[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Aliphatic Organo-functional Siloxanes. IV. Direct Synthesis of Organosiloxane Esters and Acids from Halomethylsiloxanes and Halomethylethoxysilanes[1]

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A new and improved synthesis of aliphatic organo-functional siloxanes, in which the silicon atom may be mono- or difunctional, is effected by reaction of halomethylsiloxanes or halomethylethoxysilanes with sodiomalonic ester or sodiocyanoacetic ester. Ethanol and diethyl carbitol are suitable solvents for the reactions of chloromethyldimethylethoxysilane and chloromethylmethyldiethoxysilane with sodiomalonic ester. Diethyl carbitol is a useful solvent for the above reactions of halomethylsiloxanes. However, an ethanol solvent gives a complex mixture of products with chloromethylpentamethyldisiloxane and sodiomalonic ester. Reaction of sodiomalonic ester and bis-(halomethyl)-tetramethyldisiloxanes results in the formation of a new organosiloxane ring system; a *6-ring disiloxane-diester* is produced.

In previous publications from this Laboratory on aliphatic organo-functional siloxanes[2-4] our objectives in studying this relatively unexplored area of chemistry have been set forth and need not be repeated here. Through use of the reaction with concd. sulfuric acid of a variety of organo-functional silanes to give selective cleavage of one methyl group from trimethylsilyl, Me_3Si,[2,4,5] it was found possible to prepare a large number of interesting organo-functional siloxanes. Thus, the synthesis and physical properties of sixteen organopolysiloxane diesters are reported in a recent publication.[4]

As a basis for discussion, the following reported preparation of a disiloxane-diacid, I,[2] will serve to illustrate the synthetic route to aliphatic organo-functional siloxanes which uses methyl–silicon cleavage by concd. sulfuric acid as the key reaction.

$$Me_3SiCl \xrightarrow{Cl_2} ClCH_2Me_2SiCl \xrightarrow{MeMgBr}$$

$$Me_3SiCH_2Cl \xrightarrow[\text{Ester}]{\text{Malonic}} Me_3SiCH_2CH_2CO_2H \xrightarrow[2,\ H_2O]{1,\ H_2SO_4} \underset{\text{I}}{O(SiMe_2CH_2CH_2CO_2H)_2} + 2CH_4$$

From examination of the above reaction sequence it is clear that *methylation* of the silicon atom is involved at one stage (step 2) and *demethylation* at a later stage.

Elimination of these two stages would obviously provide a shorter and more desirable route to the synthesis of aliphatic organo-functional siloxanes. However, we were long prevented from realization of this objective by two factors: (1) Overgeneralization of the reported facts concerning base-catalyzed carbon–silicon cleavage of $ClCH_2$–Si in structures having one or more electronegative substituents linked to silicon[6] (chloromethylpentamethyldisiloxane undergoes chloromethyl–silicon cleavage with even so weak a base as alcoholic ammonia); (2) an experiment performed several years ago in which chloromethylpentamethyldisiloxane gave none of the desired disiloxane-diester when treated with sodiomalonic ester in ethanol solvent.[7]

More recently, re-examination of the above situation from a theoretical standpoint led us to speculate that the bulky malonic ester anion with its negative charge delocalized by resonance is indeed quite different from smaller more localized bases such as hydroxide and ethoxide anions, and might, therefore, more selectively attack the carbon–chlorine bond in a $ClCH_2Me_2Si$–O–Si-grouping.[8]

Malonic Ester Synthesis with Halomethylsiloxanes.—Sodiomalonic ester, *prepared in a toluene solvent to ensure against the presence of anions other than malonate*, was heated (105°) with iodomethylpentamethyldisiloxane (45 hours) and gave the disiloxanediester, compound II, in 50% yield.

$$ICH_2Me_2SiOSiMe_3 + \overset{\ominus}{C}H(CO_2Et)_2 \xrightarrow{\text{toluene}} \underset{\text{II}}{Me_3SiOSiMe_2CH_2CH(CO_2Et)_2}$$

The use of diethyl carbitol (diethylene glycol diethyl ether) as a solvent was next investigated and proved to have several advantages over toluene. Homogeneous solutions of sodiomalonic ester in diethyl carbitol are readily prepared and are more reactive toward halomethylsiloxanes than are suspensions of sodiomalonic ester in toluene. Use of diethyl carbitol gave compound II in 75% yield from iodomethylpentamethyldisiloxane and in 58–75% yields from chloromethylpentamethyldisiloxane.

Hydrolysis and decarboxylation of compound II are readily carried out by heating with concd. hydrochloric–glacial acetic acid solutions which also equilibrate the siloxane bond and furnish hexamethyldisiloxane and compound I in yields (94%) approaching the theoretical.

$$2\text{II} \xrightarrow[\text{HCl}]{\text{HOAc}} (Me_3Si)_2O + 4CH_3CO_2Et + \underset{\text{I}}{O(SiMe_2CH_2CH_2CO_2H)_2}$$

Thus, I is now available in 70–74% over-all yields by a 2-step process from chloromethylpentamethyldisiloxane. The latter substance is easily prepared by cohydrolysis of chloromethyldimethylchlorosilane and trimethylchlorosilane.[6a]

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[1] Paper 50 in a series on organosilicon chemistry. For paper 49 see P. D. George, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **77**, 6647 (1955).

[2] L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, *ibid.*, **75**, 2932 (1953).

[3] L. H. Sommer and R. P. Pioch, *ibid.*, **75**, 6337 (1953).

[4] L. H. Sommer, W. D. English, G. R. Ansul and D. N. Vivona, *ibid.*, **77**, 2485 (1955).

[5] L. H. Sommer, G. M. Goldberg, G. H. Barnes and L. S. Stone, Jr., *ibid.*, **76**, 1609 (1954).

