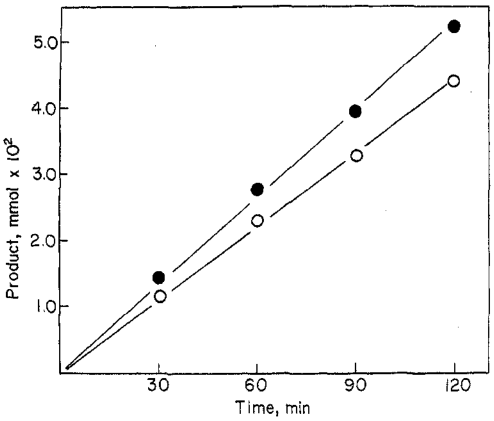

Figure 5.—The determination of the quantum yield of formation of (●) *m*-methoxybenzyl methyl ether and (○) *m*-methoxytoluene from the photolysis of *m*-methoxybenzyltrimethylammonium chloride in methanol.

with a catalytic amount of hydrogen chloride in the presence of 5,5-dimethylcyclohexane-1,3-dione, the dimedone derivative was formed.[29] The nmr spectrum of the compound prepared in this manner was compared with an authentic specimen obtained by reacting aqueous formaldehyde. When a portion of the photolysate was treated in a similar manner, the dimedone derivative was formed, as indicated by its nmr spectrum, but it was not analyzed quantitatively.

Product Analysis.—All quantitative analyses were performed by gas chromatography on a Varian Aerograph Model 1200 gas chromatograph equipped with a flame ionization detector. Products were identified by comparing their retention times with those of authentic samples on at least two columns whose separation characteristics differed. Analyses were performed by the internal standard method with a marker chosen, where possible, which had a similar functional group and a retention time close to that of the compound being analyzed.

Photolysis Studies.—Samples of ammonium salts were weighed into 10-ml volumetric flasks and diluted to volume with the appropriate solvent. The solution was then transferred to a cylindrical quartz tube (15 × 1.5 cm) and degassed by passing a slow stream of nitrogen through the solution for 10 min. The tube was sealed with a rubber septum. The photolyses were carried out in a Rayonet RPR-100 photochemical reactor (The Southern New England Ultraviolet Co.) using sixteen 253-nm lamps and rotated with a Rayonet MGR-100 merry-go-round.

Quantum Yield Measurements.—Aliquots (3.0 ml) of standard solutions were transferred to 10 × 1 cm quartz tubes and degassed as above. The solutions were photolyzed in a merry-go-round apparatus (F. G. Moses, Co., Wilmington, Delaware). A helix coil low-pressure Hg lamp (Mr. Charles Shott, University of Alberta), operating on 100 mA from a 5000-V transformer, was placed in the center of the apparatus. More than 97% of the light was centered about a sharp band at 254 nm. A shutter was arranged so that photolysis was allowed only after the lamp was warmed. A constant temperature of 32° was maintained in the reactor. Chloroacetic acid was used for actinometry and a value of 0.370 chosen as the quantum yield for chloride formation at 32°.[30] The flux of light through each slit was found to be $7.22 \pm 0.08 \times 10^{-5}$ einsteins hr^{-1} by this method (average of 20 separate runs). The formation of each product was followed periodically up to 5% conversion as shown in Figure 5 for the photolysis of *m*-methoxybenzyltrimethylammonium chloride in methanol. The quantum yield (moles einstein^{-1}) was obtained by dividing the slope (mole hour^{-1}) by the flux (einsteins hour^{-1}).

Registry No.—$PhCH_2N(CH_3)_3^+$ Br^-, 5350-41-4; $(PhCH_2)_2N(CH_3)_2^+$ Cl^-, 100-94-7; $(PhCH_2)_3NCH_3^+$ Br^-, 31246-85-2; $PhCH_2N(CH_3)_3^+$ Cl^-, 56-93-9; $(PhCH_2)_2N(CH_3)_2^+$ EtO^-, 31280-85-0; $(PhCH_2)_3NH^+$ Cl^-, 7673-07-6; $PhCH_2N(n\text{-}Hex)_3^+$ Br^-, 31280-89-4; $(PhCH_2)_2NH(CH_3)^+$ Cl^-, 5441-24-7; $(PhCH_2)_2NH_2^+$ Cl^-, 20455-68-9; $PhCH_2NH_3^+$ Cl^-, 3287-99-8; $PhCH_2N(CH_3)CH_2OCH_2CH_3$, 31280-93-0; benzyl ethyl ether, 539-30-0; benzyl methyl ether, 538-86-3; *m*-methoxybenzyl methyl ether, 1515-82-8; *m*-methoxytoluene, 100-84-5.

Acknowledgment.—We wish to thank the National Science Foundation, the Petroleum Research Fund of the American Chemical Society, and the Edgewood Arsenal, U. S. Army, for generous financial support and the Miles Chemical Co. for samples of some benzylammonium salts.

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Syntheses of (3-Aminoalkyl)silicon Compounds

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The syntheses and chemical properties of some 54 compounds are described, all having structural units including ≡SiCCCN= with either methyl, phenyl, siloxy, alkoxy, or amino groups on silicon and H, alkyl, or phenyl groups on nitrogen. Thirteen of the compounds are novel substituted heterocyclic 1-aza-2-silacyclopentanes and one is a 1-aza-2-silacyclohexane.

During the course of some years we have had occasion in these laboratories to prepare large numbers of 3-silylalkylamino compounds. Nearly all of these amines had either methyl, alkoxy, or siloxy groups attached to silicon and hydrogen, alkyl, aryl, or other groups attached to nitrogen.

Only a few compounds of this kind were previously known. Some examples are 3-trimethylsilylpropylamine (**2**)[2a] which was first made by reduction of 3-trimethylsilylpropionitrile with lithium aluminum hydride[2b] and later by hydrogenation of the same intermediate.[3] Comparable hydrogenation of 2-cyanoethylalkoxysilanes has also been described.[3a,4]

Examples of the alkylation of amines or ammonia with 3-silylalkyl chlorides are also known.[3b,5]

In this paper many structures of this kind, including

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(1) Many of the experiments in this paper were carried out by G. K. Menzie (deceased).

(2) (a) Throughout this paper the numbers in parentheses, (**2**), refer to compounds as listed in Table II. (b) L. H. Sommer and J. Rockett, *J. Amer. Chem. Soc.*, **73**, 5130 (1951).

