[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY]

Preparation of Dimethylphenyl- and Methyldiphenylsilanecarboxylic Acids and Some of Their Derivatives

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Dimethylphenyl- and methyldiphenylsilanecarboxylic acids were prepared by carbonation of the corresponding silyllithium reagents, and their methyl esters prepared through reaction with diazomethane. As a structure proof, the methyl ester of dimethylphenylsilanecarboxylic acid was reduced with lithium aluminum hydride to the same carbinol obtained by reaction of the silyllithium reagent with formaldehyde. An increasing stability to base in ethanol solution was observed in the order of triphenyl-, methyldiphenyl-, dimethylphenylsilanecarboxylic acid.

Benkeser and Severson,[1] in their initial investigation of the preparation and properties of triphenylsilylpotassium, found that this compound reacted with carbon dioxide to produce a white crystalline solid. This material was stable at room temperature, but when heated, decomposed to form carbon monoxide and a mixture of triphenylsilanol and hexaphenyldisilane. On the basis of its analysis and general behavior, they concluded that this carbonation product was triphenylsilanecarboxylic acid, $(C_6H_5)_3SiCOOH$. Proof of the structure of this compound was later obtained by preparation of the methyl ester, and its reduction by lithium aluminum hydride to the known triphenylhydroxymethylsilane.[2]

Triphenylsilanecarboxylic acid has also been prepared by the carbonation of triphenylsilyllithium.[3] The only other silanecarboxylic acid that has been reported is tri-*p*-tolylsilanecarboxylic acid, prepared by carbonation of the silylpotassium reagent.[4]

The chemistry of the silanecarboxylic acids is different from that of other carboxylic acid systems. Benkeser and Severson[1] found that their crude acid decomposed upon heating with the evolution of carbon monoxide. Later studies by Brook[5] have shown that all known organosilicon compounds in which the silicon is attached directly to a carboxylic acid or ester group undergo thermal rearrangements accompanied by the elimination of the carbonyl group as carbon monoxide.

Complete decomposition of the acid with evolution of carbon monoxide occurs rapidly after treatment with only catalytic amounts of sodium hydroxide or sodium ethoxide in absolute ethanol, and more slowly with sodium methoxide in absolute methanol or with aqueous pyridine.[2]

We are now reporting the preparation of two silanecarboxylic acids that can be extracted from their carbonation mixtures by aqueous base in good yields. The carbonation of dimethylphenylsilyllithium, extraction of the reaction mixture with chilled 2% sodium hydroxide solution, acidification with dilute hydrochloric acid, and immediate extraction with ether gave dimethylphenylsilanecarboxylic acid in 47% yield.

Confirmatory evidence for the structure of the acid was obtained by following the procedure for the structural proof of triphenylsilanecarboxylic acid.[2] Dimethylphenylsilanecarboxylic acid was converted to its methyl ester, methyl dimethylphenylsilanecarboxylate, by reaction with diazomethane. Reduction of the ester with lithium aluminum hydride gave an hydroxy compound which was identical with the compound obtained from dimethylphenylsilyllithium and formaldehyde gas.

$$\begin{tikzcd}
(CH_3)_2(C_6H_5)SiLi \arrow[r, "CO_2"] \arrow[dd, "CH_2O"] & (CH_3)_2(C_6H_5)SiCO_2H \arrow[d, "CH_2N_2"] \\
 & (CH_3)_2(C_6H_5)SiCOOCH_3 \arrow[dl, "LiAlH"'] \\
(CH_3)_2(C_6H_5)SiCH_2OH &
\end{tikzcd}$$

The carbonation of methyldiphenylsilyllithium gave methyldiphenylsilanecarboxylic acid, which also could be extracted with chilled aqueous base. Reaction of the acid with diazomethane gave the expected methyl methyldiphenylsilanecarboxylate.

It is important to carry out the basic extraction of the acids at low temperature and as rapidly as possible. When the extraction of dimethylphenylsilanecarboxylic acid was carried out slowly at room temperature, the yield was reduced to 12.0%.

Dimethylphenylsilanecarboxylic acid melts at 56–58° without decomposition; however, when heated to 125°, it decomposes with the evolution of carbon monoxide. Methyldiphenylsilanecarboxylic acid decomposes at its melting point, 133.5–136°, also with the evolution of carbon monoxide.

