TABLE I

AMINOALKANE HYDROCHLORIDES

Alkane	M.p. of hydrochloride, °C. 1-NH$_2$	2NH$_2$	3-NH$_2$	Method of prepn.[a] 1-NH$_2$
Nonane	185–186[b]	81–82	103–104	B
Decane	182–183[d]	84–85	107–108	[c]
Undecane	190–192[e]	83–85	110–111	B
Dodecane	185–187[f]	91–92	109–110	A
Tridecane	192–193[f]	87–88	112–113	B
Tetradecane	194–195[g]	86–88	109–109.5	A
Pentadecane	199–200[e]		112–114	B
Hexadecane	155–156[h]			A
Heptadecane	158–160[e]			B
Octadecane	160–161[i]			A

[a] The A and B refer to the methods described in the Experimental. The 2- and 3-aminoalkanes were all prepared by method C as given in the Experimental. [b] A decomposition point. [c] Purchased from Matheson, Coleman and Bell as the free amine. [d] J. von Braun, W. Teuffert and K. Weissbach, *Ann.*, **272**, 121 (1929). [e] C. Naegeli, L. Guntuch and P. Lendorff, *Helv. Chim. Acta*, 12, 240 (1929). [f] E. Lutz, *Ber.*, **19**, 1440 (1886). [g] F. Krafft, *ibid.*, **23**, 2360 (1890). [h] H. P. Teunissen, *Rec. trav. chim.*, **46**, 209 (1927). [i] N. K. Adam and J. W. W. Dyer, *J. Chem. Soc.*, **127**, 73 (1925).

TABLE II

ANALYSES[a] OF AMINOALKANE HYDROCHLORIDES

Alkane	Nitrogen, % Calcd.	Found 2-NH$_2$	3-NH$_2$
Nonane	7.75	7.44	7.83
Decane	7.20	7.51	7.01
Undecane	6.71	7.03	6.29
Dodecane	6.29	6.00	6.66
Tridecane	5.92	5.80	6.03
Tetradecane	5.59	5.99	5.17
Pentadecane	5.25	..	5.10

[a] Analyses by micro-Kjeldahl method.

pears when the amino group is on the 12th carbon of a straight chain, *i.e.*, 1-aminodecane, 2-aminotridecane and 3-aminotetradecane. These results are somewhat similar to Fuller's observations.[7] A high degree of surface activity, as evidenced by foaming and emulsifying properties, accompanies *in vitro* antimicrobial activity in all three series of amines.

Experimental[8]

The Preparation of Aminoalkane Hydrochlorides. (A) **Reduction of Amides.**—The amides were prepared from the acid chlorides by a standard procedure.[9] The amides were reduced by placing an ether solution of an excess of lithium aluminum hydride in the boiler and the amide in the thimble of a Soxhlet extraction apparatus and heating at reflux until all the amide was consumed. The reaction mixture was decomposed with water, the ether layer separated and dried over stick potassium hydroxide. After decantation from the drying agent, dry hydrogen chloride was bubbled into the ether solution until there was no further precipitation. The precipitate was filtered and crystallized from chloroform and petroleum ether. Over-all yields from amide to amine hydrochloride were 50–62%.

(B) **The Hofmann Rearrangement.**—The following procedure, when rigidly adhered to, gave yields of 85–95% methyl alkylcarbamate. Any deviations in order and speed of addition of the reagents gave yields of 95–98% acylalkylurea. A solution of 0.03 *M* of amide dissolved in 27 g. of methanol was placed in a flask equipped with a vigorous stirrer and reflux condenser. While stirring as rapidly as possible a solution, made by adding 1.8 g., 0.075 *M*, of sodium to 45 g. of methanol, was added as rapidly as possible. *Immediately in one portion*, 6 g, 0.0375 *M* of bromine was added. After the initially vigorous reaction subsided, the solution was heated to reflux temperature for 10 minutes. The isolation of the alkylcarbamate and its hydrolysis to the amine followed the described procedure.[4] The amine was dissolved in ether and precipitated and crystallized as in (A) above. Over-all yields from amide to amine hydrochloride were 60–78%.

