[CONTRIBUTION FROM DOW CORNING CORPORATION, MIDLAND, MICHIGAN]

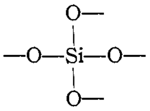
Organo-Silicon Polymers. The Cyclic Dimethyl Siloxanes*

BY M. J. HUNTER, J. F. HYDE, E. L. WARRICK AND H. J. FLETCHER

Cyclic structures in conventional organic chemistry have been well established. Early workers thought only five and six membered carbon rings were possible, but it was later shown[1] that strained rings of three and four members could exist. Continued studies with cyclic hydrocarbons[2] led to the preparation of much larger unstrained rings containing up to eighteen carbon atoms. Carothers and Hill[3] believed all the larger rings may not be entirely without strain, but they pointed out the effect of oxygen in the ring as a means of reducing strain.

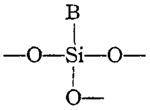
Cyclic structures have also been shown to exist in inorganic chemical systems. Particularly in the field of mineral silicates, Bragg[4] has shown by X-ray analysis, cyclic structures containing six, eight, and twelve alternate oxygen and silicon atoms in the form of polyvalent ions.

These cyclic inorganic silicate polymer structures are involved fundamentally in the structure of quartz and glass.[5,6] In such a completely cross-linked or netted polymer, each silicon is surrounded by four oxygen atoms



$$\begin{array}{c} O- \\ | \\ -O-Si-O- \\ | \\ O- \end{array}$$

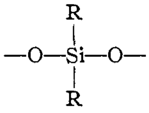
If one of the oxygen bond positions were blocked, the polymer would still be cross linked



$$\begin{array}{c} B \\ | \\ -O-Si-O- \\ | \\ O- \end{array}$$

but if two positions are substituted with a blocking group, a linear polymer would be expected. These difunctional silicon polymers would conceivably be either open chain or cyclic structures. This concept is borne out by the linear and cyclic silicon oxyhalide structures of Schumb and Holloway[7] where two positions on the silicon atom are replaced with chlorine. Only one cyclic, the tetramer form $(Cl_2SiO)_4$, was characterized.

When two positions on the silicon atom are blocked with hydrocarbon radicals



$$\begin{array}{c} R \\ | \\ -O-Si-O- \\ | \\ R \end{array}$$

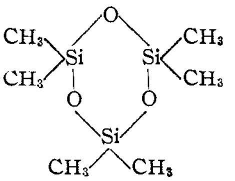
similar structural possibilities may be assumed to exist. Early work by Kipping[8] on disubstituted dichlorosilanes was carried out with the idea of obtaining $R_2Si{=}O$ configurations analogous to $R_2C{=}O$ structures in organic chemistry. These $R_2Si{=}O$ compounds were to be called "silicones" corresponding to conventional ketones. Instead of finding $(C_6H_5)_2Si{=}O$ from the hydrolysis of dichlorodiphenylsilane, Kipping found mainly the diol or linear and cyclic low polymer products. A cyclic trimer, hexaphenylcyclotrisiloxane, melting at 188°, and a cyclic tetramer, octaphenylcyclotetrasiloxane, melting at 201° were isolated and described.

Similar cyclic structures from the hydrolysis of dialkyl dichlorosilanes were reported by Hyde and DeLong[9] in work which was originally planned to determine the effects of the introduction of organic radicals into silicate structures of a vitreous nature. From the hydrolysis of dichlorodiethylsilane, a cyclic trimer was isolated. Similarly from dichlorodimethylsilane a corresponding trimer in impure state was obtained.

The object of this paper is to describe the preparation and properties of a series of highly purified cyclic dimethylsiloxanes of the formula $[(CH_3)_2SiO]_x$ where x is three to eight inclusive.

Description of Results

This series of compounds is unusual in that it represents the most extensive series of closely related cyclic polymeric structures that has been described up to the present time. These polymers contain ring structures of alternate silicon and oxygen atoms with six to sixteen members. The nature of these cyclic compounds is represented by the following two structures



Hexamethylcyclotrisiloxane

I

---

* The material contained in this paper was presented in large part before the High Polymer Conference at Gibson Island, June 25, 1945, by E. L. Warrick, of the Mellon Institute of Industrial Research; M. J. Hunter and H. J. Fletcher with Dow-Corning Corporation, and J. F. Hyde with the Corning Glass Works.

(1) Baeyer, *Ber.*, **18**, 2277 (1885).

