

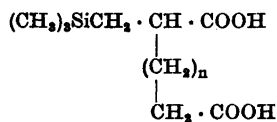
The Synthesis of Some Aliphatic Organosilicon Dicarboxylic Acids. II*

LENNART EBERSON

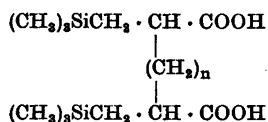
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This paper deals with the preparation of some α,α' -bis-[trimethylsilylmethyl]-alkanedioic acids by way of the reaction between diethyl trimethylsilylmethylsodiomaltonate and iodine and α,ω -dihalogenides. Thus, the α,α' -bis-[trimethylsilylmethyl]-glutaric, -adipic, -pimelic, and -suberic acids have been prepared, whereas the succinic acid derivative could not be synthesized by this method. The acids have all been separated into two isomers, corresponding to the *meso* and racemic forms. An anomalous cleavage of one carbethoxy group in the reaction between diethyl trimethylsilylmethylsodiomaltonate and methylene bromide has been described and diethyl trimethylsilylmethyl-bromomethylmalonate has been prepared.

In a previous paper¹ was described the preparation of some α -mono-[trimethylsilylmethyl]-substituted dicarboxylic acids of the general formula I. It would be of interest from several points of view to develop a preparative route to the corresponding α,α' -bis-[trimethylsilylmethyl]-substituted dicarboxylic acids (II).



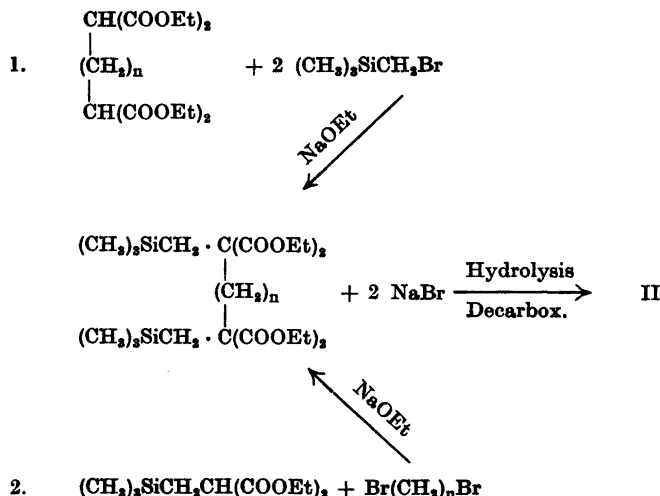
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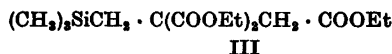
II

There were two possible ways of attacking the problem, which can be represented by the following formulae:

* Part I. *Acta Chem. Scand.* 8 (1954) 1183.



Of these two methods the latter seemed to be the more attractive one. Firstly, it could be expected to give better yields as there was evidence that the introduction of the trimethylsilylmethyl group into a monosubstituted malonic ester goes rather slowly. Thus, in the preparation of triethyl trimethylsilylmethylcarboxymethylmalonate (III) a much better over-all yield was obtained when the

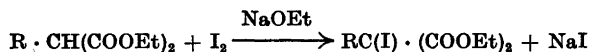


trimethylsilylmethyl group was introduced before the carbethoxymethyl group¹. Similarly, Sommer and Marans² found that it was impossible to introduce a trimethylsilylmethyl group into ethyl α -methyl- or α -ethylacetoacetate. In this case the negative result could not be explained by the non-reactivity of the halogen atom, as iodomethyltrimethylsilane was used in the experiments. A case where the nonreactivity could be explained on this basis has been described by the author³. Secondly, method 2 has never been studied systematically for the same alkyl-substituted malonic ester, and the synthetic possibilities of the method for the preparation of a series of α, α' -dialkyl-substituted dicarboxylic acids are therefore not satisfactorily known. Finally, this method permits a more direct study of the manner in which the trimethylsilylmethyl group differs from other groups which do not contain silicon.

Some of these aspects will be discussed more in detail under the descriptions of the reactions between the diethyl trimethylsilylmethylsodiummalonate and the individual dihalogenides.