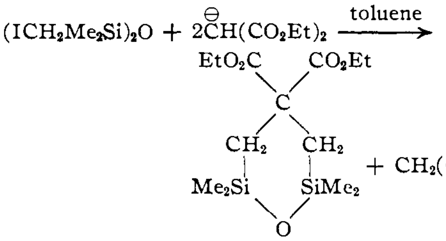
[6] For rapid cleavage of $ClCH_2$–Si in structure having one or more oxygen substituents bonded to Si see: (a) R. H. Krieble and J. R. Elliott, *ibid.*, **67**, 1810 (1945); 2291 (1946); (b) J. L. Speier, *ibid.*, **71**, 273 (1949); (c) C. F. Roedel, *ibid.*, **71**, 269 (1949).

[7] G. M. Goldberg, Ph.D. Thesis, Pennsylvania State University, 1949.

[8] A more nearly complete theoretical discussion will appear in a later publication after more data have been accumulated.

Reaction of sodiomalonic ester with chloromethylpentamethyldisiloxane in *t-butyl alcohol* gave II in 48% yield. Reinvestigation of the use of ethanol as a solvent gave a complex mixture of products none of which corresponded to compound II.[8a]

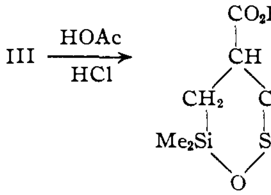
Treatment of bis-(iodomethyl)-tetramethyldisiloxane (0.5 mole) with sodiomalonic ester (1.2 moles) in toluene gave the cyclic diester, compound III, in 61% yield.



III

Use of the less reactive bis-(chloromethyl)-tetramethyldisiloxane in a toluene solvent gave only 28% yield of compound III. In diethyl carbitol solvent, bis-(chloromethyl)-tetramethyldisiloxane gave a 61% yield of somewhat impure III which could be converted to the cyclic monocarboxylic acid, IV, to give an over-all yield of 50% for the acid based on bis-(chloromethyl)-tetramethyldisiloxane. Thus, the most convenient synthesis of IV involves use of diethyl carbitol as a solvent in the malonic ester step.

The cyclic diester is readily hydrolyzed and decarboxylated by heating with concd. hydrochloric-glacial acetic acid solution and gives the cyclic acid, IV, as hard, shiny, white crystals, m.p. 145°, in 91% yield.

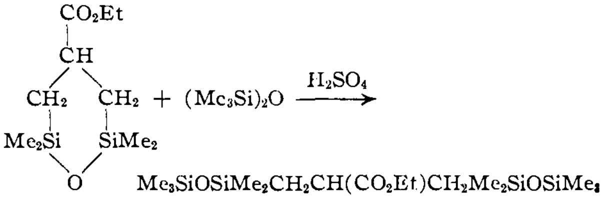


IV

The high yield of IV is of considerable interest since it clearly indicates a high order of stability for the 6-ring disiloxane system present in compound IV. Ring-opening followed by intermolecular condensation in the presence of the acidic reagent employed (see above for equilibration of the siloxane bond in conversion of II to I) would, of course, lead to linear polymers having the structural unit

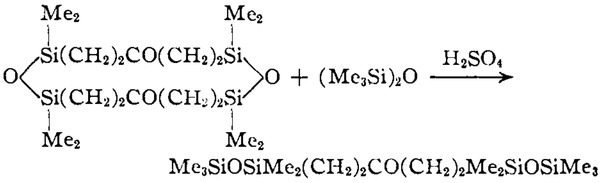
$$\text{—SiMe}_2\text{CH}_2\text{CH(CO}_2\text{H)CH}_2\text{Me}_2\text{Si—O—}$$

Stability of the 6-ring disiloxane system was also evident in another series of experiments. Conventional esterification with ethanol and concd. hydrochloric acid as a catalyst gave the ethyl ester V. When the latter (0.78 mole) was treated with hexamethyldisiloxane (2.3 moles) and a small amount of concd. sulfuric acid (under conditions which smoothly give linear trimethylsiloxy end-blocked polymethylpolysiloxanes by equilibration of octamethylcyclotetrasiloxane or hexamethylcyclotrisiloxane with hexamethyldisiloxane)[9] starting material was recovered in large amount and only a 17% yield of VI was obtained.



V VI

The above results may also be compared with the 41% yield obtained in the following equilibration under similar conditions.[2]



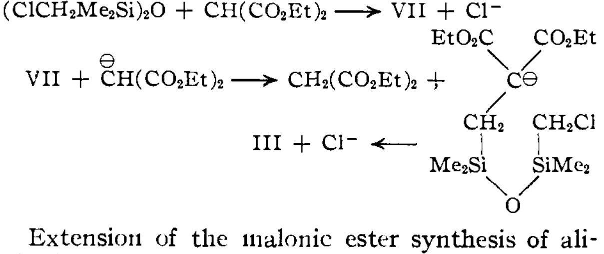
The cyclic monocarboxylic acid IV and its ethyl ester V both have the infrared absorption maximum for the siloxane linkage at 10.1 μ. Open-chain organodisiloxanes usually have siloxane absorption maxima in the range of 9.4–9.5 μ. Young and co-workers[10] have shown in studies of methyl-, ethyl- and phenylcyclopolysiloxanes that this absorption maximum is shifted to shorter or longer wave lengths depending on ring size. Thus, the 6-ring cyclotrisiloxanes have absorption maxima for the siloxane linkage in the range 9.8–9.9 μ, while the 8-ring cyclotetrasiloxanes have maxima at 9.15–9.25 microns. The 6-ring disiloxanes herein reported show the highest wave length absorption maximum for the siloxane linkage thus far reported.

