cooled and decomposed with 32 ml. of cold 25% sulfuric acid. Upon addition of the acid the imine salt crystallized out in small yellow flakes. The solid was heated under reflux with 200 ml. of 8 *N* sulfuric acid for 48 hours, at which time all the solid had gone into solution. The solution was cooled to room temperature and washed twice with water. The toluene layer was separated, dried over Drierite, concentrated and the residue fractionated under reduced pressure. The viscous yellow oil obtained weighed 11.7 g., b.p. 240–243 (1.5 mm.) (81%). The oil was crystallized from a water–ethanol mixture yielding 11 g. of white crystals melting at 83–84°.

Anal. Calcd. for $C_{25}H_{20}O$: C, 89.25; H, 5.98. Found: C, 89.13; H, 6.06.

The other ketones were prepared in a similar way.

TABLE II

NEW KETONES (III)

R	Yield, %	M.p., °C.	B.p., °C.	Mm.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H	80	103–104	248–251	1	89.79	89.40	5.43	5.78
2′-CH_3	81	83–84	240–243	1.5	89.25	89.13	5.98	6.06
3′-CH_3	80	114–115			89.25	89.11	5.98	6.21
4′-CH_3	84	77–78	248–251	3	89.25	89.19	5.98	6.17

10-Phenyl-1,2-benzanthracene (IV, R = H).—A solution of 0.50 g. of 2-(1-naphthylmethyl)-benzophenone (III, R = H) in 24 ml. of glacial acetic acid and 6 ml. of 48% hydrobromic acid was heated under reflux for 2.5 hours, during which time the product had crystallized. The mixture was cooled and the solid filtered, washed thrice with water and dried *in vacuo* yielding 0.48 g. (98%) of crystals, m.p. 182–184°. Two recrystallizations from an ethanol-benzene mixture gave 0.45 g. of white crystals, m.p. 183–184°.

Anal. Calcd. for $C_{24}H_{16}$: C, 94.70; H, 5.29. Found: C, 94.84; H, 5.24.

Two of the analogs IV, R = 2′-CH_3, and IV, R = 4′-CH_3, also were prepared by the acid cyclization of the corresponding ketone.

TABLE III

NEW HYDROCARBONS[a] (IV)

R	Yield, %	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
H[b]	98	183–184	94.70	94.84	5.30	5.24
2′-CH_3	74	132.5–133	94.30	94.57	5.70	5.60
3′-CH_3	88	110–111	94.30	94.49	5.70	5.73
4′-CH_3	80	121–122	94.30	94.02	5.70	5.78

[a] The ultraviolet spectra of the hydrocarbons were taken with a Beckman spectrophotometer (model DU, 1-cm. silica cell) at a concn. of 10 mg./l. using 95% EtOH as the solvent. The maxima for all four hydrocarbons appear at the same wave lengths. The optical density values at these wave length maxima are listed for the hydrocarbons in the same order as the hydrocarbons appear in Table III: λ 222 mμ (1.47, 1.34, 1.51, 1.54); λ 259 mμ (1.08, 0.98, 0.97, 0.98); λ 271 mμ (1.33, 1.16, 1.23, 1.20); λ 281 mμ (2.25, 2.05, 1.99, 1.89); λ 291 mμ (2.76, 2.32, 2.38, 2.31); λ 335 mμ (0.24, 0.23, 0.23, 0.22); λ 351 mμ (0.31, 0.30, 0.29, 0.28); λ 366 mμ (0.23, 0.22, 0.22, 0.22). [b] Prepared in 35% yield by cyclizing the corresponding ketimine hydrochloride thermally.

BLACKSBURG, VIRGINIA

[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, UNIVERSITY OF TORONTO AND IOWA STATE COLLEGE]

Base-catalyzed Elimination Reactions of Triphenylsilanecarboxylic Acid and its Derivatives

BY A. G. BROOK AND HENRY GILMAN

RECEIVED JUNE 7, 1954

The preparations of triphenylsilanecarboxylic acid and its methyl ester are described. It is shown that these compounds are subject to base-catalyzed elimination of carbon monoxide by a variety of nucleophilic reagents. Methyl triphenylsilanecarboxylate is readily reduced to triphenylhydroxymethylsilane by lithium aluminum hydride. Triphenylmethoxysilane has been prepared.