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TABLE I

$RCl + R'R''NH \rightarrow$ PRODUCTS $+ R'R''NH_2^+Cl^-$

R	R′	R″	Products	Yield, %	No.[a]
$ClMe_2Si(CH_2)_3-$	H	$-CH_2CH_2NH_2$	$Me_2\overline{Si(CH_2)_3N}CH_2CH_2NH_2$	50	9
$ClMe_2SiCH_2CHMeCH_2$	H	$-CH_2CH_2NH_2$	$Me_2\overline{SiCH_2CHMeCH_2NH}CH_2CH_2NH_2$	76	13
$MeOMe_2Si(CH_2)_3-$	H	$-CH_2CH_2NH_2$	$MeOMe_2Si(CH_2)_3NHCH_2CH_2NH_2$	55	20
$(MeO)_2MeSi(CH_2)_3-$	H	$-CH_2CH_2NH_2$	$(MeO)_2MeSi(CH_2)_3NHCH_2CH_2NH_2$	80	21
$(MeO)_3Si(CH_2)_3-$	H	$-CH_2CH_2NH_2$	$(MeO)_3Si(CH_2)_3NHCH_2CH_2NH_2$	87	22
$Me_3SiCH_2CHMeCH_2-$	H	$-CH_2CH_2NH_2$	$Me_3SiCH_2CHMeCH_2NHCH_2CH_2NH_2$	67	25
$(MeO)_2MeSiCH_2CHMeCH_2-$	H	$-CH_2CH_2NH_2$	$(MeO)_2MeSiCH_2CHMeCH_2NHCH_2CH_2NH_2$	85	27
$(MeO)_3SiCH_2CHMeCH_2-$	H	$-CH_2CH_2NH_2$	$(MeO)_3SiCH_2CHMeCH_2NHCH_2CH_2NH_2$	82	28
$(EtO)_3Si(CH_2)_3-$	H	$-CH_2CH_2NH_2$	$(EtO)_3Si(CH_2)_3NHCH_2CH_2NH_2$	62	36
$ClMe_2Si(CH_2)_4-$	H	Me	$Me_2\overline{Si(CH_2)_4N}Me$	65	5
$ClMe_2SiCH_2CHMeCH_2-$	H	Me	$Me_2\overline{SiCH_2CHMeCH_2N}Me$	76	6
$ClMeOMeSiCH_2CHMeCH_2-$	H	Me	$MeOMe\overline{SiCH_2CHMeCH_2N}Me$	36	7
$(MeO)_3Si(CH_2)_3-$	H	Me	$(MeO)_3Si(CH_2)_3NHMe$	69	8
			$[(MeO)_3Si(CH_2)_3]_2NMe$	19	44
$Cl_2MeSiCH_2CHMeCH_2-$	H	Me	$MeNH\overline{SiCH_2CHMeCH_2N}Me$	100[b]	10
			$MeN[\overline{SiCH_2CHMeCH_2N}Me]$	b	41
$(MeO)_2MeSi(CH_2)_3-$	H	Me	$(MeO)_2MeSi(CH_2)_3NHMe$	79	12
$(EtO)_3Si(CH_2)_3-$	H	Me	$(EtO)_3Si(CH_2)_3NHMe$	73	32
$ClPhMeSiCH_2CHMeCH_2-$	H	Me	$PhMe\overline{SiCH_2CHMeCH_2N}Me$	65	38
$(MeO)_3Si(CH_2)_3-$	Me	Me	$(MeO)_3Si(CH_2)_3NMe_2$	79	19
$(MeO)_3Si(CH_2)_3-$	H	$-CH_2CH{=}CH_2$	$(MeO)_3Si(CH_2)_3NHCH_2CH{=}CH_2$	59	23
$(MeO)_3Si(CH_2)_3-$	Morpholine		$(MeO)_3Si(CH_2)_3\overline{NCH_2CH_2OCH_2CH_2}$		
$(MeO)_3Si(CH_2)_3-$	H	n-Bu	$(MeO)_3Si(CH_2)_3NH$-n-Bu	50	33
$Me_3Si(CH_2)_3-$	H	H	$Me_3Si(CH_2)_3NH_2$	45	2
			$[Me_3Si(CH_2)_3]_2NH$	18	41
$(MeO)_3Si(CH_2)_3-$	H	H	$(MeO)_3Si(CH_2)_3NH_2$	31	4
$(EtO)_2MeSi(CH_2)_3-$	H	H	$(EtO)_2MeSi(CH_2)_3NH_2$	51	17
			$[(EtO)_2MeSi(CH_2)_3]_2NH_2$	32	49
$(EtO)_3Si(CH_2)_3-$	H	H	$(EtO)_3Si(CH_2)_3NH_2$	31	17
$ClMe_2Si(CH_2)_3-$	H	H	$MeOMe_2Si(CH_2)_3NH_2$[b]	30	3
			$[MeOMe_2Si(CH_2)_2]_2NH$[b]	25	41
$ClMe_2SiCH_2CHMeCH_2-$	H	H	$Me_2\overline{SiCH_2CHMeCH_2N}H$	18	1
			$ClCH_2CHMeCH_2Me_2Si\overline{NSiMe_2CH_2CHMeCH_2}$	40	b

[a] Example number in Table II. [b] See Experimental Section.

novel heterocyclic aminosilanes, are described along with unusual chemical reactivities they exhibit.

Results and Discussion

Six (3-chloroalkyl)silicon compounds were heated with from 9 to 18 mol of liquid ammonia per equivalent of chloride to see what yields of corresponding amino derivatives would be obtained (Table I). The chloroalkyl groups gave yields of primary amines usually from 30 to 51%, with secondary amines and higher boiling products accounting for the remainder even when a large excess of ammonia was used.

$$RCl \xrightarrow[-NH_4Cl]{NH_3} RNH_2 \xrightarrow[-NH_4Cl]{RCl\text{-}NH_3} R_2NH$$

Chlorosilanes formed silazanes in such a process at very much faster rates.

$$\equiv SiCl \xrightarrow[-NH_4Cl]{NH_3} \equiv SiNH_2 \xrightarrow{-0.5NH_3} 0.5(\equiv Si)_2NH$$

Silazanes and amines react as follows.

$$\equiv SiN< + R_2NH \rightleftharpoons \equiv SiNR_2 + HN<$$

By way of these reactions very complex structures were easily possible, especially with ammonia and any chlorosilylalkyl chloride. The use of primary amines in these systems simplifies them, and secondary amines such as dimethylamine yield simple products in an easily understood manner.

