mole, of compound III. There was then added over a period of 15 minutes 9.2 g., 0.40 atom, of sodium metal, a vigorous evolution of hydrogen occurring. After heating at reflux to complete the reaction, the contents of the flask were cooled to 0° and a solution of 57.5 g., 0.42 mole, of freshly distilled bromoacetone in an equal volume of dry ether was added dropwise. The reaction mixture was then permitted to come to room temperature, refluxed for one hour, and a solution of 37 ml. of concd. hydrochloric acid in 100 ml. of water was added slowly. Separation of the ether layer and ether extraction of the acidic aqueous layer were followed by drying and then distillation of the ether, the last traces of ether being removed under vacuum. There remained 116 g. of crude compound IV which was used directly without further purification.

Refluxing a solution of 58 g. of the above product in 50 ml. of ethanol with 200 ml. of an 8% aqueous sodium hydroxide solution for 1.75 hours was followed by cooling, acidification with dilute sulfuric acid and extraction with two 50-ml. portions of ether. After drying of the product and distillation of the ether, fractionation gave compound V, 14.3 g., 0.079 mole, b.p. 118° at 21 mm., $n^{20}\text{D}$ 1.4827, 39% yield based on the amount of crude compound IV used. This material had a yellow-green color and a very pleasant odor.

Anal. Calcd. for $C_{10}H_{18}OSi$: Si, 15.4. Found: Si, 15.3.

The oxime was prepared and after recrystallization from methanol there was obtained a white crystalline solid, m.p. 108–108.5°.

Anal. Calcd. for $C_{10}H_{19}ONSi$: Si, 14.2. Found: Si, 14.2.

When a mid-fraction from the above distillation was chilled in a Dry Ice–ether bath it solidified. After warming to room temperature, melting on the steam-bath and cooling to room temperature the material again solidified. Recrystallization from hexane gave beautiful white crystals, m.p. 58–58.5°, subliming at 45° and having the same odor as the original liquid. The ultraviolet spectrum of the solid in absolute ethanol was the same as that for the liquid, maximum at 248 mμ and log ε 4.08. Thus pure compound V is a solid, m.p. 58–58.5°.

Synthesis of Ethyl 2-(β-Trimethylsilyl-ethyl)-5-methyl-3-furoate (VI).—In a 500-ml. round-bottomed flask fitted with a condenser there were placed 60 g. of crude compound IV, 10 ml. of concd. sulfuric acid, 150 ml. of glacial acetic acid and 20 ml. of water. The solution was refluxed for 1.25 hours, cooled, and then the organic layer was separated. The aqueous layer was extracted with three 100-ml. portions of ether and the combined ether and organic layers washed with water, dried, and then distilled to remove the ether. Fractionation gave 21.4 g., 0.0843 mole, 38% yield of compound VI, b.p. 90° at 2 mm., $n^{20}\text{D}$ 1.4695.

Anal. Calcd. for $C_{13}H_{22}O_3Si$: Si, 11.03; mol. wt., 254. Found: Si, 11.3; mol. wt. in benzene, 254, 257.

The ultraviolet absorption spectrum of the furan in absolute ethanol shows a maximum at 257 mμ and log ε 3.74.

Synthesis of 9,9-Dimethyl-9-siladecane-2,6-dione (VII).—To a solution of 0.05 mole of sodium ethoxide in 15 ml. of ethyl alcohol there was added rapidly a solution of 64.8 g., 0.30 mole, of compound III in 200 ml. of dry ether. A solution of 23.1 g., 0.33 mole, of freshly distilled methyl vinyl ketone in 500 ml. of dry ether was then added during 1.5 hours at room temperature with stirring. The reaction mixture was stirred for an additional 2.5 hours after addition was completed and a solution of 10 ml. of glacial acetic acid in 100 ml. of water was then added and the ether layer separated, washed with water and dried. After distillation of the ether, fractionation gave a mid-fraction consisting mostly of solid and liquid fractions of varied refractive index. Recrystallization of the mid-fraction from hexane gave 9.2 g. of glistening white plates, m.p. 49.5–50°.

Anal. Calcd. for $C_{11}H_{22}O_2Si$: Si, 13.05. Found: Si, 13.1.

A disemicarbazone was prepared.

Anal. Calcd. for $C_{13}H_{28}O_2N_6Si$: Si, 8.53. Found: Si, 8.68.

