VI, as no ethyl glyoxylate-DNP could be found when the reaction was carried out at room temperature with excess DNPH. The product V cannot reasonably be obtained except through the unstable hydrazonium intermediate IV, and, with excess chloral, once the formation of V is complete, the remaining "mono-DNP" undergoes the hydrolysis-esterification reaction to VII.²⁵ The chloroform solution spectrum of V contained absorption maxima at 385 m μ (ϵ 4.01 \times 10⁴) and 435 m μ (ϵ 4.81 \times 10⁴) while in alcoholic sodium hydroxide λ_{max} 540 m μ (ϵ 5.42 \times 10⁴), the results being in complete agreement with the spectral properties previously reported for other bis-DNP's of 1,2-dicarbonyl compounds.¹¹

The above reaction scheme implies that the tri-

(25) The mono-DNP of chloral, m.p. 131°, has been reported by F. L. Roduta and C. Quiblan, *Rev. Filipina med. farm.*, 27, 123 (1936), *Chem. Abstr.*, 31, 98. As the derivative was prepared from methanol, it seems likely the methyl glyoxylate DNP was the derivative isolated. chloromethyl-group is activated by the conjugated unsaturation of the DNP moiety and, further, that a similar π -electron system should react in an analogous fashion. To test this hypothesis, DNPH was treated at elevated temperatures with an excess of benzotrichloride and yielded the anomalous "benzoyl chloride-DNP." Similarly, benzal chloride was used in the preparation of the benzaldehyde derivative. These results offer support for the reaction mechanism proposed and indicate that the DNP portion of the derivative has an activating effect similar to that of the phenyl groups in the benzyl halides.²³

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COLLEGE STATION, TEX.

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY OF LOWELL TECHNOLOGICAL INSTITUTE AND THE LOWELL TECHNOLOGICAL INSTITUTE RESEARCH FOUNDATION]

Chemistry of the Silylamines. I. The Condensation of Monofunctional Silylamines with Monofunctional Silanols¹

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The rates of reaction of triphenyl- and triethylsilanol with a series of silylamines in bis(2-methoxyethyl) ether have been measured under a variety of conditions. The effect on the reaction rate of the structure of the reacting species, the addition of acid catalyst, and the observed second-order kinetics indicate a bimolecular type mechanism. This condensation reaction offers an alternate route for the formation of siloxane bonds.

Numerous reports in the literature indicate that silylamines are susceptible to attack by various nucleophilic reagents resulting in the cleavage of the silicon-nitrogen bond.

 $\begin{array}{c} R-X: + \equiv Si - N = \longrightarrow R-X-Si \equiv + H: N= \\ \downarrow \\ H & X \text{ may be 0, NH, or S} \end{array}$

Rochow² states that an ---NH₂ group attached to silicon is easily replaced by an ---OH group upon hydrolysis, generating ammonia. The treatment of triethylsilylamine with hydrogen sulfide resulted in the formation of the corresponding thiol compound, triethylsilanthiol.³ The reaction of hexamethyldisilazane with alcohols gives aliphatic trimethylsilyl ethers.⁴ Langer and co-workers⁵ have recently extended this reaction to prepare a large number of silvl ethers belonging to this class. Smith⁶ has treated triethylsilanol with di-*tert*-butoxydiaminosilane and isolated $(C_2H_5)_3Si-O-Si-(t-C_4H_9O)_2-NH_2$.

In each of the above reactions of silylamines or silazanes with water, primary amines, alcohols, hydrogen sulfide, or a silanol, it appears that a nucleophilic displacement on silicon occurs,⁵ which results in the formation of a new \equiv Si-O-, \equiv Si-N= or \equiv Si-S- linkage.

Since this displacement reaction is of considerable practical importance for the synthesis of a variety of useful silicone intermediates and products, a program has been initiated in these laboratories to obtain fundamental information concerning the behavior of silylamines toward various nucleophilic reagents.