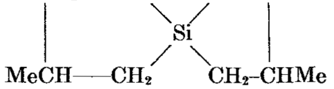
Reagents such as $Me_2ClSiCH_2CH_2CH_2Cl$ and ammonia underwent all of these reactions, to form a liquid mixture of polymers including units of $-SiMe_2(CH_2)_3NH-$ and $-SiMe_2(CH_2)_3NH(CH_2)_3SiMe_2NH-$. This mixture reacted vigorously with dry methanol to form 3-(methoxydimethylsilylpropylamine), $MeOMeSi(CH_2)_3NH_2$ (**3**), 30%, and bis(3-methoxydimethylsilylpropyl)amine, $[MeOMe_2Si(CH_2)_3]NH$ (**42**), 25%, along with higher boiling products that decomposed on distillation. The reaction with methanol was a well-known one by which the Si–N structures were methanolyzed.

$$\equiv SiN< + MeOH \longrightarrow \equiv SiOMe + HN<$$

In a very comparable example, 3-chloro-2-methylpropyldimethylchlorosilane, $ClCH_2CHMeCH_2SiMe_2Cl$, was first converted into the corresponding disilazane,

TABLE II

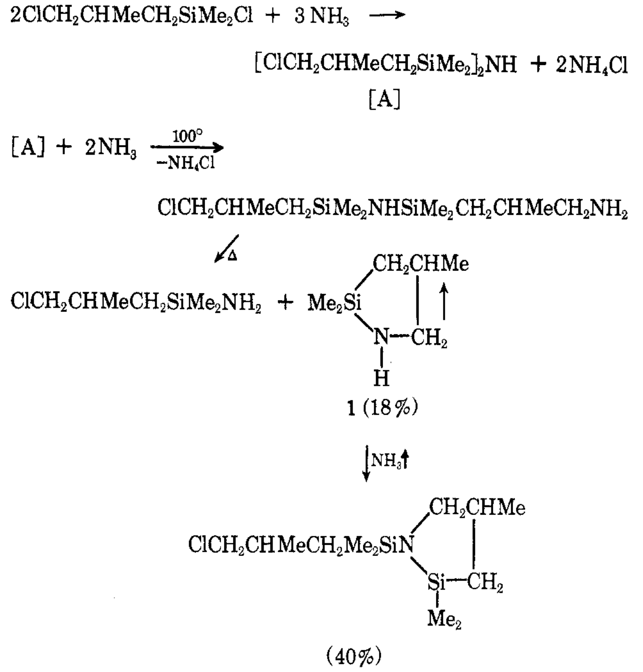
(AMINOALKYL)SILICON COMPOUNDS

No.	Structure	Bp		n^{25}_D	d^{25}_4	R_D		Empirical formula	Neut equiv		Si, %	
		°C	mm			Found	Calcd		Found	Calcd	Found	Calcd
1	$Me_2SiCH_2CHMeCH_2NH$	17.8	46	1.4661–7	0.8883	0.312	0.312	$C_6H_{15}NSi$	128.8	129.3	22.0	21.7
2	$Me_3SiCH_2CH_2CH_2NH_2$[a]	58	30	1.4260	0.7831	0.327	0.328	$C_6H_{17}NSi$	134	131		
3	$MeOMeSiCH_2CH_2CH_2NH_2$	87	50	1.4301	0.8696	0.297	0.297	$C_6H_{17}ONSi$	153	147	18.1	19.1
4	$(MeO)_3SiCH_2CH_2CH_2NH_2$[b]	104	30	1.4188	1.009	0.251	0.253	$C_6H_{17}O_3NSi$	185	179		
5	$Me_2Si(CH_2)_4NMe$	64	55	1.4451	0.8446	0.315	0.316	$C_7H_{17}NSi$	144	143	19.5	19.6
6	$Me_2SiCH_2CHMeCH_2NMe$	136	744	1.4308	0.8132	0.318	0.316	$C_7H_{17}NSi$	143	143	19.7	19.6
7	$(MeO)MeSiCH_2CHMeCH_2NMe$	63	30	1.4285	0.8943	0.289	0.289	$C_7H_{17}ONSi$	158	159	17.4	17.6
8	$(MeO)_3SiCH_2CH_2CH_2NHMe$	106	30	1.4194	0.9767	0.259	0.260	$C_7H_{19}O_3NSi$	195	193	$pK_b{}^{25}{}_{H_2O} = 5.18$	
9	$Me_2SiCH_2CH_2CH_2NCH_2CH_2NH_2$	95	33	1.4897	0.9410	0.307	0.307	$C_7H_{18}N_2Si$	78.6	79.2	17.7	17.7
10	$(MeHN)MeSiCH_2CHMeCH_2NMe$	30	1	1.4450	0.8721	0.305	0.305	$C_7H_{18}N_2Si$	86	79.2	17.6	17.7
11	$MeOMe_2SiCH_2CHMeCH_2NH_2$			1.4361	0.8711	0.307	0.300	$C_7H_{19}ONSi$	158	161	17.8	17.4
12	$(MeO)_2MeSiCH_2CH_2CH_2NHMe$	93	25	1.4224	0.9173	0.277	0.278	$C_7H_{19}O_2NSi$	180	177	16.4	15.8
13	$Me_2SiCH_2CHMeCH_2NCH_2CH_2NH_2$	209	757	1.4754	0.9085	0.310	0.310	$C_8H_{20}N_2Si$	84	86	16.0	16.3
14	$MeOMeSiCH_2CHMeCH_2NCH_2CH_2NH_2$	87	4	1.4740	0.9841	0.286	0.287	$C_8H_{20}ON_2Si$	103	102	15.0	14.9
15	$(MeO)_2SiCH_2CHMeCH_2NCH_2CH_2NH_2$	Mp 70–78° dec						$C_8H_{20}O_2N_2Si$	103	102	13.8	13.7
16	$MeOMe_2SiCH_2CHMeCH_2NHMe$			1.4299	0.8526	0.303	0.303	$C_8H_{21}ONSi$	174	175	15.8	16.0
17	$(EtO)_2MeSiCH_2CH_2CH_2NH_2$[c]	110	30	1.4243	0.9081	0.281	0.281	$C_8H_{21}O_2NSi$			14.9	14.7
18	$(MeO)_2MeSiCH_2CHMeCH_2NHMe$	84	12	1.4257	0.9109	0.281	0.282	$C_8H_{21}O_2NSi$	189	191	14.6	14.7
19	$(MeO)_3SiCH_2CH_2CH_2NMe_2$	106	30	1.4150	0.9479	0.264	0.265	$C_8H_{21}O_3NSi$	215	207	13.2	13.5
20	$MeOMe_2SiCH_2CH_2CH_2NHCH_2CH_2NH_2$	116	14	1.4518	0.9082	0.297	0.298	$C_8H_{22}ON_2Si$	93	95.2	14.5	14.7
21	$(MeO)_2MeSiCH_2CH_2CH_2NHCH_2CH_2NH_2$	139	25	1.4500	0.9675	0.278	0.278	$C_8H_{22}O_2N_2Si$	103	103		
22	$(MeO)_3SiCH_2CH_2CH_2NHCH_2CH_2NH_2$	146	15	1.4418	1.0152	0.261	0.261	$C_8H_{22}O_3N_2Si$	111	111	12.5	12.6
23	$(MeO)_3SiCH_2CH_2CH_2NHCH_2CH{=}CH_2$	121	15	1.4326	0.9706	0.268	0.268	$C_9H_{21}O_3NSi$	222	229	12.7	12.8
24	$(EtO)_3SiCH_2CH_2CH_2NH_2$[d]	115	19	1.4185	0.9414	0.268	0.267	$C_9H_{23}O_3NSi$	220	221		
25	$Me_3SiCH_2CHMeCH_2NHCH_2CH_2NH_2$	76	2	1.4520	0.8400	0.321	0.321	$C_9H_{24}N_2Si$	94	94.2		
26	$MeOMe_2SiCH_2CHMeCH_2NHCH_2CH_2NH_2$	140	30	1.4513	0.900	0.299	0.300	$C_9H_{24}ON_2Si$	102	102	13.7	13.8
27	$(MeO)_2MeSiCH_2CHMeCH_2NHCH_2CH_2NH_2$	123	7.5	1.4508	0.9648	0.279	0.279	$C_9H_{24}O_2N_2Si$	111	110	13.0	12.7
28	$(MeO)_3SiCH_2CHMeCH_2NHCH_2CH_2NH_2$			1.4459	1.009	0.266	0.266	$C_9H_{24}O_3N_2Si$	119	118	12.2	11.9
29		86	10	1.4666	0.9236	0.300	0.303	$C_{10}H_{22}N_2Si$	100	99.2	14.3	14.2
30	*tert*-$BuOMeSiCH_2CHMeCH_2NMe$	40	1	1.4300	0.8646	0.299	0.298	$C_{10}H_{23}ONSi$	202	201	13.8	14.0
31	$(MeO)_3SiCH_2CH_2CH_2NCH_2CH_2OCH_2CH_2$	133	10	1.4450	1.045	0.255	0.257	$C_{10}H_{23}O_4NSi$			11.3	11.3
32	*i*-$PrOMe_2SiCH_2CHMeCH_2NHMe$	30	0.1	1.4266	0.8342	0.308	0.307	$C_{10}H_{25}ONSi$	203	203	13.7	13.8
33	$(MeO)_3SiCH_2CH_2CH_2NHn$–Bu	102	3.5	1.4246	0.9415	0.271	0.272	$C_{10}H_{25}O_3NSi$	234	235	11.8	11.9
34	$(EtO)_3SiCH_2CH_2CH_2NHMe$	121	30	1.4186	0.9280	0.272	0.272	$C_{10}H_{25}O_3NSi$			11.7	11.9
	hydrochloride	Mp 106–107°							% Cl 13.0	13.0	10.2	10.5
35	$AcOMe_2SiCH_2CHMeCH_2NMeAc$			1.4575	0.9863	0.274	0.276	$C_{11}H_{23}O_3NSi$	245	247		