The monosemicarbazone requires 10.32% Si.

Synthesis of 3-(β-Trimethylsilylethyl)-cyclohex-2-ene-1-one (VIII).—A solution of 2.14 g., 0.01 mole, of compound VII in 25 ml. of 5% alcoholic potassium hydroxide was refluxed for one hour. The solution was cooled and extracted three times with ether and the combined ether layers washed with water and dried over sodium sulfate. The ether and residual ethanol were removed at atmospheric pressure and the crude organic material was fractionated at reduced pressure. There was obtained 1.5 g. of compound VIII, b.p. 125° at 6 mm., $n^{20}\text{D}$ 1.4888.

Anal. Calcd. for $C_{11}H_{20}OSi$: Si, 14.30. Found: Si, 14.6.

The ultraviolet absorption spectrum had a maximum at 238 mμ, log ε 4.13. A semicarbazone readily was prepared and had m.p. 204–207°. The ultraviolet absorption in ethanol for this semicarbazone showed a maximum at 266 mμ.

STATE COLLEGE, PENNA.

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

Malonic Ester Syntheses with Organosilicon Compounds. New Silicon-containing Malonic Esters, Mono- and Dicarboxylic Acids, Barbituric Acids and a Disiloxanetetracarboxylic Acid[1]

BY L. H. SOMMER, G. M. GOLDBERG, G. H. BARNES AND L. S. STONE, JR.

RECEIVED OCTOBER 1, 1953

The malonic ester synthesis has been successfully applied in the preparation of four monosubstituted malonates containing the following organosilicon groups: Me_3SiCH_2–, $C_6H_5Me_2SiCH_2$–, $Me_3SiCH_2SiCH_2$– and $Me_3SiCH_2CH_2CH_2$–. Methyl, allyl and cyanoethyl groups, but not a second trimethylsilylmethyl group, could be introduced into trimethylsilylmethylmalonic ester. The series of ω-trimethylsilyl-substituted monocarboxylic acids has been extended to include the valeric and caproic acid derivatives, and properties for all of the acids in the series are compared. Trimethylsilylmethyl derivatives of glutaric and barbituric acid, a disiloxanetetracarboxylic acid and a disilaheptanoic acid are described.

In this paper we report the synthesis of silicon-containing mono- and disubstituted malonic esters; their hydrolysis and decarboxylation to give monocarboxylic acids; their conversion to barbituric acids by treatment with urea, and an example of cyanoethylation with acrylonitrile to give, after hydrolysis and decarboxylation, a trimethylsilylmethylglutaric acid. Two new aliphatic organofunctional siloxanes are also reported.

Organosilicon Malonates.—Reaction of ethyl malonate with haloalkylsilanes having structures I–IV proceeded smoothly in the presence of sodium ethoxide using ethyl alcohol as the solvent.

Me_3SiCH_2Cl (I) $Me_3SiCH_2CH_2CH_2Br$ (III)
$C_6H_5Me_2SiCH_2Cl$ (II) $Me_3SiCH_2SiMe_2CH_2I$ (IV)

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[1] Paper 41 in a series on organosilicon chemistry. For Paper 40 see THIS JOURNAL, 76, 1606 (1954).

TABLE I

ORGANOSILICON MALONATES $R-C(CO_2Et)_2-R'$

Cpd.	Structure R	R'	Yield, %	B.p., °C.	Mm.	$n^{20}D$	d^{20}	MR_D Found	MR_D Calcd.	Sapn. equiv. Found	Sapn. equiv. Calcd.	Silicon, % Found	Silicon, % Calcd.
V	Me_3SiCH_2	H	67	119	13	1.4312	0.9680	65.9	66.1	124	123	11.4	11.4
VI	Me_3SiCH_2	CH_3	72	122	15	1.4352	0.9663	70.3	70.7	130	130	10.7	10.8
VII	Me_3SiCH_2	$CH_2=CH-CH_2$	71	89	2	1.4472				142	143	9.8	9.8
VIII	$C_6H_5Me_2SiCH_2$	H	73	132	1	1.4900	1.042	85.6	86.1	153	154	9.2	9.1
IX	$Me_3SiCH_2Me_2SiCH_2$	H	61	88	1	1.4460	0.9516	89.3	89.5	159	159	17.6	17.5
X	$Me_3SiCH_2CH_2CH_2$	H	63	114	2	1.4330	0.9472	75.3	75.4	137	137	10.3	10.2

