TABLE II
ISOMERIZATION PROPERTIES OF SOME *cis–trans* ISOMERS

Compound	Conditions	Isomerization rate, min.$^{-1}$
A, *cis*-1-Bromo-1-propene	0°, dark	0.341×10^{-5}
	0°, light	Apx. same
	40°, dark	0.403×10^{-3}
	66.7°, dark	0.0126
	100°, dark	Apx. 0.25
trans-1-Bromo-1-propene	0°, dark	0.801×10^{-5}
	0°, light	Greater than 0.80×10^{-5}
	40°, dark	0.910×10^{-3}
	40°, light	Greater than 0.910×10^{-3}
	66.7°, dark	0.0302
	100°, dark	Apx. 0.6
B, *cis*-1-Chloro-1-propene	139°, light	0
trans-1-Chloro-1-propene	139°, light	0
C, *cis*-1,3-Dibromopropene	30°, light, dark	0
trans-1,3-Dibromopropene	30°, light, dark	0
D, *cis*-3-Bromo-2-propen-1-ol	30°, light, dark	0
trans-3-Bromo-2-propen-1-ol	30°, light, dark	0
E, *cis*-1-Bromo-3-chloro-1-propene	0°, dark	0
	40°, dark	Less than *cis*-BrCH=CH—CH_3
	40°, light	Increased
trans-1-Bromo-3-chloro-1-propene	0°, dark	0
	40°, dark	Less than *trans*-BrCH=CH—CH_3
	40°, light	Increased
F, 3-Bromo-1-chloro-2-fluoro-1-propene	Room temp., light	Isomerizes

viously described.[4] A sample of the pure *cis* isomer was obtained by distillation and a pure sample of the *trans* isomer was obtained by recrystallization at −78°.

3-Bromo-2-propen-1-ols.—The 3-bromo-2-propen-1-ols were prepared by hydrolysis of a mixture of the 1,3-dibromopropenes with an excess of 5% aqueous sodium carbonate solution at 75° for 24 hours as previously described.[4] The isomers were separated by distillation.

1-Bromo-3-chloro-1-propene.—The 1-bromo-3-chloro-1-propenes were prepared by the action of an excess of concentrated hydrochloric acid on a mixture of the 3-bromo-2-propen-1-ols at 65° for 5 hours.[4] The isomers were separated by distillation through a 100-plate column.

Isomerization, Thermal.—Approximately 0.5 ml. of freshly distilled isomer was injected into a 1-ml. Pyrex ampoule with a hypodermic syringe and the ampoule sealed while surrounded by Dry Ice. Each ampoule was then wrapped in aluminum foil to exclude light. Six or seven ampoules were usually filled at the same time and with the same material. The group was then placed in a constant temperature bath and individual ampoules withdrawn at appropriate intervals of time and their contents immediately analyzed by infrared spectra.

Isomerization in the Presence of Light.—The procedures used for the isomerizations in the presence of light were identical with those in the dark except that the ampoules were not wrapped and their contents were exposed to light of measured intensity. In the 40° runs a 250 watt tungsten spot lamp was used to provide the light (1600 ft.-candles) and in the 0° runs the illumination was provided by a 40 watt fluorescent lamp (400 ft.-candles). The light intensity at the surface of the ampoules was measured by a photoelectric exposure meter.

Infrared Spectra.—A Perkin–Elmer model 12 infrared spectrometer was used throughout the work. Liquid samples were analyzed in a cell having sodium chloride windows, and with a spacing of 0.025 mm.

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The Preparation of Long Chain Alkylamine Hydrochlorides[1a]

BY BROWN L. MURR AND CHAS. T. LESTER[1b]

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The observation by Cummings that certain alkylamine salts inhibited the *in vitro* growth of tubercle bacilli and certain pathogenic fungi[2] led us to prepare a number of such compounds. These compounds are all salts of primary aliphatic amines, containing nine or more carbons, with the amino group on the 1-, 2- or 3-position.

The 1-aminoalkanes were prepared from the appropriate acid amide, either by reduction with lithium aluminum hydride[3] or by a Hofmann rearrangement.[4] This latter reaction we found even more sensitive to reaction conditions than we expected despite some literature warning concerning its sensitivity.[5] The 2- and 3-aminoalkanes were prepared from the appropriate methyl and ethyl ketones by means of a Leuckart[6] reaction. The amines prepared are listed in Tables I and II. Although all the 1-amino compounds have been previously reported, they are included for comparison.

The complete details of the testing will be reported elsewhere. Maximum *in vitro* activity ap-

(1) (a) Taken in part from the M.S. Thesis of B. L. Murr, Emory University, 1953, and supported in part by a grant from the National Tuberculosis Association and in part by a grant from the U. S. Public Health. Presented at the Regional Conclave of the American Chemical Society, New Orleans, La., Dec., 1953. (b) To whom inquiries should be addressed.

(2) M. M. Cummings, P. C. Hudgins, E. H. Runyon, M. Tagar and C. T. Lester, *Trans. Nat. Tuber. Assoc.*, **49**, 1 (1953).

(3) W. G. Brown in "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 469.

(4) E. S. Wallis and J. F. Lane in "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 267.

(5) L. Jeffreys, *Am. Chem. J.*, **22**, 14 (1899).

(6) M. L. Moore in "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 301.

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[g]		112–114	B
Hexadecane	155–156[h]			A
Heptadecane	158–160[g]			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[5] 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%.

(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-

(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).