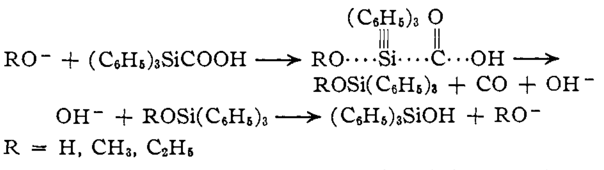
Triphenylsilanecarboxylic acid (I), originally reported by Benkeser and Severson,[1] has been prepared in good yield, free from other products, by the carbonation of triphenylsilylpotassium.[2]

$$(C_6H_5)_3Si{-}Si(C_6H_5)_3 \xrightarrow{Na/K} (C_6H_5)_3SiK \xrightarrow{CO_2}$$

$$\underset{I}{(C_6H_5)_3SiCOOH} \xrightarrow{CH_2N_2} \underset{II}{(C_6H_5)_3SiCOOMe} \xrightarrow{LiAlH_4} \underset{III}{(C_6H_5)_3SiCH_2OH}$$

The yields of acid from this reaction were reproducible only with difficulty, due to a base-catalyzed decomposition which the acid undergoes with great facility, in which triphenylsilanol and carbon monoxide are produced. When this decomposition was avoided by working rapidly in the cold, reproducible yields in excess of 80% were obtained.

While crude triphenylsilanecarboxylic acid is relatively unstable, decomposing in warm absolute ethanol with the evolution of carbon monoxide,[1] purified samples are relatively stable and fail to decompose in absolute ethanol or in ethanol–pyridine solutions. Complete decomposition of the pure acid, with evolution of carbon monoxide occurs rapidly by treatment of the acid with only catalytic amounts of aqueous sodium hydroxide or sodium ethoxide in absolute ethanol, and more slowly with sodium methoxide in absolute methanol, or with aqueous pyridine. In each case the only products isolated from the reaction are carbon monoxide, liberated quantitatively, and triphenylsilanol. These reactions are summarized in the equations



$$RO^- + (C_6H_5)_3SiCOOH \longrightarrow RO\cdots\overset{(C_6H_5)_3}{\overset{|||}{Si}}\cdots\overset{O}{\overset{\|}{C}}\cdots OH \longrightarrow ROSi(C_6H_5)_3 + CO + OH^-$$

$$OH^- + ROSi(C_6H_5)_3 \longrightarrow (C_6H_5)_3SiOH + RO^-$$

R = H, CH_3, C_2H_5

It appears probable that a nucleophilic attack by the base on the acid occurs, and that triphenylalkoxysilane, carbon monoxide and hydroxyl ion are initially formed. This latter species then competes with the alkoxyl ion for the remaining acid and, further, causes hydrolysis of the triphenylalkoxy-

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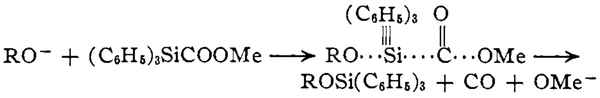
[1] R. A. Benkeser and R. G. Severson, THIS JOURNAL, **73**, 1424 (1951).

[2] Henry Gilman and T. C. Wu, *J. Org. Chem.*, **18**, 753 (1953).

silane already formed, so that only triphenylsilanol is isolated. Evidence for these reactions was obtained by treatment of triphenylsilanecarboxylic acid with 1.3 equivalents of sodium ethoxide in absolute ethanol. Carbon monoxide was evolved but no triphenylethoxysilane could be detected, and a 79% yield of triphenylsilanol was obtained. Under the same conditions, triphenylethoxysilane, when treated with 1.3 equivalents of sodium hydroxide in absolute ethanol, yielded 73% of triphenylsilanol and only 8% of recovered triphenylethoxysilane.

No evidence has been found that the decomposition of triphenylsilanecarboxylic acid is acid catalyzed. The compound is stable to brief refluxing in ethanol containing a trace of aqueous hydrochloric acid. Prolonged refluxing of the carboxylic acid with 6 *N* sulfuric acid, or in solution with ethanol and 6 *N* sulfuric acid, resulted in partial elimination of carbon monoxide, but an equivalent amount of decomposition occurred when the sulfuric acid was replaced by distilled water.

