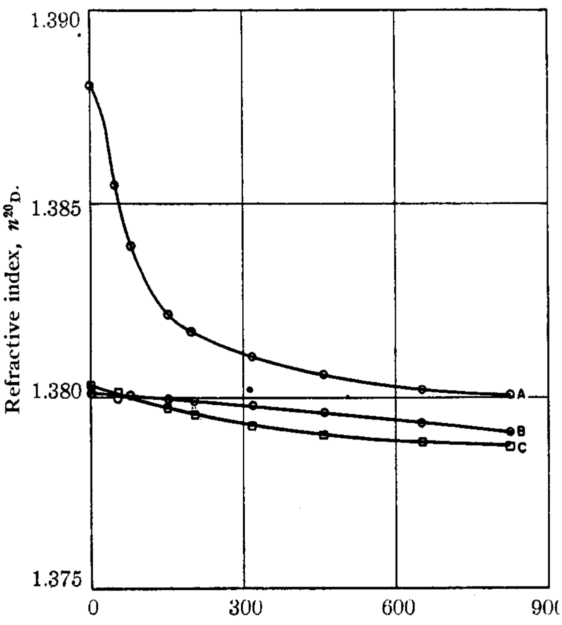

Fig. 1.—Dehydration of trimethylsilanol: A, pure silanol over K_2CO_3; B, azeotrope over Al_2O_3; C, azeotrope over K_2CO_3.

Hexamethyldisiloxane is a colorless, water-insoluble, inflammable liquid with a mild odor reminiscent of trimethylsilanol. No oxidation appears to occur upon boiling the siloxane with concentrated nitric acid for short periods of time. This is probably due to the insolubility of the two materials. Phosphoric anhydride or the

---

[1] The nomenclature used in this paper has been discussed recently [Sauer, *J. Chem. Education*, **21**, 303 (1944)].

[2] Rochow and Gilliam, THIS JOURNAL, **63**, 798 (1941).

[3] Hyde and DeLong, *ibid.*, **63**, 1194 (1941).

[4] Rochow, U. S. Patent 2,258,218 (1941).

[5] Stock, *Ber.*, **50**, 1754 (1917).

[6] For example, the following silanols distill with no reported decomposition: (a) triethyl-, b. p. 154° (760 mm.) [Ladenburg, *Ann.*, **164**, 318 (1872)]; (b) tri-*n*-propyl-, b. p. 206–208° (760 mm.) [Pape, *ibid.*, **222**, 367 (1884)]; (c) triisoamyl-, b. p. 269–270° (760 mm.) [Taurke, *Ber.*, **38**, 1666 (1905)].

[7] Taylor and Walden, THIS JOURNAL, **66**, 842 (1944); Gilliam and Sauer, *ibid.*, **66**, 1793 (1944).

[8] Hydrolysis of ethyltriethylsilylamine [Kraus and Nelson, THIS JOURNAL, **56**, 195 (1934)] and of α-methyl-*p*-triethylsilylbenzyl alcohol [Grüttner and Cauer, *Ber.*, **51**, 1288 (1918)] by hydrochloric acid and cleavage of hexaethyldisiloxane by sulfuric acid[6a] have been employed.

[9] Kipping and Hackford, *J. Chem. Soc.*, **99**, 138 (1911).

phosphoric acids apparently cleave the siloxane linkage; slow distillation of hexamethyldisiloxane from phosphoric anhydride converts a portion of the siloxane to tri-(trimethylsilyl) phosphate.

The trimethylalkoxysilanes were prepared by alcoholysis of trimethylchlorosilane, preferably employing a tertiary amine to remove the hydrogen chloride. Several azeotropes of these ethers and the alcohols used in the preparations were encountered. In this respect the trimethylalkoxysilanes resemble the analogous carbon ethers.[10] Several of the azeotropic compositions were determined.

The best values of the physical constants for hexamethyldisiloxane, trimethylsilanol and its simple carbon ethers appear in Table I while Table II gives a comparison of the boiling points of some carbon and silicon compounds of similar structure. It is noteworthy that in this latter table the only appreciable difference in boiling points appears in the compounds containing hydrogen bonded to oxygen or nitrogen.