(2) Ruzicka, Stoll and Schinz, *Helv. Chim. Acta*, **9**, 249 (1926).

(3) Carothers and Hill, THIS JOURNAL, **55**, 5043 (1933).

(4) W. L. Bragg, "Atomic Structure of Minerals," Cornell University Press, Ithaca, N. Y., 1937, pp. 139–146.

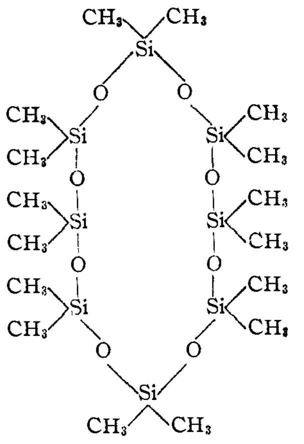
(5) W. L. Bragg, "Introduction to Crystal Analyses," G. Bell and Sons, Ltd., London, 1928, p. 83.

(6) W. H. Zachariasen, THIS JOURNAL, **54**, 3841 (1932).

(7) Schumb and Holloway, *ibid.*, **63**, 2753 (1941).

(8) Kipping and Robinson, *J. Chem. Soc.*, **105**, 484–500 (1914).

(9) Hyde and DeLong, THIS JOURNAL, **63**, 1194 (1941).



Hexadecamethylcycloöctasiloxane
II

For convenience in discussion, I has been called "cyclic trimer," and II, "cyclic octamer," etc.

On hydrolysis of diethyoxydimethylsilane[10] there was formed a mixed polymer fluid which was separated by distillation under vacuum at 250° into a non-volatile portion 70–80% and a low polymer volatile portion 20–30%. When all of the ethoxyl groups were removed, the low polymer portion was essentially a mixture of cyclic dimethyl siloxane polymers containing four to eight silicon atoms with smaller amounts of higher boiling fractions.

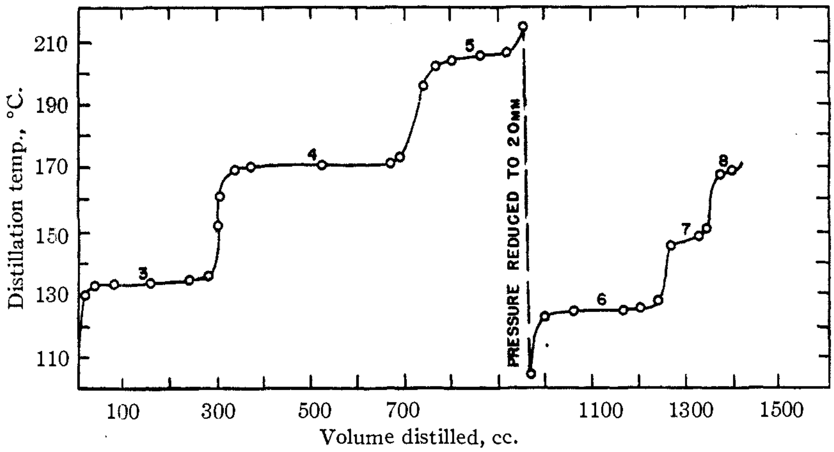


Fig. 1.—Fractional distillation curve for mixed cyclic dimethylsiloxanes obtained from the destructive distillation of high polymer fluids. Numbers on plateaus refer to number of silicon atoms in each cyclic compound.

A similar result was obtained from the hydrolysis of dichlorodimethylsilane.[11] In this case, the cyclic trimer was also found in the low polymer portion, if the hydrolysis was carefully performed.

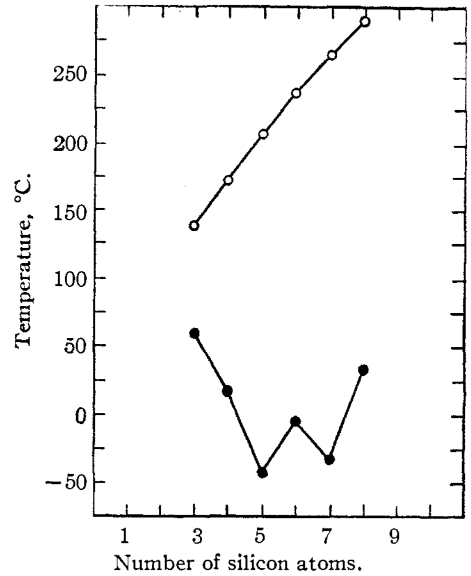


Fig. 2.—Boiling points and freezing points of cyclic dimethylsiloxanes; ○, atmospheric boiling points; ●, freezing points.

