

The Synthesis of Some Aliphatic Organosilicon Dicarboxylic Acids

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In order to prepare some organosilicon compounds containing several functional groups attached to carbon, the trimethylsilylmethylsuccinic, α -[trimethylsilylmethyl]-glutaric, and α -[trimethylsilylmethyl]-adipic acids have been synthesized in good yields *via* diethyl trimethylsilylmethylmalonate.

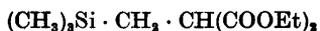
Relatively few aliphatic organosilicon compounds containing two or more functional groups ($-\text{OH}$, $-\text{NH}_2$, $-\text{COOH}$ *etc.*) not directly attached to a silicon atom have been reported in the literature. This type of compound would be of considerable interest as starting materials in the formation of organosilicon polymers, in which the bonds between the single units consist not only of silicon and oxygen atoms but also of other atoms or groups.

Sommer and co-workers^{1,2} have prepared several bifunctional organosiloxanes by utilization of the reaction between the $(\text{CH}_3)_3\text{Si}$ -group and concentrated sulphuric acid. Noll, Speier and Daubert³ have similarly synthesized organosiloxanes containing two amino groups attached to carbon.

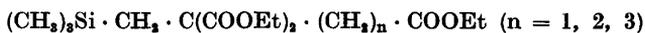
In order to investigate some triorganosilyl-substituted aliphatic dibasic acids, the reaction between diethyl trimethylsilylmethylmalonate (I) in the form of its sodium compound and the ω -bromoesters of some fatty acids has been studied. In connection with this work the addition of I to acrylonitrile has been performed. The preparation of I from chloromethyltrimethylsilane and diethylmalonate was first reported by Sommer, Gold, Goldberg and Marans⁴. However, they never isolated the pure compound but hydrolysed and decarboxylated the crude product directly to form β -trimethylsilylpropionic acid. No attempts to introduce a second group into I have been described.

In this laboratory I was prepared from bromomethyltrimethylsilane, which was available in large quantities, and diethyl malonate in 80—85 % yield. The ω -bromoesters used were ethyl bromoacetate, methyl β -bromopropionate, and ethyl γ -bromobutyrate. They readily reacted with I to form the

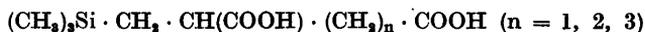
corresponding triethyl trimethylsilylmethyl- ω -carboxyalkylmalonates * (II) in yields of 89, 89 and 80 %, respectively. Subsequent hydrolysis and decarboxylation gave good yields of the α -[trimethylsilylmethyl]-succinic, -glutaric, and -adipic ** acids (III)



I



II



III

An attempt to prepare the triester II, $n = 1$, from triethyl carboxymethylmalonate and bromomethyltrimethylsilane was not very successful, the yield being only about 30 %.

Addition of I to acrylonitrile gave a diethyl trimethylsilylmethylcyanoethylmalonate (IV or V) in good yield.



IV



V

After hydrolysis and decarboxylation there was obtained α -[trimethylsilylmethyl]-glutaric acid, identical with that synthesized from I and methyl β -bromopropionate, thus indicating that the formula IV must be assigned to the addition product.

The dibasic acids thus prepared gave, similarly to β -trimethylsilylpropionic acid¹, by treatment with concentrated sulphuric acid methane amounting to 95–100 % of the theoretically calculated volume (one mole of methane/one mole of acid). The nature of the products obtained after treatment of the reaction mixture with water is being investigated.

EXPERIMENTAL

All reagents used were carefully dried and fractionated in a glass-helix packed column of about ten theoretical plates. In the malonic ester syntheses precautions were taken to exclude moisture from the reaction vessels.

Diethyl trimethylsilylmethylmalonate (I). Several reactions of bromomethyltrimethylsilane with sodiomalonic ester gave yields of I ranging from 80 to 85 %. The following synthesis is typical.

In a 1-liter, three-necked flask equipped with a stirrer, a dropping funnel, a reflux condenser, and a thermometer reaching into the flask, sodium ethylate was prepared by the addition of 23.0 g (1.00 g.at.) of sodium to 300 ml of absolute ethanol. To this was added, during a few minutes, 160 g (1.00 mole) of diethyl malonate, followed by the dropwise addition of 167 g (1.00 mole) of bromomethyltrimethylsilane, while the temperature of the reaction mixture was maintained at 70–80°. The reaction mixture was stirred and heated under reflux for twenty-four hours, after which time its reaction was neutral

* In the case of methyl β -bromopropionate *trans*-esterification took place.