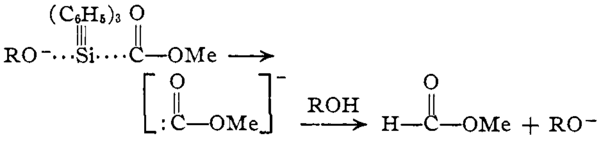
Treatment of triphenylsilanecarboxylic acid with excess diazomethane gave an 84% yield of methyl triphenylsilanecarboxylate (II), the first-reported α-silanecarboxylic acid ester. The compound is a reasonably stable solid melting at 109°, but like the parent acid, is very sensitive to alkaline reagents. Treatment of the compound at room temperature with catalytic amounts of sodium hydroxide, sodium methoxide or sodium ethoxide yielded triphenylsilanol, triphenylmethoxysilane and triphenylethoxysilane, respectively, each in good yield, as well as carbon monoxide. These reactions are summarized by the following equation. The reactions presumably pass through a pentacovalent intermediate in accordance with recent studies of the displacement reactions of silicon.[3]



$$RO^- + (C_6H_5)_3SiCOOMe \longrightarrow RO\cdots\overset{(C_6H_5)_3}{\overset{|||}{Si}}\cdots\overset{O}{\overset{\|}{C}}\cdots OMe \longrightarrow ROSi(C_6H_5)_3 + CO + OMe^-$$

$R = H, CH_3, C_2H_5$

It has recently been found in this Laboratory that in these decompositions carbon monoxide is not liberated quantitatively, although the triphenylalkoxysilane is obtained in nearly quantitative yield, and none of the ester is recovered. It appears probable that some methyl formate is formed.[4]



$$RO^-\cdots\overset{(C_6H_5)_3}{\overset{|||}{Si}}\cdots\overset{O}{\overset{\|}{C}}—OMe \longrightarrow \left[:\overset{O}{\overset{\|}{C}}—OMe\right]^- \xrightarrow{ROH} H—\overset{O}{\overset{\|}{C}}—OMe + RO^-$$

This reaction is being investigated.

Treatment of methyl triphenylsilanecarboxylate with lithium aluminum hydride led to a smooth reduction of the compound to triphenylhydroxymethylsilane (III).

The elimination of carbon monoxide from a carboxylic acid under such mild conditions has not hitherto been observed in organic chemistry. The facility with which these decompositions occur is significant in that it clearly demonstrates the marked susceptibility of silanes bearing electron-attracting substituents to attack by nucleophilic reagents. Evidence will be presented in a future communication relating to the thermal instability of organosilicon and organogermanium compounds that elimination of carbon monoxide is generally characteristic of α-silane- and α-germanecarboxylic acids and their esters.

Experimental[5]

Triphenylsilanecarboxylic Acid.—Triphenylsilylpotassium, prepared by cleavage of 20.0 g. (0.0386 mole) of hexaphenyldisilane with 3.5 ml. of 1:5 sodium–potassium alloy in 100 ml. of dry ether over 18 hours, was amalgamated with mercury,[2] and after removal of the amalgam through a stopcock in the bottom of the flask, the suspension was dripped onto Dry Ice slurried in ether. As soon as the reaction mixture had warmed to room temperature, 100 ml. of ice-cold water was added, and without attempting to dissolve all the solids, the ether layer was removed with a separatory funnel and was discarded. The aqueous suspension was rapidly acidified to *p*H 4 with cold 5% hydrochloric acid, and the precipitated material was immediately filtered off and washed with several portions of ice-cold water. It was then thoroughly dried in a vacuum desiccator at room temperature at 2 mm. pressure for 12 hours. This 20.5 g. (87%) of crude triphenylsilanecarboxylic acid melted at 175–177° with evolution of a gas. Comparable yields were obtained when this procedure was repeated, but when attempts were made to get all the solid into solution prior to separation of the ether layer through use of dilute sodium hydroxide, or when triphenylsilylpotassium dissolved in ethylene glycol dimethyl ether[6] was employed, much lower yields of acid were obtained which were badly contaminated with triphenylsilanol. Under thesel atter conditions, considerable triphenylsilanol could also be recovered from the ether layer.

Recrystallization was achieved by adding 50 ml. of boiling benzene to 5.0 g. of the crude acid slurried in about 5 ml. of benzene. This mixture was then rewarmed to boiling, and the almost clear solution was filtered. To the hot filtrate was added 50 ml. of boiling petroleum ether (b.p. 60–70°) and from this solution 3.68 g. (74%) of pure triphenylsilanecarboxylic acid, m.p. 183–184° with evolution of gas, precipitated as shiny crystals. The infrared spectrum was similar to that of triphenylacetic acid, except for some shift in the position of the absorption bands due to the substitution of silicon for carbon.[7]

Anal. Calcd. for $C_{19}H_{16}O_2Si$: C, 75.0; H, 5.3. Found: C, 75.1; H, 5.4.