The reaction between diethyl trimethylsilylmethylsodiomalonate and iodine

The reaction between the sodium derivatives of alkylsubstituted malonic esters and iodine has been studied in some detail by Bischoff *et al.*^{4, 5} They concluded that the coupling of the malonic ester residues to form the tetraester was only a side-reaction, the major part reacting according to the formula:



However, their results might be explained by the fact that they used equimolecular amounts of the reactants instead of the proportion 2:1 which is required for the formation of the tetraester.

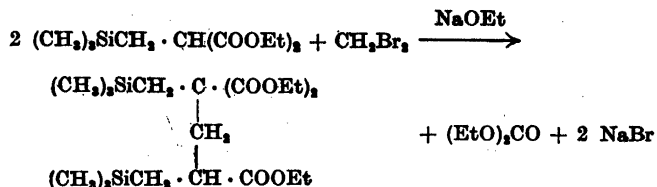
When the sodium compound of diethyl trimethylsilylmethylmalonate reacted with iodine in ethanol-ether or toluene solution in the molecular proportion 2:1 a good yield of the expected tetraester was obtained. The only indication of the formation of diethyl trimethylsilylmethyliodomalonate was the appearance of minute amounts of iodine in the foreruns when the reaction product was distilled. No attempts to synthesize this iodine compound were undertaken as it could be expected to be unstable (β -silicon effect).

The best yields were obtained when the reaction was performed in toluene solution. This might be attributed to the non-solvolytic conditions, allowing only a minimum of side-reactions to occur. However, it was a very slow process to dissolve sodium cut into pieces or in the form of wire in a solution of the malonic ester in toluene or benzene. After boiling the mixture for 8 hours there still remained small fragments of sodium undissolved. This difficulty was overcome by the use of the highly reactive sodium-toluene dispersion described by Hansley⁶ and Frampton and Nobis⁷. Using this dispersion the sodium dissolved in a period of 2—3 minutes and undesirable side-reactions were avoided. (All malonic ester syntheses carried out in toluene solution which are described in this paper were made according to this method).

Unfortunately, the tetraester thus prepared was very resistant to hydrolysis and, in fact, could not be hydrolysed under conditions which did not cause cleavage of methyl groups from the silicon atoms. The following conditions were tried: (1) boiling with concentrated aqueous alkali for 48 hours; (2) boiling with 10 % ethanolic alkali for 48 hours; (3) heating with 10 % ethanolic alkali at 170° in an autoclave for 24 hours. In this case probably both hydrolysis and methyl-silicon cleavage occurred, an alkali-soluble tar being obtained as the major product; (4) boiling with 64 % hydrobromic acid for 48 hours; (5) boiling with sulphuric acid of various strengths. In the last case no hydrolysis was observed at concentrations below 70 % and above this concentration methyl-silicon cleavage set in, only tar products being obtained.

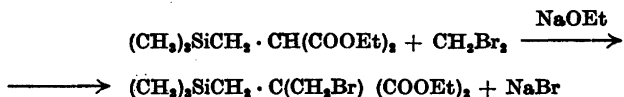
The reaction between diethyl trimethylsilylmethylsodiomalonate and methylene bromide

This reaction exhibited an abnormal course as *one* carbethoxy group was eliminated when the reaction was performed in ethanolic solution, according to the formula:



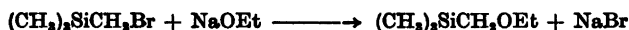
Souther⁸ has described a similar reaction between diethyl phenylsodiummalonate and methylene iodide, in which case *two* carbethoxy groups were eliminated and diethyl α, α' -diphenylglutarate was formed.

In the hope of obtaining the normal product, the reaction was undertaken in toluene solution. In this case, however, no tetraester was formed but instead the diethyl trimethylsilylmethyl-bromomethylmalonate formed by the reaction



This compound could also be prepared from diethyl trimethylsilylmethylsodiummalonate and methylene bromide in excess in ethanolic solution.