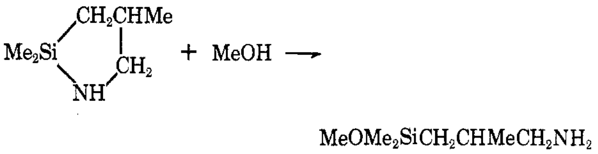
36	$tert$-BuOMe$_2$SiCH$_2$CHMeCH$_2$NHMe	65	4	1.4295	0.8369	0.308	0.309	$C_{11}H_{27}ONSi$	219	217	12.7	12.9
37	(EtO)$_3$SiCH$_2$CH$_2$CH$_2$NHCH$_2$CH$_2$NH$_2$	156	15	1.4367	0.9629	0.272	0.273	$C_{11}H_{28}O_3N_2Si$	133	132	10.6	10.6
38	PhMeSiCH$_2$CHMeCH$_2$NMe	116	15	1.5133	0.9434	0.319	0.317	$C_{12}H_{19}NSi$	206	205	13.7	13.7
39	MeOMe$_2$SiCH$_2$CH$_2$CH$_2$NHPh			1.5236	0.9742	0.314	0.311	$C_{12}H_{21}ONSi$			13.0	12.6
40	(MeO)$_3$SiCH$_2$CH$_2$CH$_2$NH-c-C$_6$H$_{11}$	160	15	1.4505	0.9909	0.271	0.272	$C_{12}H_{27}O_3NSi$	258	261	10.9	10.7
41	[Me$_3$SiCH$_2$CH$_2$CH$_2$]$_2$NH	150	30	1.4409	0.802	0.330	0.238	$C_{12}H_{31}NSi_2$	244	246	22.2	22.8
42	[MeOMe$_2$SiCH$_2$CH$_2$CH$_2$]$_2$NH	132	1	1.4461	0.888	0.301	0.309	$C_{12}H_{31}O_2NSi_2$	270	278	22.0	22.2
43	MeN[MeSiCH$_2$CHMeCH$_2$NMe]$_2$	90	1	1.4734	0.929	0.302	0.302	$C_{13}H_{31}N_3Si_2$	99	95	19.8	19.7
44	EtMe$_2$SiOSiMe$_2$CH$_2$CH$_2$CH$_2$NH-$tert$-Bu	61	1	1.4255	0.830	0.308	0.309	$C_{13}H_{33}ONSi_2$	277	276		
	Hydrochloride	Mp 175–176.5°										
45	[(MeO)$_3$SiCH$_2$CH$_2$CH$_2$]$_2$NMe	165	16	1.4288	1.021	0.252	0.253	$C_{13}H_{33}O_6NSi_2$	346	356	15.6	15.8
46	Me$_3$SiOSiMe$_2$CH$_2$CH$_2$CH$_2$NHPh	80	1	1.4872	0.925	0.311	0.305	$C_{14}H_{27}ONSi_2$	% N 5.1	5.0	19.9	20.0
47	O[SiMe$_2$CH$_2$CH$_2$CH$_2$CH$_2$NMeH]$_2$	166	15	1.4456	0.878	0.303	0.306	$C_{14}H_{36}ON_2Si_2$	154	152	18.8	18.5
48	O[SiMe$_2$CH$_2$CH$_2$CH$_2$NMe$_2$]	165	30	1.4353	0.848	0.308	0.308	$C_{14}H_{36}ON_2Si_2$	154	152	18.7	18.5
49	[(EtO)$_2$MeSiCH$_2$CH$_2$CH$_2$]$_2$NH			1.4385	0.937	0.281	0.280	$C_{16}H_{39}O_4NSi_2$	360	365		
50	O[SiMe$_2$CH$_2$CH$_2$CH$_2$NMe$_3{}^+$Cl$^-$]$_2$	Mp 264–267° (sinters at 250°)						$C_{16}H_{42}OClN_2Si_2$	% Cl 17.3	17.5	13.8	13.9
51	O[SiMe$_2$CH$_2$CHMeCH$_2$NHCH$_2$CH$_2$NH$_2$]$_2$	207	7	1.4689	0.924	0.302	0.302	$C_{16}H_{42}ON_4Si_2$			15.2	15.5
52	O[SiMe$_2$CH$_2$CH$_2$CH$_2$NHn-Bu]$_2$	130	1	1.4411	0.862	0.308	0.310	$C_{18}H_{44}ON_2Si_2$	189	180		
53	O[SiMe$_2$CH$_2$CHMeCH$_2$NCH$_2$CH$_2$OCH$_2$CH$_2$]$_2$	160	1	1.4654	0.960	0.288	0.290	$C_{20}H_{44}O_3N_2Si_2$				
	dihydrochloride	Mp 199–200° dec									% Cl 14.4	14.5

[a] Reference 2 reported n^{20}_D 1.4301, d^{20}_4 0.7866. [b] Reference 3a reported bp 91–92° (15.5 mm), n^{20}_D 1.4235, d^{20}_4 1.0265. [c] Reference 3b reported bp 85–88° (8 mm), n^{25}_D 1.4260, d^{20}_4 0.9162. [d] Reference 6 reported bp 119–122° (29 mm), n^{25}_D 1.4220, d^{25}_4 0.9477.

