was quickly pipetted in and the reaction mixture shaken vigorously. At suitable intervals, 5-ml. samples were withdrawn for titration of the developed acid using *ca.* 0.02 *N* standard sodium hydroxide solution with methyl red as the indicator. The total halide present was determined from an "infinity" titration made after a lapse of ten to twenty half-lives. The rate constants were determined from the least squares plot of log $b/(b - x)$ *vs.* t where b is the value of the infinity titration and x the value of the titration of the sample taken at time t. All the bath temperatures were set by Beckmann thermometers standardized in the bath against the same platinum resistance thermometer and Mueller bridge arrangement, sensitive to a few ten-thousandths of a degree. The temperature accuracy, not limited by the calibration standard, should be of the order of ±0.01° or less.

Materials.—The 80% aqueous alcohol was prepared by mixing eight volumes of anhydrous ethanol and two volumes of water. Dimethylisopropylcarbinol, b.p. 117° (750 mm.), $n^{25}\text{D}$ 1.4155, was prepared *via* the Grignard reaction from methyl isopropyl ketone and methyl iodide. Dimethylisopropylcarbinyl chloride, b.p. 110° (750 mm.), $n^{25}\text{D}$ 1.4178, was made by treatment of the alcohol with concd. hydrochloric acid. The *t*-amyl chloride, b.p. 84.5° (740 mm.), $n^{25}\text{D}$ 1.4036, and the *t*-butyl chloride, b.p. 50.5° (740 mm.), $n^{25}\text{D}$ 1.3855, were commercial products. Tetramethylethylene, b.p. 71–72° (750 mm.), $n^{25}\text{D}$ 1.4095, was prepared by distillation from a mixture of phosphoric acid and dimethylisopropylcarbinol. All of the above organic compounds, except the ethanol and the methyl iodide, were carefully fractionated through a 50 × 1 cm. glass helix packed column with partial take-off head.

Preparation of 3-Deutero-2,3-dimethyl-2-chlorobutane.—A sample of 2.0 g. (0.10 mole) of deuterium oxide was dropped slowly, over a period of 48 hr., into a solution of 22.0 g. (0.28 mole) of acetyl chloride and 7.3 g. (0.087 mole) of tetramethylethylene. After the addition was complete the solution was refluxed for two hours, hydrolyzed on ice and extracted with ether. The ether solution was dried with potassium carbonate and the product recovered by distillation; b.p. 109.5–110° (740 mm.), $n^{25}\text{D}$ 1.4182, yield 7.5 g. (0.062 mole), 72%.

BLOOMINGTON, INDIANA

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

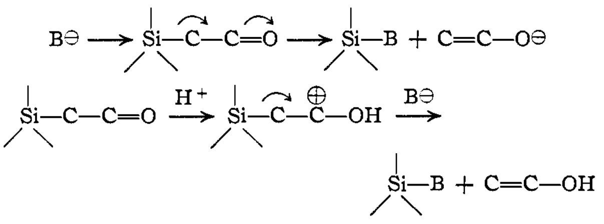
Further Studies on Silicon-containing Carbonyl Compounds: Diketones, Ketoesters and Cyclic Unsaturated Ketones[1]

BY LEO H. SOMMER AND RICHARD P. PIOCH[2]

RECEIVED OCTOBER 1, 1953

The use of $Me_3SiCH_2CH_2COMe$ and $Me_3SiCH_2CH_2CO_2Et$ as starting materials in a variety of condensation reactions has permitted the synthesis of a number of new silicon-containing carbonyl compounds which include β-diketones and their copper chelates, β-ketoesters, cyclic α,β-unsaturated ketones, pyrazolones, a δ-diketone and a furoic ester.

It has been demonstrated that organosilicon carbonyl compounds having the structure Si—C—C=O readily undergo cleavage of the organo-functional group from silicon by electrophilic and nucleophilic reagents.[3]



Thus, while trimethylsilylacetone, $Me_3SiCH_2COCH_3$, recently has been synthesized, attempts to prepare the 2,4-dinitrophenylhydrazone derivative under the usual acidic conditions employed gave instead the derivative of acetone.[4] Further, ethyl trimethylsilylacetate, $Me_3SiCH_2CO_2Et$, also undergoes cleavage of the carboethoxymethyl group from silicon with acids and bases.[3] Because of the fact that ketones and esters of the type Si—C—C—C=O are structurally incapable of undergoing cleavage of the organo-functional group from silicon by the simple electronic processes shown above, a study of these compounds and their reactions has been undertaken.