Finally, no tetraester was formed when reaction scheme 1 was tried. Only a reacted starting material and ethoxymethyltrimethylsilane formed according to the formula



were obtained. This was further evidence that the trimethylsilylmethyl group should be introduced first in syntheses of this type.

The triester was readily hydrolyzed by ethanolic alkali.

The reaction between diethyl trimethylsilylmethylsodiummalonate and ethylene bromide, trimethylene bromide, and tetramethylene bromide

These dihalogenides reacted with diethyl trimethylsilylmethylsodiummalonate in the proportions 1:2 in ethanolic solution to give the expected tetraesters. However, in the case of ethylene bromide the reaction had to be performed in toluene solution to obtain reasonable yields of the tetraester, as Kitzing⁹ already has pointed out.

These tetraesters were readily hydrolyzed by ethanolic alkali.

* This reaction will be more closely investigated with alkylmalonic esters in a coming paper.

The α,α' -bis-[trimethylsilylmethyl]-alkanedioic acids
(II, $n = 1-4$)

These acids contain two identical asymmetric carbon atoms and thus must be expected to exist in *meso* and racemic forms. This was also found to be the fact and all the α,α' -bis-[trimethylsilylmethyl]-substituted dicarboxylic acids could be separated more or less readily into two forms.

The α,α' -bis-[trimethylsilylmethyl]-succinic acid could not be prepared by this method as has already been mentioned.

The crude mixture of α,α' -bis-[trimethylsilylmethyl]-glutaric acids obtained from the decarboxylation of the corresponding triacid was separated into the two forms by a simple crystallization from ethyl acetate in which solvent the high-melting isomer was much less soluble than the low-melting one. One recrystallization from ethyl acetate gave the high-melting form in the pure state, m. p. 187—188°, whereas the low-melting form required three recrystallizations from 80 % acetic acid before being obtained in a pure state, m. p. 118—120°.

Both isomers were converted into their anhydrides by boiling with acetyl chloride. The melting points of the anhydrides were 44—44.5° and 36—38°, respectively. The anhydrides were easily converted to the corresponding acids by treatment with dilute sodium hydroxide.

The two forms of the α,α' -bis-[trimethylsilylmethyl]-adipic acid were also easily separated by a simple crystallization from ethyl acetate and the final purification was achieved by recrystallizing the acids twice from 80 % acetic acid. The melting points were 122—123° and 102—104°, respectively.

However, in the case of the α,α' -bis-[trimethylsilylmethyl]-pimelic acids the difference in solubility between the isomers was rather small and a laborious and time-consuming fractionated crystallization from benzene was necessary to obtain a separation. The final purification was again performed by several recrystallizations from 80 % acetic acid. The difference in melting points was very small too, the acids melting at 91.5—93° and 87.5—89.5°, respectively. That the acids were not identical was proved by the mixed fusion method according to Kofler¹⁰, and further by converting the acids into the dianilides, which melted at 192—193° and 162—165°, respectively.

The two α,α' -bis-[trimethylsilylmethyl]-suberic acids also presented difficulties in the separation but a four-stage fractionated crystallization from ether-petroleum ether gave the isomers in an almost pure state. Final purification was performed by two recrystallizations from 80 % acetic acid. The melting points were 102—103° and 83—86°, respectively.

It would be of interest to compare the melting points of the acids prepared here with those of the corresponding α,α' -dimethyl- and α,α' -diethylsubstituted dicarboxylic acids. These data are given in Table 1.

As is seen from Table 1, the silicon-containing acids except the glutaric are in accordance with the statement made by Batzer and Wiloth¹¹ that α,α' -dialkylsubstituted dicarboxylic acids with an even number of carbon atoms in the chain exhibit greater differences in the melting points of the diastereoisomers than those with an odd number. In the case of the α,α' -bis-[trimethylsilylmethyl]-glutaric acid the difference in both melting points and

Table 1. Melting points of α,α' -dialkyl-substituted dicarboxylic acids.