(C) **The Leuckart Reaction.**—The ketones from which the amines were prepared were all synthesized from the appropriate acid chloride and alkylcadmium compound.[10] The Leuckart reactions were run as described[6] for conversion of laurophenone to the corresponding amine, the only significant departure being in the workup at the conclusion of the reaction. The organic layer was separated from the aqueous layer and heated with concentrated hydrochloric acid until the mixture became homogeneous. On cooling this solution, the salt of the amine crystallized. The crystals were collected by filtration and the compound recrystallized from petroleum ether. Over-all yields from ketone to aminoalkane hydrochloride were 50–63%.

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[7] A. T. Fuller, *Biochem. J.*, **36**, 548 (1942), reported on the inhibiting action of a large number of organic bases, using a variety of microörganisms. He found maximum activity in the 12–16 carbon range for 1-amino compounds.

[8] All melting points reported are uncorrected.

[9] J. Cason and M. Rapoport, "Laboratory Text in Organic Chemistry", Prentice-Hall, Inc., New York, N. Y., 1950, p. 86.

[10] J. Cason, *Chem. Revs.*, **40**, 22 (1947).

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Methylvinylpolysiloxanes

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Although a number of vinyl-containing silicon compounds have been reported,[1–3] diorganosiloxanes containing both methyl and vinyl groups attached to silicon have not been investigated in detail. Such compounds are interesting since they can be polymerized through the vinyl group as well as through siloxane bond rearrangement. They can be used to introduce unsaturation into a wide variety of organosiloxane materials, and provide a starting point for the preparation of a number of different derivatives.

The hydrolysis of methylvinyldiethoxysilane with hydrochloric acid results in the formation of a methylvinylsiloxane oil with apparently no loss of unsaturation. A similar oil is formed by the hydrolysis of methylvinyldichlorosilane.[2] It is necessary in the rectification of this crude siloxane oil to take special precautions to avoid polymerization through the vinyl unsaturation, and *p*-*t*-butylcatechol has been employed as an inhibitor. By careful distillation we have obtained three pure cyclic methylvinylsiloxanes in a combined yield of 32%. The individual pure siloxanes isolated were 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane, $[(CH_3)(CH_2{=}CH)SiO]_4$, 1,3,5,7,9-pentamethyl-1,3,5,7,9-pentavinylcyclopentasiloxane, $[(CH_3)(CH_2{=}CH)SiO]_5$ and 1,3,5,7,9,11-hexamethyl-1,3,5,7,9,11-hexavinylcyclohexasiloxane, $[(CH_3)(CH_2{=}CH)SiO]_6$. These siloxanes and some of their physical properties are listed in Table I. The last com-

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[1] E. G. Rochow, "Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951, pp. 171–187.

[2] D. T. Hurd, THIS JOURNAL, **67**, 1813 (1945).

[3] L. H. Sommer, R. M. Murch and F. A. Mitch, *ibid.*, **76**, 1619 (1954).

TABLE I

METHYLVINYLSILOXANES

Siloxane	B.p. °C.	Mm.	ΔHv, kcal. mole^{-1}	M.p., °C.	n^{20}D	$d^{20}{}_4$	MRD Calcd.[a]	MRD Found
$[(CH_3)(CH_2{=}CH)SiO]_4$	111–112	10	14.7 ± 1	− 43.5 ± 0.1	1.4342	0.9875	91.20	90.93
	224–224.5	758						
$[(CH_3)(CH_2{=}CH)SiO]_5$	145–146	13	15.6 ± 1	−140 to −136[b]	1.4373	0.9943	114.00	113.58
	261–262	758						
$[(CH_3)(CH_2{=}CH)SiO]_6$	160.5–161	5						
	172–172.5	11	17.6 ± 1	−123 to −119[b]	1.4400	1.0050	136.80	135.58
	296–297	758						
$[(CH_3)_2(CH_2{=}CH)Si]_2O$	139	760	......	− 99.7 ± 0.1	1.4123	0.811[c]	57.24	57.23