Application of the acetoacetic ester synthesis to iodomethyltrimethylsilane in previous work gave good yields of the following monoketones[3]: $Me_3SiCH_2CH_2COCH_3$, $Me_3SiCH_2CH(CH_3)COCH_3$ and $Me_3SiCH_2CH(C_2H_5)COCH_3$. Self-condensation of ethyl β-trimethylsilylpropionate using the excellent reagent of Frostick and Hauser, diisopropylaminomagnesium bromide,[5] gave a symmetrical ketone containing two silicon atoms, $Me_3SiCH_2CH_2COCH_2CH_2SiMe_3$.[6] Since these syntheses, which were carried out in the presence of strong bases or acids, confirmed our conclusions based on the above mechanistic reasoning, it was of interest to attempt the synthesis of a group of carbonyl compounds of more complex nature, including diketones, ketoesters and cyclic unsaturated ketones.

The methods available for the preparation of such carbonyl compounds generally involve esters and ketones as starting material. In the present work, ethyl β-trimethylsilylpropionate[3] and 5,5-dimethyl-5-silahexane-2-one were used. For the preparation of the latter, a convenient method[7] involving the low-temperature (−65°) reaction of β-trimethylsilylpropionyl chloride with methylmagnesium bromide in the presence of a small amount of ferric chloride gave the desired ketone in good yield.

Synthesis of β-diketones containing silicon was of interest in view of the fact that these compounds are excellent chelating agents for metal ions and

---

[1] Paper 40 in a series on organosilicon chemistry. For Paper 39 see THIS JOURNAL, **76**, 1186 (1954).

[2] Taken from the Ph.D. thesis of R. P. Pioch, The Pennsylvania State College, 1952.

[3] *Cf.* L. H. Sommer and N. S. Marans, THIS JOURNAL, **72**, 1935 (1950).

[4] C. R. Hauser and C. R. Hance, *ibid.*, **74**, 5091 (1952).

[5] F. C. Frostick and C. R. Hauser, *ibid.*, **71**, 1350 (1949).

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

[7] W. C. Percival, R. B. Wagner and N. C. Cook, *ibid.*, **75**, 3731 (1953).

because of certain theoretical implications which the properties of such substances would have for the mechanism of substitution at a silicon atom.[8] In the present study 7,7-dimethyl-7-silaoctane-2,4-dione (I) was synthesized by condensation of 5,5-dimethyl-5-silahexane-2-one with ethyl acetate. Sodium amide was the base used following the work of Adams and Hauser[9] who showed that this reagent is superior to sodium ethoxide in the synthesis of β-diketones.

$$Me_3SiCH_2CH_2COCH_3 + CH_3CO_2Et \longrightarrow Me_3SiCH_2CH_2COCH_2COCH_3 \quad (I)$$

While anion formation usually occurs at the methyl carbon for ordinary aliphatic ketones in these condensations, it was possible, but not probable, that the presence of the silicon atom might induce anion formation at the methylene carbon thus giving a β-diketone of the structure $Me_3SiCH_2CH(COCH_3)COCH_3$. Structure I for the β-diketone obtained was clearly established when it was found that condensation of ethyl β-trimethylsilylpropionate with acetone gave the same product.

Synthesis of a symmetrical β-diketone containing two silicon atoms resulted from the reaction

$$Me_3SiCH_2CH_2COCH_3 + Me_3SiCH_2CH_2CO_2Et \xrightarrow{NaNH_2} Me_3SiCH_2CH_2COCH_2COCH_2CH_2SiMe_3 \quad (II)$$

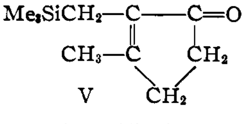
Acid dissociation constants for compounds I and II in a 74.5 volume per cent. dioxane–water solvent, and formation constants for their chelate compounds with copper, nickel and barium ions have been reported.[10] In harmony with the *inductive effect* of electron release relative to alkyl found for trimethylsilyl, Me_3Si–,[11] compounds I and II have lower acid dissociation constants (pK_D, 13.50 and 12.90, respectively) than acetylacetone (pK_D 12.70). Chelate formation constants of the silicon-containing β-diketones compare favorably with those for acetylacetone.[10] Copper chelates of I and II were prepared in the present work and contain as expected, 2 molecules of ketone per Cu^{++} ion.