Yields of the monosubstituted malonates obtained with these halides compare favorably with those obtained using more conventional alkyl halides, as shown in Table I, thus indicating that no significant amount of carbon–silicon cleavage occurred in these reactions. As shown previously,[2] the structure Si–C–CO_2Et readily undergoes cleavage of the carbethoxymethyl group from silicon with electrophilic and nucleophilic reagents. Therefore, organosilicon malonates which might be obtained by treatment of R_3SiCl with malonic ester would be of little use for further synthesis, and organosilicon malonates of the type here reported comprise structures having the silicon atom in the most proximate relation to the malonic ester grouping compatible with chemical stability. Further, β-haloalkylsilanes, which have the structure Si–C–C–X, react with strong as well as weak bases to give very rapid β-eliminations involving silicon, resulting in cleavage of the haloalkyl group from silicon with formation of halide ion and olefin,[3] thereby making necessary the use of a γ-haloalkylsilane (III) as the next useful higher homolog of compound I.

Treatment of sodiotrimethylsilylmethylmalonic ester with methyl iodide and allyl bromide gave compounds VI and VII, respectively, in excellent yield. Sodium ethoxide and an ethanol solvent also were used in these preparations.

When an attempt was made to introduce a second trimethylsilylmethyl group into the malonic ester molecule by treatment of sodiotrimethylsilylmethylmalonic ester with chloromethyltrimethylsilane, half of the halide used was recovered as such or in the form of trimethylsilylmethyl ethyl ether, the product of a Williamson type reaction of the halide with sodium ethoxide. Some alkylation may have taken place since only 63% of the ethyl trimethylsilylmethylmalonate was recovered. However, no constant-boiling fraction was obtained from the products boiling above this ester.

Organosilicon Monocarboxylic Acids.—In a previous publication we reported that sodioacetoacetic ester reacts with iodomethyltrimethylsilane in the presence of excess sodium ethoxide to give a 70% yield of ethyl β-trimethylsilylpropionate.[4] This ester was hydrolyzed to β-trimethylsilylpropionic acid in 89% yield. Thus, the over-all yield of the acid by this procedure is 62%. In extension of previous work which gave a 69% yield of β-trimethylsilylpropionic acid as prepared by the malonic ester synthesis from chloromethyltrimethylsilane without isolation of the intermediate ester,[5] compounds V, VI, VII, VIII, IX and X were converted to the corresponding monocarboxylic acids.[6]

With the synthesis of 5-trimethylsilylvaleric acid from compound X, a series of ω-trimethylsilyl-substituted straight-chain carboxylic acids of the general formula $Me_3Si(CH_2)_nCO_2H$ was complete through a value of $n = 4$. To extend this series to the next higher member, the Grignard reagent of 5-bromopentyltrimethylsilane[7] was carbonated with Dry Ice giving 6-trimethylsilylcaproic acid. Table II gives melting points and dissociation constants for this series of acids. It is of some interest that the alternating effect characteristic of the melting points of ordinary *n*-carboxylic acids is not found in this series.

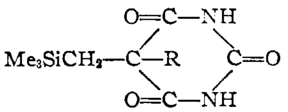
TABLE II

$Me_3Si(CH_2)_nCO_2H$

n	M.p., °C.	Solubility, g./liter	$K \times 10^5$
1[a]	40	12.01	0.60
2[a]	22	2.04	1.24
3[b]	4	0.58	1.30
4	−2	.19	1.09
5	−7.5	.06	0.87

[a] Ref. 12. [b] Ref. 9a.

Organosilicon Barbituric Acids.—As a beginning study in the preparation of silicon-containing structures that are of interest from the standpoint of physiological properties, we have synthesized three silicon-containing barbituric acids by reaction of compounds V, VI and VII with urea, giving compounds XI, XII and XIII, respectively.



XI, R = H—
XII, R = CH_3—
XIII, R = $CH_2=CH-CH_2$—

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[2] J. R. Gold, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **70**, 2874 (1948).

[3] L. H. Sommer, D. L. Bailey and F. C. Whitmore, *ibid.*, **70**, 2869 (1948).

[4] L. H. Sommer and N. S. Marans, *ibid.*, **72**, 1935 (1950).