TABLE I

PHYSICAL PROPERTIES OF THE COMPOUNDS $(CH_3)_3SiOR$

R	B. p. °C.	B. p. Mm.	n^{20}_D	d^{20}_4 (vac.)
—H	98.6	752	1.3880	0.8112
$—CH_3$	57	760	1.3678	....
$—C_2H_5$	75	745	1.3743	.7573
$—C_4H_9$-*n*	124	760	1.3925	.7774
$—Si(CH_3)_3$[a]	100.4	757	1.3772	.7638

[a] M. p. *ca.* −59°C.

TABLE II

COMPARISON OF THE BOILING POINTS OF SILICON AND CARBON COMPOUNDS OF SIMILAR STRUCTURE

Type formula	Boiling points T = Si	Boiling points T = C
$(CH_3)_3TCl$	58	52
$(CH_3)_3T—OH$	99	83
$(CH_3)_3T—OCH_3$	57	55
$(CH_3)_3T—OC_2H_5$	75	73
$(CH_3)_3T—OC_4H_9$-*n*	124	124
$(CH_3)_3T—O—T(CH_3)_3$	100	107[11]
$(CH_3)_3T—NH—T(CH_3)_3$	126	92–95[12]

Experimental

Technique for Analyzing Volatile Samples for Active Hydrogen.—A "Grignard machine" was constructed and operated generally as described by Shriner.[13] The modification necessitated by the volatility of the samples (b. p. 90–100°) was the freezing of the liquid sample while sweeping out the system with dry nitrogen. The effectiveness of this sweeping out process was increased by extending the addition tube in the reaction flask to within 1 cm. of the bottom of the flask.

Hexamethyldisiloxane.—Trimethylchlorosilane (b. p. 57.3–57.5° (753 mm.)) was hydrolyzed with boiling water; 51 g. (0.47 mole) gave 32.7 g. (86%) of hexamethyldisiloxane, b. p. 99.5–100.6°. Redistillation of this from phosphoric anhydride gave a more anhydrous product, b. p. 100.0–100.9°, n^{20}_D 1.3774, d^{20}_4 (vac.) 0.7619.

Anal. Calcd. for $C_6H_{18}Si_2O$: C, 44.39; H, 11.18; Si, 34.57. Found: C, 44.3, 44.5; H, 10.9, 11.3; Si, 34.2, 34.6.

Repetition of this hydrolysis at room temperature by agitating as little as 5 g. of trimethylchlorosilane with 400 cc. of water gave only hexamethyldisiloxane, n^{20}_D 1.3771–1.3772. When one mole of trimethylchlorosilane was swept with dry nitrogen into a vigorously stirred solution of one mole of sodium bicarbonate and 255 cc. of water over a three and one-half hour period, the water-white layer which separated (69.8 g.) gave fractions of b. p. 99.6–100.1° and n^{20}_D 1.3772–1.3774. The following procedures, however, gave in addition to hexamethyldisiloxane considerable amounts of a material, b. p. 89–91° n^{20}_D 1.3800–1.3797, which was later identified as azeotropic hexamethyldisiloxane–trimethylsilanol: (a) hydrolysis of an ethereal solution of trimethylchlorosilane by 20% aqueous potassium hydroxide (one mole KOH/mole chlorosilane) at 0°, and (b) hydrolysis of trimethylchlorosilane (or an ethereal solution thereof) by dilute aqueous ammonia at 0–6°, or at room temperature. When the ethereal solution was used in (b) nearly all the product was azeotrope, b. p. 90.4–90.6°, n^{20}_D 1.3800.

Hexamethyldisilazine.—A solution of 109 g. (1.0 mole) of trimethylchlorosilane (b. p. 57.1–57.3° (750 mm.), 32.2% Cl) in 500 cc. of anhydrous ether was placed in a 1-liter, round-bottom flask fitted with an efficient reflux condenser and bearing a side arm through which was inserted a gas inlet tube from a cylinder of ammonia. Upon the introduction of ammonia a white precipitate immediately appeared and a very slight warming of the mixture was noted. The reaction mixture was brought to reflux temperature and a slow flow of ammonia maintained for six hours. The ammonium chloride was allowed to settle and the ethereal solution was decanted and filtered. The powdery white solid was washed with three 50-cc. portions of anhydrous ether. After distillation of ether from the combined extracts the product was fractionated in a glass packed column having 10–12 theoretical plates giving 23.4 g. of hexamethyldisilazine, b. p. 125.4–125.6°, n^{20}_D 1.4080, d^{20}_4 (vac.) 0.7742.