[a] Calculated using bond refraction data of Warrick, THIS JOURNAL, **68**, 2455 (1946). [b] Sample froze to a glass. [c] Determined with a Fischer–Davidson gravitometer.

pound in the table, the linear tetramethyldivinyldisiloxane, was obtained by the hydrolysis of dimethylvinylethoxysilane.

The rather wide ranges of the melting points of the pentamer and hexamer probably result from the presence of isomers.[4] Once the individual methylvinylsiloxanes were purified, they were found to be much more stable at elevated temperatures, and could be distilled unchanged at atmospheric pressure without the use of a polymerization inhibitor. This stability is remarkable in view of the number of unsaturated groups present in these compounds, and vinylsiloxanes are, thus, considerably different from allylsiloxanes in this respect.

All the siloxanes added bromine quantitatively to give the corresponding polybromides; for example, the tetramer, $[(CH_3)(CH_2{=}CH)SiO]_4$, added eight bromine atoms to give the corresponding bromide, $[(CH_3)(CH_2BrCHBr)SiO]_4$. The bromine adducts of the siloxanes reacted quantitatively with potassium hydroxide in methanol to give vinyl bromide, and the corresponding potassium silanolate salt, thus

$$[(CH_3)(CH_2BrCHBr)SiO]_4 + 16KOH \xrightarrow{CH_3OH} 4CH_3Si(OK)_3 + 4KBr + 4CH_2{=}CHBr$$

The cyclic siloxanes $[CH_3(CH_2{=}CH)SiO]_{4-6}$, all polymerized through vinyl unsaturation to cross-linked insoluble resins in 15 minutes with 2% benzoyl peroxide at 100°. The vinylsiloxanes could be copolymerized with cyclic dimethylsiloxanes by siloxane bond rearrangement using strongly basic catalysts. Thus the pentamer was copolymerized with octamethylcyclotetrasiloxane using cesium hydroxide[5] as a catalyst to form a high molecular weight silicone gum containing silicon-bonded vinyl groups. These gums have been found useful in the covulcanization of silicone rubber with various other rubber materials, such as Butyl, Neoprene, GRS, Perbunan and natural rubber.

Experimental

Densities were measured at 20.00 ± 0.02° with a calibrated 10-ml. pycnometer. Melting points were obtained with a calibrated platinum resistance thermometer and a Müller bridge.

Cyclic Methylvinylsiloxanes.—A mixture of 1000 g. (6.24 moles) of redistilled methylvinyldiethoxysilane[6] (b.p. 133°, n^{20}D 1.4001, $d^{20}{}_4$ 0.8620) and 1000 ml. of 6 *N* hydrochloric acid was refluxed for 72 hours. The lower phase was washed four times with distilled water, then dried over anhydrous potassium carbonate and filtered. There was obtained 484.5 g. (90% yield) of a mixed methylvinylsiloxane oil. Attempts to distil this oil without the use of a polymerization inhibitor were unsuccessful since the oil polymerized rapidly to a resinous material at elevated temperatures.

To separate individual components of the methylvinylsiloxane oil 4.8 g. (1%) of *p*-*t*-butylcatechol was added and the mixture rapidly distilled at 0.5 mm. using a 12″ Vigreux column. A total of 169.4 g. of cyclic methylvinylsiloxanes (mostly the tetramer, pentamer and hexamer) was stripped from the mixture between 60 and 135° at 0.5 mm.; this corresponds to a 32% yield based on the original weight of methylvinyldiethoxysilane. The 315 g. of high boiling still-pot residue polymerized violently to a resin when it was heated to 200° at atmospheric pressure under nitrogen atmosphere.