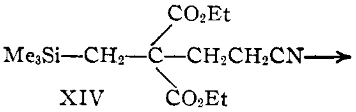
[5] L. H. Sommer and J. Rockett, *ibid.*, **73**, 5130 (1951).

[6] While the yields of desired product in the acetoacetic ester synthesis compare favorably with those obtained by the malonic ester method, we have found the latter to be more convenient in relatively large-scale preparations. A further advantage of the malonic ester synthesis over the acetoacetic ester method lies in the use of chloromethyltrimethylsilane and chloromethylphenyldimethylsilane in the former synthesis; the chloromethylsilanes give virtually none of the desired product in the acetoacetic ester synthesis, a Williamson type reaction with sodium ethoxide comprising the major reaction path. Use of compound IV instead of the corresponding chloride resulted from the availability of the former at the time this work was done.

[7] L. H. Sommer, R. E. Van Strien and F. C. Whitmore, THIS JOURNAL, **71**, 3056 (1949).

The physiological effects of these substances are being studied and will be reported at a later date.

Organosilicon Di- and Tetracarboxylic Acids and the Ethyl Esters.—Cyanoethylation of ethyl trimethylsilylmethylmalonate (V) with acrylonitrile in a dioxane solvent in the presence of Triton B gave ethyl trimethylsilylmethyl-2-cyanoethylmalonate (XIV), which upon refluxing with a mixture of hydrochloric and acetic acids gave a 67% yield of α-trimethylsilylmethylglutaric acid (XV),[8] m.p. 62–63°.



$$\mathrm{Me_3Si{-}CH_2{-}\overset{CO_2Et}{\underset{CO_2Et}{C}}{-}CH_2CH_2CN} \longrightarrow$$

XIV

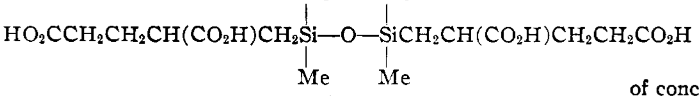
$$\mathrm{Me_3SiCH_2CH(CO_2H)CH_2CH_2CO_2H}$$

XV

Diethyl α-trimethylsilylmethylglutarate (XVI) and the anhydride of α-trimethylsilylmethylglutaric acid, compound XVII were prepared from compound XV by conventional procedures.

In extension of a new reaction in organosilicon chemistry which involves cleavage of one methyl group from trimethylsilyl, Me₃Si, by concd. sulfuric acid,[9] compound XV was converted to a disiloxanetetracarboxylic acid (XVIII).

$$\mathrm{2Me_3SiCH_2CH(CO_2H)CH_2CH_2CO_2H} \xrightarrow[(2)\ \mathrm{H_2O}]{(1)\ \mathrm{H_2SO_4}}$$



$$\mathrm{HO_2CCH_2CH_2CH(CO_2H)CH_2\overset{Me}{\underset{Me}{Si}}{-}O{-}\overset{Me}{\underset{Me}{Si}}CH_2CH(CO_2H)CH_2CH_2CO_2H}$$

XVIII

Compound XVIII is a micro-crystalline white solid, m.p. 85–86°. Methyl–silicon cleavage of compound XVI with sulfuric acid gave the tetraethyl ester derived from XVIII, as an oil (XIX).

Experimental

Haloalkylsilanes.—The synthesis of compound I and III has been reported previously.[7,10] Compound II, chloromethyldimethylphenylsilane, was prepared in 67–76% yields from the reaction of phenylmagnesium bromide with chloromethyldimethylchlorosilane using a procedure similar to that employed for compound I. Compound II has b.p. 135° (48 mm.), $n^{20}\mathrm{D}$ 1.5218, d^{20} 1.031, MR_D 54.63 (calcd. 54.94).

Anal. Calcd. for $\mathrm{C_9H_{13}SiCl}$: Cl, 19.2; Si, 15.2. Found: Cl, 19.3; Si, 15.4.

Compound IV was prepared in 90% yield from the reaction of 2,2,4,4-tetramethyl-2,4-disila-1-chloropentane[11] with sodium iodide in dry acetone. Compound IV has b.p. 98° (15 mm.), $n^{20}\mathrm{D}$ 1.4945, d^{20} 1.257, MR_D 66.37 (calcd. 66.51).

Anal. Calcd. for $\mathrm{C_7H_{19}Si_2I}$: Si, 18.9. Found: Si, 19.1.