HN[SiMe$_2$CH$_2$CHMeCH$_2$Cl]$_2$, which was then heated with ammonia at 100° for 46 hr. The reaction was only about 70% complete after this time, indicating a considerable retarding effect of the 2-methyl group upon the rate of reaction of the 1-chloride with ammonia. This reaction, however, produced two novel cyclic structures. The products from this experiment can be most plausibly explained by a sequence of reactions such as



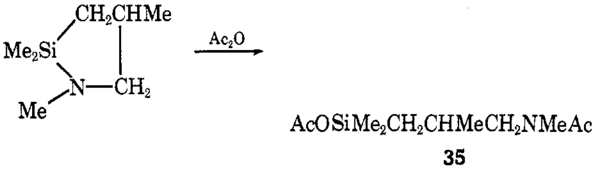
2,2,4-Trimethyl-1-aza-2-silacyclopentane (**1**) above reacted vigorously with dry methanol to form (3-methoxydimethylsilyl)-2-methylpropylamine (**11**).



(1)

11

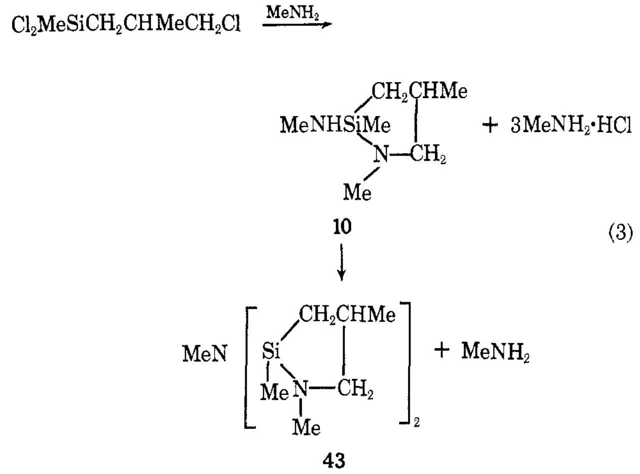
A similar series of experiments was carried out with nine chloroalkylsilicon compounds and methylamine (Table I). Only about 7–10 mol of methylamine to 1 equiv of chloride was used to obtain good to excellent yields of distillable products. 4-Chlorobutyldimethylchlorosilane gave a 65% yield of 1,2,2-trimethyl-1-aza-2-silacyclohexane (**5**). 3-Chloro-2-methylpropyldimethylchlorosilane gave 76% 1,2,2,4-tetramethyl-1-aza-2-silacyclopentane (**6**). Both of these cyclic aminosilanes were very reactive toward water or alcohols, with the ring opening as shown in eq 1. Water, methanol, and 2-propanol reacted vigorously with liberation of heat. *tert*-Butyl alcohol reacted in the same way but slowly, so that the reaction was not noticeably exothermic. Acetic anhydride reacted violently. When acetic anhydride was added slowly to the aminosilane in a flask packed in ice, a vigorous reaction proceeded quantitatively according to eq 2.



(2)

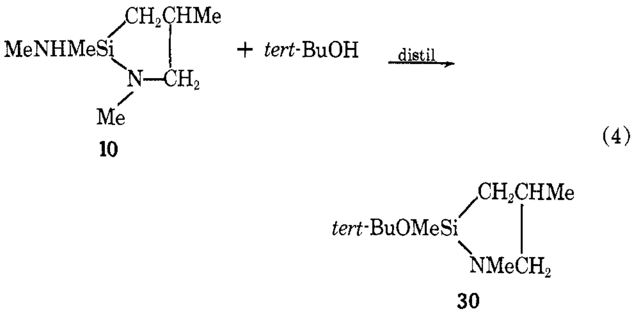
35

3-Chloro-2-methylpropylmethyldichlorosilane and methylamine gave rise to an especially interesting example. Nearly a quantitative yield of 1,2,4-trimethyl-2-methylamine-1-aza-2-silacyclopentane (**10**) was formed. Upon distillation **10** lost methylamine to form a novel bicyclodisilazane (**43**) according to eq 3.



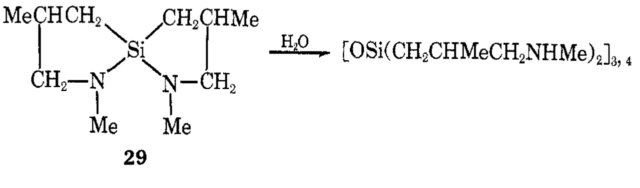
(3)

Methanol and **10** reacted vigorously as expected to form 3-(methyldimethoxysilyl)-2-methylpropylamine (**18**). However, *tert*-butyl alcohol replaced only the methylamino group from silicon and reacted no further even upon distillation.



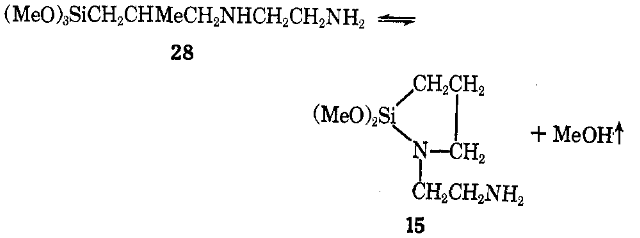
(4)

Bis(3-chloro-2-methylpropyl)dichlorosilane gave a 41% yield of a new kind of spiro derivative, 1,3,-6,8-tetramethyl-1,6-diaza-5-sila[4.4]spirononane (**29**). With an equimolar amount of water **29** formed a mixture of tri- and tetracyclosiloxanes.



A similar set of experiments was carried out with nine 3-chloropropylsilicon compounds and anhydrous ethylenediamine (Table I). Usually 5 mol of ethylenediamine was used for each equivalent of chloride. The reactions were very rapid at about 100° and in each case the products separated very well at room temperature into two liquid layers. The top layer contained the organic products and a small amount of ethylenediamine. The bottom layer was a solution of ethylenediamine hydrochloride in ethylenediamine.

Slow distillation of compounds like 2-(3-trimethoxysilyl-2-methylpropylamino)ethylamine (**28**) liberated methanol and revealed that the silylation of alcohols by cyclic aminosilanes is reversible.



In the same way **27** slowly **14** and **18** formed **7**. Methanol was liberated more rapidly from trimethoxysilyl compounds than from dimethoxymethylsilyl compounds under similar conditions.

Aminopropylsiloxane compounds were also prepared in good yields by warming allylamines of the formula $CH_2{=}CHCH_2NRR'$ (R = alkyl or phenyl, R′ = H or alkyl) with siloxane hydrides. In this way with chloroplatinic acid as the catalyst, **44**, **46**, **48**, and **52** were prepared. Allylamine under such conditions leads to a complex mixture of products and liberated hydrogen.[6] The secondary allylamines did not liberate hydrogen to any noticeable extent. They acted very much as the allylaminosilanes did[6] under similar conditions.