Fresh inhibitor was added to the stripped methylvinylsiloxanes and the mixture was fractionated under reduced pressure in a 1/2″ × 16″ Protruded-packed column. The following fractions were obtained: (1) b.p. 111–112° at 10 mm., wt. 44.0 g., corresponding to the cyclic tetramer $[(CH_3)(CH_2{=}CH)SiO]_4$; (2) b.p. 115–143° at 11 mm., wt. 79.0 g., of which 76.5 g. boiled at 141.5–143° at 11 mm.. corresponding to the cyclic pentamer, $[(CH_3)(CH_2{=}CH)SiO]_5$; (3) b.p. 143–172.5° at 11 mm., wt. 30.2 g., of which 28.7 g. boiled at 172–172.5° at 11 mm., corresponding to the cyclic hexamer $[(CH_3)(CH_2{=}CH)SiO]_6$; and a residue of 11.6 g. probably consisting mostly of hexamer. The percentages of the siloxanes in the distillable fractions were approximately 30% tetramer, 50% pentamer and 20% hexamer. Fraction 2, as obtained, was a cloudy liquid from which *ca.* 2 ml. of *p*-*t*-butylcatechol separated on standing.

Fraction 1 corresponded to the tetramer, and was sufficiently pure for analysis.

Anal. Calcd. for $C_{12}H_{24}Si_4O_4$: C, 41.8; H, 7.02; Si, 32.6; mol. wt., 344.7. Found: C, 41.9; H, 7.2; Si, 32.5; mol. wt., 346. The molecular weight was determined cryoscopically using a solution of 0.240 g. of the siloxane in 19.17 g. of cyclohexane. A 7-ml. sample of $[(CH_3)(CH_2{=}CH)SiO]_4$ was distilled in a small Vigreux column at atmospheric pressure without polymerization or decomposition, b.p. 224–224.5° at 758 mm.

Fraction 2 was washed with 25-ml. portions of 1% sodium carbonate until the *p*-*t*-butylcatechol was removed (as evidenced by a negative ferric chloride test on the aqueous solution). The oil was dried over anhydrous potassium carbonate and distilled under reduced pressure in a 1/2″ × 16″ Protruded-packed column. The pentamer distilled at 145–146° at 13 mm.; the fraction isolated weighed 71 g.

Anal. Calcd. for $C_{15}H_{30}Si_5O_5$: C, 41.8; H, 7.02; Si, 32.6; mol. wt., 430.8. Found: C, 41.6; H, 7.2; Si, 32.8; mol. wt., 437.

This siloxane could be distilled at atmospheric pressure without polymerization or decomposition, b.p. 261–262° at 750 mm.

Fraction 3 was redistilled under reduced pressure in a 1/2″ × 16″ Protruded-packed column to give the pure hexamer, b.p. 160.5–161° at 5 mm., wt. 28.1 g.

Anal. Calcd. for $C_{18}H_{36}Si_6O_6$: C, 41.8; H, 7.02; Si, 32.6; mol. wt., 517.0. Found: C, 41.3; H, 7.1; Si, 31.3; mol. wt., 536.

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(4) C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, THIS JOURNAL, **70**, 3758 (1948).

(5) D. T. Hurd, R. C. Osthoff and M. L. Corrin, *ibid.*, **76**, 249 (1954).

(6) M. Cohen and J. R. Ladd, *ibid.*, **75**, 988 (1953).

This compound could be distilled at atmospheric pressure without polymerization, b.p. 296–297° at 750 mm., but some slight decomposition due to oxidation occurred, and a slight odor of formaldehyde was noted in the product.

The densities, refractive indices, molar refractions, melting points and heats of vaporization of the siloxanes are listed in Table I. The latent heats of vaporization were obtained from the slopes of straight line plots of log p *vs.* T^{-1} using the boiling points of the siloxanes at various temperatures.