Organosilicon Malonates.—The synthesis of compounds V and VI will be described as representative of the procedures employed for the malonates listed in Table I. To a solution of 1 mole of sodium ethoxide in 500 ml. of absolute ethanol was added 168 g., 1.05 moles, of ethyl malonate during 30 minutes. Heat was then applied by use of a steam-bath and 122.5 g., 1.0 mole, of compound I was added over a period of one hour. After refluxing for 24 hours, the reaction mixture was made acid to litmus by addition of 1.5 ml. of glacial acetic acid and most of the ethanol was then distilled. The residual salts were dissolved in 250 ml. of water and the resulting product was extracted with two 100-ml. portions of ether and one 100-ml. portion of benzene. Combination of the extracts and distillation of mixed solvents was followed by fractionation of the residue to give compound V. In addition to the latter, there was obtained a 7% yield of ethyl β-trimethylsilylpropionate[4] produced by a cleavage of compound V.

$$\mathrm{Me_3SiCH_2CH(CO_2Et)_2 + EtOH} \xrightarrow{\mathrm{NaOEt}} \mathrm{(CH_3)_2SiCH_2CH_2CO_2Et + (EtO)_2CO}$$

Compound V was smoothly alkylated with methyl iodide the following procedure: To a solution of 0.25 mole of sodium ethoxide in 125 ml. of ethanol there was added during 10 minutes 61.5 g., 0.25 mole, of compound V. This was followed by addition of 39.0 g., 0.27 mole, of methyl iodide during 25 minutes. After refluxing for 36 hours, the ethanol was distilled, the residual salts dissolved in water and compound VI was isolated in the manner described above for compound V.

Organosilicon Monocarboxylic Acids.—The conversion of compound VI to the corresponding monocarboxylic acid will be described as representative of the procedure used. In a 200-ml. round-bottomed flask fitted with a reflux condenser there was placed a solution of 40 g., 0.72 mole, of potassium hydroxide in 40 ml. of water. The solution was heated to 90° and there was added through the condenser 47 g., 0.18 mole, of compound VI. Saponification took place rapidly. The resulting solution was heated at 90° for one hour and then the condenser was removed and the solution evaporated to dryness. The residual salts were dissolved in 100 ml. of water and this solution was acidified by the addition of 80 ml. of concd. hydrochloric acid. The layers were separated and the water layer was extracted with two 50-ml. portions of ether. After removal of ether by distillation, the residue was returned to the original flask and decarboxylated by heating at 150° for eight hours. Benzene, 50 ml., was then added and distilled to remove water, and the dry acid was fractionated. There was obtained an 85.5% yield of α-methyl-β-trimethylsilylpropionic acid, b.p. 118° (13 mm.), $n^{20}\mathrm{D}$ 1.4312, d^{20} 0.9102, MR_D 45.55 (calcd. 45.60).

Anal. Calcd. for $\mathrm{C_7H_{16}O_2Si}$: Si, 17.5; neut. equiv., 160.3. Found: Si, 17.5; neut. equiv., 159.3.

β-Trimethylsilylpropionic acid[12] was prepared from compound V in 67% yield, b.p. 130° (34 mm.), $n^{20}\mathrm{D}$ 1.4279.

β-Phenyldimethylsilylpropionic acid[4] was prepared from compound VII in 86% yield by a procedure which differed from that described above in one important respect. Acidification with concd. hydrochloric acid prior to decarboxylation was performed while cooling the reaction product in a salt–ice-bath to prevent phenyl–silicon cleavage. The product obtained when this precaution was not observed is a silalactone, $\mathrm{Me_2\underbrace{SiCH_2CH_2CO}_{O}}$, which has since been prepared by a better method and will be reported in a forthcoming publication. The properties of the β-phenyldimethylsilylpropionic acid as prepared in the present work are b.p. 116° (1 mm.), $n^{20}\mathrm{D}$ 1.5148 as compared to b.p. 132° (2 mm.), $n^{20}\mathrm{D}$ 1.5149 given in ref. 4.

4,4,6,6-Tetramethyl-4,6-disilaheptanoic acid was prepared from compound IX in 46% yield and had b.p. 123° (4 mm.), m.p. −2°, $n^{20}\mathrm{D}$ 1.4521, d^{20} 0.9165, MR_D 217.9 (calcd. 218.4).