Cyclics in high yields are more readily prepared, however, by the depolymerization of dimethylsiloxane high polymers. This may be done by heating the polymers to 350–400° at which temperature cyclics are formed by rearrangement of siloxane linkages. When this operation is carried out under vacuum at lower temperatures, but with sodium hydroxide as a catalyst, above 90% yields of cyclic low polymers may be obtained. Fractional distillation of these low polymer products, from a typical run obtained by the use of alkali catalyst, gives the curve plotted in Fig. 1. This curve shows a series of progressively higher boiling plateaus which are the boiling points of the six cyclic compounds to be described in this paper. The physical properties of these cyclic polymers after careful purification either by redistillation or recrystallization are shown in Table I.

The atmospheric boiling points (Fig. 2) show a regular progression as the molecular weight increases. A complete range of vapor pressures at different temperatures is shown in the Cox Chart (Fig. 3). The freezing points (Fig. 2) display a marked fluctuation entirely independent of the molecular weight. The cyclic pentamer and heptamer with ten and fourteen membered rings seem to have the greatest difficulty in establishing the regularized orientation required for crystallization, as indicated by their low freezing points.

[10] (a) U. S. Patent 2,380,057, July 10, 1945, by McGregor and Warrick. (b) U. S. Patent 2,384,384, February 26, 1945, by McGregor and Warrick.

[11] (a) Gilliam, Liebhafsky and Winslow, This Journal, 63, 801 (1941); (b) U. S. Patent 2,286,763, December 26, 1940, by Rochow.

TABLE I

PHYSICAL PROPERTIES AND ANALYSES OF CYCLIC DIMETHYLSILOXANE LOW POLYMERS

1	Cyclic polymer size	Trimer	Tetramer	Pentamer	Hexamer	Heptamer	Octamer
2	Name	Hexamethyl-cyclotri-siloxane	Octamethyl-cyclotra-siloxane	Decamethyl-cyclopenta-siloxane	Dodeca-methyl-cyclohexa-siloxane	Tetradeca-methyl-cyclohepta-siloxane	Hexadeca-methyl-cycloöcta-siloxane
3	Formula	$[(CH_3)_2SiO]_3$	$[(CH_3)_2SiO]_4$	$[(CH_3)_2SiO]_5$	$[(CH_3)_2SiO]_6$	$[(CH_3)_2SiO]_7$	$[(CH_3)_2SiO]_8$
4	Boiling points, °C.	133	171	204.5	236	147°/20 mm.	168°/20 mm.
5	Melting points, °C.	64.5	17.4	−44	−3.0	−32	31.5
6	Viscosity, centistokes at 25°	...	2.30	3.87	6.62	9.47	13.23[a]
7	Density at 25°	...	0.9497	0.9531	0.9613	0.9664	...
8	Density of crystals	1.12	1.06	...	...	...	1.177
9	Refractive index $n^{25}\text{D}$		1.3935	1.3958	1.3996	1.4018	1.4039[a]
10	Molecular refraction	...	74.47	93.24	111.87	130.45	...
11	Atomic refraction of silicon	...	5.53	5.57	5.57	5.56	...
12	Surface tension, dynes/cm. 25°	...	17.37	17.42	17.61	18.30	...
13	Parachor	...	637	794	948	1110	...
14	Parachor equivalent for silicon	...	27.1	26.7	25.8	26.4	...
15	Victor Meyer, mol. wt.	219	300	376	444	...	...
16	Mol. wt. freezing cyclohexane	227	296	369	430	515	587
17	Mol. wt. calcd.	222.38	296.51	370.64	444.77	518.90	593.02
18	% Carbon found	33.3	33.8	32.5	32.2	32.7	32.2
19	% Carbon calcd.	32.4	32.4	32.4	32.4	32.4	32.4
20	% Silicon found	37.7	37.9	37.9	37.7	37.8	37.9
21	% Silicon calcd.	37.9	37.9	37.9	37.9	37.9	37.9

[a] Determined on the supercooled liquid.

The higher melting points of the cyclic trimer and octamer are indicative of a more symmetrical geometric structure.