| Name of the parent dicarboxylic acid | Number of C-atoms in the chain | α,α' -substituent | | |
|--------------------------------------|--------------------------------|-------------------------------|---------------------------------|---|
| | | CH ₃ - | C ₂ H ₅ - | (CH ₃) ₃ SiCH ₂ - |
| Succinic acid | 4 | 192° | 192° | — |
| | | 123–124° | 129° | — |
| Glutaric acid | 5 | 128° | 119–120° | 187–188° |
| | | 102–104° | 93.5–94.5° | 118–120° |
| Adipic acid | 6 | 142° | 136° | 122–123° |
| | | 70–72° | 51–53° | 102–104° |
| Pimelic acid | 7 | 81–81.5° | Not separated | 91.5–93° |
| | | 76–76.5° | | 87.5–89.5° |
| Suberic acid | 8 | Not separated | Not separated | 102–103° |
| | | | | 83–86° |

solubilities of the diastereoisomers was abnormally great as compared with the dimethyl- and diethyl-derivatives. Unfortunately, the succinic acid derivative was not available for comparison, and therefore conclusions regarding this anomaly could not be drawn. Other methods of preparing this acid are 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. The reactions with sodium dispersions were performed in an atmosphere of nitrogen to prevent oxidation of the sodium. Determinations of the melting points were made with a Kofler micro hot stage¹⁰.

Preparation of sodium dispersions. A 20 % sodium dispersion in toluene was prepared by melting 50 g of sodium in 200 g of toluene and stirring the mixture for 10 minutes at 105° with a special high-speed stirrer at 4000 r.p.m.; 1 % of oleic acid was added as a stabilizer. The sodium particles of the dispersion thus prepared had an average size of about 10 μ which was sufficient for this work. The dispersion was very reactive and had to be handled with great care. It could be stored in thick-walled glass-bottles in an atmosphere of nitrogen for several months without losing its reactivity.

1,2-bis-[trimethylsilylmethyl]-1,1,2,2-tetracarboethoxyethane. A. In a 1000 ml three-necked flask equipped with a mechanical stirrer, a dropping funnel, a reflux condenser, and a thermometer reaching into the flask 4.6 g (0.2 mole) of sodium was dissolved in a mixture of 60 ml of absolute ethanol and 150 ml of absolute ether. After the addition of 49.2 g of diethyl trimethylsilylmethylmalonate the flask was cooled in an ice-bath until the temperature was below 5°. A solution of 25.4 g (0.1 mole) of iodine in 200 ml of absolute ether was added at such a rate that the temperature was kept below 10°. Each drop of iodine gave a light brown colour which disappeared almost instantaneously. The mixture was allowed to reach room temperature and finally boiled for half an hour. After cooling, 150 ml of water was added, the ethereal layer was separated and washed with water, sodium thiosulphate solution, and water again. The ether solution was dried with anhydrous magnesium sulphate, the ether distilled off and the residue distilled *in vacuo*. This method gave 15.1 g of recovered diethyl trimethylsilylmethylmalonate, slightly discoloured by iodine, and 21.5 g (0.044 mole) of the tetraester, a 63 % yield based on un-

recovered material. The tetraester was a very viscous oil which solidified completely after standing for 3 weeks at room temperature. On account of its very bad crystallizing properties it could not be made to crystallize from any solvent. B. p. 196–198°/11 mm, 171–173°/2 mm, m. p. 44–46°. (Found: C 53.7; H 8.6; Si 11.4; Calc. for $C_{22}H_{42}O_8Si_2$: C 53.8; H 8.6; Si 11.4).

B. In a 500 ml flask equipped as in the foregoing synthesis there was placed 11.5 g of a 20 % sodium-toluene dispersion (0.1 mole) together with 50 ml of sodium-dried toluene and 24.6 g (0.1 mole) of diethyl trimethylsilylmethylmalonate was added cautiously. After 5 minutes all the sodium had dissolved and a clear yellow solution resulted. The flask was cooled in an ice-bath and 12.7 g (0.05 mole) of iodine in 40 ml of toluene was added. The temperature was kept below 10°. After heating at 40° for one hour the reaction mixture was worked up as before. This procedure gave 5.6 g of the recovered malonic ester and the tetraester amounted to 14.5 g (0.030 mole), a 77 % yield, based on unrecovered malonic ester.