In order to investigate the mode of formation of the 6-ring disiloxane system, its logical precursor in the malonic ester synthesis, a chloromethyldisiloxane diester, compound VII, was synthesized

$$(\text{ClCH}_2\text{Me}_2\text{Si})_2\text{O} + \text{Me}_3\text{SiOSiCH}_2\text{CH(CO}_2\text{Et)}_2 \xrightarrow{\text{H}_2\text{SO}_4} \text{ClCH}_2\text{Me}_2\text{SiOSiCH}_2\text{CH(CO}_2\text{Et)}_2$$

VII

Treatment of VII with 1 mole equivalent of sodiomalonic ester in diethyl carbitol gave the cyclic diester, III, in 66% yield. Thus, a probable mechanism is



Extension of the malonic ester synthesis of aliphatic organo-functional siloxanes to compounds in which the silicon atom is difunctional is, of course, quite important as a first step in making such substances available for incorporation in the main chains of organopolysiloxanes. This objective was

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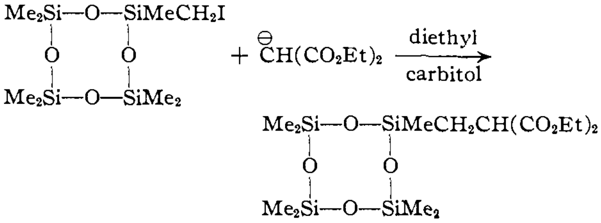
[8a] This reaction is still under investigation and will be reported in detail later. See the Experimental part for preliminary data.

[9] W. I. Patnode and D. F. Wilcock, THIS JOURNAL, **68**, 361 (1946).

[10] C. W. Young, P. C. Servais, C. C. Currie and M. J. Hunter, *ibid.*, **70**, 3758 (1948).

first realized in the present work by treatment of iodomethylheptamethylcyclotetrasiloxane with sodiomalonic ester in diethyl carbitol solvent.



VIII

Compound VIII was synthesized in 45% yield by this procedure. Chloromethylheptamethylcyclotetrasiloxane is much less reactive than the iodo analog and gave only a 23% yield of VIII.

Ethyl cyanoacetate was used instead of ethyl malonate for a reaction with iodomethylpentamethyldisiloxane in diethyl carbitol solvent. The product, compound IX, was formed in 50% yield.

$$ICH_2Me_2SiOSiMe_3 + \overset{\ominus}{C}H(CN)CO_2Et \xrightarrow[\text{carbitol}]{\text{diethyl}} Me_3SiOSiMe_2CH_2CH(CN)CO_2Et$$

IX

Malonic Ester Synthesis with Chloromethylethoxysilanes.—Chloromethylethoxysilanes, which are readily available from the corresponding chlorosilanes by simple ethanolysis, would have certain advantages over the chloromethylsiloxanes for use in malonic ester synthesis because of the ease with which the ethoxy–silicon bond in the product could be hydrolyzed as a means of incorporating the organo-functional unit into a polysiloxane structure. Furthermore, it seemed of considerable theoretical interest to determine whether reaction would take place at the carbon–chlorine or the carbon–silicon bond in chloromethylethoxysilanes when these compounds are treated with sodiomalonic ester in various solvents.

In the first of a series of experiments, chloromethyldimethylethoxysilane[11] was treated with sodiomalonic ester in diethyl carbitol solvent and gave the diester, compound X, in 61% yield.

$$ClCH_2Me_2SiOEt + \overset{\ominus}{C}H(CO_2Et) \xrightarrow[\text{carbitol}]{\text{diethyl}} EtOSiMe_2CH_2CH(CO_2Et)_2$$

X

Thus far, chloromethylethoxysilanes simulate the chloromethylsiloxanes in their reactions with sodiomalonic ester.

However, when sodiomalonic ester in *ethanol solvent* was treated with chloromethyldimethylethoxysilane, a 60% yield of X was obtained. Compound X gave the disiloxane-diacid, I, in 95% yield after heating with concd. hydrochloric–glacial acetic acid solution.

The above studies were next extended to include chloromethylmethyldiethoxysilane. Reaction of this substance with sodiomalonic ester in diethyl carbitol solvent gave the desired diester, compound XI, in 61% yield.

$$ClCH_2MeSi(OEt)_2 + \overset{\ominus}{C}H(CO_2Et)_2 \xrightarrow[\text{carbitol}]{\text{diethyl}} (EtO)_2SiMeCH_2CH(CO_2Et)_2$$

XI

Chloromethylmethyldiethoxysilane was next treated with sodiomalonic ester in *ethanol solvent.* Compound XI was obtained in 66% yield.

Use of ethyl cyanoacetate in place of ethyl malonate with chloromethylmethyldiethoxysilane in ethanol solvent gave XII in 46% yield.

$$ClCH_2MeSi(OEt)_2 + \overset{\ominus}{C}H(CN)CO_2Et \xrightarrow{\text{ethanol}} (EtO)_2SiMeCH_2CH(CN)CO_2Et$$

XII

We choose to postpone any discussion of the theoretical significance of the above facts until precise and complete data are available concerning the nature of the reactions which occur during treatment of chloromethylpentamethyldisiloxane with sodiomalonic ester in *ethanol* solvent.

Apart from their probable importance for a better understanding of structure–reactivity relationships in organosilicon chemistry, the reactions reported herein provide a new and useful route to aliphatic organo-functional siloxanes which should further stimulate activity in this area.

Experimental

Malonic Ester Synthesis with Halomethylsiloxanes

A. Reactions of Halomethylpentamethyldisiloxanes in Diethyl Carbitol and Toluene Solvents.—Reaction of sodium with malonic ester using diethyl carbitol as a solvent proceeds smoothly at room temperature with some heating being required for reaction of the last portions of sodium. Preparation of sodium "sand" is unnecessary and the reaction has the further advantage of providing a homogeneous solution of sodiomalonic ester in a solvent which possesses no "active" hydrogen.