Neutralization equivalents for the acids were determined by sodium hydroxide titration of a 70:30 ethanol-water solution of the acid. Dimethyl-

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(1) R. A. Benkeser and R. G. Severson, *J. Am. Chem. Soc.*, **73,** 1424 (1951).

(2) A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **77,** 2322 (1955).

(3) M. V. George and H. Gilman, *J. Am. Chem. Soc.*, **81,** 3288 (1959).

(4) A. G. Brook and R. J. Mauris, *J. Am. Chem. Soc.*, **79,** 971 (1957).

(5) A. G. Brook, *J. Am. Chem. Soc.*, **77,** 4827 (1955).

phenylsilanecarboxylic acid gave very good values, but the values for methyldiphenylsilanecarboxylic acid were slightly greater than the theoretical value. It was found that an ethanol solution of methyldiphenylsilanecarboxylic acid will slowly decarbonylate when treated with a few drops of aqueous sodium hydroxide. It is possible that this may have interfered with the titration. Dimethylphenylsilanecarboxylic acid will also decarbonylate under the same conditions, but the reaction appears to be much slower. This is in contrast to triphenylsilanecarboxylic acid which reacts quite rapidly.

Based upon the stabilities at their melting points and the rates at which ethanol solutions of the acids react with base, the following appears to be the order of stability:

$$(CH_3)_2(C_6H_5)SiCOOH > (CH_3)(C_6H_5)_2SiCOOH > (C_6H_5)_3SiCOOH$$

The decarbonylation of silanecarboxylic acids has been proposed to occur by means of attack of a nucleophilic species upon silicon.[2,4] If one considers the inductive effects of alkyl *versus* aryl, the replacement of a phenyl by a methyl group would increase the electron density around silicon. This in turn would decrease the ease of nucleophilic attack, in agreement with the order of acid stability observed in our reactions.

EXPERIMENTAL[6]

Carbonation of dimethylphenylsilyllithium. Dimethylphenylsilyllithium[7] (0.074 mole in tetrahydrofuran solution) was carbonated by pouring into a Dry Ice–ether slurry. The solution was allowed to warm to slightly above 0°. This was extracted as rapidly as possible with 200 ml. of chilled 2% sodium hydroxide. The chilled extract was immediately acidified to *p*H 5–6 with dilute hydrochloric acid. Ether extraction was employed, and the extracts dried over anhydrous sodium sulfate. The ether was decanted from the sodium sulfate and evaporated under an air-jet to leave 7.35 g. (55.2%) of crude dimethylphenylsilanecarboxylic acid, m.p. 51–56°. Several recrystallizations from petroleum ether (b.p. 30–50°), cooled to ice-bath temperature, gave 4.65 g. (34.9%) of white crystals, m.p. 56–58°. It is necessary to cool the petroleum ether to ice-bath temperature and filter while chilled due to the high solubility of the acid, even at room temperature, in this solvent.

Anal. Calcd. for $C_9H_{12}O_2Si$: C, 59.95; H, 6.71; neut. equiv., 180.28. Found: C, 59.90, 59.95; H, 6.60, 6.62; neut. equiv., 181.63, 181.71.

The infrared spectrum of this compound in carbon disulfide showed absorption bands at 6.04, 8.00, and 8.99 μ, characteristic of COOH, Si-methyl, and Si-phenyl groups, respectively. There was also a broad band starting at 2.95 and ending at 3.95 μ, with peaks at 3.30, 3.55, 3.70, and 3.95 μ. This is probably an associated O—H running into the C—H region.

This reaction was repeated twice to give the acid in crude yields of 71.0 and 47.0% (pure yields of 50.2 and 30.0%), respectively.

Carbonation of methyldiphenylsilyllithium. A tetrahydrofuran solution of 0.06 mole of methyldiphenylsilyllithium[7] was carbonated by pouring into a Dry Ice–ether slurry. The same rapid work-up at low temperatures as described previously for dimethylphenylsilanecarboxylic acid was employed to obtain 9.80 g. (67.5%) of crude methyldiphenylsilanecarboxylic acid, m.p. 124–132° dec. Several recrystallizations from petroleum ether (b.p. 80–110°) gave 4.8 g. (33.1%) of white crystals, m.p. 133.5–136° dec.

Anal. Calcd. for $C_{14}H_{14}O_2Si$: C, 69.5; H, 5.83; neut. equiv., 242.34. Found: C, 69.45, 69.55; H, 5.66, 5.72; neut. equiv., 247.3, 250.0, 257.4.