⁽¹⁾ Presented at the 137th meeting of the American Chemical Society, Division of Organic Chemistry, at Cleveland, Ohio, April 11, 1960.

⁽²⁾ E. G. Rochow, Chemistry of the Silicones, John Wiley and Sons, New York, New York, 2nd ed., 1951, p. 58.

⁽³⁾ E. Larsson and R. Mjorne, Acta. Chem. Scand., 5, 964 (1951).

⁽⁴⁾ J. L. Speir, J. Am. Chem. Soc., 74, 1003 (1952).

⁽⁵⁾ S. H. Langer, S. Connell, and I. Wender, J. Org. Chem., 23, 50 (1958).

⁽⁶⁾ B. Smith, Svensk. Kem. Tidskr., 65, 101 (1953); Chem. Abstr., 48, 9907g (1954).

The present paper describes a general experimental technique for measuring the rates of the displacement reactions on silylamines and illustrates this technique with a study of the condensation of monofunctional silanols with monofunctional silylamines.

$$R_sSiOH + R_s'SiNR'_2 \longrightarrow R_sSi-O-SiR_s' + HNR'_2$$

This condensation reaction offers an alternate route for the formation of siloxane linkages, \Longrightarrow Si-O---Si \equiv . Furthermore, it offers an approach to the formation of siloxane linkages in which control of the structure of the end product may be exercised. Previous methods for forming siloxane bonds such as treatment of chlorosilanes with alkoxy or hydroxy silanes,⁷ condensation of alkoxysilanes with silanols in the presence of metallic sodium,⁶ condensation of selected silanols,⁸ and the equilibration of preformed silicone cyclic intermediates⁹ are mainly random type reactions.

EXPERIMENTAL

General method. Ammonia or an amine is liberated when a silylamine reacts with a nucleophilic reagent. The rate of reaction, therefore, can be followed by measurement of the rate of formation of the amine. The method adopted for the present work is a modification of that described by Ma and Zuazaga, 10 concerned with the determination of nitrogen by a Micro Kjeldahl procedure. In this procedure the ammonia evolved on decomposition of the organic compound was absorbed in a 2 wt. % solution of boric acid and the liberated borate anion titrated with standard hydrochloric acid solution. To check this method for the present work, weighed samples of freshly distilled diethylamine were added to a 2 wt. % solution of boric acid followed by titration with a standard hydrochloric acid solution. The indicator used was methylpurple modified methylorange. Ninety-nine and fourtenths per cent of the diethylamine was accounted for using this technique.

The rate runs were carried out using bis(2-methoxyetbyl) ether as the solvent. The amine, as it formed, was removed from the reaction site by a stream of nitrogen passing through the system at a constant rate. Duplicate runs of several of the condensation reactions were carried out; excellent duplication was obtained.

Apparatus. The rate studies were carried out in a 30-ml. round bottom flask fitted with an inlet tube and a 12-inch water condenser. An outlet tube was connected from the top of the condenser to a 125-ml. Erlenmeyer flask. The reaction vessel was immersed in a constant temperature bath, the temperature of which was controlled to within $\pm 0.5^{\circ}$. The inlet tube reached to the bottom of the flask through which nitrogen gas was passed at a constant rate. The gas rate was held constant at two bubbles/sec. formed as the nitrogen swept out the reaction flask, through the condenser and outlet tube and passed through approximately 20 ml. of freshly prepared 2 wt. % boric acid solution contained in the Erlenmeyer flask. The amine generated during the reaction was thus removed from the reaction site. The

(7) D. T. Hurd, British Patent 585,400, February 6, 1947.

(8) W. T. Grubb, J. Am. Chem. Soc., 76, 3408 (1954).