Densities and refractive index values are shown in Fig. 4. The atomic refractions of silicon may be calculated using literature values for the other atoms, and as may be noted, are rather constant values. Bygden[12] has reported atomic refraction

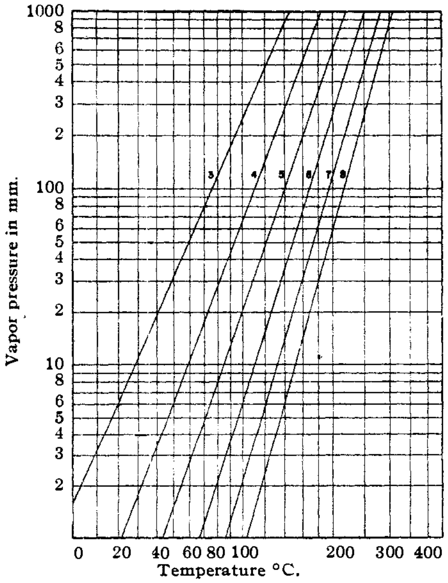


Fig. 3.—Cox chart curves for cyclic dimethylsiloxanes. Numbers on curves refer to number of silicon atoms in rings.

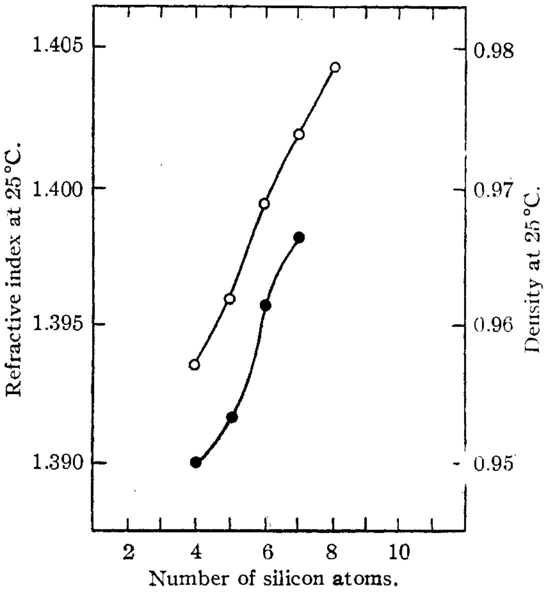


Fig. 4.—Refractive index and density of cyclic dimethylsiloxanes: ○, refractive index values, ●, density determinations.

---

[12] Bygden, *Z. physik. Chem.*, **90**, 243 (1915).

for a number of variously substituted silanes. Tetra alkyl or aryl silanes show values in the range of 7.07 to 7.59 while dichloroethylpropylsilane yields an atomic refraction for silicon of 5.70. The degree of substitution and type of substituent seem to influence markedly the value. The constancy of the atomic refraction for silicon for this series of cyclic dimethylsiloxanes (see Table I, line 11) is further evidence of their membership in a homologous series where the degree of substitution of the silicon is constant. Since only in cyclic systems is the degree of substitution constant, this is confirmation of cyclic structure.

The surface tension values were determined on the non-crystalline cyclics and found to be very low. From these data the parachors and parachor equivalents for silicon in dimethylsiloxanes have been calculated, using the values obtained from Glasstone.[13] These results are found in Table I, lines 12, 13 and 14.

Viscosities of the cyclic polymers at different temperatures are shown in Fig. 5. When these data are plotted as log η *vs.* $\sqrt{M}$, a straight line is obtained. It is thought that a comparison of these viscosity relationships to a series of open chain polymers, which are to be described in a later paper, will give new insight to the problem of shape factor in viscosity studies of polymeric systems.

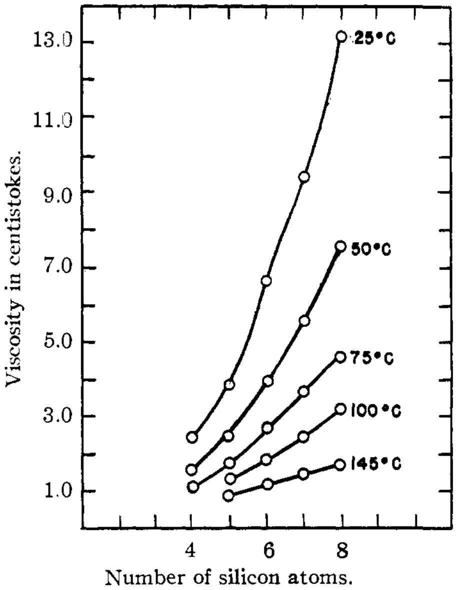


Fig. 5.—Viscosities of cyclic dimethylsiloxanes at different temperatures.