The infrared spectrum of this compound in carbon disulfide is almost identical with that of dimethylphenylsilanecarboxylic acid except for an intensification of the C—H aromatic peak and a decrease of the C—H aliphatic and Si-methyl peaks.

A repeat of this reaction gave the acid in 84.0% crude yield (66.5% pure yield).

Stability of acids towards heat and base. Dimethylphenylsilanecarboxylic acid melts at 56–58° without decomposition. However, upon raising the temperature to 125°, decomposition with gas evolution occurs. Methyldiphenylsilanecarboxylic acid decomposes with gas evolution at its melting point, 133.5–136°. The gas which was evolved was carbon monoxide as evidenced by a black deposit on paper saturated with 5% palladium chloride.[8]

Methyldiphenylsilanecarboxylic acid was stable when treated with 10% aqueous sodium hydroxide. However, when an absolute ethanol solution was treated with a few drops of 10% aqueous sodium hydroxide, a slow evolution of carbon monoxide was detected by the palladium chloride test. The reaction with base in ethanol solution and not in the aqueous system was probably due to the solubility of the acid in ethanol. Dimethylphenylsilanecarboxylic acid, in absolute ethanol, reacted more slowly with aqueous sodium hydroxide, as evidenced by the very slow appearance of a dark stain on the palladium chloride paper. It appears that dimethylphenylsilanecarboxylic acid is not so sensitive to base attack as is methyldiphenylsilanecarboxylic acid. In contrast, triphenylsilanecarboxylic acid very rapidly gave a positive test.

Reaction of dimethylphenylsilanecarboxylic acid with diazomethane. Five grams (0.0278 mole) of dimethylphenylsilanecarboxylic acid was dissolved in 50 ml. of ether and agitated by means of a magnetic stirrer. The diazomethane in ether solution was added slowly at room temperature. The addition was completed in 5 min. The solution was yellow, but this color was lost after a minute of stirring. The ether was allowed to evaporate in a hood overnight. The resulting colorless oil was distilled at reduced pressure to give 3.15 g. (57.9%) of methyl dimethylphenylsilanecarboxylate, b.p. 46–48° (0.03 mm.), n_{D}^{20} 1.5068, d_{20}^{20} 1.0226.

Anal. Calcd. for $C_{10}H_{14}O_2Si$: C, 61.82; H, 7.26; MR_D, 56.48. Found: C, 61.69, 61.66; H, 7.45, 7.45; MR_D, 56.53.

The infrared spectrum in carbon disulfide showed absorption bands at 3.25, 3.40, 5.95, 8.00, and 8.79 μ, characteristic of C—H aryl, C—H aliphatic, ester carbonyl, Si-methyl, and Si-phenyl, respectively.

A repeat of this reaction gave the ester in 90.2% yield, b.p. 79–81° (1.2 mm.), n_{D}^{20} 1.5069.

Reaction of methyldiphenylsilanecarboxylic acid with diazomethane. Nine grams (0.0372 mole) of methyldiphenylsilanecarboxylic acid was esterified by diazomethane in ether solution and worked up as described in the previous experiment. Distillation of the resulting oil at reduced pressure gave 6.60 g. (69.3%) of methyl methyldiphenylsilanecarboxylate, b.p. 115–116° (0.02 mm.), n_{D}^{20} 1.5645, d_{20}^{20} 1.0926.

Anal. Calcd. for $C_{15}H_{16}O_2Si$: C, 70.28; H, 6.29; Si, 10.92; MR_D, 76.37. Found: C, 70.64, 70.81; H, 6.48, 6.52; Si, 10.82, 10.90; MR_D, 76.38.

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(6) Organometallic reactions were carried out under an atmosphere of dry, oxygen-free nitrogen. Melting points are uncorrected.

(7) H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

(8) R. Nowicki, *Chem. Ztg.*, **35**, 1120 (1911).

The spectrum is similar to that of methyl dimethylphenylsilanecarboxylate, with the same change in intensities associated with the replacement of a methyl by a phenyl group.