Experimental Section

Reagents.—The 3-chloropropyl- and 3-chloro-2-methylpropylsilanes used in this work were prepared as described by Ryan, Menzie, and Speier.[7] 4-Chlorobutyldimethylchlorosilane was prepared as described by Smith, Ryan, and Speier.[8] Neutralization equivalents of the amines were obtained by titration with 1 *N* HCl in aqueous alcohol or, if a precipitate formed, by titration with 1 *N* $HClO_4$ in glacial acetic acid. Specific refractions R_D were calculated with published values for bond refractions.[9]

Syntheses.—The following examples illustrate the methods used to prepare the compounds listed in Table II.

3-Trimethylsilylpropylamine (2) and Bis(trimethylsilylpropyl)-amine (41).—3-Chloropropyltrimethylsilane (226 g, 1.5 mol), methanol (144 g), and ammonia (408 g, 24 mol) were heated for 20 hr at 100° in a stainless steel autoclave. The vessel was cooled to room temperature and opened to permit ammonia to evaporate. The residue was stirred with water and petroleum ether (bp 30–60°). The organic layer was separated, dried, and distilled to yield **2** (37 g, 0.28 mol, 19% yield) and **41** (37 g, 0.15 mol, 18% yield). The aqueous layer was made strongly alkaline with NaOH, whereupon an organic liquid separated. This was distilled and found to be nearly pure **2** (51 g, 0.39 mol, 26% yield) having the properties shown in Table II.

3-Diethoxymethylsilylpropylamine (17) and Bis(3-diethoxymethylsilylpropyl)amine (49).—3-Chloropropylmethyldiethoxysilane (422 g, 2 mol) and ammonia (617 g, 36.3 mol) were heated for 15 hr at 90° as above. The vessel was then cooled to room temperature and the lower liquid phase was separated by means of a stainless steel tube extending to the bottom of the vessel. This layer was then distilled to give **17** (196 g, 51% yield) and **49** (117 g, 32% yield).

2,2,4-Trimethyl-1-aza-2-silacyclopentane (1) and 2,2,4-Trimethyl-1-(3-chloro-2-methylpropyl)dimethylsilyl-1-aza-2-silacyclopentane.—(3-Chloro-2-methylpropyl)dimethylchlorosilane (741 g, 4 mol) was dissolved in 1 l. of pentane. Ammonia was bubbled through the solution until the solution was saturated. The mixture was filtered free of ammonium chloride, which was washed with pentane and dried (yield 221 g, 4 mol of NH_4Cl weighs 214 g). The filtrate and washings were combined and the pentane was evaporated under vacuum to leave a cloudy liquid presumed

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[6] J. C. Saam and J. L. Speier, *J. Org. Chem.*, **24**, 119 (1959).

[7] J. W. Ryan, G. K. Menzie, and J. L. Speier, *J. Amer. Chem. Soc.*, **82**, 3601 (1960).

[8] A. G. Smith, J. W. Ryan, and J. L. Speier, *J. Org. Chem.*, **27**, 2183 (1962).

[9] A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

to be 1,3-bis(3-chloro-2-methylpropyl)-1,1,3,3-tetramethyldisilazane, (552 g, 1.76 mol, 88% yield): neut equiv 324.8; calcd for $(\mathrm{ClCH_2CHMeCH_2Me_2Si})_2\mathrm{NH}$, 314.4.

All of this material was heated with ammonia (620 g, 37 mol) in a 2.9-l. stainless steel autoclave at 100° for 46 hr. The products were cooled. Ammonia was permitted to evaporate and the residue was filtered. The solids were washed with pentane, dried, and weighed (123 g). This would represent a 70% yield of ammonium chloride based upon the chloride content of the disilazane.

The liquid product and washings were combined and distilled to yield **1** (82 g, 18% yield) with the properties shown in Table II. Methanol (3.2 g, 0.1 mol) was added to **1** (12.9 g, 0.1 mol). The solution spontaneously grew warm. Vapor phase chromatography showed 3-methoxydimethylsilyl-2-methylpropylamine (**11**), essentially pure, containing no **1** or methanol.

The next fraction was collected at about 0.03 mm over the range of 99–106°, 219 g, $n^{25}\mathrm{D}$ 1.4678, 40% yield. A sample was shown to contain chlorine by heating it with ethylenediamine and testing the solution for chloride ion.

Anal. Calcd for $\mathrm{ClCH_2CHMeCH_2SiMe_2}\overline{\mathrm{NSiMe_2CH_2CHMeCH_2}}$: Si, 20.2; neut equiv, 278. Found: Si, 20.2; neut equiv, 264.

1,2,2-Trimethyl-1-aza-2-silacyclohexane (5).—4-Chlorobutyldimethylchlorosilane (115 g, 0.6 mol) was heated in a stainless steel autoclave at 100° for 19 hr with methylamine (317 g, 10.3 mol). The vessel was cooled and opened. The supernatant liquid (156 g) was separated and distilled to give 73 g of methylamine followed by **5** (58 g, 65% yield) and a viscous residue which was not identified.

1,2,2,4-Tetramethyl-1-aza-2-silacyclopentane (6).—3-Chloro-2-methylpropyldimethylchlorosilane (556 g, 3 mol) and methylamine (640 g, 20.6 mol) were used as above to yield **6** (392 g, 76% yield).

(3-Methoxydimethylsilyl-2-methylpropyl)methylamine (16).—A sample of **6** (72 g, 0.5 mol) with dry methanol (16 g, 0.5 mol) grew warm spontaneously and very soon vpc showed only one component with the properties shown in Table II for **16**.

(2-Propoxydimethylsilyl-2-methylpropyl)methylamine (32).—In the same fashion **6** (43 g, 0.3 mol) mixed with 2-propanol (20 g, 0.33 mol) at room temperature rose very quickly to 78°. The product was essentially all **32** with the properties shown in Table II.

***N*-(3-Acetoxydimethylsilyl)-2-methylpropyl-*N*-methylacetamide (35).**—A sample of **6** (14.3 g, 0.1 mol) and acetic anhydride (10.2 g, 0.1 mol) were stirred together in a flask packed in ice to control a very exothermic reaction. Vapor phase chromatography then showed only one peak with a long retention time. This product easily dissolved in water and was titrated as a typical acetoxysilane with 0.1 *N* sodium hydroxide to a pH of 8.1 to get the value shown in Table II for **35**.

3-*tert*-Butoxydimethylsilyl-2-methylpropylmethylamine (36).—A sample of **6** (21.5 g, 0.15 mol) and *tert*-butyl alcohol (11.1 g, 0.15 mol) were mixed. Although no reaction was apparent, distillation gave **36** in nearly 100% yield.