Anal. Calcd. for $C_6H_{19}Si_2N$: C, 44.66; H, 11.87; Si, 34.78; N, 8.68; N. E., 161.3; act. H, 1.00. Found: C, 44.7, 44.3; H, 11.1, 10.9; Si, 34.6, 34.8; N, 8.65, 8.54; N. E., 159 (methyl orange), 159 (brom phenol blue); act. H, 0.88, 0.94.

The white solid, which contained much ether, was dissolved in 300 cc. of water and the ether layer separated. Distillation of this ethereal solution gave four fractions totaling 29.1 g., b. p. 124–126°, n^{20}_D 1.4080. The total yield of hexamethyldisilazine by this procedure was then 52.5 g. (65%). This synthesis has been repeated with yields of 61–68%.

Trimethylsilanol from Dimethyl Silicone.—A methylmagnesium iodide solution in dibutyl ether was prepared by adding 142 g. (1 mole) of methyl iodide in 125 cc. of dibutyl ether to 36 g. of magnesium in 300 cc. of dibutyl ether. A portion of the solution was withdrawn and found by titration with dilute hydrochloric acid to be 2.16 *M*.

By means of nitrogen pressure 425 ml. (containing 0.92 mole of methylmagnesium iodide) of this solution was filtered and transferred to a dry 1-liter three-neck flask fitted with a vigorous mechanical stirrer and an addition funnel. From the latter was added 66.0 g. (0.89 equivalent of $(CH_3)_2SiO$) of a liquid dimethyl silicone[14] over a forty-five-minute period, the contents of the flask being

---

(10) See, for example, Evans and Edlund, *Ind. Eng. Chem.*, **28**, 1188 (1936); Lécat, *Rec. trav. chim.*, **46**, 243 (1927); Popelier, *Bull. soc. chim. Belg.*, **32**, 193 (1923).

(11) Erickson and Ashton, THIS JOURNAL, **63**, 1769 (1941).

(12) Klages, Nober, Kircher and Bock, *Ann.*, **547**, 1 (1941); *C. A.*, **35**, 4346 (1941).

(13) R. L. Shriner, "Quantitative Analysis of Organic Compounds," Edwards Brothers, Inc., Ann Arbor, Mich., 1938, pp. 57–60.

(14) This was obtained from Dr. W. I. Patnode who prepared it by hydrolyzing pure dimethyldichlorosilane. This material was tested in the "Grignard machine" and found to contain 61 mg. atoms of active hydrogen per kg.

heated with a boiling water-bath. Heating and stirring were continued for two hours. The reaction mixture was then allowed to cool, much white solid, $(CH_3)_3SiOMgI$, separating. With vigorous stirring and ice cooling aqueous saturated ammonium chloride solution was slowly admitted through the addition funnel, a considerable amount of methane being evolved. The magnesium salts failed to dissolve completely and an emulsion appeared. The reaction mixture was transferred to a separatory funnel and the clear upper layer separated (Solution A).

The entire lower layer, which contained the emulsion, was diluted to twice its volume with water and refluxed for an hour. After cooling dilute hydrochloric acid was added until the solution became acid to methyl orange. The solution was filtered by suction and extracted with 100 cc. of dibutyl ether. This ether layer (Solution B) was then dried over sodium carbonate.

From Solution A the following fractions were obtained by distillation in a small glass-packed column having 5–6 theoretical plates: I, b. p. 76–92°, $n^{20}{}_{\mathrm{D}}$ 1.3810, 6.1 g.; II, b. p. 92–97°, $n^{20}{}_{\mathrm{D}}$ 1.3854, 2.2 g.; III, b. p. 97–99°, $n^{20}{}_{\mathrm{D}}$ 1.3880, 8.3 g.; IV, b. p. 99–100°, $n^{20}{}_{\mathrm{D}}$ 1.3880, 3.3 g.