(9) E. G. Rochow, Chemistry of the Silicones, John Wiley and Sons, New York, New York, 2nd ed., 1951, p. 69; A. R. Gilbert and S. W. Kantor, J. Polymer Sci. 40, 35 (1959)

Gilbert and S. W. Kantor, J. Polymer Sci., 40, 35 (1959). (10) T. S. Ma and G. Zuasaga, Ind. Eng. Chem. (Anal. Ed.), 14, 280 (1942). borate anion was then titrated at regular intervals with standard hydrochloric acid solution.

Timing procedure. Timing of the reaction was begun when the silylamine was added to the solution of the silanol in bis(2-methoxyethyl) ether solution. Nitrogen was swept through this solution for 5 min. and passed into the boric acid solution before the amine was added. The boric acid solution was changed at timed intervals and titrated with standard hydrochloric acid. Duplication of runs gave excellent results as previously mentioned. This fact appears to justify the validity of the timing procedure outlined above.

Materials. Commercial triphenylsilanol was recrystallized from benzene. The resulting material had m.p. 148-150°; lit.,¹¹147-149°.

Triethylsilanol was prepared by the hydrolysis of triethylchlorosilane using a procedure similar to that described by Sommer¹⁹ for the hydrolysis of triethylfluorosilane. Distillation of the isolated product through a semimicro column¹³ gave b.p. 153°, n_D^{26} 1.4299; lit.,¹² b.p. 153.5°, n_D^{20} 1.4329.

N,N-Diethylaminotrimethylsilane was prepared by the treatment of trimethylchlorosilane with diethylamine as described by Sauer and Hasek.¹⁴ The purified material had b.p. 126-127°, n_{2}^{56} 1.4062; lit.,¹⁴ b.p. 126.3°, n_{2}^{50} 1.4112.

N-n-Butylaminotrimethylsilane was prepared by treatment of *n*-butylamine with hexamethyldisilazane.⁵ The material had b.p. 132-136.6°, n_D^{25} 1.4060; lit.,⁵ 132-135°, n_D^{20} 1.4058.

N-tert-Butylaminotrimethylsilane was obtained by treatment of trimethylchlorosilane with tert-butylamine using a procedure similar to that by which N,N-diethylaminotrimethylsilane was prepared.¹⁴ The purified material had b.p. 120-121°, n_{25}^{25} 1.4054.

120-121°, n⁵ 1.4054. Anal. Calcd. for C₇H₁₉SiN: Neut. Equiv., 145. Found: Neut. Equiv. 148.5.

N,N-Diethylaminotriethylsilane was prepared by treatment of triethylchlorosilane with diethylamine using a procedure similar to that described for N,N-diethylaminotrimethylsilane.⁴ The purified material had b.p. 198-200°, n_D^{25} 1.4360; lit.,¹⁵ b.p. 200.5°, n_D^{20} 1.4400.

N-Ethylaminotriethylsilane was prepared from triethylchlorosilane and ethylamine. The purified material had b.p. 170.5°, n_D^{25} 1.4254; lit.¹⁶ b.p. 170.3°, n_D^{20} 1.4290.

N-N-Diethylaminotri-n-butylsilane was prepared by treatment of tri-n-butylchlorosilane with diethylamine in ether solvent. The purified material had b.p. 118-128° (5.0 mm.), n_{D}^{sp} 1.4450-1.4455.

Anal. Caled. for $C_{16}H_{37}NSi$: Si, 10.32%. Found: Si, 10.2 \pm 0.5%.

Commercial n-propylalcohol was dried over "Molecular Sieve" and distilled.¹⁶

Commercial bis(2-methoxyethyl) ether was passed through a 12-inch column of "Molecular Sieve" to remove water and peroxides.

Baker Chemical Company reagent grade boric acid was used throughout this investigation. For each time interval the 2 wt. % boric acid solution was freshly prepared using distilled water. It was necessary to prepare the solution immediately before use since on standing the pH of the boric

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(12) L. H. Sommer, E. W. Pietrusza, and F. C. Whitmore, J. Am. Chem. Soc., 68, 2282 (1946).

(13) C. W. Gould, Jr., G. Holzman, and C. Neimann, Anal. Chem., 20, 361 (1948).