Attempts to hydrolyze the 1,2-bis-[trimethylsilylmethyl]-1,1,2,2-tetracarboethoxyethane. 1) 4.9 g (0.01 mole) of the tetraester was boiled for 48 hours with a solution of 6.7 g (0.12 mole) of potassium hydroxide in 20 ml of water. After cooling the mixture was extracted twice with ether and the aqueous layer was acidified with hydrochloric acid. No oil or solid could be extracted from the solution. From the ether layer 92 % of the tetraester was recovered.

2) Boiling for 48 hours with 10 % ethanolic potassium hydroxide (0.12 mole in 80 ml of ethanol) of 0.01 mole of the tetraester gave as above about 90 % of the tetraester in recovery and no alkali-soluble matter was obtained.

3) 4.9 g (0.01 mole) of the tetraester and 0.12 mole of potassium hydroxide in 80 ml of ethanol was heated in an autoclave at 150–160° for 24 hours. Working up the dark brown reaction mixture yielded 0.5 g of the tetraester and 3.4 g of a dark, alkali-soluble tar which did not solidify even upon prolonged standing in a vacuum desiccator over concentrated sulphuric acid.

4) 4.9 g of the tetraester + 35 ml of 66 % hydrobromic acid was boiled in a flask equipped with a 60 cm Vigreux column for 48 hours. No formation of ethyl alcohol or ethyl bromide could be detected, and almost all the tetraester was recovered.

5) When boiling the tetraester with sulphuric acid of various concentrations no effect was observed at concentrations below 70 % even after several days' of boiling. At 70 %, however, small amounts of methane were formed but no hydrolysis was observed.

4.9 g of the tetraester was boiled with 20 ml of 75 % sulphuric acid for 15 minutes. Methane was evolved. The reaction mixture was diluted with water and a sticky solid was formed which was filtered and dried. On titration with standard alkali solution it showed an equivalent weight of 155 and it had no definite melting point.

1,3-bis-[trimethylsilylmethyl]-1,1,3-tricarboethoxypropane. A. In the apparatus mentioned previously 11.5 g (0.5 mole) of sodium was dissolved in 150 ml of absolute ethanol. 123 g (0.5 mole) of diethyl trimethylsilylmethylmalonate was added, followed by the dropwise addition of 43.5 g (0.25 mole) of methylene bromide at a temperature of about 80°. After refluxing for twenty hours the reaction mixture was neutralized with some glacial acetic acid and the alcohol distilled off on a water-bath through a short column. The residue was washed with water and dried with anhydrous magnesium sulphate. The following fractions were obtained after distillation *in vacuo*: I, b. p. 65–68°/100 mm, 14.5 g; II, b. p. 88–90°/2 mm, 35.0 g; III, b. p. 158–161°/2 mm, 67.3 g. Fraction I was redistilled, b. p. 124–125°/760 mm, and identified as diethyl carbonate by means of refractive index and density, n_D^{20} 1.3841, and d_4^{20} 0.9753, (data from handbook: n_D^{20} 1.3845; d_4^{20} 0.9751). Fraction II consisted of diethyl trimethylsilylmethylmalonate while III was the triester, n_D^{20} 1.4527, d_4^{20} 0.9874. The yield based on unrecovered material was 85 %. (Found: C 55.7; H 9.4; Si 12.9; r_D 0.2736. Calc. for $C_{20}H_{40}O_6Si_3$: C 55.5; H 9.3; Si 13.0; r_D 0.2742).

B. In the same apparatus 0.2 mole of sodium was dissolved in 70 ml of absolute ethanol. 0.1 mole of 1,1,3,3-tetracarboethoxypropane was added followed by 0.2 mole of bromomethyltrimethylsilane. After refluxing for 24 hours 150 ml of water was added, the organic layer was washed with water 3 times and finally dried with anhydrous magnesium sulphate. Distillation yielded 10.5 g (0.080 mole) of ethoxymethyltrimethylsilane, b. p. 101–103°/760 mm, n_D^{20} 1.3935, and d_4^{20} 0.7538 (handbook: n_D^{20} 1.3940, d_4^{25} 0.755), a

40 % yield, and most of the 1,1,3,3-tetracarbethoxypropane in recovery. No higher-boiling fractions were obtained.