Iodomethylpentamethyldisiloxane, 115 g. (0.4 mole), was added rapidly with stirring to a solution prepared from sodium, 9.2 g. (0.4 mole), diethyl malonate, 64 g. (0.4 mole) and 210 ml. of diethyl carbitol. Heating at 100° gave rapid formation of a white granular precipitate of sodium iodide and was continued with stirring for 15 hours. The reaction mixture was then washed with two 100-ml. portions of water to remove sodium iodide. The first washing layered out satisfactorily, but the second washing required a few ml. of benzene to break the emulsion which formed. The water washings were extracted with benzene, the benzene extract added to the main product, and the whole distilled through a Claisen flask. This procedure gave 106 g. of crude product which was fractionated to give 96.5 g. (0.30 mole, 75% yield) of II, 1,1-dicarbethoxy-3,3,5,5-tetramethyl-3,5-disila-4-oxahexane, b.p. 127–128° (7 mm.), n^{20}_D 1.4240, d^{20} 0.9717.

Anal. Calcd. for $C_{13}H_{28}O_5Si_2$: Si, 17.5; sap. equiv., 160; mol. wt., 320; MR_D, 84.9. Found: Si, 17.9; sap. equiv., 160; mol. wt. 310; MR_D, 84.2.

The saponification equivalents were determined by heating weighed samples of the diester in diethylene glycol–KOH solution for 9 hours on the steam-bath.

When the above procedure was used for the reaction of chloromethylpentamethyldisiloxane with sodiomalonic ester, the yields of fractionated compound II were 58–75%.

Reaction of iodomethylpentamethyldisiloxane with sodiomalonic ester in toluene as solvent was carried out as follows. Iodomethylpentamethyldisiloxane, 142 g. (0.49 mole), was added during 30 minutes with stirring and heating at 50° to sodiomalonic ester prepared from diethyl malonate, 96 g. (0.6 mole) and a suspension of 12 g. (0.52 mole) of sodium "sand" in 750 ml. of toluene. The reaction temperature was then raised to 105° and stirring and heating at that temperature were continued for 45 hours. After cooling and removal of sodium iodide by filtration, Claisen distillation followed by fractionation gave a 50% yield of compound II

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[11] H. Freiser, M. V. Eagle and J. Speier, This Journal, **75**, 2824 (1953).

having properties identical with those of the product obtained using diethyl carbitol as the solvent.

B. Reactions of Bis-(halomethyl)-tetramethyldisiloxanes in Diethyl Carbitol and Toluene Solvents.—Bis-(iodomethyl)-tetramethyldisiloxane, b.p. 120° (6 mm.), $n^{20}\mathrm{D}$ 1.5255, Si, 13.3% (calcd., 13.5% Si), (prepared from bis-(chloromethyl)-tetramethyldisiloxane and sodium iodide in acetone solvent), 207 g. (0.5 mole) was added during 30 minutes with stirring and heating at 50° to sodiomalonic ester prepared from diethyl malonate, 192 g. (1.2 moles) and a suspension of 23 g. (1 mole), of sodium "sand" in 1.4 l. of toluene. After heating at reflux temperature for 50 hours, the reaction product was cooled, filtered to remove sodium iodide, Claisen distilled, and then fractionated to give 97 g. (0.305 mole, 61% yield) of compound III, 1,1-dicarbethoxy-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane, b.p. 134° (6–7 mm.), $n^{20}\mathrm{D}$ 1.4485, d^{20} 1.043.

Anal. Calcd. for $C_{13}H_{26}O_5Si_2$: Si, 17.6; sap. equiv., 159; mol. wt., 318; MR_D 82.7. Found: Si, 17.9; sap. equiv., 157; mol. wt., 315; MR_D 81.8.

Compound III required heating with diethylene glycol-KOH on the steam-bath for 20 hours to effect complete saponification.

When the above procedure was used for the reaction of bis-(chloromethyl)-tetramethyldisiloxane with sodiomalonic ester, the yield of fractionated compound III was only 28%.

Reaction of bis-(chloromethyl)-tetramethyldisiloxane with sodiomalonic ester in *diethyl carbitol* as a solvent was carried out as follows. Bis-(chloromethyl)-tetramethyldisiloxane, 67 g. (0.29 mole), was added during 5 minutes at 40° to sodiomalonic ester prepared as described previously from diethyl malonate, 96 g. (0.6 mole) and sodium, 13.8 g. (0.6 mole) in 250 ml. of diethyl carbitol. The reaction mixture was then heated to 110–115° with stirring. Heating and stirring were continued for 18 hours and then the reaction product was filtered. Claisen distillation of the filtrate gave 58.2 g. (0.183 mole) of crude (b.p. 141–142° (10 mm.), $n^{20}\mathrm{D}$ 1.4430–1.4480), cyclic diester, a 63% yield of crude product. This material was carefully fractionated but the fractions collected, although having the approximately correct boiling points, gave $n^{20}\mathrm{D}$ 1.4440–1.4455. Since the fractionation failed to yield material corresponding to the correct index of refraction ($n^{20}\mathrm{D}$ 1.4485), (indicating the presence of an impurity which could not easily be separated by fractionation), the distillate was hydrolyzed and decarboxylated to the solid cyclic acid (see below). After recrystallization from petroleum ether, there was obtained 30 g. of compound IV, m.p. 144°.

When bis-(iodomethyl)-tetramethyldisiloxane was treated with sodiomalonic ester in diethyl carbitol results were obtained which were very similar to those reported above for bis-(chloromethyl)-tetramethyldisiloxane. Thus, the reaction of bis-(halomethyl)-tetramethyldisiloxanes with sodiomalonic ester in diethyl carbitol (a procedure which is more convenient to use than that involving toluene) gives the cyclic acid in over-all yield of about 50%.

