ACTA CHEMICA SCANDINAVICA 10 (1956) 629—632

The Synthesis of Some Aliphatic Organosilicon Dicarboxylic Acids. III *

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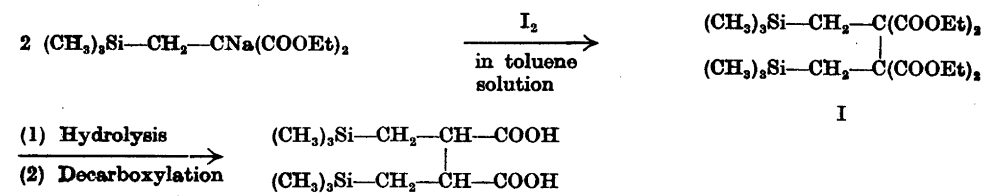
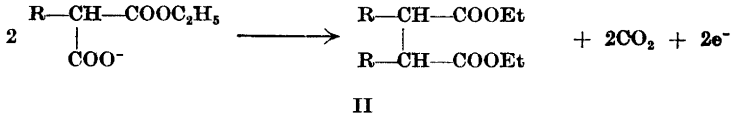
The preparation of α,α′-bis-[trimethylsilylmethyl]-succinic acid by electrolysis of monoethyl trimethylsilylmethylmalonate is described. The acid is found to exist in two forms, corresponding to the *meso* and racemic forms.

During attempts to prepare α,α′-bis-[trimethylsilylmethyl]-succinic acid by the following sequence of reactions



it was found [1] that the intermediate tetraester (I) could not be hydrolyzed under conditions which did not cause cleavage of methyl groups from the silicon atoms.

Another method for the preparation of α,α′-dialkylsubstituted succinic acids is the Crum Brown-Walker modification of the Kolbe electrolytic synthesis [2], namely the electrolysis of a half ester of an alkylmalonic acid according to the formula



II

* Part II: see Ref.[1].

In this paper the application of this reaction to monoethyl trimethylsilylmethylmalonate will be described.

The half ester was readily obtained in the crude state by half saponification of the corresponding diester, but could not be purified by distillation on account of its thermal instability. When heated to a temperature above 120° it decomposed into ethyl β-trimethylsilylpropionate, similarly to other monoethyl alkylmalonates. Attempts to purify the half ester by conversion into its calcium salt and recrystallization were not successful, as there was considerable loss of material during this procedure. However, the use of the crude ester in the electrolyses gave reasonably good yields and therefore no other purification methods were tried.

The electrolysis was carried out in anhydrous methanolic solution, where the conditions for optimum yields are not so critical as in aqueous solution. In water solution the yield of diester was much smaller, and besides which large amounts of polymeric material were obtained. The latter was probably polyacrylic ester, which could be formed by β-elimination of an intermediate radical. The presence of this polymer made the separation of the reaction products very difficult. In methanolic solution the reaction proceeded smoothly and a 40 % yield of the diester (II), R = $(CH_3)_3Si—CH_2$-, was obtained. (II) was then readily hydrolyzed by boiling with ethanolic potassium hydroxide to give a mixture of the *meso* and racemic forms of α,α'-bis-[trimethylsilylmethyl]-succinic acid. The separation of the diastereoisomers was easily affected by a simple crystallization from acetone, in which the high-melting acid was rather insoluble. The acids were finally recrystallized from 70 % acetic acid, giving the pure isomers of the melting points 241—244° (decomp.) and 160—162°, respectively.

The two forms could readily be converted into their anhydrides by boiling them with acetyl chloride. The anhydride of the high-melting acid melted at 74—76°, while the other was obtained as an oil, which did not crystallize. The anhydrides were hydrolyzed by boiling aqueous sodium hydroxide to form the corresponding acids. The above-mentioned decomposition of the high-melting acid at its melting point was found to be due to an elimination of water with the formation of the anhydride of the *low*-melting acid. The low-melting acid, in turn, on heating to 80—100° above its melting point gave its own anhydride. This was in line with the behavior of other α,α'-dialkyl-substituted succinic acids, *e. g.*, α,α'-diethylsuccinic acid [3].

With the preparation of these two acids the series of α,α'-bis-[trimethylsilylmethyl]-substituted *n*-dicarboxylic acids from the succinic to the suberic acid derivative has been completed. The work on these acids is now being continued to determine which of the forms can be resolved into optically active acids.

EXPERIMENTAL

Monoethyl trimethylsilylmethylmalonate. 49.2 g (0.2 mole) of diethyl trimethylsilylmethylmalonate was added to a solution of 11.2 g (0.2 mole) of potassium hydroxide in 250 ml of absolute ethanol, and the mixture was allowed to stand at room temperature for two hours. Then 100 ml of water was added and the ethanol was distilled off on a water-bath. The aqueous solution was extracted four times with 30 ml portions of ether

to remove unreacted diester and then acidified with concentrated hydrochloric acid with cooling in an ice-bath. (The recovered diester amounted to 7.2 g, 14 %). The organic layer was taken up in ether and the ether solution was washed twice with water, the ether distilled off and 100 ml of benzene was added. By distilling the benzene the contaminating water was removed from the half ester and a dry product was obtained. During the distillation the temperature of the flask content was not allowed to exceed 100° in order to prevent decarboxylation. The yield of crude ester was 85 % (based on unrecovered material) and it could be used directly in the electrolysis experiments.