Diethyl trimethylsilylmethyl-bromomethylmalonate. A. In ethanolic solution. In the usual apparatus 4.6 g (0.2 mole) of sodium was dissolved in 70 ml of absolute ethanol and a mixture of 49.2 g (0.2 mole) of diethyl trimethylsilylmethylmalonate and 69.6 (0.4 mole) of methylene bromide was added slowly. The mixture was then boiled under reflux for 2 hours and worked up as before, giving 44.4 g of diethyl trimethylsilylmethyl-bromomethylmalonate, b. p. 153–156°/15 mm, n_D^{20} 1.4603, d_4^{20} 1.1884, a 65 % yield. (Found: Br 23.3; Si 8.3; r_D 0.2306. Calc. for $C_{15}H_{23}O_4BrSi$: Br 23.6; Si 8.3; r_D 0.2305).

B. In toluene solution. In the usual apparatus 11.5 g of a 20 % sodium-toluene dispersion (0.1 mole) was placed together with 50 ml of toluene. 24.6 g (0.1 mole) of diethyl trimethylsilylmethylmalonate was added carefully. When the sodium had dissolved 0.05 mole of methylene bromide was added dropwise and the reaction mixture was refluxed for 8 hours. After the usual treatment 6.0 g of diethyl trimethylsilylmethyl-bromomethylmalonate was obtained, b. p. 116–117°/2 mm, n_D^{20} 1.4597, and d_4^{20} 1.1883, a 35 % yield (based on methylene bromide). No higher-boiling fractions were obtained.

a,a'-bis-[trimethylsilylmethyl]-glutaric acid. 61.5 g (0.142 mole) of the 1,3-bis-[trimethylsilylmethyl]-1,1,3-tricarbethoxypropane was hydrolyzed by boiling with excess ethanolic potassium hydroxide for 20 hours. To the solution was added 200 ml of water and the ethanol was distilled off. Upon acidification with hydrochloric acid the triacid precipitated. It was filtered, washed thoroughly with water and finally air-dried. A small quantity was recrystallized from acetone, m. p. 163–169° (decomp.). (Found: C 47.9; H 8.2; Si 16.2. Calc. for $C_{14}H_{22}O_6Si_2$: C 48.2; H 8.1; Si 16.1).

The main bulk of the crude triacid, 48.0 g (0.138 mole), was decarboxylated by heating to 180–200° for 15 minutes. After cooling the acid mixture was dissolved in 350 ml of boiling ethyl acetate, filtered and allowed to stand for 6 hours. The crystals formed (19.5 g) were filtered and washed with ethyl acetate, m. p. 185–187°. The filtrate was evaporated to a volume of 40 ml, whereafter a new portion of crystals (4.0 g) was obtained, m. p. 183–187°. These two fractions were combined and recrystallized once from ethyl acetate, m. p. 187–188°. The mother liquor was evaporated to dryness and the residue was recrystallized 3 times from 80 % acetic acid, yielding 9.5 g of the low-melting form, m. p. 118–120°. The yields were 56 and 23 %, respectively. (Found for the high-melting form: C 51.2; H 9.3; Si 18.5; equiv. wt. 152.7. Found for the low-melting form: C 51.1; H 9.1; Si 18.5; equiv. wt. 152.1. Calc. for $C_{13}H_{20}O_6Si_2$: C 51.3; H 9.3; Si 18.5; equiv. wt. 152.3).

Anhydrides of the glutaric acids. 0.01 mole of each acid was refluxed with 5 ml of acetyl chloride for 3 hours. The excess acetyl chloride was distilled off and the residue distilled *in vacuo*. Both acid anhydrides boiled at 155–156°/2.5 mm and were formed in about 85 % yields. They were viscous oils which soon solidified. The anhydride of the high-melting acid melted at 44.5–45° and that of the low-melting one at 36–38°. No attempts to recrystallize the anhydrides were made. (Found for the high-melting form: C 54.4; H 9.1; Si 19.6; equiv. wt. 143.6. Found for the low-melting form: C 54.4; H 9.1; Si 19.5; equiv. wt. 143.2. Calc. for $C_{13}H_{20}O_5Si_2$: C 54.5; H 9.1; Si 19.6; equiv. wt. 143.3).