Hunsdiecker[12] has found that certain γ-dicarbonyl systems, *e.g.*, α-acyl levulinates, readily give ring-closure with formation of a cyclopentenone structure. For the synthesis of a silicon-containing cyclopentenone, 5,5-dimethyl-5-silahexane-2-one was used as the starting material in the reaction sequence

$$Me_3SiCH_2CH_2COCH_3 + (EtO)_2CO \xrightarrow{NaH} Me_3SiCH_2CH_2COCH_2CO_2Et(III) \xrightarrow[Na]{BrCH_2COCH_3}$$

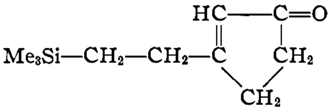
$$Me_3SiCH_2CH_2COCH(CO_2Et)CH_2COCH_3 \xrightarrow[H_2O]{NaOH}$$

IV



V

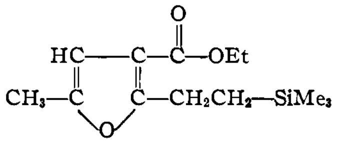
Hunsdiecker[12] has shown that intramolecular condensation of α-acyl levulinates proceeds in such a manner as to leave the terminal methyl group intact, thus indicating that our cyclopentenone has the structure V. Confirmation of V is found in the position of the ultraviolet absorption maximum found for the cyclopentenone, *e.g.*, 248 mμ, as compared to a calculated value of 249 mμ for structure V using Woodward's rules.[13] The alternate structure which would result from condensation involving the terminal methyl group is



This compound should have a maximum at 239 mμ.

The cyclopentenone V was originally obtained as a yellow liquid of pleasant odor. When a portion of the liquid was chilled in an ether–Dry Ice-bath there was obtained a white crystalline solid, m.p. 58–58.5°, and having the same ultraviolet spectrum as the original liquid.

In contrast to the formation of cyclopentenone structures when treated with bases, γ-dicarbonyl systems are readily converted to furan derivatives by acids.[14] Refluxing the acyl levulinate (IV) with a mixture of concd. sulfuric acid, acetic acid and water gave compound VI



(VI)

The infrared spectrum shows strong bands at 5.88 μ, conjugated ester; 6.34, carbon to carbon double bond; 7–7.2, furan ring.[15] It is interesting to note that ring closure occurred more readily than hydrolysis and decarboxylation of the β-ketoester grouping in IV, and that the resulting ethyl furoate was not hydrolyzed under the acid conditions used.[16]

For the synthesis of a cyclohexenone containing silicon the preparation of a 2,6-diketone was necessary. The latter was prepared by a Michael condensation of compound III with methyl vinyl ketone.

$$Me_3SiCH_2CH_2COCH_2CO_2Et + CH_3{-}COCH{=}CH_2 \xrightarrow{NaOEt} Me_3SiCH_2CH_2COCH_2CH_2CH_2COCH_3 \quad (VII)$$

Compound VII, 9,9-dimethyl-9-siladecane-2,6-dione, is a white crystalline solid, m.p. 49.5–50° which gives a disemicarbazone.

In contrast to the 2,5-structures, aliphatic 2,6-dicarbonyl compounds are readily cyclized to cyclohexenones by either acid or base and not to 1,4-

---

[8] The latter will be discussed in a forthcoming publication.

[9] J. T. Adams and C. R. Hauser, THIS JOURNAL, **66**, 1220 (1944).

[10] L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 457 (1953).

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

[12] H. Hunsdiecker, *Ber.*, **75B**, 447 (1942).

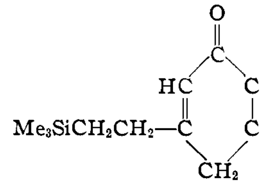
[13] R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941); **64**, 76 (1942).

[14] A. A. Morton, "The Chemistry of Heterocyclic Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 3.

[15] H. M. Randall, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949.