** The preparation of β -trimethylsilyladipic acid by oxidation of 4-trimethylsilylhexanol has been reported in the patent literature².

to litmus. After cooling, the reaction product was poured into 600 ml of water, the organic layer was separated and the aqueous solution extracted twice with ether. The combined extracts were washed several times with water and then dried over anhydrous calcium chloride. Fractionation gave 202 g (82 % yield) of compound I, b.p. 113–115°/10 mm, n_D^{20} 1.4313, d_4^{20} 0.9688. (Found: C 53.4; H 9.1; Si 11.4; r_D 0.2673. Calc. for $C_{11}H_{22}O_4Si$: C 52.6; H 9.0; Si 11.4; r_D 0.2672.)

Triethyl trimethylsilylmethyl-carboxymethylmalonate. A. From diethyl trimethylsilylmethylmalonate and ethyl bromoacetate. In a 500 ml, three-necked flask equipped with a stirrer, a dropping funnel, a reflux condenser, and a thermometer reaching into the flask, 4.6 g (0.200 g.at.) of sodium was dissolved in 60 ml of absolute ethanol. 49.2 g (0.200 mole) of I was added in one portion, followed by the addition of 33.4 g (0.200 mole) of ethyl bromoacetate during two hours. The temperature of the reaction mixture was maintained at 70–80°. The solution was then stirred and heated under reflux for one hour, after which time it reacted neutrally to litmus. Working up the reaction mixture in the usual manner gave 50.6 g (0.152 mole) of triethyl trimethylsilylmethyl-carboxymethylmalonate, b.p. 163–164°/11 mm, n_D^{20} 1.4443, d_4^{20} 1.0280. A small amount, 7.0 g, of compound I was recovered. The yield, based on unrecovered material, was 89 %. (Found: C 53.7; H 8.5; Si 8.4; r_D 0.2585. Calc. for $C_{18}H_{38}O_6Si$: C 54.2; H 8.5; Si 8.4; r_D 0.2588.)

B. From triethyl carboxymethylmalonate and bromomethyltrimethylsilane. Triethyl carboxymethylmalonate, 24.6 g (0.100 mole) was added to a well-stirred solution of 2.30 g (0.100 g.at.) of sodium in 30 ml of absolute ethanol. After the addition of 16.7 g (0.100 mole) of bromomethyltrimethylsilane, the reaction mixture was stirred and heated under reflux for forty-eight hours. Working up in the usual manner gave 10.3 g of triethyl trimethylsilylmethyl-carboxymethylmalonate. Yield 31 %, n_D^{20} 1.4443, d_4^{20} 1.0281.

Trimethylsilylmethyl-carboxymethylmalonic acid. 67.5 g (1.20 moles) of potassium hydroxide was dissolved in a small quantity of water and absolute ethanol was added until a homogeneous solution was obtained. To this was added 50.0 g (0.150 mole) of triethyl trimethylsilylmethyl-carboxymethylmalonate and the resulting mixture was refluxed for twenty-four hours. After cooling, the solution was neutralized with concentrated hydrochloric acid and evaporated to near dryness on a waterbath. Acidification with 20 % hydrochloric acid precipitated the tribasic acid which was filtered, washed with a small volume of water and dried over concentrated sulphuric acid in a vacuum desiccator. The yield of crude product was 33.5 g (90 %). A small quantity was recrystallised from hot water, m.p. 160° (decomp.). (Found: C 43.6; H 6.6; Si 11.4. Calc. for $C_8H_{14}O_6Si$: C 43.5; H 6.5; Si 11.3.)

Trimethylsilylmethylsuccinic acid. The crude trimethylsilylmethylcarboxymethylmalonic acid was decarboxylated by heating to 190–200° for ten minutes. After cooling, the oil solidified and the crystals were recrystallised from a mixture of benzene and petroleum ether. A 75 % yield of pure trimethylsilylmethylsuccinic acid, m.p. 106–107°, was obtained. (Found: C 43.7; H 6.6; Si 13.8; equiv. weight 102.7. Calc. for $C_8H_{16}O_4Si$: C 43.5; H 6.5; Si 13.7; equiv. weight 102.2.)

Triethyl trimethylsilylmethyl- β -carboxyethylmalonate. This compound was prepared from 4.60 g (0.200 g.at.) of sodium in 60 ml of absolute ethanol, 49.2 g (0.200 mole) of I and 33.4 g (0.200 mole) of methyl β -bromopropionate in the same way as the carboxymethyl derivative. There was obtained 59.0 g of triethyl trimethylsilylmethyl- β -carboxyethylmalonate, b.p. 175–177°/11 mm, n_D^{20} 1.4481, d_D^{20} 1.0289. 2.5 g of I was recovered. Yield 89 % based on unrecovered material. (Found: C 55.2; H 8.8; Si 8.1; r_D 0.2602. Calc. for $C_{16}H_{30}O_6Si$: C 55.5; H 8.7; Si 8.1; r_D 0.2617.)

α -[Trimethylsilylmethyl]-glutaric acid. Triethyl trimethylsilylmethyl- β -carboxyethylmalonate was hydrolysed with alcoholic potassium hydroxide as before to yield 90 % of the corresponding tribasic acid. A small quantity was recrystallised from hot water, m.p. 165° (decomp.). (Found: C 45.6; H 6.9; Si 10.9. Calc. for $C_{10}H_{18}O_6Si$: C 45.8; H 6.9; Si 10.7.)