Reduction of methyl dimethylphenylsilanecarboxylate with lithium aluminum hydride. Lithium aluminum hydride, 3.26 g. (0.086 mole), was added in small portions to 20.0 g. (0.013 mole) of methyl dimethylphenylsilanecarboxylate dissolved in 200 ml. of ether and cooled to ice-bath temperature. Vigorous refluxing occurred as each portion was added. The ice bath was removed upon completion of addition, and the reaction mixture was allowed to stir at room temperature for 4.5 hr. The solution was then poured onto crushed ice acidified with sulfuric acid. The usual work-up was employed. Distillation of the solvent left a colorless oil which was distilled at reduced pressure to give 13.55 g. (79.3%) of a colorless oil later shown to be dimethylphenylhydroxymethylsilane, b.p. 130–135° (30 mm.), n_D^{20} 1.5220. This was redistilled to give 12.05 g. (70.4%), b.p. 132–135° (27 mm.), n_D^{20} 1.5225, d_{20}^{20} 0.9899.

Anal. Calcd. for $C_9H_{14}OSi$: C, 65.00; H, 8.48; MR_D, 51.65. Found: C, 64.39, 64.56; H, 7.57, 7.74; MR_D, 51.24.

The infrared spectrum in carbon disulfide showed the absorption bands mentioned previously for C—H aromatic and aliphatic, Si-methyl, and Si-phenyl, and, in addition, bands at 2.97 and 10.00 μ indicative of an associated OH and hydroxymethyl, respectively.

Reaction of dimethylphenylsilyllithium with formaldehyde. Formaldehyde gas, prepared by heating 20.0 g. of paraformaldehyde, was passed over a rapidly stirred solution of 0.148 mole of dimethylphenylsilyllithium in tetrahydrofuran solution. The reaction mixture became quite warm and mild refluxing occurred. A water bath was applied to avoid overheating. The solution became lighter in color, until after 1 hr. it was light brown-orange. Color Test I[9] was then negative. Stirring at room temperature was continued for 2 hr. Hydrolysis was effected with water and the usual work-up employed. Evaporation of the solvent left a colorless oil which was distilled at reduced pressure to give 11.15 g. (45.3%) of dimethylphenylhydroxymethylsilane, b.p. 111–117° (11 mm.), n_D^{20} 1.5256. This oil was redistilled to give 8.80 g. (35.8%), b.p. 113–117° (11 mm.), n_D^{20} 1.5251.

Anal. Calcd. for $C_9H_{14}OSi$: C, 65.0; H, 8.48; MR_D, 51.65. Found: C, 64.43, 64.57; H, 8.02, 8.19; MR_D, 50.35.

The infrared spectrum is superimposable with that of the oil obtained in the lithium aluminum hydride reduction of methyl dimethylphenylsilanecarboxylate.

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[9] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE POLYTECHNIC INSTITUTE OF BROOKLYN]

Hydrogenolyses of Aromatic Halides with Triphenyltin Hydride[1]

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Triphenyltin hydride is postulated to be a by-product of the intermediate in the Diels-Alder reaction between triphenylvinyltin and tetracyclone. The hydride serves as a reducing agent for tetracyclone and is also capable of hydrogenolyzing aromatic halides selectively.

Tetracyclone, (tetraphenylcyclopentadienone, I) has been reported to undergo a Diels-Alder reaction with organomercury[5,6] and organoarsenic[6] compounds. With a view toward preparing new organometallic compounds *via* this reaction, I was treated with triphenylvinyltin (II). No evidence of reaction was obtained when the components were heated in benzene, but in refluxing bromobenzene (IX) the color of I was discharged and a reducing gas was evolved. From the reaction mixture, tetraphenyltin (III), 2,3,4,5-tetraphenylcyclopent-2-enone (IV), triphenyltin bromide (V), and 1,2,3,4-tetraphenylbenzene (VI) were isolated by fractional crystallization. When the reaction was conducted in refluxing nitrobenzene III and VI were isolated.

In order to understand the appearance of these products, II was heated in refluxing bromobenzene and it slowly disproportionated to give III. That V had not been obtained suggested that another tin containing compound had reacted with the solvent.

It was then assumed that I underwent the Diels Alder reaction with II and afforded an unstable adduct (A) which eliminated carbon monoxide (the reducing gas?) and triphenyltin hydride (VII) to give fully aromatic VI. Hydrogenolysis of the solvent by VII would give V and reduction of I would give IV. In support of this suggested

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[1] A preliminary report of part of this work appeared in *J. Org. Chem.*, **24**, 294 (1959).

[2] Taken from a portion of the dissertation presented to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1960.

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[4] Sponsored in part by the Office of Ordnance Research, U. S. Army.

[5] V. S. Abramov and L. V. Shapshinskaya, *Doklady Akad. Nauk S.S.S.R.*, **59**, 1291 (1948).

[6] V. S. Abramov, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, **1945**, 330.