C. Reaction of Halomethylheptamethylcyclotetrasiloxanes in Diethyl Carbitol.—Iodomethylheptamethylcyclotetrasiloxane, 149 g. (0.35 mole, b.p. 66° (0.7 mm.), $n^{20}\mathrm{D}$, 1.4449, d^{20} 1.2897, MR_D, 87.2 (calcd., MR_D, 87.4), Si, 26.6 (calcd., 26.6% Si) (prepared in 83% yield from the chloro analog and sodium iodide in acetone)), was dissolved in 50 ml. of diethyl carbitol, heated to 100°, and sodiomalonic ester, prepared from 8.0 g. (0.35 mole) of sodium and diethyl malonate, 56 g. (0.35 mole), in 250 ml. of diethyl carbitol, was added with stirring during 2 hours. Reaction seemed to proceed quite rapidly as evidenced by precipitation of sodium iodide. After addition had been completed, titration of a 1-ml. aliquot of the reaction mixture required only 1 ml. of 0.025 *N* H_2SO_4, indicating almost complete reaction. After cooling to room temperature, 300 ml. of ether was added and the product was washed with 500 ml. of 0.5 *N* HCl to remove any base which could cause siloxane-bond rearrangement. This was followed by washing with 500 ml. of distilled water, ether extraction of the water layer, and drying over Drierite. Fractional distillation gave 72 g. (0.16 mole) of compound VIII, β,β-(dicarbethoxyethyl)-heptamethylcyclotetrasiloxane, 45% yield, b.p. 136° (2 mm.), $n^{20}\mathrm{D}$ 1.4251, d^{20} 1.0542.

Anal. Calcd. for $C_{15}H_{34}O_8Si_4$: Si, 24.7; sap. equiv., 227; MR_D, 110.5. Found: Si, 24.9; sap. equiv., 229; MR_D, 110.3.

Saponification equivalents were obtained by refluxing with methyl cellosolve KOH for 4 hours.

When chloromethylheptamethylcyclotetrasiloxane was treated with sodio-malonic ester in diethyl carbitol according to the usual procedure employed with chloromethylpentamethyldisiloxane in the carbitol solvent, a 24% yield of compound VIII was obtained, b.p. 114° (0.3 mm.), $n^{20}\mathrm{D}$ 1.4254. Reaction with chloromethylheptamethylcyclotetrasiloxane proceeds much more slowly than with the iodomethyl analog. Thus, the chloromethyl compound required 20 hours of heating at 100° to effect complete reaction.

D. Reaction of Chloromethylpentamethyldisiloxane in *t*-Butyl Alcohol Solvent.—Sodium, 11.5 g. (0.5 mole) in 200 ml. of *t*-butyl alcohol was heated to 75° in the presence of diethyl malonate, 83 g. (0.52 mole). After completion of the reaction, the flask contents comprised a clear homogeneous solution which when cooled to 50° "solidified" to a gel. To the latter was added chloromethylpentamethyldisiloxane, 0.5 mole, and the mixture was then heated and stirred, causing it to become nearly clear again. After heating for one hour at 85° a considerable amount of sodium chloride formed and the reaction mixture was then stirred and heated at 75° for 15 hours. The flask contents were then cooled and washed with two 100-ml. portions of water. After benzene extraction of the water layer, the product was Claisen distilled followed by fractionation which gave compound II, 76.0 g. (0.238 mole), b.p. 127° (7 mm.), $n^{20}\mathrm{D}$ 1.4240, in 48% yield.

E. Reaction of Chloromethylpentamethyldisiloxane in Ethyl Alcohol.—To a refluxing solution of sodiomalonic ester prepared from 1 mole of sodium and 1.2 moles of diethyl malonate in 500 ml. of absolute alcohol there were added 10 g. of sodium iodide (for the purpose of exchange with the chloromethyl groups) and 196 g. (1 mole) of chloromethylpentamethyldisiloxane. Formation of a white precipitate was immediately observed. Reaction appeared to be complete after 6 hours of stirring and heating as evidenced by the constancy of the volume of 0.05 *N* sulfuric required to neutralize 1-ml. aliquots of the reaction mixture. At the end of 6 hours the amount of standard acid required had decreased from 7.70 to 0.55 ml. The precipitated salts were removed from the product by centrifugation since filtration of the gel-like precipitate was not practical. The liquid product was then distilled through a Claisen flask and crudely separated into two fractions. Careful fractionation of the lower-boiling material gave 28 g. (21%) of trimethylethoxysilane as slightly impure trimethylethoxysilane–ethanol azeotrope containing 30% ethanol, b.p. 65° (724 mm.), $n^{20}\mathrm{D}$ 1.3720 (lit.[12] b.p. 66°, $n^{20}\mathrm{D}$ 1.3729), and chloromethyldimethylethoxysilane, 15.2 g. (10%), b.p. 58° (47 mm.), $n^{20}\mathrm{D}$ 1.4164; (lit.[11] b.p. 132° (741 mm.), $n^{25}\mathrm{D}$ 1.4124); we have obtained $n^{20}\mathrm{D}$ 1.4164 for this compound in numerous preparations using chloromethyldimethylchlorosilane and ethanol). Fractionation of the higher-boiling fraction gave 26.2 g. (13%) of unreacted diethyl malonate, b.p. 91° (13 mm.), $n^{20}\mathrm{D}$ 1.4151, 26.2 g. (9.6%) of diethyl dimethylethoxysilylmethylmalonate, b.p. 125° (4.5 mm.), $n^{20}\mathrm{D}$ 1.4299 (see below); and no compound II.