Anal. Calcd. for $\mathrm{C_9H_{22}O_2Si_2}$: Si, 25.7; neut. equiv., 218.4. Found: Si, 25.3; neut. equiv., 217.9.

5-Trimethylsilylvaleric acid was prepared from compound X in 74.7% yield and had b.p. 134° (14 mm.), $n^{20}\mathrm{D}$ 1.4358, d^{20} 0.9047, MR_D 50.35 (calcd. 50.23).

Anal. Calcd. for $\mathrm{C_8H_{18}O_2Si}$: Si, 16.1; neut. equiv., 174.3. Found: Si, 16.2; neut. equiv., 174.9.

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[8] The synthesis of 3-trimethylsilyladipic acid from oxidation of 4-trimethylsilylcyclohexanol with nitric acid has been reported; J. L. Speier, THIS JOURNAL, **74**, 1003 (1952).

[9] (a) L. H. Sommer, N. S. Marans, G. M. Goldberg, J. Rockett and R. P. Pioch, *ibid.*, **73**, 882 (1951); (b) L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, *ibid.*, **75**, 2932 (1933); (c) L. H. Sommer, W. P. Barie and J. R. Gould, *ibid.*, **75**, 3765 (1953).

[10] F. C. Whitmore, L. H. Sommer and J. Gold, *ibid.*, **69**, 1976 (1947).

[11] L. H. Sommer, F. A. Mitch and G. M. Goldberg, *ibid.*, **71**, 2746 (1949).

[12] L. H. Sommer, J. R. Gold, G. M. Goldberg and N. S. Marans, *ibid.*, **71**, 1509 (1949).

6-Trimethylsilylcaproic acid was prepared by carbonation of the Grignard reagent derived from 5-bromopentyltrimethylsilane in 53% yield and had b.p. 260° (738 mm.), $n^{20}D$ 1.4390, d^{20} 0.8923, *MR*D 55.50 (calcd. 54.98).

Anal. Calcd. for $C_9H_{20}O_2Si$: Si, 14.9; neut. equiv., 188.3. Found: Si, 14.9; neut. equiv., 189.0.

Dissociation constants for 5-trimethylsilylvaleric acid and 6-trimethylsilylcaproic acid, as given in Table II, were determined by the method used in ref. 12.

Organosilicon Barbiturates.—The synthesis of 5-trimethylsilylmethylbarbituric acid will be described as representative of the procedure used. To a solution of 0.5 mole of sodium ethoxide in 350 ml. of absolute ethanol was added 123 g., 0.5 mole, of compound V in 10 minutes. To the stirred solution of sodiotrimethylsilylmethylmalonate there was then added 30.0 g., 0.5 mole, of urea dissolved in 250 ml. of ethanol at 70°. The reaction mixture was heated at reflux temperature for 12 hours during which time a white solid precipitated. A solution of 45 ml. of concd. hydrochloric acid in 500 ml. of warm (50°) water was then added to the reaction mixture. The white solid was filtered, washed with three 100-ml. portions of cold water and dried by means of an infrared lamp, giving 75.6 g., 71% yield of compound XI, m.p. 240–241° dec.

Anal. Calcd. for $C_8H_{14}O_3N_2Si$: Si, 13.10. Found: Si, 13.05.

Compound XII, 5-methyl-5-trimethylsilylmethylbarbituric acid, was prepared from compound VI in 51% yield, m.p. 180–181°.

Anal. Calcd. for $C_9H_{16}O_3SiN_2$: Si, 12.3. Found: Si, 12.7.

Compound XIII, 5-allyl-5-trimethylsilylmethylbarbituric acid, was prepared from compound VII in 57% yield, m.p. 116–118°.

Anal. Calcd. for $C_{11}H_{18}O_3N_2Si$: Si, 11.0. Found: Si, 10.7.

Synthesis of Ethyl Trimethylsilylmethyl-2-cyanoethyl Malonate (XIV).—Compound V, 246 g. (1.0 mole), Triton B (10 ml.) and dioxane (50 ml.) were heated to 80° and acrylonitrile, 60 g. (1.14 mole) was added with stirring over a period of 10 minutes. After heating at 110° for 24 hours the product was separated from the aqueous layer, acidified with concd. hydrochloric acid, dried, and then fractionated. There was obtained 275 g. of compound XIV, a clear, colorless liquid, b.p. 138° (1.2 mm.), $n^{20}D$ 1.4519, 92% yield.