1,2,4-Trimethyl-2-methylamino-1-aza-2-silacyclopentane (10) and Bis-2-(1,2,4-trimethyl-1-aza-2-silacyclopentyl)methylamine (43).—3-Chloro-2-methylpropylmethyldichlorosilane (3674 g, 18 mol) and methylamine (4224 g, 136 mol) were heated at 100° for 22 hr and worked up as for **5** above to give 2856 g (100% yield calculated as pure **10**) of a liquid organic layer which was distilled. Methylamine was continuously liberated during the distillation of the first major fraction, **10**. When methylamine no longer was being liberated, the second major fraction, **43**, was collected smoothly. These two fractions constituted a very high yield of products, but the exact yield of each became uncertain in this experiment. Apparently, the methylaminosilane **10** was nearly the exclusive product of the reaction. During distillation it lost methylamine to form the disilazane **43**.

(3-Dimethoxymethylsilyl-2-methylpropyl)methylamine (18).—A sample of **10** (above) was mixed with 2 equiv of methanol and distilled to give a 94% yield of **18**.

1,2,4-Trimethyl-2-*tert*-butoxy-1-aza-2-silacyclopentane (30).—A second sample of the above **10** (79 g, 0.5 mol) was dissolved in an equal volume of pentane. To this solution *tert*-butyl alcohol was added (37 g, 0.5 mol). Vapor phase chromatography showed that essentially all the *tert*-butyl alcohol and all the **10** reacted to form one new product, **30**. A second portion of *tert*-butyl alcohol (37 g, 0.5 mol) was then added. This did not react. The solution was then distilled to remove first methylamine and pentane, then half of the *tert*-butyl alcohol and finally **30** (74 g, 74% yield) having the properties shown in Table II.

1,3,6,8-Tetramethyl-1,6-diaza-5-silaspiro[4.4]nonane (29).—Bis((3-chloro-2-methylpropyl)dichlorosilane (169 g, 0.6 mol) and methylamine (409 g, 13.2 mol) were heated for 8 hr at 100° in a stainless steel autoclave. The vessel was then cooled and a top layer was separated. The bottom layer was evaporated to dryness to leave methylammonium chloride. This solid was washed with pentane and the washings were added to the top layer, which was then distilled. The dried, washed salt weighed 157 g. The calculated weight for $\mathrm{MeNH_3^+Cl^-}$ is 162 g. Distillation gave 49 g (41%) of **29** having the properties given in Table II.

A sample of this spirane (9.92 g, 0.05 mol) was mixed with water (0.9 g, 0.05 mol) and stirred with a thermometer. The temperature very slowly rose as the droplets of water began to disperse. Rather suddenly the water dissolved and the temperature rose abruptly to 142°. A clear, viscous polysiloxane formed. Infrared analysis indicated that it was chiefly a mixture of cyclotri- and -tetrasiloxanes, $n^{25}\mathrm{D}$ 1.4832, d^{25} 0.9824, R_D 0.290 (calcd 0.283), neut equiv 108.7 (calcd 108.2).

Products from Ethylenediamine.—Chlorides shown in Table I were heated to about 100° with a 5 to 7 mole ratio of anhydrous ethylenediamine. The reactions were usually exothermic and rapid. When the products were cooled to room temperature, they formed two liquid layers. The top layer was distilled to give the products and yields shown in Table II.

1-(2-aminoethyl)-2,4-dimethyl-2-methoxy-1-aza-2-silacyclopentene (14).—2-(3-Dimethoxymethyl)-2-methylpropylaminoethylamine (**27**) (331 g, 1.5 mol) was heated to reflux in a small still of about 25 plates and periodically over 52 hr methanol was removed until 35 g (1.1 mol) had been collected. The rate of formation of methanol became very slow. Vacuum was applied and the product was distilled to give **14** (170.3 g, 60% yield) on a constant-boiling plateau leaving a viscous residue.

1-(2-Aminoethyl)-2,2-dimethoxy-4-methyl-1-aza-2-silacyclopentane (15).—Under similar conditions, 2-(3-trimethoxysilyl-2-methylpropylamino)ethylamine (**28**) formed crystalline **15** in approximately the same yield but at a much more rapid rate. The crystals were very difficult to handle. They appeared to change on standing to become slushy even in sealed containers and no means to purify them by recrystallization could be found. Methanol reacted with these crystals to liberate heat and to reform **28** quantitatively.

Bis[3-(2-aminoethylamino)-2-methylpropyl]tetramethyldisiloxane (51).—*sym*-Bis(3-chloro-2-methylpropyl)tetramethyldisiloxane (409 g, 1.3 mol) was added to a solution of ethylenediamine (774, g, 12.9 mol) in 300 ml of methanol and heated to reflux for 19.5 hr. Most of the methanol and some ethylenediamine was then removed by distillation. The residue then separated into two layers. The top layer was separated and distilled to give **51** (332 g, 72% yield).

3-Trimethoxysilylpropyldimethylamine (19).—3-Chloropropyltrimethoxysilane (696 g, 3.5 mol), dimethylamine (632 g, 14 mol), and 400 ml of Skellysolve-F were heated for 22 hr at 100° in a rocking autoclave. The mixture was then cooled and filtered and the filtrate was distilled to obtain **19** (570 g, 79% yield) and almost no residue.

3-Trimethoxysilylpropylallylamine (23).—3-Chloropropyltrimethoxysilane (788 g, 4 mol) was heated to reflux for 60 hr with allylamine (832 g, 14.6 mol). Sodium methoxide (4 mol) in methanol was then added and the mixture was filtered and distilled to obtain **23** (517 g, 59% yield).

***N*-(3-Trimethoxysilylpropyl)morpholine (31).**—3-Chloropropyltrimethoxysilane (268 g, 1.35 mol) was added to refluxing morpholine (466 g, 4.1 mol) and kept at 125–130° for 75 min. When the mixture had cooled to room temperature, crystalline morpholine hydrochloride was filtered from it and the filtrate was distilled to give **31** (266 g, 79% yield).

***N*-(3-Trimethoxysilylpropyl)butylamine (33).**—3-Chloropropyltrimethoxysilane (1590 g, 8 mol) and *n*-butylamine (2120 g, 29 mol) treated in the above manner gave **33** (940 g, 50% yield). Skellysolve-F was used to assist filtration of the amine hydrochloride in this example.

***N*-(3-Ethyldimethylsiloxydimethylsilylpropyl)-*tert*-butylamine (44).**—*tert*-Butylallylamine (19 g, 0.17 mol) and 1-ethyl-1,1,3,3-tetramethyldisiloxane were heated to 100°. At this temperature two or three drops of 0.1 *N* chloroplatinic acid in 2-propanol was added. When the exothermic reaction subsided, the mixture was distilled to give **44** (39 g, 84% yield). The product gave only one peak by glc analysis. The H′ nmr spectrum consisted of the sharp singlet for $SiCH_3$, τ 9.96, a triplet for NCH_2, 7.53, and complex absorptions from 8.3 to 9.7.