[16] The synthesis of 2-furyltrimethylsilane, 5-trimethylsilyl-2-furoic acid and 2-acetyl-5-trimethylsilylfuran, compounds having silicon directly linked to the 2-position in furan, has been reported. The furyl–silicon bond is readily cleaved by bromine: R. A. Benkeser and R. B. Currie, THIS JOURNAL, **70**, 1780 (1948).

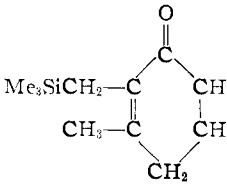
pyrans.[17] When compound VII was refluxed with dilute alcoholic sodium hydroxide an 80% yield of a ketone assigned structure VIII was obtained.



(VIII)

This ketone is a liquid having a light yellow color and a pleasant odor. A semicarbazone was prepared. The presence of the α,β-unsaturated carbonyl system was proven by the ultraviolet absorption spectrum in absolute alcohol which had a maximum at 238 mμ, log ϵ 4.13. Further proof is afforded by the position of the absorption maximum of the semicarbazone,[18] in ethanol, 266 mμ.

An alternate structure for the cyclohexenone would result from condensation of compound VII in such a manner as to involve the methylene group beta to the silicon atom



(IX)

Structure VIII is shown to be the correct one by the position of the ultraviolet maximum, 238 mμ (calcd. for VIII by Woodward's rules, 239 mμ; for IX, 249 mμ).

The above syntheses furnish additional confirmation of our view[3] that organosilicon compounds having a carbonyl group two carbons removed from the silicon do not readily undergo cleavage of the organo-functional group from silicon.

Experimental

A New Preparation of 5,5-Dimethyl-5-silahexane-2-one.—In a 500-ml., 3-necked, round-bottomed flask fitted with a dropping funnel, a mercury-sealed stirrer and a small condenser, and immersed in a Dry Ice–acetone cooling bath, were placed 39.5 g., 0.24 mole, of β-trimethylsilylpropionyl chloride,[3] 0.25 g. of anhydrous ferric chloride and 50 ml. of dry ether. A solution of 0.24 mole of methylmagnesium bromide in 200 ml. of ether was then added with vigorous stirring during 2.5 hours. Vigorous stirring was maintained for 1 hour after addition was completed. The flask was then removed from the cooling bath and the ether distilled. The solid residue was heated on the steam-bath for 1.5 hours and then decomposed with 250 ml. of water followed by treatment with acid, separation of the organic layer, and extraction of the aqueous layer with two 100-ml. portions of ether. Fractionation gave 19.2 g., 0.133 mole, of 5,5-dimethyl-5-silahexane-2-one, b.p. 81° at 45 mm., $n^{20}\mathrm{D}$ 1.4222, 56% yield.

Synthesis of 7,7-Dimethyl-7-silaoctane-2,4-dione (I).—To a stirred suspension of 0.6 mole of sodium amide in 300 ml. of ether was added at room temperature a solution of 43.2 g., 0.30 mole, of 5,5-dimethyl-5-silahexane-2-one in 50 ml. of dry ether. After stirring for 15 minutes, a solution of 52.9 g., 0.60 mole, of ethyl acetate in 50 ml. of dry ether was added and the reaction mixture was stirred and heated on the steam-bath for an additional hour. Treatment with water and acid followed by separation and drying of the organic material gave, after fractionation, 5.3 g. of recovered 5,5-dimethyl-5-silahexane-2-one, and 33.7 g., 0.124 mole, of compound I, b.p. 105° at 15 mm., $n^{20}\mathrm{D}$ 1.4623, d^{20} 0.9155, 69% yield.

Anal. Calcd. for $C_9H_{18}O_2Si$: Si, 15.05. Found: Si, 15.05.

Treatment of the β-diketone with a hot methanol–water solution of copper acetate gave, after recrystallization from methanol–water, a light blue copper chelate, m.p. 101–102°.

Anal. Calcd. for $C_{18}H_{34}O_4Si_2Cu$: Cu, 14.6. Found: Cu, 14.6.

Condensation of ethyl β-trimethylsilylpropionate with acetone by a procedure similar to that used above gave, in 65% yield, a substance identical with the above β-diketone which also yielded a copper chelate, m.p. 101–102°, m.p. 101–102°.