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(15) B. N. Dolgov. N. P. Kharitonov, and M. G. Vorarkov, Zhur. Obshcheš Khim., 24, 678 (1954); Chem. Abstr., 49, 5272 (1955).

(16) "Molecular Sieve" is available from the Linde Company, Union Carbide Corp., Tonawanda, N. Y.

		TABLE I		
Condensation	OF	SILYLAMINES	WITH	SILANOLS

			Concentration (mole/l.) ^b		Special	Specific Reaction ^{c} Rate Constant, k .
System	Silanol	Silylamine	Silanol	Silylamine	Conditions	$(1-mole^{-1} \sec^{-1})^{f}$
I	(C ₆ H ₅) ₃ SiOH	$(CH_3)_3SiN(C_2H_5)_2$	0.1810	0.1810		5.91 × 10 ⁻⁴
II	(C6H5)3SiOH	$(CH_3)_3SiN(C_2H_5)_2$	0.1710	0.1775	Run at 40°	3.01×10^{-4}
III	(C6H5)3SiOH	$(CH_3)_3SiN(C_2H_5)_2$	0.1760	0.1805	(CH ₂) ₂ SiCl added ^d	$7.85 imes 10^{-4}$
IV	(C6H5)3SiOH	$(CH_2)_3 SiN(C_2H_5)_2$	0.2100	0.1900	(n-C4H2)3N added	$5.99 imes 10^{-4}$
v	(C ₆ H ₅) ₃ SiOH	$(CH_3)_3SiN(C_2H_5)_2$	0.3610	0.1715	•••	$5.32 imes 10^{-4}$
VI	(C ₆ H ₅) ₃ SiOH	(CH3)3SiNH-C4H9-t	0.1845	0.1851		$3.00 imes 10^{-4}$
\mathbf{VII}	$(C_2H_5)_3SiOH$	$(CH_3)_2 SiN(C_2H_5)_2$	0.4065	0.1855		$1.60 imes 10^{-4}$
VIII	(C ₂ H ₅) ₃ SiOH	$(CH_{3})_{3}SiN(C_{2}H_{5})_{2}$	0.4130	0.3840		1.67×10^{-4}
IX	(C ₂ H ₅) ₃ SiOH	(CH ₃) ₃ SiNH-C ₄ H ₉ -n	0.3775	0.3805		$7.15 imes 10^{-5}$
X	$n-C_3H_7-OH$	$(CH_3)_3SiN(C_2H_5)_2$	0.1934	0.1420		8.33×10^{-4}
XI	(C ₆ H ₅) ₃ SiOH	$(C_2H_5)_3SiN(C_2H_5)_2$	0.1810	0,1505		3.11×10^{-4}
XII	(C ₆ H ₅) ₃ SiOH	$(C_2H_5)_3SiNHC_2H_5$	0.1720	0.1575	· · · ·	$2.86 imes 10^{-4}$
XIII	$(C_6H_5)_3SiOH$	$(C_2H_5)_3SiNHC_2H_5$	0.1850	0.1830	quinoline solvent	4.89×10^{-4}
XIV	$(C_6H_5)_3SiOH$	$(n-\mathrm{C_4H_9})_3\mathrm{SiN}(\mathrm{C_2H_5})_2$	0.1905	0.1655		$5.36 imes10^{-5}$

^a All runs were carried out at 50 \pm 0.5° except for System II as noted. ^b The solvent in each run was bis(2-methoxyethyl) ether except in system XIII as noted. ^e k values were determined from the second order rate plots examples of which are shown in Fig. 1. ^d Concentration of (CH₄)₂SiCl, 0.0017 mole/l. ^e Concentration of (n-C₄H₉)₂N, 0.0014 mole/l. ^f The probable error in the k values is estimated to be $\pm 10.0\%$.

acid solution was found to change as much as 1 pH unit over the course of a week.