Occasionally, samples of triphenylsilanecarboxylic acid were found to contain triphenylsilanol, resulting from decarbonylation. This was best removed, with some loss of acid, by refluxing the mixture in carbon tetrachloride (5 ml. per g.) in which the acid is only slightly soluble, and filtering the suspension hot, the triphenylsilanol being removed in the solution.

Behavior of Triphenylsilanecarboxylic Acid. In Solution.—A solution of 1.0 g. (0.0033 mole) of the crude acid in 15 ml. of warm absolute ethanol slowly evolved a gas after about 1 minute. This was shown to be carbon monoxide since filter paper dipped in a 5% aqueous palladium chloride solution and held in the mouth of the flask rapidly turned black.[8] The solution was cooled at once and from it separated 0.2 g. (20%) of acid, m.p. 182–183° with evolution of gas, and from the mother liquor was isolated 0.5 g. (55%) of triphenylsilanol, m.p. 147–149°, identified by mixed melting point with an authentic specimen.

When the purified acid was treated similarly, no carbon monoxide was liberated after 20 minutes refluxing and the acid, m.p. 182–184°, was recovered unchanged in 80% yield.

With Sodium Hydroxide.—When 1.0 g. (0.0033 mole) of pure triphenylsilanecarboxylic acid in 15 ml. of absolute

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(3) C. G. Swain, R. M. Esteve and R. H. Jones, THIS JOURNAL, **71**, 965 (1949).

(4) J. A. Christiansen and J. C. Gjaldbaek, *Kgl. Danske Videnskab. Selskab.. Math.-fys. Medd.*, **20**, No. 3, 22 (1942) [*C. A.*, **38**, 3898 (1944)].

(5) Melting points are uncorrected.

(6) A. G. Brook and H. Gilman, THIS JOURNAL, **76**, 278 (1954).

(7) We are indebted to Dr. V. A. Fassel, Mr. M. Margoshes and the Ames Laboratory for the infrared data.

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

ethanol was treated at room temperature with 2 drops of 10% aqueous sodium hydroxide, an immediate and rapid evolution of carbon monoxide occurred. Removal of the solvent under reduced pressure, and recrystallization from petroleum ether (b.p. 90–100°), yielded 0.07 g. (8%) of hexaphenyldisiloxane, m.p. 222–224°, identified by mixed melting point, and 0.85 g. (90%) of triphenylsilanol, m.p. 148–150°, identified by mixed melting point with an authentic specimen. The formation of hexaphenyldisiloxane was undoubtedly due to the dehydration of triphenylsilanol by the trace of base present, for if instead of removing the ethanol to recover the product the ethanol solution was poured into excess water and neutralized, the product isolated was pure triphenylsilanol, m.p. 149–150°, obtained in 92% yield, and no trace of hexaphenyldisiloxane could be found.

The carbon monoxide evolved from these base-catalyzed decarbonylations was quantitatively measured by connecting a flask containing 0.38 g. (0.00125 mole) of triphenylsilanecarboxylic acid in 15 ml. of absolute ethanol with a mercury-filled gas buret. After equilibration of the system 0.5 ml. of 10% sodium hydroxide was added and the system was magnetically stirred for 0.5 hour. Over this time a total of 28.0 ml. (0.00114 mole, 91%) of gas was collected at 25°, 758 mm. Approximate correction for the carbon monoxide dissolved in the ethanol raised this yield to 99%. No carbon dioxide could be detected when the gas was bubbled through a barium hydroxide solution. From the ethanol solution was isolated 0.29 g. (84%) of triphenylsilanol, m.p. 148–150°, identified by mixed melting point.

With Sodium Methoxide.—When 0.1 g. (0.00033 mole) of triphenylsilanecarboxylic acid in 5 ml. of anhydrous methanol was treated with 0.03 ml. (0.00026 mole) of a solution of 0.1 g. of sodium in 5 ml. of anhydrous methanol at room temperature, carbon monoxide was very slowly evolved. After about 30 minutes the reaction mixture was worked up and 0.09 g. of crude solid melting from 151–166° with evolution of gas was isolated. The mixed melting point with authentic triphenylsilanol was slightly depressed. The crude material was again treated with 0.03 ml. of the same sodium methoxide solution for an additional 3 hours. Additional carbon monoxide was evolved during this period. After working up the reaction a total of 0.05 g. (55%) of triphenylsilanol, m.p. 150–151°, was isolated which did not depress the mixed melting point when admixed with an authentic specimen. No triphenylmethoxysilane could be detected.