1,4-bis-[trimethylsilylmethyl]-1,1,4,4-tetracarbethoxybutane. This compound was prepared in the usual manner from 23.0 g of 20 % sodium dispersion (0.2 mole) in 100 ml of toluene, 49.2 g (0.2 mole) of diethyl trimethylsilylmethylmalonate, and 18.8 g (0.1 mole) of ethylene bromide. The reaction mixture was refluxed for 20 hours before working up. 8.5 g of the malonic ester was recovered and the tetraester amounted to 21.2 g, b. p. 188–191°/2.5 mm, a 50 % yield (based on unrecovered material). The distillate soon solidified and had the melting point 53–54°. (Found: C 55.6; H 9.0; Si 10.8. Calc. for $C_{24}H_{44}O_8Si_4$: C 55.6; H 8.9; Si 10.8).

a,a'-bis-[trimethylsilylmethyl]-adipic acid. 31.2 g (0.060 mole) of the tetraester was hydrolyzed with ethanolic potassium hydroxide as before. A small quantity of the tetraacid was recrystallized from acetone-petroleum ether, m. p. 202° (decomp.). (Found: C 47.4; H 7.4; Si 13.8. Calc. for $C_{16}H_{26}O_6Si_2$: C 47.3; H 7.4; Si 13.8).

24.0 g (0.059 mole) of the tetraacid was decarboxylated at 200–210° for 20 minutes. The crude acid mixture was dissolved in 60 ml of boiling ethyl acetate, filtered, and allowed to cool. After 3 hours the crystals (5.9 g) were filtered and washed with ethyl acetate, m. p. 115–120°. After 2 recrystallizations from 80 % acetic acid the acid was

obtained in a pure state, 4.5 g, m. p. 122–123°. The mother liquor was evaporated to dryness and the residue recrystallized twice from 80 % acetic acid. The low-melting form was thus obtained pure, 9.5 g, m. p. 102–104°. The yields were 24 and 51 %, respectively. (Found for the high-melting form: C 52.8; H 9.6; Si 17.6; equiv. wt. 159.3. Found for the low-melting form: C 52.8; H 9.5; Si 17.6; equiv. wt. 159.4. Calc. for $C_{14}H_{30}O_4Si_2$: C 52.8; H 9.5; Si 17.6; equiv. wt. 159.3).

1,5-bis-[trimethylsilylmethyl]-1,1,5,5-tetracarboethoxypentane. This synthesis was performed as a conventional malonic ester synthesis from 4.6 g (0.2 mole) of sodium dissolved in 70 ml of absolute ethanol, 49.2 g (0.2 mole) of diethyl trimethylsilylmethylmalonate, and 20.2 g (0.1 mole) of trimethylene bromide. The mixture was boiled for 2 hours. 39.0 g (0.073 mole) of the expected tetraester was obtained, b. p. 202–203°/2 mm, m. p. 67–68°. 10.0 g of the malonic ester was recovered. The yield based on unrecovered material was 91 %. (Found: C 56.5; H 9.2; Si 10.5. Calc. for $C_{25}H_{44}O_8Si_2$: C 56.4; H 9.1; Si 10.5).

α,α' -bis-[trimethylsilylmethyl]-pimelic acid. The tetraester was hydrolyzed as before giving the corresponding tetraacid in 97 % yield. A small amount was recrystallized from acetone-petroleumether, m. p. 180–183° (decomp.). (Found: C 48.7; H 7.8; Si 13.5. Calc. for $C_{17}H_{32}O_8Si_2$: C 48.5; H 7.7; Si 13.5).