The cylic methylvinylsiloxanes had similar infrared absorption spectra, but with slight shifts in certain peaks with different compounds. The tetramer exhibited the following principal peaks: 3.28 μ (C–H); 3.33 μ (C–H); 3.39 μ (C–H); 6.25 μ (C=C); 7.11 μ (C–H); 7.95 μ (C–H); 9.32 μ (Si–O); 9.94 μ (C=C); 10.43 μ (C=C); 12.14 μ (Si–C); 13.02 μ; 13.36 μ; and 14.65 μ.

1,3-Divinyltetramethyldisiloxane.[7]—A mixture of 100 ml. of acetone, 10 ml. of 0.1 N hydrochloric acid and 20.9 g. of vinyldimethylethoxysilane[6] (b.p. 99°, n^{20}_D 1.3982, d^{20}_4 0.7934) was refluxed for 4 hours. The acetone was then distilled and the oil was washed with water, dried over calcium chloride and distilled to give 13.0 g. (61%) of 1,3-divinyltetramethyldisiloxane, b.p. 139°. The properties of this siloxane are listed in Table I.

Addition of Bromine to Methylvinylsiloxanes.—The addition of bromine to the methylvinylsiloxanes in carbon tetrachloride or carbon disulfide solution was slow but quantitative. The addition reaction was found to be very rapid in acetic acid solution or in the absence of solvent.

(a) $[(CH_3)(CH_2{=}CH)SiO]_4$.—A solution of 1.00 g. of the tetramer in 10 ml. of acetic acid absorbed 1.90 g. of Br_2 corresponding to 103% of the theoretical amount. The solvent was removed under vacuum and residual octabromide remained as a liquid, n^{20}_D 1.5621. A solution of bromine in CCl_4 (0.113 g. of Br_2 per g. of solution) was added over a period of 4 hours at −30 to −10° to a solution of 1.00 g. of $[(CH_3)(CH_2{=}CH)SiO]_4$ in 10 ml. of CCl_4 until 3 drops of bromine solution caused a yellowish-brown color lasting for 1 hour. A total of 16.0 g. of solution (1.81 g. Br_2) was used, equivalent to 98% of the theoretical amount. The solvent could be removed under vacuum, leaving the liquid octabromide as before.

(b) $[(CH_3)(CH_2{=}CH)SiO]_5$.—A solution of 1.05 g. of the pentamer in 10 ml. of acetic acid absorbed 1.94 g. of Br_2 corresponding to 100% of the theoretical amount. The decabromide separated during the reaction but did not interfere with the titration. The solvent was removed under vacuum to leave the liquid decabromide, n^{20}_D 1.5663.

(c) $[(CH_3)(CH_2{=}CH)SiO]_6$.—One gram of the hexamer in 10 ml. of acetic acid absorbed 1.80 g. of Br_2 corresponding to 98% of the theoretical amount. The dodecabromide was quite insoluble in acetic acid. The last traces of acid were removed under vacuum to leave the liquid dodecabromide, n^{20}_D 1.5680.

(d) $[(CH_3)_2(CH_2{=}CH)Si]_2O$.—One gram of $[(CH_3)_2(CH_2{=}CH)Si]_2O$ in 10 ml. of acetic acid absorbed 1.74 g. of bromine corresponding to 101% of the theoretical amount. The solvent was removed under vacuum to leave the liquid tetrabromide, n^{20}_D 1.5322.

Reaction of Methyldibromoethylsiloxanes with Methanolic Potassium Hydroxide.—A solution of 14.3 g. (0.0145 mole) of $[(CH_3)(CH_2BrCHBr)SiO]_4$ in 250 ml. of methanol was placed in a 500-ml. 3-necked flask equipped with addition tube, stirrer and a water-cooled condenser, the top of which was connected to a trap immersed in a Dry Ice-acetone bath. The open end of the trap was protected with a by-pass stream of dry nitrogen. A solution of 25 g. of 85% potassium hydroxide (0.38 mole) in 80 ml. of methanol was added to the stirred and refluxing methanol solution over a period of one-half hour, during which time a precipitate of potassium bromide formed in the flask and vinyl bromide collected in the trap. The mixture was refluxed for an additional one-half hour, then most of the methanol was removed by distillation. The residue in the flask was dissolved in 150 ml. of water. Upon acidification of this solution with 6 N HCl, a precipitate of polymethyltrisiloxane (methyl-T gel) was formed. It was filtered and air-dried to a constant weight of 3.85 g., 99% of the theoretical amount.