RESULTS AND DISCUSSION

To investigate the cleavage of the \equiv Si-N= bond in the subject condensation reaction, kinetic studies employing triphenyl- and triethylsilanol were carried out with a selected series of silylamine derivatives under a variety of conditions. The systems investigated are summarized in Table I. In order to compare the reactivity of an organic alcohol to the silanols, the condensation of 1propanol with N,N-diethylaminotrimethylsilane was also investigated. Information as to the effect of temperature, concentration of the reacting species, added catalyst, and the structure of the silanol and silylamine on the rate of the condensation reaction was obtained.

Identification of reaction products. To establish that the condensation of silanols with silylamines results in the formation of a new =Si-O-Si= linkage, the product from the treatment of triphenylsilanol with N,N-diethylaminotrimethylsilane (Table I, System I) was isolated and identified. The treatment of a monofunctional silanol with a monofunctional silvlamine should result in the formation of a disiloxane, *i.e.*, System I, should yield triphenyltrimethyldisiloxane. This disiloxane was isolated from the reaction mixture of System I by concentration of the product solution over a period of several weeks at room temperature. The material (0.75 g.) had m.p. 49-50°, lit.,¹⁷ m.p. 49.5-51.0°. This reaction was carried to 82% completion, which theoretically should yield 1.04 g. (0.00298 mole) of triphenyltrimethyldisiloxane. The actual amount of product isolated (0.75 g.) corresponds to 72.5% conversion. This result may indicate that the main side reaction, *i.e.*, the selfcondensation of the silanol,⁸ occurs to a small extent in the subject systems. However, hexaphenyldisiloxane was not isolated.

Determination of specific reaction rates. As outlined in the experimental section, the rates of the subject condensation reactions were followed by measuring the rate at which the amine was evolved from the reaction mixture.

In the majority of the runs approximately the stoichiometric ratio of reactants was used. Second order kinetics were expected and, therefore, specific reaction rate constants, k, were obtained by the method of constructing second order rate plots¹⁸ (as illustrated in Fig. 1) based on the equation $kt = \frac{x}{a(a-x)}$. From the slope of the lines the value for the second order rate constants were calculated employing the relationship, slope = 1/k. (See Systems I, II, III, VI VIII, IX, XII, and XIII in Table I.) For the other runs summarized in Table I (Systems IV, V, VII, X, XI, and XIV) k values were obtained by constructing second order rate plots based on the equation $k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$ where slope = $\frac{2.303}{k(a-b)}$. The results clearly demonstrate that the rate of condensation of a silanol with a

silylamine obeys second order kinetics. The general rate expression may be represented by $+ d[RN-H_2]/dt = k$ [Silylamine] [Silanol] where RNH₂ represents the organic amine formed during the course of the reaction.

⁽¹⁷⁾ W. H. Daudt and J. Hyde, J. Am. Chem. Soc., 74, 386 (1952); U. S. Patent, 2,444,555.

⁽¹⁸⁾ S. Glasstone, *Textbook of Physical Chemistry*, D. Van Nostrand Co., Inc., New York, New York, 2nd ed., 1946, p. 1054.



TIME IN SECONDS (10")

Fig. 1. Second order reaction rate plots. △ System I, ● System II, ○ System VIII, × System XIII

The effect of a change in the ratio of reactants on the subject condensation reactions is seen in a comparison of System I with V and System VII with VIII in Table I. Within experimental error, the k values obtained were similar.

Effect of temperature. In the present work the system N,N - diethylaminotrimethylsilane - triphenylsilanol (Table I, Systems I and II) was used to investigate the effect of temperature on the subject reaction. As noted in Table I, an increase in the temperature of 10° resulted in the rate constant being increased by a factor of 2. Since at 50° the majority of the reactions could be carried out over a convenient period of time, this temperature was used for the various systems in this work.