This product (28 g, 0.1 mol) with ammonium chloride (5 g, 0.1 mol) was heated to reflux in 100 ml of benzene for 24 hr. The solution was permitted to cool slowly and crystals of the amine hydrochloride formed in 68% yield, mp 175-176.5°.

***N*-(3-Pentamethyldisiloxanylpropyl)aniline (46).**—*N*-Allylaniline and pentamethyldisiloxane with chloroplatinic acid treated as above gave **46** in 75% yield.

1,3-Bis(3-dimethylaminopropyl)tetramethyldisiloxane (48).—To 50 ml of refluxing xylene that contained 10^{-4} mol of $H_2PtCl_6 \cdot 6H_2O$ was added a solution of 1,1,3,3-tetramethyldisiloxane (134 g, 1 mol) in dimethylallylamine (170 g, 2 mol). A rapid exothermic reaction occurred. When it subsided, the solution was distilled. About 20 ml as a precut was impure $HSiMe_2OSiMe_2(CH_2)_3NMe_2$ followed by **48** (233 g, 77% yield).

1,3-Bis(3-trimethylaminopropyl)tetramethyldisiloxane Dichloride (50).—1,3-Bis(3-chloropropyl)tetramethyldisiloxane (345 g, 1.2 mol) and trimethylamine (285 g, 4.8 mol) were heated together for 65 hr at 150° in an autoclave. The vessel was then cooled and opened to let excess trimethylamine evaporate. The residue was 463 g of sparkling white crystals (95% yield).

Bis-1,3-(3-*n*-butylaminopropyl)tetramethyldisiloxane (52).—*n*-Butylallylamine (20 g, 0.18 mol) and 1,1,3,3-tetramethyldisiloxane (12 g, 0.09 mol) were heated together to 103°, when one drop of 0.1 *N* $H_2PtCl_6 \cdot 6H_2O$ in 2-propanol was added. The temperature quickly rose to 185°. The product was distilled to give **52** (22.5 g, 67% yield).

1,3-Bis(3-*N*-morpholine-2-methylpropyl)tetramethyldisiloxane (53).—1,3-Bis(3-chloro-2-methyl)tetramethyldisiloxane (98.8 g, 0.314 mol) was added to refluxing morpholine (300 g, 3.44 mol) and refluxed for 13 hr. The solution was then cooled. Morpholine hydrochloride precipitated and was filtered off. The filtrate was distilled to give **53** (98 g, 75% yield).

Registry No.—**1**, 31024-74-5; **2**, 18187-14-9; **3**, 31024-26-7; **4**, 13822-56-5; **5**, 18387-18-3; **6**, 18387-19-4; **7**, 31024-30-3; **8**, 3069-25-8; **9**, 31024-32-5; **10**, 31024-33-6; **11**, 31024-34-7; **12**, 31024-35-8; **13**, 18246-33-8; **14**, 18441-77-5; **15**, 31024-38-1; **16**, 31024-39-2; **17**, 3179-76-8; **18**, 31024-41-6; **19**, 2530-86-1; **20**, 3069-33-8; **21**, 3069-29-2; **22**, 1760-24-3; **23**, 31024-46-1; **24**, 919-30-2; **25**, 31024-48-3; **26**, 31024-49-4; **27**, 23410-40-4; **28**, 2530-82-7; **29**, 18037-12-2; **30**, 31024-53-0; **31**, 31024-54-1; **32**, 31024-55-2; **33**, 31024-56-3; **34**, 6044-50-4; **34** HCl, 31024-58-5; **35**, 31024-59-6; **36**, 31024-60-9; **37**, 5089-72-5; **38**, 18052-23-8; **39**, 31024-63-2; **40**, 3068-78-8; **41**, 31024-65-4; **42**, 31024-66-5; **43**, 31024-67-6; **44**, 31024-68-7; **44** HCl, 31024-69-8; **45**, 31024-70-1; **46**, 31024-71-2; **47**, 17907-36-7; **48**, 26526-97-6; **49**, 31020-47-0; **50**, 31020-48-1; **51**, 18547-06-3; **52**, 31020-50-5; **53**, 31020-51-6; **53** 2HCl, 31020-52-7.

Mechanism of the Reaction of Benzyl Alcohols with a Cyclic Trans Carbonate[1a]

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The mechanism of carbonate ring opening of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-carbonate (I) by various para-substituted benzyl alcohols in the presence of triethylamine was studied. The reaction is first order in both I and the amine-alcohol complex. The rate of carbonate ring opening was in the order $NO_2 > Cl$, $Br > H > CH_3$ for the para-substituted benzyl alcohols. This order correlates with the shift of the OH stretching frequency obtained when benzyl alcohol derivatives are complexed with triethylamine. The effect of solvent on the reaction rate of I with benzyl alcohol was determined for 16 solvents. Rate values correlate well with the hydrogen bonding and dielectric properties of the solvents.

Facile preparations of sugar trans carbonates[3] and their reactions with alcohols, mercaptans, and amines[4] prompted further investigation of these reactions. Our work[5] showed that methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2, 3-carbonate (I) reacted readily with primary and secondary amines. For reaction with thiols and alcohols to form the acyclic carbonates, a basic catalyst such as triethylamine was required.[5] In this paper we describe a study of (a) the mechanism of the amine-catalyzed reaction of the cyclic carbonate I with various para-substituted benzyl alcohols and (b) the effects of solvents of widely varying basicity and dielectric strength on this reaction.

Kinetics and Mechanism of the Reaction.—Preliminary rate comparisons of carbonate ring opening in I by benzyl alcohol, α-toluenethiol, and benzylamine at 100° in the presence of triethylamine are reported in Table I.

TABLE I

RATES OF CARBONATE RING OPENING OF I BY BENZYL ALCOHOL, α-TOLUENETHIOL, AND BENZYLAMINE AT 100°

Nucleophile	Mole ratio Nucleophile	Mole ratio $(C_2H_5)_3N$	Mole ratio I	$t_{1/2}$,[a] min
Benzyl alcohol	4	7	1	210
α-Toluenethiol	4	7	1	111
Benzylamine	4	. . .	1	16

[a] $t_{1/2}$ = the time required for one-half of methyl 4,6-*O*-benzylidene-α-D-glucopyranoside 2,3-carbonate (I) to react.

Under the reaction conditions used, the order of reactivity is amine > thiol > alcohol and their ratio of half-life is 1:7:13. This order correlates with predicted nucleophilicities of these compounds.[6] The reaction

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(1) (a) Based in part of the M.S. thesis submitted by E. I. Stout to Bradley University, 1968, and presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 13-18, 1969. (b) Northern Regional Research Laboratory. (c) Bradley University.

(2) This is a laboratory of the Northern Marketing and Nutrition Research Division, Agricultural Research Service, U. S. Department of Agriculture, Peoria, Ill. 61604. The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

(3) W. M. Doane, B. S. Shasha, E. I. Stout, C. R. Russell, and C. E. Rist, *Carbohyd. Res.*, **4**, 445 (1967).

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