The structure of these cyclic compounds is established by both analysis and molecular weights, as well as by the regularities in the relationships of their physical properties. These results are further amply confirmed by X-ray examination.[14] Caution is desirable in the molecular weight determinations of such compounds and careful comparison of various procedures is necessary. When cyclohexane with its normal constant[15] was employed, the values were uniformly low. Use of the Victor Meyer method on the lower members gave results in good agreement with calculated values for these compounds. These volatile members were in turn employed to establish new constants for cyclohexane which then gave satisfactory confirmation of the molecular weights for the heptamer and octamer (constant for hydrocarbons = 203; constant for polydimethylsiloxanes = 231).

The distribution of the cyclic members as shown in Fig. 1 may be varied considerably depending upon the pressure employed, and catalyst used. Depolymerization at atmospheric pressure may yield as high as 60–70% of cyclic tetramer, while under reduced pressure the higher membered polymers are obtained in greater quantities. The relative amounts of higher membered cyclics gradually decrease in order of their size, because the probability of formation becomes less with increased length, and because their boiling points are so high that they tend to be broken down before volatilization can occur.

From the higher yields of eight and ten membered tetramer and pentamer rings, it would seem as though these are the most stable ring structures whereas the five and six membered rings of hydrocarbon chemistry are the most stable. The six membered cyclic trimer appears to have less stability than the tetramer and pentamer, and apparently is under a slight strain since preliminary X-ray data indicate that all atoms in the ring lie in a single plane. The sixteen membered cyclic octamer ring, on the other hand, is probably not under strain since X-ray data[14] show the ring is not planar.

Experimental

Into a one-liter round-bottomed flask with a ground glass joint and thermometer well was placed 300 g. of high polymer dimethylsiloxane fluid[10b] (927 centistokes at 25°) which was thoroughly mixed with 8 g. of powdered sodium hydroxide. A glass elbow (0.5 in. diam.) was used to connect the flask with a receiver, and two Dry Ice traps were placed between the receiver and the vacuum pump. The system was evacuated to 1 mm. pressure and the flask heated gently with an open flame. The voluminous white fumes given off were condensed in the receiver and Dry Ice traps. The temperature inside the reaction mass was usually 230–240°, but most of the decomposition appeared to take place where the high polymer came in contact with the hot glass surface. The distillate weighed 281 g. (93.7%) and the residue 27 g.

Several distillates by the above procedure were combined and distilled through a well insulated fractionating column (4 ft. × 1.25 in.) packed with 0.25-inch Fenske single turn glass helices. A Corad head operating at 10% on the plateaus and 5% take off on the intermediate cuts was used on the column to obtain the curve shown in Fig. 1. Further purification of the compounds was accomplished

---

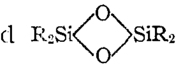
[13] Glasstone, "Text Book of Physical Chemistry," D. Van Nostrand, New York, N. Y., 1940, p. 516.

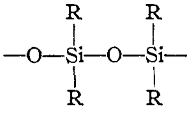
[14] Frevel and Hunter, This Journal, **67**, 2275 (1945).

[15] Muscarelli and Devati, *Gazz. chim. ital.*, **37B**, 642 (1909).

by careful redistillation of the individual members and also recrystallization whenever possible.

Theoretical Discussion

The possible existence of such structures as $R_2Si{=}O$ and  has been considered by Kipping.[16] Attempts to obtain evidence for the existence of such structures yielded negative results. The work described here in the dimethyl series confirms the above findings, and shows that the normal result of hydrolysis and condensation is the formation of polymers.



$$\begin{array}{ccccc} & R & & R & \\ & | & & | & \\ -O- & Si & -O- & Si & - \\ & | & & | & \\ & R & & R & \end{array}$$

Kipping's isolation of $(C_6H_5)_2Si(OH)_2$ and other closely related intermediate hydroxyl structures[16a] indicated a manner in which cyclic polymers may be formed. Condensation appears to occur more readily in the dimethyl series under comparable conditions indicating an effect that is dependent on the nature of the substituent groups.

The cyclic dimer of this series was not found under the conditions employed, but some of its characteristics could be predicted by extension of the physical property curves.