Effect of catalyst. Langer and co-workers⁵ demonstrated the catalytic effect of acid catalyst on the condensation of silazanes with alcohols. As might be expected, a similar catalytic effect should operate in the present reactions. This was found to be the case. Comparison of the k values listed in Table I for Systems I and III shows that the addition of a trace of acid catalyst increases the rate constant from 5.91 \times 10⁻⁴ to 8.34 \times 10⁻⁴ 1-mole⁻¹ sec.⁻¹; this is not a large difference, but higher concentrations of catalyst may result in a larger increase. It was also of interest to determine if an organic base might have a catalytic effect on the rate of the above system. It was found that the addition of a trace of tri-n-butylamine had no effect on the rate (compare Systems I and IV, Table I). However, the use of quinoline as a solvent did result in an increase in the rate of condensation (compare Systems XII and XIII).

Effect of structure. From the specific reaction rates summarized in Table I it is apparent that the nature of the organic groups attached to the silicon atom in the silanol and in the silylamine have an effect upon the rate of the reaction. The following general observations may be made from the data:

(1) The rate of condensation of a given silanol with monofunctional silylamines of the type $R_4SiNR_1R_2$, in which R remains constant and R_1 , R_2 are varied, decreases in the order of $-N_1N_1$ -dialkyl > --NH-alkyl (compare System I with VI, System VIII with IX, and System XI with XII in Table I).

(2) The rate of condensation of a given silanol with monofunctional silylamines of the type $R_3SiNR_1R_2$, in which R is varied and R_1 , R_2 remain constant, decreases in the order $(CH_2)_3Si-$ > $(C_2H_5)_3Si-$ > $(n-C_4H_9)_3Si-$ (compare System I, System XII, and System XIV).

(3) The rate of condensation of monofunctional silanols toward a given silylamine decreases in the order of triaryl-> trialkyl- (compare System I with VIII in Table I).

(4) Toward the same silylamine, 1-propanol condensed at a faster rate than triphenyl- or triethylsilanol (compare System X with Systems I and VIII).

Mechanism. From the data accumulated in this investigation it appears that the condensation of silanols with silylamines involves an attack of the oxygen atom of the silanol on the silicon atom of the silylamine accompanied by deprotonization of the silanol. The result of this attack is the formation of an \Longrightarrow Si—O—Si \Longrightarrow linkage with cleavage of the \Longrightarrow Si—N \Longrightarrow bond in the silylamine molecule. Further investigation is necessary to formulate a detailed mechanism of the condensation reaction but on the basis of the accumulated evidence the reaction may be pictured involving a four centered type intermediate.



The data demonstrate that triphenylsilanol is a more effective condensation reagent than triethylsilanol toward the same silylamine. This order can be correlated with the acid strengths of the silanols. West and Baney measured the acid strengths of a series of silanols and showed triphenyl-silanol to be a stronger acid than a series of trialkylsilanols.^{19,20} On this basis triphenylsilanol would be expected to give a faster rate than triethylsilanol. On the other

⁽¹⁹⁾ R. West and R. H. Baney, J. Inorg. & Nuclear Chem., 7, 297 (1958).

⁽²⁰⁾ R. West and R. H. Baney, J. Am. Chem. Soc., 81, 6145 (1959).

hand, the more basic silylamine would be expected to condense at a faster rate. The observation that N,N-dialkylaminosilanes react at a faster rate than N-alkylaminosilanes can be correlated with the base strengths of the silylamines. Ebsworth and Emeléus²¹ demonstrated that N,N-dimethylsilylamines are appreciably stronger bases than the monomethylated silylamines. Furthermore, a more basic solvent was shown to result in an increase in the rate of the reaction. It should be pointed out however, in comparing the N,N-dialkylsubstituted silylamines vs. the N-alkyl derivatives toward the

(21) E. A. V. Ebsworth and H. J. Emeléus, J. Chem. Soc., 2150 (1958).

same silanol that several of the N-alkyl types investigated are quite bulky. It is reasonable to expect that a steric factor may also account for the observed decrease in rate.

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