The vinyl bromide was distilled in a low-temperature Podbielniak column, b.p. 0° at 400 mm.

Similarly, the other bromo derivatives $[(CH_3)(CH_2BrCHBr)SiO]_5$, $[(CH_3)(CH_2BrCHBr)SiO]_6$ and $[(CH_3)_2(CH_2BrCHBr)Si]_2O$ reacted with methanolic potassium hydroxide to produce vinyl bromide and the corresponding potassium silanolates.

Polymerization of Methylvinylsiloxanes.—A solution of 6 g. of $[(CH_3)(CH_2{=}CH)SiO]_5$ in 200 g. of octamethylcyclotetrasiloxane, $[(CH_3)_2SiO]_4$, was heated to 150° and 0.02 g. of solid cesium hydroxide was added with stirring. The catalyst dissolved, and within 10 minutes the mixture had become a very stiff, rubbery polymer (gum). This gum was soluble in toluene, but it could be cross-linked and rendered insoluble by treating it with 0.1% benzoyl peroxide at 120°.

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[7] This compound was first obtained by this method in this Laboratory by M. Cohen and J. R. Ladd.

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cis- and *trans*-2-Styrylquinolinium Compounds[1a]

BY LESTER HORWITZ

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2-Styrylquinolines and their salts may exist as *cis* and *trans* isomers, although such isomers never have been reported. Räth and Lehmann[1b] have isolated *cis* and *trans*-2-*o*-nitrostilbazole, which they were able to separate by fractional crystallizations. During a study of the preparation of 1-methyl-2-(*m*-nitrostyryl)-6-ethoxyquinolinium methosulfate, photographically important as a desensitizing dye, it appeared that this compound could be prepared in *cis* and *trans* forms with different ultraviolet absorption spectra. The methods employed were extended to the preparation of other *cis* and *trans*-2-styrylquinolinium salts.[1c]

It seems possible to assign a *trans* configuration to the 2-styrylquinolinium compounds prepared by the piperidine-catalyzed condensation of quinaldinium salts with aromatic aldehydes (Table I) on the basis of ultraviolet spectra. The main peaks of these compounds generally appeared at longer wave length of 25 to 75 mμ than did the main peaks of their isomers, prepared by the quaternation of 2-styrylquinolines, obtained from the condensation of quinaldines with aromatic aldehydes in acetic anhydride (Table III). To these latter compounds a *cis* structure is assigned. In the case of the *cis* configuration, coplanarity of the entire molecule is expected to be inhibited which would prevent full chromophoric conjugation. Depending on the degree of steric hindrance, there will be either a displacement of the absorption peak to shorter wave lengths or a fall in the extinction coefficient (or both) displayed by the spectrum of the *cis* when compared to that of the *trans* form.[2a] A change occurring only in the intensity of absorption with steric inhibition of coplanarity has been suggested as resulting from a transition between a non-planar

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(1) (a) Presented before the Organic Division of the American Chemical Society at New York City, Sept., 1954; (b) C. Räth and E. Lehmann, *Ber.*, **58B**, 342 (1925). (c) The extension of these methods to the stilbazole series will be the subject of a future communication.

(2) (a) E. A. Braude, E. R. H. Jones, H. P. Koch, R. W. Richardson, F. Sondheimer and J. B. Toogood, *J. Chem. Soc.*, 1890 (1949); (b) E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature*, **173**, 117 (1954).