Anal. Calcd. for $C_{14}H_{25}NO_4Si$: Si, 9.37. Found: Si, 9.35.

α-Trimethylsilylmethylglutaric Acid (XV).—Compound XIV, 75 g., 0.25 mole, 65 ml. of concd. hydrochloric acid and 100 ml. of glacial acetic acid were placed in a 500-ml. flask attached to a distilling column. The mixture was refluxed for 94 hours while removing ethyl acetate at frequent intervals. Next, the excess of hydrochloric acid and acetic acid was removed by distillation. The residue was then diluted with ether and filtered to remove 12.6 g. of ammonium chloride. The ether was evaporated on the steam-bath, and the residue recrystallized from petroleum ether, giving 36.4 g., 67% yield of compound XV, m.p. 61.5–62.5°. Recrystallization from petroleum ether gave m.p. 63–64°.

Anal. Calcd. for $C_9H_{18}O_4Si$: Si, 12.8; neut. equiv., 109. Found: Si, 12.8; neut. equiv., 109.

5,5,7,7-Tetramethyl-5,7-disila-6-oxa-1,3,9,11-hendecanetetracarboxylic Acid (XVIII).—Compound XV, 22 g., 0.1 mole, was placed in a 500-ml. three-necked flask equipped with a mercury-sealed stirrer, a dropping funnel and a water-cooled condenser. The flask was immersed in an ice-bath and concd. sulfuric acid was added from the dropping funnel. After seven hours of stirring at ice-temperature, the reaction product was poured onto ice giving an organic layer which was a viscous liquid. The latter was separated and dissolved in ether and the aqueous layer was extracted twice with ether. After removal of the ether, a viscous liquid was obtained which when seeded with a small amount of solid compound XVIII gave a micro-crystalline white solid, m.p. 82–84°, 17 g., 80% yield of compound XVIII. This compound could not be recrystallized, but after washing alternately with benzene and water the m.p. was 85–86°.

Anal. Calcd. for $C_{16}H_{30}O_9Si_2$: Si, 13.3; neut. equiv., 106. Found: Si, 13.3; neut. equiv., 107.

In the first preparation of compound XVIII considerable difficulty was encountered in effecting crystallization. After standing at −5° for two months, the substance finally solidified. Recrystallization from organic solvents could not be effected because of a strong tendency of compound XVIII to come out of solution as an oil.

Tetraethyl 5,5,7,7-Tetramethyl-5,7-disila-6-oxa-1,3,9,11-hendecanetetracarboxylate (XIX).—Diethyl α-trimethylsilylmethylglutarate was prepared by refluxing compound XV, 21.2 g., with a mixture of ethanol and benzene in the presence of 0.2 ml. of hydrochloric acid. After removal of water as an azeotrope and distillation of the excess ethanol and benzene, fractionation gave 18.1 g., 66% yield of compound XVI, b.p. 122° (4.5 mm.), $n^{20}D$ 1.4598.

Anal. Calcd. for $C_{13}H_{26}O_4Si$: Si, 10.2; sapn. equiv., 137. Found: Si, 10.3; sapn. equiv., 137.

The above ester, 17.6 g., was treated with concd. sulfuric acid by the procedure described above for the corresponding acid. After addition of the product to ice, the organic product was extracted with ether and the ether solution was shaken with aqueous potassium hydroxide sufficient to neutralize any residual acid. The ether solution was then dried and fractionated giving 5.5 g. of compound XIX, b.p. 205° (2 mm.), $n^{20}D$ 1.4500, a 31% yield. This ester was also prepared by esterification of compound XVIII.

Anal. Calcd. for $C_9H_{18}O_4Si$: Si, 10.5; sapn. equiv., 134. Found: Si, 10.6; sapn. equiv., 136.

α-Trimethylsilylmethylglutaric Anhydride (XVII).—α-Trimethylsilylmethylglutaric acid, 11.7 g., 0.03 mole, was refluxed with 11 g. of acetyl chloride until HCl evolution ceased. Fractionation of the product gave 7.3 g. of compound XVII, a clear, colorless liquid, b.p. 142° (5 mm.), $n^{20}D$ 1.4712.

Anal. Calcd. for $C_9H_{16}O_3Si$: Si, 14.0; neut. equiv., 100. Found: Si, 13.9; neut. equiv., 101.

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