46.0 g (0.110 mole) of the tetraacid was decarboxylated at 180–200° for 20 minutes yielding 36 g (0.108 mole) of the crude pimelic acids. This mixture was submitted to a four-stage fractionated crystallization from benzene. The fractions could then be combined to give 2 main bulks of the melting points 82–89° (13.5 g) and 87–93° (16.2 g). Each fraction was recrystallized 4 times from 80 % acetic acid to give the pure acids, m. p. 87.5–89.5° (8.0 g) and 91.5–93° (13.1 g). The eutectic melting point was determined by the mixed fusion method and was 65°. The yields of the pure acids were 22 and 36 %, respectively. (Found for the acid with m. p. 91.5–93°: C 54.3; H 9.7; Si 16.9; equiv. wt. 166.4. Found for the acid with m. p. 87.5–89.5°: C 54.2; H 9.7; Si 16.9; equiv. wt. 166.6. Calc. for $C_{15}H_{30}O_4Si_2$: C 54.2; H 9.7; Si 16.9; equiv. wt. 166.3).

Preparation of the anilides. The anilides were prepared by refluxing 0.6 g of each of the acids with 1 ml of thionyl chloride for 15 minutes, evaporation of the excess thionyl chloride, and addition of 0.8 g of aniline in 10 ml of benzene. The mixture was boiled for 10 minutes, water added, the benzene layer separated, and washed twice with dilute hydrochloric acid and finally with water. The benzene was distilled off and the residue recrystallized 4 times from 70 % ethanol. The high-melting acid gave an anilide melting at 192–193°, while the low-melting one gave an anilide melting at 162–165°. (Found for the high-melting isomer: C 67.2; H 8.7; Si 11.5. Found for the low-melting isomer: C 67.0; H 8.7; Si 11.5. Calc. for $C_{27}H_{42}O_2N_2Si_2$: C 67.2; H 8.8; Si 11.6).

1,6-bis-[trimethylsilylmethyl]-1,1,6,6-tetracarboethoxyhexane. In the usual apparatus 4.6 g (0.2 mole) of sodium was dissolved in 70 ml of absolute ethanol, and 49.2 g (0.2 mole) of diethyl trimethylsilylmethylmalonate was added. 21.6 g (0.1 mole) of tetramethylene bromide was added dropwise at such a rate that the mixture refluxed gently. After the addition the reaction mixture was boiled under reflux for 2 hours. Then it was neutralized with a few drops of glacial acetic acid, the ethanol distilled off and 150 ml of water added. The oil solidified immediately and was filtered, washed with water and air-dried. It was sufficiently pure for direct use in the preparation of the suberic acids. The yield was 45.4 g (0.083 mole), 83 %. A small quantity was recrystallized from petroleum-ether, m. p. 93–94°. (Found: C 57.1; H 9.2; Si 10.3. Calc. for $C_{26}H_{50}O_8Si_2$: C 57.1; H 9.2; Si 10.3).

α,α' -bis-[trimethylsilylmethyl]-suberic acid. The tetraester was hydrolyzed as before yielding 98 % of the corresponding tetraacid. A small quantity was recrystallized from acetone-petroleumether, m. p. 205–210° (decomp.). (Found: C 50.0; H 7.9; Si 13.0. Calc. for $C_{18}H_{34}O_8Si_2$: C 49.8; H 7.9; Si 12.9).

33.0 g of the crude acid mixture obtained after decarboxylation at 210–220° for 10 minutes was submitted to a four-stage fractionated crystallization from ether-petroleum-ether. The fractions were combined into 2 main bulks of the melting points 93–100° (8.0 g) and 81–87° (16.3 g). The high-melting portion required 2 recrystallizations from 80 % acetic acid before being obtained pure, m. p. 102–103° (5.5 g) whereas the low-melting one required 4 recrystallizations from the same solvent, m. p. 83–86° (11.2 g). The yields of the pure acids were 17 and 33 %, respectively. (Found for the high-melting form: C 55.3; H 9.8; Si 16.3; equiv. wt. 173.1. Found for the low-melting form: C 55.5;

H 9.9; Si 16.2; equiv. wt. 172.9. Calc. for $C_{16}H_{34}O_8Si_2$: C 55.4; H 9.9; Si 16.2; equiv. wt. 173.3).

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