When a suspension of 0.05 g. of triphenylsilanecarboxylic acid in 3 ml. of ethanol, 0.5 ml. of pyridine and 0.5 ml. of water was left at room temperature for 3 hours, carbon monoxide was evolved slowly.[8] However, when a solution of 0.05 g. of the acid in 3 ml. of absolute ethanol and 0.5 ml. of anhydrous pyridine were refluxed for 5 minutes, no carbon monoxide was evolved.

With Sodium Ethoxide.—When 1.0 g. (0.0033 mole) of triphenylsilanecarboxylic acid in 20 ml. of absolute ethanol was treated at room temperature with 2 drops (approx. 0.00035 mole) of a solution of 0.1 g. of sodium in 5 ml. of absolute ethanol, an immediate evolution of carbon monoxide occurred. The reaction was worked up to give 0.9 g. (98%) of crude triphenylsilanol, m.p. 137–147°, which when admixed with authentic triphenylsilanol melted at 146–149°. Recrystallization from petroleum ether (b.p. 90–100°) yielded 0.8 g. of pure triphenylsilanol, m.p. 149–150°. No triphenylethoxysilane could be found.

To 0.5 g. (0.00165 mole) of triphenylsilanecarboxylic acid in 5 ml. of anhydrous ethanol was added 0.00217 mole of sodium ethoxide in ethanol. After 10 minutes the reaction was worked up as above to yield 0.41 g. (90%) of crude triphenylsilanol, m.p. 135–145°, which after recrystallization from petroleum ether (b.p. 60–70°) weighed 0.36 g. (79%) and melted at 148–151°. A mixed melting point with an authentic sample was not depressed.

As a comparison to this result, the hydrolysis of triphenylethoxysilane was studied. To 0.5 g. (0.00165 mole) of triphenylethoxysilane in 5 ml. of ethanol was added 0.086 g. (0.00215 mole) of sodium hydroxide in 1.7 ml. of absolute ethanol. After 12 minutes the reaction was drowned in water and worked up to yield 0.33 g. (73%) of triphenylsilanol, m.p. 151–152°, and 0.04 g. (8%) of recovered triphenylethoxysilane, m.p. 59–62°, both products being identified by mixed melting points.

With Acid.—When 1.0 g. (0.0033 mole) of pure triphenylsilanecarboxylic acid in 10 ml. of absolute ethanol was refluxed for 2 minutes in the presence of 2 drops of 10% aqueous hydrochloric acid, no carbon monoxide was evolved.[8] When a suspension of 0.2 g. of the acid in 5 ml. of 6 *N* sulfuric acid was refluxed, carbon monoxide was detected after 23 minutes. After a total of 30 minutes refluxing, the suspension was cooled and the solid filtered, washed and dried. A total of 0.14 g. (70%) of triphenylsilanecarboxylic acid, m.p. 181–183° with gas evolution, was recovered which was identified by mixed melting point with an authentic sample. For comparison, a blank run was carried out in which 0.2 g. of the acid was refluxed in 5 ml. of distilled water. Carbon monoxide was detected after 15 minutes. After 30 minutes, the reaction mixture was worked up as above and 0.14 g. (70%) of triphenylsilanecarboxylic acid, m.p. 183–184° with evolution of carbon monoxide, was isolated and identified by a mixed melting point with an authentic specimen.

A solution of 0.13 g. of triphenylsilanecarboxylic acid in 6 ml. of ethanol and 1 ml. of 6 *N* sulfuric acid was refluxed for 20 minutes. Carbon monoxide was detected after 11 minutes. After 20 minutes under reflux, the reaction mixture was worked up to yield 0.11 g. of crude material which melted from 142–155° with evolution of gas. Recrystallization from ethanol yielded 0.065 g. (50%) of triphenylsilanecarboxylic acid, m.p. 183–184° with evolution of carbon monoxide, which did not depress the mixed melting point with an authentic sample.