Hydrolysis and decarboxylation of the unfractionated products obtained from treatment of sodiomalonic ester, 2 moles, with an equivalent amount of chloromethylpentamethyldisiloxane in ethanol solvent, using the procedure described below for authentic compound II, gave only 3 g. of disiloxane diacid, compound I.

Synthesis of 1-Carboxy-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane (Compound IV).—In a 1-liter glass-jointed distillation flask were placed 120 g. (0.377 mole) of III, 500 ml. of glacial acetic acid and 150 ml. of concd. hydrochloric acid. The flask was then attached to a glass-helix packed fractionating column and heated to reflux for 12 hours. After removal of ethyl acetate and cooling, 62 g. of hard, shiny, white crystals separated and were filtered. Evaporation of the filtrate to a volume of 50 ml. yielded a second crop of crystals, 15 g. Recrystallization from petroleum ether (b.p. 67–92°) gave 75 g. of compound IV, m.p. 145°, 91% yield.

Anal. Calcd. for $C_8H_{18}Si_2O_3$: Si, 25.7; neut. equiv., 218. Found: Si, 26.1; neut. equiv., 218.

Preparation of 4,4,6,6-Tetramethyl-4,6-disila-5-oxanonanedioic Acid (Compound I).—Compound II, 192 g.,

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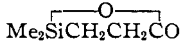
(12) R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944).

0.60 mole, together with 500 ml. of glacial acetic acid and 150 ml. of concd. hydrochloric acid was placed in a flask attached to a fractionation column and heated at reflux temperature for 24 hours. After slow distillation of the resulting ethyl acetate most of the acetic and hydrochloric acids were removed by distillation. The residue was then distilled through a Claisen flask under vacuum to yield 75 g. (0.58 mole) of the silalactone,  $Me_2SiCH_2CH_2CO$, which will be reported in a forthcoming publication as being the product obtained from heating compound I.[13] Treatment of the silalactone with 10 ml. of water followed by vigorous stirring gave 78 g. (0.281 mole) of compound I, m.p. and mixed m.p. 54°,[2] neutral equivalent 139 (calcd., 139), in 94% yield.

Synthesis of 1-Cyano-1-carbethoxy-3,3,5,5-tetramethyl-3,5-disila-4-oxahexane (Compound IX).—Ethyl cyanoacetate, 35 g. (0.31 mole), was added to 7.1 g. (0.31 mole) of sodium and 300 ml. of diethyl carbitol and the reaction mixture heated at 100° until all of the sodium had reacted. Unlike sodiomalonic ester which is completely soluble in warm diethyl carbitol, the present reaction gave an insoluble granular precipitate. The flask contents were cooled to room temperature and iodomethylpentamethyldisiloxane 86 g. (0.3 mole) was added over 5 minutes. The reaction mixture was then heated at 100° with stirring for 20 hours. Filtration followed by Claisen distillation and fractionation gave compound IX, 40.4 g. (0.148 mole), b.p. 140° (17 mm.), $n^{20}\mathrm{D}$ 1.4260, d^{20} 0.9605, in 50% yield.

Anal. Calcd. for $C_{11}H_{23}O_3Si_2N$: Si, 20.6; MR_{D}, 73.6. Found: Si, 20.8; MR_{D}, 73.1.

An attempt was made to obtain a saponification equivalent by heating the cyano ester for 1.5 hours on the steam-bath and then titrating with standard acid. The values obtained were 256 and 259 (theoretical for saponification of the ester function only is 273), thus indicating that very little hydrolysis of the nitrile group had taken place under these conditions.

Following the procedure detailed above for the preparation of compound I from compound II, the cyano ester was converted to compound I in 85% yield, m.p. and mixed m.p. 54°.

Preparation of 1-Carbethoxy-3,3,5,5-tetramethyl-3,5-disila-4-oxacyclohexane (Compound V).—Refluxing (18 hours) of a solution comprising 60 g. (0.275 mole) of the cyclic acid, compound IV, 500 ml. of absolute alcohol and 5 ml. of concd. hydrochloric acid, was followed by slow distillation (10 hours) in a fractionation column of ethanol and ethanol–water azeotrope. Fractionation under vacuum then gave compound V, b.p. 102° (11 mm.), $n^{20}\mathrm{D}$ 1.4392, d^{20} 0.9718, 65 g. (0.264 mole) in 96% yield.

Anal. Calcd. for $C_{10}H_{22}Si_2O_3$: Si, 22.8; sap. equiv., 247; mol. wt., 247; MR_{D}, 67.1. Found: Si, 23.0; sap. equiv., 246; mol. wt., 248; MR_{D}, 66.7.

Equilibration of Compound V with Hexamethyldisiloxane.—The cyclic monoester, compound V, 192 g. (0.777 mole), was added slowly to a mixture of hexamethyldisiloxane, 378 g. (2.33 moles) and 20 ml. of concd. sulfuric acid. The addition was carried out during 45 minutes with vigorous stirring at room temperature. No heat was evolved. The reaction mixture was then stirred at room temperature for 24 hours. The lower sulfuric acid layer was separated and then the product was washed with three 75-ml. portions of water. The product was then dried over potassium carbonate, and fractionation gave 99.9 g. (0.41 mole) of slightly impure recovered compound V, b.p. 109° (16 mm.), $n^{20}\mathrm{D}$ 1.4375 and the tetrasiloxane, 2,2,4,4,8,8,10,10-octamethyl-2,4,8,10-tetrasila-3,9-dioxa-6-carbethoxyundecane, 54.7 g. (0.135 mole), b.p. 115° (2 mm.), $n^{20}\mathrm{D}$ 1.4253, d^{20} 0.9073, 17.4% yield. Analytical data for compound VI are as follows.