Anal. Calcd. for $C_3H_{10}SiO$: C, 39.96; H, 11.18; Si, 31.12; act. H, 1.00. Found (Fract. IV): C, 40.2, 39.8; H, 10.9, 10.7; Si, 31.2, 31.1; act. H, 0.98, 0.99.

No pure silanol could be isolated from Solution B by distillation, although fractions having $n^{20}{}_{\mathrm{D}}$ values from 1.3801 to 1.3880 were obtained.

Trimethylsiloxymagnesium Iodide.—About 0.5 g. of trimethylsilanol was treated with excess methylmagnesium iodide in the "Grignard machine." After standing overnight with the reagent, the crystals were washed four times with 20-cc. portions of dry ethyl ether. The large crystals remaining after decantation of the ether were dried at 2–3 mm. pressure and 100° for two hours, and then analyzed by the Volhard technique.

Anal. Calcd. for $C_3H_9SiOMgI$: I, 52.8. Found: I, 52.4.

Trimethylsilanol from Hexamethyldisilazine.—To a vigorously stirred mixture of 70.0 g. (0.435 mole) of hexamethyldisilazine, 250 cc. of dibutyl ether, 50 g. of water and a few drops of methyl orange indicator was added dropwise dilute aqueous hydrochloric acid (1.06 *N*). The mixture became slightly acidic after 387 ml. of acid had been added (two and one-quarter hours) and a pinch of potassium carbonate was then added, making the aqueous layer basic. The ether layer was separated and dried over potassium carbonate. Distillation in an 18-plate column gave 17 g. of azeotropic trimethylsilanol-hexamethyldisiloxane, b. p. 89.8–90.2° (752 mm.), $n^{20}{}_{\mathrm{D}}$ 1.3798, and 35 g. of trimethylsilanol, b. p. 98.6–99.0°, $n^{20}{}_{\mathrm{D}}$ 1.3880, d^{20}_{4} (vac.) 0.8112. On total reflux the boiling point of the pure silanol was found to fall from 98.6 to 88.0° over a ninety-minute period, thus demonstrating spontaneous dehydration at its boiling point.

Trimethylmethoxysilane.—To a solution of 50.0 ml. (0.62 mole) of pyridine and 20.0 ml. (0.497 mole) of absolute methanol in 200 ml. of dry toluene was added a solution of 54.0 g. (0.497 mole) of trimethylchlorosilane in 100 ml. of dry toluene. The product consisted of (A) azeotropic methanol-trimethylmethoxysilane, b. p. 49.6–50.0° (760 mm.), $n^{20}{}_{\mathrm{D}}$ 1.3636–1.3638, 14.5 g., and (B) trimethylmethoxysilane, b. p. 57.0° (760 mm.), $n^{20}{}_{\mathrm{D}}$ 1.3678–1.3680, 7.4 g. A portion of A was washed twice with water and redistilled giving trimethylmethoxysilane, b. p. 57.0–57.3° (758 mm.), $n^{20}{}_{\mathrm{D}}$ 1.3678–1.3679.

The preparation was repeated using one mole of the chlorosilane and ether as the solvent. After washing the reaction mixture with water and drying the resulting ethereal solution, there was obtained by distillation 38.7 g. (46%) of pure trimethylmethoxysilane, b. p. 56.5–56.7° (747 mm.), $n^{20}{}_{\mathrm{D}}$ 1.3678–1.3679.

Anal. Calcd. for $C_4H_{12}SiO$: Si, 26.93. Found: Si, 26.8, 27.0.

Trimethylethoxysilane.—This was prepared in the same manner as trimethylmethoxysilane, except that xylene was used as the solvent. Distillation gave three fractions (25.7 g., 44%) of trimethylethoxysilane, b. p. 74.9–75.0° (745 mm.), $n^{20}{}_{\mathrm{D}}$ 1.3741–1.3743, d^{20}_{4} (vac.) 0.7573.

Anal. Calcd. for $C_5H_{14}SiO$: C, 50.79; H, 11.94. Found: C, 50.4; H, 12.4.