Diethyl α,α'-bis-[trimethylsilylmethyl]-succinate. 21.8 g (0.1 mole) of monoethyl trimethylsilylmethylmalonate and 2 g of potassium hydroxide were dissolved in 100 ml of dry methanol. The solution was placed in a cell consisting of a 200 ml beaker fitted with a platinum spiral anode (surface area 3.0 cm²), a platinum net cathode (total surface area *ca.* 50 cm²), and a thermometer reaching into the liquid. The cell was cooled by immersion in an ice-bath (internal temperature of cell was kept all the time about 30°) and a current of 1.5 amp. was passed until the electrolyte became approximately neutral. This required *ca.* 20 % longer time than that calculated on the basis of the current and the amount of half ester employed.

The product was isolated by dilution of the cell contents with water, distilling off the methanol on a water-bath and taking up the organic layer in ether. The extract was washed with very dilute (2 %) sodium hydroxide solution to remove small amounts of starting material, then with water and finally dried with anhydrous magnesium sulphate. After evaporation the remaining oil was distilled in *vacuo*, b.p. 136—138°/4 mm, n_D^{20} 1.4448, d_4^{20} 0.9363, yield 6.9 g (40 %). (Found: C 55.3; H 9.8; Si 16.0; r_D 0.2841. Calc. for $C_{16}H_{34}O_4Si_2$: C 55.4; H 9.9; Si 16.2; r_D 0.2843.)

α,α'-Bis-[trimethylsilylmethyl]-succinic acid. 5.1 g (0.015 mole) of the above diester was hydrolyzed by boiling with excess 10 % ethanolic potassium hydroxide for 24 hours. The solution was diluted with water and the ethanol distilled off on a water-bath. Acidification with 5 N hydrochloric acid precipitated the mixture of the diastereoisomers. The crystals were filtered, washed thoroughly with water and air-dried. They were dissolved in 100 ml of boiling acetone, filtered to remove insoluble matter and left to crystallize. A yield of 1.4 g melting at 235° (decomp.) was obtained. The filtrate was evaporated to a volume of 10 ml and then gave an additional 0.4 g with the same melting point. The two fractions were combined and recrystallized from 70 % acetic acid giving a product, m. p. 242—244° (decomp.), which was not increased by further recrystallization. Yield 1.5 g.

The mother-liquor from the second filtration was evaporated to dryness and the residue recrystallized twice from 70 % acetic acid to give 1.4 g of the low-melting acid, m. p. 160—162°. The yields of the pure isomers were 34 and 32 %, respectively. (Found for the high-melting acid: C 49.3; H 9.1; Si 19.2; equiv. wt. 145.2. Found for the low-melting acid: C 49.8; H 9.1; Si 19.3; equiv. wt. 145.0. Calc. for $C_{12}H_{26}O_4Si_2$: C 49.6; H 9.0; Si 19.3; equiv. wt. 145.3.)

Preparation and hydrolysis of the anhydrides. I. 0.5 g of the high-melting acid was boiled with 3 ml of acetyl chloride until the crystals had completely dissolved, which required about 20 hours. Evaporation of the excess acetyl chloride and the acetic acid formed gave a residue which soon solidified, m. p. 71—76°, yield 0.4 g. The crude product was recrystallized from petroleum ether, to give the m. p. 74—76°. Upon hydrolysis with hot sodium hydroxide solution the high-melting acid was quantitatively recovered.

II. After treating the low-melting acid in the same manner as above an oil was obtained which did not solidify. It was vacuum-distilled, b. p. 130—135°/12 mm. The product gave the low-melting acid on hydrolysis as before. (Found for the anhydride, m. p. 74—76°: C 52.7; H 8.8; Si 20.6. Found for the liquid anhydride: C 52.9; H 8.8; Si 20.5; Calc. for $C_{12}H_{24}O_3Si_2$: C 52.9; H 8.9; Si 20.6.)

Anhydrization of the acids by heat. 160 mg of the high-melting acid was heated in a small test-tube to 250° in an oil-bath for 15 minutes. The crystals melted and drops of water condensed in the upper end of the test-tube. The product was liquid and consisted of the anhydride of the low-melting acid, as identified by its almost quantitative conversion into the low-melting acid by hydrolysis. (150 mg, m. p. 159—162°).

The low-melting acid on the same treatment gave exclusively its own anhydride.

The author wishes to express his sincere gratitude to Professor Erik Larsson for his kind interest in this work.

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Received January 23, 1956.