Anal. Calcd. for $C_{16}H_{40}O_4Si_4$: Si, 27.5; sap. equiv., 409; MR_{D}, 116.0. Found: Si, 27.9; sap. equiv., 409; MR_{D}, 115.4.

Synthesis and Ring-closure of the Presumed Open-chain Intermediate in the Formation of Compound III.—A mixture of compound II, 96.0 g. (0.3 mole) and bis-(chloromethyl)-tetramethyldisiloxane, 104 g. (0.45 mole) to which 6 ml. of concd. sulfuric acid had been added, was stirred at room temperature for 20 hours. After separation of the sulfuric acid layer, the product was washed with three 30-ml. portions of salt solution. Addition of 50 ml. of benzene was followed by fractionation. After removal of chloromethylpentamethyldisiloxane (0.16 mole), bis-(chloromethyl)-tetramethyldisiloxane (0.252 mole), and compound II (0.076 mole), there was obtained 54.7 g. (0.154 mole) of compound VII, 1,1-dicarbethoxy-3,3,5,5-tetramethyl-3,5-disila-4-oxa-6-chlorohexane, b.p. 172° (16 mm.), $n^{20}\mathrm{D}$ 1.4405, d^{20} 1.052, in 51% yield.

Anal. Calcd. for $C_{13}H_{27}Si_2O_5Cl$: Si, 15.8; sap. equiv., 178; MR_{D}, 89.7. Found: Si, 16.3; sap. equiv., 176; MR_{D} 89.1.

Sodiomalonic ester was prepared from sodium metal, 4.0 g. (0.174 mole) and diethyl malonate, 28 g. (0.175 mole) in 100 ml. of diethyl carbitol in the usual manner. The reaction mixture was cooled to room temperature and compound VII, 60 g. (0.169 mole), was added during ten minutes. The reaction mixture was then heated to 100° with stirring and maintained at that temperature for 20 hours. After cooling, washing with three 50-ml. portions of water, and benzene extraction of the water-washings the product was fractionated. There was obtained 35.6 g. (0.112 mole) of cyclic diester, compound III, b.p. 152° (17 mm.), $n^{20}\mathrm{D}$ 1.4485, 66% yield.

Malonic Ester Synthesis with Chloromethylethoxysilanes. A. Reactions of Chloromethyldimethylethoxysilane in Ethanol and Diethyl Carbitol Solvents.—Sodiomalonic ester was prepared in the usual manner from 11.5 g. (0.5 mole) of sodium and diethyl malonate, 85 g. (0.53 mole) in 250 ml. of dry *ethanol*. Chloromethyldimethylethoxysilane, 76.3 g. (0.5 mole), was added during 15 minutes and the reaction mixture was then refluxed for 18 hours. After filtration, Claisen distillation followed by fractionation gave compound X, diethyl dimethylethoxysilylmethylmalonate, 83.1 g. (0.30 mole), b.p. 142° (15 mm.), $n^{20}\mathrm{D}$ 1.4295, d^{20} 1.001, in 60% yield.

Anal. Calcd. for $C_{12}H_{24}O_5Si$: Si, 10.2; sap. equiv., 138; MR_{D}, 71.6. Found: Si, 10.5; sap. equiv., 136; MR_{D}, 71.1.

Treatment of chloromethyldimethylethoxysilane, 61 g., (0.4 mole) with sodiomalonic ester prepared from 9.7 g. (0.42 mole) of sodium metal and 72 g. (0.45 mole) of diethyl malonate in 200 ml. of diethyl carbitol gave compound X in 61% yield after stirring and heating at 120° for 18 hours followed by filtration and fractionation.

As further proof for the assigned structure of compound X, 4,4,6,6-tetramethyl-4,6-disila-5-oxanonanedioic acid was prepared from it as follows.

Compound X, 41.1 g. (0.149 mole), was treated with glacial acetic acid and concd. hydrochloric acid by the procedure described above for the conversion of compound II to the disiloxane–diacid (compound I). There was obtained a 95% yield of compound I, m.p. and mixed m.p. 54°.

B. Reactions of Chloromethylmethyldiethoxysilane in Ethanol and Diethyl Carbitol.—Sodiomalonic ester was prepared in the usual manner from 23 g. (1 mole) of sodium and diethyl malonate, 190 g. (1.2 moles) in 500 ml. of dry ethanol. After heating to reflux, 10 g. of sodium iodide was added as a catalyst followed by 182.6 g. (1 mole) of chloromethylmethyldiethoxysilane. From the titer of 1-ml. aliquots, the reaction was found to be almost complete after 14 hours. The reaction mixture was filtered and Claisen distilled. Fractionation then gave compound XI, diethyl methyldiethoxysilylmethylmalonate, 199.5 g. (0.66 mole), b.p. 172° (26 mm.), $n^{20}\mathrm{D}$ 1.4258, d^{20} 1.0264, in 66% yield.

Anal. Calcd. for $C_{13}H_{26}O_6Si$: Si, 9.15; sap. equiv., 153; MR_{D}, 77.1. Found: Si, 9.23; sap. equiv., 157; MR_{D}, 76.4.

Sodiomalonic ester in diethyl carbitol, when treated with chloromethylmethyldiethoxysilane in the usual manner, gave compound XI in 61% yield.

Chloromethylmethyldiethoxysilane, b.p. 77° (38 mm.), Si, 14.1% (calcd., Si, 14.2%), was prepared by conventional ethanolysis of chloromethylmethyldichlorosilane in 71% yield.