A small amount of material (3–4 g.) was obtained distilling at 65–66°. To 15 g. of trimethylethoxysilane was added 25 ml. of absolute ethanol and the solution distilled giving the ethanol–trimethylethoxysilane azeotrope, b. p. 66.4° (760 mm.), $n^{20}{}_{\mathrm{D}}$ 1.3729.

Trimethyl-*n*-butoxysilane.—To 109 g. (1.0 mole) of trimethylchlorosilane (b. p. 57.2–57.5°, 32.5–32.7% Cl) was added 76.5 g. (1.03 moles) of *n*-butanol. Fractionation in a glass packed column having 10–12 theoretical plates gave two principal materials: I, b. p. 111.0–111.5° (754 mm.), $n^{20}{}_{\mathrm{D}}$ 1.3962–1.3963, 37.8 g., and II, b. p. 123.4–123.6° (754 mm.), $n^{20}{}_{\mathrm{D}}$ 1.3925, 39.0 g. The lower boiling material was azeotropic *n*-butanol–trimethyl-*n*-butoxysilane. Redistillation of II gave pure trimethyl-*n*-butoxysilane, b. p. 124.5–124.7° (761 mm.), $n^{20}{}_{\mathrm{D}}$ 1.3925, d^{20}_{4} (vac.) 0.7774.

Anal. Calcd. for $C_7H_{18}SiO$: Si, 19.18. Found: Si, 19.4, 19.0.

Tri-(trimethylsilyl) Phosphate.—To 150 cc. of hexamethyldisiloxane which had previously been dried by distillation from sodium was added 5–8 g. of phosphoric anhydride. The hexamethyldisiloxane was slowly distilled over a two-day period. At the end of this time no solid phosphoric anhydride remained, and the residue was a heavy oil. Distillation at reduced pressure gave tri-(trimethylsiloxy) phosphate, b. p. 85–87° (4 mm.), $n^{20}{}_{\mathrm{D}}$ 1.4090. This was analyzed by titration with *N*/2 sodium hydroxide solution to the methyl orange end-point, using a reference standard containing monosodium phosphate.

Anal. Calcd. for $C_9H_{27}Si_3PO_4$: $PO_4^{\equiv}$, 30.21. Found: $PO_4^{\equiv}$, 30.4, 29.8, 30.0.

Composition of the Azeotropes.—Synthetic binary mixtures of the components were prepared and their refractive indices measured. By plotting refractive index against composition and assuming the unknown azeotropes to be binary mixtures a satisfactory estimate of the azeotropic compositions was obtained. The boiling point of a composition arrived at in this way was then checked by distilling such a synthetic mixture. The results are listed in Table III.

TABLE III

PROPERTIES OF THE $(CH_3)_3SiOR$—ROH AZEOTROPES

R	B. p., °C.	$n^{20}{}_{\mathrm{D}}$	Wt. % ROH
—CH_3	50	1.3637	14–16
—C_2H_5	66	1.3729	...
—C_4H_9-*n*	111	1.3963	40–44
—$Si(CH_3)_3$	90	1.3800	33–35

Acknowledgment.—The author is greatly indebted to Dr. Earl W. Balis of this Laboratory for the carbon, hydrogen and silicon analyses reported in this paper and to Dr. W. I. Patnode for a sample of liquid dimethyl silicone.

Summary

1. The following organosilicon compounds have been prepared and identified: hexamethyldisiloxane, hexamethyldisilazine, trimethylsilanol, trimethylmethoxysilane, trimethylethoxysilane, trimethyl-*n*-butoxysilane, and tri-(trimethylsilyl) phosphate.

2. Trimethylsilanol has been found to undergo dehydration more readily than the higher trialkylsilanols.

3. The boiling points and compositions for

azeotropes of certain of the trimethylsilyl ethers with their corresponding alcohols have been determined.

SCHENECTADY, NEW YORK RECEIVED AUGUST 4, 1944

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY, PRINCETON, N. J.]