The absence of a silanone type of structure, $(CH_3)_2Si{=}O$, from both the hydrolysis and destructive distillation experiments described here, illustrates one of the fundamental differences between the chemistry of carbon and analogous organo-silicon compounds: namely, the absence of the silicon double bond oxygen configuration. The name "silicone" is therefore not appropriate, from a structural point of view, for products obtained by the hydrolysis of R_2SiX_2 compounds. This term nevertheless is now being commonly used for all organo-silicon-oxygen polymers being manufactured at the present time.

An investigation of the diorgano-substituted silicon compounds leads directly into a study of linear polymers, and this field is being actively investigated. When the R groups are of such a nature that the silanediols are readily condensed, cyclization is the only method of stopping chain growth in low polymer form. Termination of linear chain growth by cyclization at low polymer stages has been discussed in a general way by polymer chemists who recognized this possibility, but the existence of cyclic structures in most linear polymer mixtures has been difficult to verify. The series of cyclic compounds found in the high polymer dimethylsiloxane preparations readily display this concept which was usually treated as a theoretical possibility.

Of special note in the physical properties of this series of cyclic dimethylsiloxanes is their very low boiling points contrasted with saturated hydrocarbon compounds of similar molecular weights. These low boiling points, considered with the vapor pressure for these compounds, suggest low molecular cohesive forces.

While the slopes of the vapor pressure curves in Fig. 3 are not truly the heats of vaporization, they are closely related to them. From these slopes a reasonably constant difference of 930 cal. is found in going from one number to the next. This is presumably the contribution of a $(CH_3)_2SiO$ group to the over-all molecular cohesion. The slopes for an homologous series of organic compounds have been shown by Dunkel[17] to possess a remarkable additivity. The contribution of individual atoms or groups to the forces of molecular cohesion may be estimated and seem to predict rather accurately the vapor pressures of the compounds. In attempting to calculate the contribution of the $(CH_3)_2SiO$ unit from Dunkel's data, the values for methyl groups and the oxygen alone are found to give 5190 cal.

The vapor pressure data for silanes and methyl-substituted silanes from calculations by Wintigen[18] show reasonable additivity with Dunkel's data. It seems evident that the siloxane structure rather than the silane structure is responsible for the greatly reduced values in the case of the dimethylsiloxane unit. In order to apply Dunkel's principles new values for the various groups would have to be obtained, taking into consideration their location in silane or siloxane structures.

The presence of a siloxane structure seems largely responsible for the over-all reduced molecular cohesion in the cyclic dimethylsiloxanes, but the complete explanation is not clear. Other physical properties are dependent upon this fundamental phenomenon of molecular cohesion or internal pressure, and seem to confirm its rather low value. The small effect of temperature on viscosity is an expression of this low molecular cohesion. This is of great practical value as well as of considerable theoretical interest.

Based on the Eyring treatment of viscous flow, Kierstead and Turkevich[19] have derived an Arrhenius type equation which they have applied to fluidity

$$\text{(Fluidity) } \phi = Ae^{-E/RT}$$

The energy of activation for viscous flow is calculated for many hydrocarbons and the influence of structure is pointed out. Similar calculations for the cyclic dimethyl siloxanes yield:

Dimethyl-siloxane units	$A \times 10^{-4}$	E, cal.	Mol. wt.
4	7.94	3060	296.51
5	7.08	3300	370.64
6	8.05	3720	444.77
7	8.65	3960	518.90
8	13.87	4430	593.02

---

[16] (a) Kipping, *J. Chem. Soc.*, **101**, 2108-2125 (1912); (b) **101**, 2125 (1912).

[17] Dunkel, *Z. physik. Chem.*, **A138**, 42 (1928).

[18] Wintigen, *Ber.*, **52**, 724 (1919).

[19] Kierstead and Turkevich, *J. Chem. Phys.*, **12**, 24 (1944).

The two cyclic hydrocarbons listed by Kierstead and Turkevich show

Cyclopentane	5.554	1878	70.13
Cyclohexane	15.21	2905	84.16

The rather rapid increase in energy of activation for viscous flow with only slight increase in molecular weights for the hydrocarbon series is contrasted with the much slower increase with larger members of the dimethylsiloxane polymer series.

Acknowledgments.—The authors wish to thank Mr. James H. McHard for his contribution to the analytical work, and Mr. R. F. Fleming for valuable assistance in some of the early work on isolation of these compounds.