Synthesis of Ethyl Methyldiethoxysilylmethylcyanoacetate (Compound XII).—Sodiocyanoacetic ester was prepared in the usual manner from sodium, 23 g. (1 mole) and ethyl cyanoacetate, 124.3 g. (1.10 moles), in 500 ml. of dry ethanol. This was heated to reflux and 10 g. of sodium iodide was added as a catalyst. Addition of chloromethylmethyldiethoxysilane, 182 g. (1 mole), over a period of 30 minutes was followed by heating to reflux and stirring for 30

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[13] Unpublished work of L. H. Sommer and R. P. Pioch.

hours. Filtration and Claisen distillation followed by fractionation gave compound XII, ethyl methyldiethoxysilylmethylcyanoacetate 120 g. (0.46 mole), b.p. 140° (8 mm.), n^{20}_D 1.4291, d^{20} 1.017, in 46% yield.

Anal. Calcd. for $C_{11}H_{21}O_4SiN$: Si, 10.8; sap. equiv. (hydrolysis of ester group only), 259; MR_D, 65.73. Found: Si, 11.0; sap. equiv., 253; MR_D, 65.74.

To prevent hydrolysis of the nitrile group very mild conditions were used for the determination of the saponification equivalent. Samples were allowed to stand at room temperature with 1 *N* potassium hydroxide in butyl cellosolve for 1 hour.

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[CONTRIBUTION FROM THE NAVAL STORES STATION, U. S. DEPARTMENT OF AGRICULTURE[1]]

Acid Isomerization of Levopimaric Acid

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The isomerization of levopimaric acid with hydrochloric, acetic, nitric, sulfuric, phosphoric and chloroacetic acids was followed by observing the changes in specific rotation. The hydrochloric acid isomerization was studied closely by stopping the isomerization at several points and analyzing the products by partition chromatography, ultraviolet absorption analysis, and levopimaric acid determination. In all these products palustric, *l*-abietic and neoabietic acids were present. Isomerization with acetic and sulfuric acids also produced these acids, although the maximum amounts of palustric and neoabietic acids produced by acid isomerization were much smaller than the amounts produced by thermal isomerization of levopimaric acid. Isomerization of *l*-abietic acid with hydrochloric acid yielded a product that contained palustric and neoabietic acids.

The work described in this paper was undertaken in order to establish the composition of the products formed by acid-catalyzed isomerization of levopimaric acid. Previous investigations of the acid isomerization of levopimaric acid[2-4] established that when hydrochloric acid was used as the catalyst, the change in specific rotation was observed to pass through a minimum, and Dupont[2] suggested the possibility of the formation of an unstable isomer at this point.

The discovery of palustric acid[5] in pine oleoresins and rosins suggested that this acid might be the intermediate isomer in the isomerization of levopimaric acid to *l*-abietic acid. Investigations with partition chromatography showed that a complete analysis of the isomerization products of levopimaric acid was possible. Studies of the products of thermally isomerized levopimaric acid[6] in this Laboratory established that palustric acid is one of the intermediate products of the thermal isomerization of levopimaric acid to *l*-abietic acid. A similar study has been made of the acid isomerization of levopimaric acid.

The changes in specific rotation during the isomerization of levopimaric acid with hydrochloric, acetic, nitric, phosphoric, sulfuric and chloroacetic (in two solvents) acids were followed (Table I). Concentrations of the acid catalyst were chosen so that the minimum point of specific rotation would be reached in two or three hours whenever possible. Since the specific rotations of the resin acids differ in various solvents and since three different solvents were used in these isomerizations, the specific rotations of *l*-abietic, levopimaric and neoabietic acids in the more common organic solvents are listed in Table II.

TABLE I

CHANGES IN SPECIFIC ROTATION[a] DURING THE ISOMERIZATION OF LEVOPIMARIC ACID WITH ACIDS

Acid	HCl	HCl	H_2SO_4	Acetic	Acetic	H_3PO_4	Chloroacetic	Chloroacetic	HNO_3
Normality	0.12	0.12	0.25	5	17.6	5.3	4.5	2.2	0.25
Solvent	95% EtOH	Abs. EtOH	Abs. EtOH	Abs. EtOH	Glacial acetic acid	Abs. EtOH	Abs. EtOH	Benzene	95% EtOH
Hours isomerized	Specific rotation								
0[b]	−275°	−275°	−275°	−265°	−275°	−275°	−275°	−250°	−275°
1/4	−159	− 78	−110			−160	−206	−124	−208
0.5	−135	− 71	−100			−143	−182	− 96	−188
1	− 91	− 70	− 94	−271	−252	−109	−174	− 48	−156
1.5	− 80	− 72	− 94		−247	− 95	−161	− 37	−133
2	− 74	− 76	− 94		−239	− 90	−147	− 34	−125
3	− 74	− 79	− 94		−228	− 88	−126	− 34	−106
4	− 74	− 84	− 94		−216	− 87	−112	− 34	− 93
5	− 74	− 87			−205	− 87	−103	− 34	− 93
8	− 74	− 88	− 93		−181	− 87	− 95	− 34	− 89
19	− 81			−255	−114				
24	− 88	− 93	− 92		−102	− 88	− 91	− 35	− 89
48	− 93	− 94	− 93		− 77	− 88	− 92	− 36	
72				−156	− 72				
96					− 72				

[a] Resin acids exhibit different specific rotations in different solvents. [b] Extrapolated values.

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[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] G. Dupont, *Compt. rend.*, **172**, 1373 (1921).

[3] R. Lombard, *Bull. soc. chim. France*, 1186 (1948).

[4] P. F. Ritchie and L. F. McBurney, THIS JOURNAL, **71**, 3736 (1949).

[5] V. M. Loeblich, D. E. Baldwin and Ray V. Lawrence, *ibid.*, **77**, 2823 (1955).

[6] V. M. Loeblich, D. E. Baldwin, R. T. O'Connor and Ray V. Lawrence, *ibid.*, **77**, 6311 (1955).