Catalytic Synthesis of Pyridine

BY CHARLES HOWARD KLINE, JR.,[1] AND JOHN TURKEVICH

The main source of pyridine is coal tar. In view of the small percentage of pyridine in this source, 0.1%,[1a] it was thought desirable to investigate various synthetic methods. The catalytic syntheses of pyridine have been extensively reported in both scientific and patent literature.[2] Nearly all of these processes fall into three classes: (a) the reaction of unsaturated hydrocarbons such as ethylene and acetylene with ammonia or hydrogen cyanide, (b) the condensation of aldehydes or ketones with ammonia, and (c) the condensation of ethanol with ammonia. Though previous investigations have indicated favorable operating conditions for the production of pyridine, no satisfactory process has been developed. Low yields, expensive reagents, and lack of specificity in the reactants are the chief drawbacks. It would appear no less difficult to purify pyridine from the products of these reactions than directly from coal tar.

Before embarking on an investigation of the synthesis of pyridine it was thought worth while to investigate the theoretical implications of the various processes. The infra-red spectrum of pyridine vapor was examined, an assignment of vibrational frequencies made and the thermodynamic properties of pyridine were calculated.[3]

Using these results the standard free energy changes at various temperatures were calculated for fifteen reactions in which pyridine is formed. These are given in Table I and because of the uncertainty in the heats of combustion should be used to indicate general trends. On the basis of this table the following general conclusions may be reached.

1. Over the whole temperature range of interest pyridine is unstable with respect to its decomposition products. Insofar as possible, catalysts must be chosen to minimize coking.
2. Syntheses based on acetylene are favorable throughout the whole temperature range.
3. Synthesis from ethylene and hydrogen cyanide is a favorable reaction over the whole temperature range considered.
4. Synthesis from pentane and ammonia is thermodynamically favorable only above 475°. Pentene, however, because of the increased energy content of the double bond over the single bond at moderate temperatures, shows a favorable equilibrium above about 400°, while pentadiene-1,4 with two double bonds would probably show a negative standard free energy change for the reaction in the liquid state at 25°.
5. Syntheses producing water as well as pyridine such as reactions 9 to 15 of Table I require a much lower temperature for favorable equilibria than similar reactions involving corresponding hydrocarbons.
6. Syntheses from formaldehyde and acetaldehyde are thermodynamically favorable even at room temperature.
7. Syntheses from furfural and its derivatives are thermodynamically favorable at room temperature.

Besides these conclusions based on available data, others may safely be drawn by reason of the close analogy between pyridine and benzene. Like benzene, pyridine is a resonating molecule being stabilized by a resonating energy of 43 kcal. and is the stable high temperature form for nitrogen carbon compounds just as benzene is the stable high-temperature form for C_6 hydrocarbons. This is supported by the fact that pyridine and benzene are products of the pyrolysis of coal tar. Just as equilibria at sufficiently high temperatures favor the formation of benzene from hexane and cyclohexane[4] it is very probable that the equilibria also favor the production of pyridine from amylamine and similar compounds at high temperatures.

Kinetic considerations suggest that an efficient process would involve the least number of reactant molecules. Thus the cyclization of amylamine, the reaction of pentamethylene oxide and ammonia or the reaction of pentadiene and ammonia are susceptible of greater catalytic control than the reaction of three molecules of acetylene with one molecule of hydrogen cyanide. The mathematical argument for this view derived from considerations of absolute reaction rate theory[5] will be the subject of another publication from the Princeton Laboratories. Thus, five-carbon chained carbons were deemed as suitable

---

[1] Ensign, U. S. N. R.

[1a] "Reilly Coal Tar Chemicals," Reilly Tar and Chemical Corporation, 1940.

[2] A good review of the literature is found in H. Maier-Bode and J. Altpeter, "Das Pyridin und seine Derivate in Wissenschaft und Technik," Halle, 1934, p. 6; W. Schmidt, Beaser and Manchen, German Patent 695,472; Natta, Mattei and Bartoletti, *Chem. Ind.* [Milano], **24**, 81–85 (1942).

[3] P. C. Stevenson and J. Turkevich, *J. Chem. Phys.*, **11**, 328 (1943); C. H. Kline, Jr., and J. Turkevich, *ibid.*, **12**, 303 (1944).

[4] Taylor and Turkevich, *Trans. Faraday Soc.*, **35**, 921–934 (1939).

[5] Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Company, New York, N. Y., 1942.