Synthesis of 2,2,10,10-Tetramethyl-2,10-disilahendecane-5,7-dione (II).—By a procedure similar to that employed for compound I, condensation of 43.2 g., 0.30 mole, of 5,5-dimethyl-5-silahexane-2-one with 104.4 g., 0.6 mole, of ethyl β-trimethylsilylpropionate in 100 ml. of ether using 0.6 mole of sodium amide gave a 59% recovery of the excess ester used and 52.3 g., 64.2% yield, of compound II, b.p. 148° at 8 mm., $n^{20}\mathrm{D}$ 1.4668, d^{20} 0.8961.

Anal. Calcd. for $C_{13}H_{28}O_2Si_2$: Si, 20.6. Found: Si, 20.9.

The copper chelate of this β-diketone was prepared and, after recrystallization from absolute ethanol, the product was obtained as steel-blue needles, m.p. 123.5–124.5°.

Anal. Calcd. for $C_{26}H_{54}O_4Si_4Cu$: Cu, 8.58. Found: Cu, 8.55.

Synthesis of Ethyl γ-(Trimethylsilylmethyl)-acetoacetate (III).—In a 2-liter, 3-necked, round-bottomed flask fitted with a mercury-sealed stirrer, a dropping funnel and a condenser and vented to the atmosphere through a Gilman trap, there were placed 250 ml. of dry ether and 48.0 g., 2.0 moles, of sodium hydride. The system was swept with dry nitrogen and 259 g., 2.2 moles, of ethyl carbonate was added rapidly. The ether was brought to reflux and there was then added with stirring during 10 hours a solution of 144.0 g., 1 mole, of 5,5-dimethyl-5-silahexane-2-one in 400 ml. of dry ether. The reaction mixture was then stirred and refluxed for 12 hours. Next, 125 ml. of glacial acetic acid was added to decompose the sodium salt followed by addition of 400 ml. of water. The organic layer was separated and the acidic aqueous layer was extracted with two 150-ml. portions of ether. The combined organic layer and ether extracts were washed with water, 10% sodium bicarbonate solution, water, and then dried over anhydrous sodium sulfate. After distillation of ether and excess ethyl carbonate, fractionation gave compound III, b.p. 126° at 14 mm., $n^{20}\mathrm{D}$ 1.4392 (after keto–enol equilibrium at room temperature was established by allowing fractions of variable index to stand for several weeks), d^{20} 0.9465, 27% yield based on the ketone used. In subsequent preparations yields of 52 and 53% were obtained.

Anal. Calcd. for $C_{10}H_{20}O_3Si$: Si, 13.0. Found: Si, 13.1.

To further characterize compound III as a β-ketoester, the pyrazolone derivative, 3-(β-trimethylsilylethyl)-pyrazolone-5, was prepared by reaction of III with hydrazine hydrate in an ether–ethanol solvent. After recrystallization from ethanol the pyrazolone had m.p. 203–204°.

Anal. Calcd. for $C_8H_{16}ON_2Si$: Si, 15.2. Found: Si, 15.3.

It is of some interest to note that there also was obtained a low yield, 8.3%, of ethyl α-(trimethylsilylmethyl)-acetoacetate, $CH_3COCH(CH_2SiMe_3)CO_2Et$,[3] which is isomeric with compound III and gave a pyrazolone, m.p. 247–248°. An authentic sample of ethyl α-(trimethylsilylmethyl)-acetoacetate[3] gave the same pyrazolone, m.p. 247–248°, 4-(trimethylsilylmethyl)-pyrazolone-5.

Anal. Calcd. for $C_8H_{16}ON_2Si$: Si, 15.2. Found: Si, 15.7.

Compound III, the major product, was readily separated from the lower-boiling isomeric ketoester, b.p. 106° at 14 mm., $n^{20}\mathrm{D}$ 1.4405.

Synthesis of 2-Trimethylsilylmethyl-3-methylcyclopent-2-ene-1-one (V).—In a one-liter, 3-necked flask fitted with a mercury-sealed stirrer, a dropping funnel and a condenser there were placed 300 ml. of dry ether and 88.0 g., 0.406

---

[17] R. C. Elderfield, "Heterocyclic Compounds," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950.

[18] L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 432 (1945).

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., $n^{20}\mathrm{D}$ 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., $n^{20}\mathrm{D}$ 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., $n^{20}\mathrm{D}$ 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)

---

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