After decarboxylation, which was effected by heating at 190–200° for ten minutes, an oil was obtained which solidified after standing overnight in a vacuum desiccator over concentrated sulphuric acid. Recrystallisation from a mixture of ethyl acetate and petroleum ether gave α -[trimethylsilylmethyl]-glutaric acid in a pure state, m.p. 61–62°.

(Found: C 45.6; H 6.9; Si 12.8; equiv. weight 109.4. Calc. for $C_9H_{18}O_4Si$: C 45.8; H 6.9; Si 12.9; equiv. weight 109.2).

Diethyl trimethylsilylmethyl- β -cyanoethylmalonate. In a 100 ml three-necked flask equipped with a stirrer, a dropping funnel, a reflux condenser and a thermometer reaching into the flask, 0.1 g of sodium was dissolved in 20 ml of absolute ethanol. 24.6 g (0.100 mole) of I was added. Then 8.0 g (0.150 mole) of newly distilled acrylonitrile was added dropwise at such a rate that the temperature of the solution did not exceed 50°. The reaction mixture was stirred for one hour at room temperature. It was neutralised with glacial acetic acid and the solvent distilled off *in vacuo* at 30°. The remaining oil was taken up in ether, the ether solution was washed twice with water and dried over anhydrous magnesium sulphate. Removal of the ether and fractionation gave 24.3 g (81 % yield) of diethyl trimethylsilylmethyl- β -cyanoethylmalonate, b.p. 189–190°/19 mm, n_D^{20} 1.4525, d_4^{20} 1.0173. (Found: N 4.7; Si 9.4; r_D 0.2654. Calc. for $C_{14}H_{25}O_4NSi$: N 4.7; Si 9.4; r_D 0.2658.)

After hydrolysis with boiling alcoholic potassium hydroxide for 48 hours and decarboxylation of the tribasic acid as usual a 78 % yield of crude dibasic acid was obtained. Recrystallisation from a mixture of ethyl acetate and petroleum ether yielded the pure compound, m.p. 61–62°, mixed m.p. with the α -[trimethylsilylmethyl]-glutaric acid above, 61–62°.

Triethyl trimethylsilylmethyl- γ -carboxypropylmalonate. This synthesis was performed as in the case of the carboxymethyl derivative, with 4.60 g (0.200 g.at.) of sodium, 49.2 g (0.200 mole) of I and 39.0 g (0.200 mole) of ethyl γ -bromobutyrate except that the reaction mixture was stirred and refluxed for forty-eight hours before working up. There was obtained 36.0 g (0.100 mole) of the triester b.p. 184–185°/11 mm, n_D^{20} 1.4488, d_4^{20} 1.0165. 18.6 g of I was recovered. The yield was 80 % based on unrecovered material. (Found: C 56.6; H 8.9; Si 7.8; r_D 0.2638. Calc. for $C_{17}H_{32}O_6Si$: C 56.6; H 8.9; Si 7.8; r_D 0.2644.)

α -[Trimethylsilylmethyl]-adipic acid. Hydrolysis of triethyl trimethylsilylmethyl- γ -carboxypropylmalonate with alcoholic potassium hydroxide as before yielded 100 % of the corresponding tribasic acid.

A small quantity was recrystallised from hot water. It melted with decomposition at 177°. (Found: C 47.4; H 7.2; Si 10.3. Calc. for $C_{11}H_{20}O_6Si$: C 47.8; H 7.3; Si 10.2.)

Decarboxylation at 180° for ten minutes gave the crude dibasic acid in 85 % yield. Recrystallisation from a mixture of benzene and petroleum ether gave pure α -[trimethylsilylmethyl]-adipic acid, m.p. 54–55°. (Found: C 51.4; H 8.5; Si 12.0; equiv. weight 116.0. Calc. for $C_{10}H_{20}O_6Si$: C 51.7; H 8.7; Si 12.1; equiv. weight 116.2.)

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REFERENCES

1. Sommer, L. H., Marans, N. S., Goldberg, G. M., Rockett, J. and Pioch, R. P. *J. Am. Chem. Soc.* **73** (1951) 882.
2. Sommer, L. H., Pioch, R. P., Marans, N. S., Goldberg, G. M., Rockett, J. and Kerlin, J. *J. Am. Chem. Soc.* **75** (1953) 2932.
3. Noll, J. E., Speier, J. L. and Daubert, B. F. *J. Am. Chem. Soc.* **73** (1951) 3867.
4. Sommer, L. H., Gold, J. R., Goldberg, G. M. and Marans, N. S. *J. Am. Chem. Soc.* **71** (1949) 1509.
5. Brit. Pat. 688178.

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