Summary

1. Cyclic dimethylsiloxane polymers from three to eight units have been prepared and their physical properties reported.

2. These cyclic structures may be isolated either from the hydrolysis products of dimethylsilane derivatives or by destructive distillation of dimethylsiloxane high polymers.

3. The phenomenally low molecular cohesion of dimethylsiloxanes compared with hydrocarbons is observed from surface tension values, vapor pressure data, and fluidity calculations.

MIDLAND, MICHIGAN RECEIVED DECEMBER 13, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Carbethoxylation of Ethyl Phenylacetate and of Ethyl α-Phenyl-*n*-butyrate Using Sodium Amide[1]

BY HOWARD G. WALKER, JR., ROBERT LEVINE,[2] ROBERT F. KIBLER AND CHARLES R. HAUSER

Wallingford, Homeyer and Jones[3] have shown that the carbethoxylation of ethyl phenylacetate with diethyl carbonate to form diethyl α-phenylmalonate may be effected in high yield by means of sodium ethoxide under forced conditions. We have found that this carbethoxylation may also be effected satisfactorily, and in considerably less time, by means of sodium amide. Since earlier workers[4] have been unsuccessful in their attempts to effect the reaction using sodium amide, our method is worthy of comment. It consists of first converting ethyl phenylacetate to its sodium derivative in the presence of excess sodium amide in liquid ammonia, replacing the ammonia by ether and adding diethyl carbonate. In this manner the self-condensation of the ethyl phenylacetate, observed by the earlier workers,[4] was avoided or at least minimized. The carbethoxylation may be represented, thus

$$C_6H_5CH_2CO_2C_2H_5 \xrightarrow{NaNH_2} Na^+(C_6H_5CHCO_2C_2H_5)^- \xrightarrow[+HCl]{(C_2H_5O)_2CO} C_6H_5CH(CO_2C_2H_5)_2$$

In a similar manner the carbethoxylation of ethyl α-phenyl-*n*-butyrate has been effected by means of sodium amide to form diethyl α-phenyl-α-ethylmalonate. However, the yield with this ester has been somewhat lower than that obtained with ethyl phenylacetate. Wallingford, Homeyer and Jones[3] have shown that ethyl α-phenyl-*n*-butyrate fails to undergo carbethoxylation in the presence of sodium ethoxide, even under forced conditions.

The sodium derivative of ethyl α-phenyl-*n*-butyrate has also been treated with ethyl chlorocarbonate to form presumably diethyl α-phenyl-α-ethylmalonate. However, the yield was lower than that with diethyl carbonate and was considerably lower than that obtained in the somewhat similar reaction of ethyl chlorocarbonate with the sodium derivative of ethyl isobutyrate, prepared by means of sodium triphenylmethide.[5]

Since ethyl propionate and higher aliphatic esters react with sodium amide to form considerable amounts of the corresponding amides,[6] no attempt has been made to carbethoxylate these esters using this base. Attempts have been made to carbethoxylate *n*-butyl and *t*-butyl acetates with diethyl carbonate using sodium amide but mixtures of condensation products appeared to be formed. Various aliphatic ethyl esters have been carbethoxylated using sodium ethoxide[3] or sodium triphenylmethide.[5,7]

Experimental

Diethyl α-Phenylmalonate.—Sodium amide (0.6 mole) was prepared in liquid ammonia as described previously.[8] Ethyl phenylacetate (0.3 mole), dissolved in 100 cc. of absolute ether, was added over a period of two minutes. The reaction flask was placed on a steam-bath and the ammonia evaporated (this takes approximately fifteen minutes), sufficient absolute ether being added so that the contents of the flask remained at approximately 300 cc. As soon as the ether began to reflux, the steam-bath

---

[1] Paper XXXIII on "Condensations"; paper XXXII, THIS JOURNAL, **68**, 26 (1946).

[2] Present address: The Mathieson Alkali Works, Niagara Falls, New York.

[3] Wallingford, Homeyer and Jones, THIS JOURNAL, **63**, 2056 (1941).

[4] Nelson and Cretcher, *ibid.*, **50**, 2760 (1928).

[5] Hudson and Hauser, *ibid.*, **63**, 3156 (1941).

[6] Hauser, Levine and Kibler, *ibid.*, **68**, 26 (1946).

[7] Baumgarten and Hauser, *ibid.*, **66**, 1037 (1944).

[8] Levine and Hauser, *ibid.*, **66**, 1768 (1944).