A blank run, made with 0.13 g. of triphenylsilanecarboxylic acid, 6 ml. of ethanol and 1 ml. of water gave essentially similar results. Carbon monoxide was detected after 6 minutes reflux, and the precipitate formed by drowning the reaction after a total of 20 minutes reflux weighed 0.09 g. and melted from 150–162° with gas evolution. Recrystallization from ethanol yielded 0.055 g. (42%) of triphenylsilanecarboxylic acid, m.p. 181–183°, identified by mixed melting point with an authentic sample. No attempt was made in these runs to isolate the triphenylsilanol formed during the decomposition.

Methyl Triphenylsilanecarboxylate.—To 1.0 g. (0.0033 mole) of triphenylsilanecarboxylic acid in 10 ml. of ether was added excess ethereal diazomethane. A gas was immediately evolved. When gas evolution had ceased, the ether and excess diazomethane were removed under reduced pressure, and the resulting solid was recrystallized from methanol. The 0.9 g. (84%) of methyl triphenylsilanecarboxylate obtained as thin plates melted at 106–108°. Recrystallization from petroleum ether (b.p. 60–70°) raised the melting point to 107–109°. The infrared spectrum was similar to that of methyl triphenylacetate except for a slight shift in the positions of the absorption bands.

Anal. Calcd. for $C_{20}H_{18}O_2Si$: C, 75.48; H, 5.70. Found: C, 75.47; H, 5.71.

Reactions of Methyl Triphenylsilanecarboxylate. A. With Aqueous Alkali.—To 0.1 g. (0.00031 mole) of methyl triphenylsilanecarboxylate in 10 ml. of ethanol was added 1 ml. of 10% aqueous sodium hydroxide. Carbon monoxide[8] was immediately evolved over a period of 5 minutes. The solution then was warmed briefly and poured into 50 ml. of water and acidified with dilute hydrochloric acid. The solid was filtered off, washed and dried. This 0.085 g. (98%) of material, m.p. 149–150°, was identified as triphenylsilanol since it failed to depress the melting point when mixed with an authentic sample.

B. **With Sodium Methoxide.**—A similar treatment of 0.2 g. (0.00063 mole) of methyl triphenylsilanecarboxylate in 5 ml. of anhydrous methanol at room temperature with 0.04 ml. (0.000035 mole of sodium methoxide) of a solution of 0.1 g. of sodium in 5 ml. of anhydrous methanol yielded carbon monoxide and an oil which crystallized yielding 0.15 g. (82%) of triphenylmethoxysilane, m.p. 53–54°. The mixed melting point with the authentic specimen prepared as described below was not depressed. The total yield of carbon monoxide, measured volumetrically, varied between 74–76% of theory for several runs.

C. **With Sodium Ethoxide.**—To a suspension of 0.1 g. (0.00031 mole) of methyl triphenylsilanecarboxylate in 5 ml. of absolute ethanol was added 0.03 ml. (0.000026 mole of sodium ethoxide) of a solution of 0.1 g. of sodium in 5 ml. of absolute ethanol. Carbon monoxide was immediately evolved. Gas evolution ceased after 10 minutes and the reaction mixture was poured into 50 ml. of water and worked up to yield 0.07 g. (73%) of triphenylethoxysilane, m.p. 59–61°, which did not depress the mixed melting point when admixed with an authentic specimen. The mixed melting point with triphenylmethoxysilane, m.p. 53–54°, was lowered to 38–45°.

Triphenylmethoxysilane.—To 0.1 g. (0.00435 g. atom) of sodium in 15 ml. of anhydrous methanol was added 1.28 g. (0.00435 mole) of triphenylchlorosilane. This mixture was refluxed for 10 minutes, during which time a white solid precipitated. The reaction mixture was then poured into 100 ml. of water and acidified with hydrochloric acid to *p*H 4. The oil which was present was thrice extracted with 10-ml. portions of chloroform which were dried over sodium sulfate. After removal of the chloroform the resulting oil was distilled and 0.88 g. (70%) collected which boiled over the range 166–168° at 1.3 mm. pressure. This oil solidified and melted at 51–53°. After recrystallization from petroleum ether (b.p. 60–70°) it melted at 53.5–54.5°.

Anal. Calcd. for $C_{19}H_{18}OSi$: Si, 9.68. Found: Si, 9.69.

Reduction of Methyl Triphenylsilanecarboxylate.—To 1.2 g. (0.0038 mole) of methyl triphenylsilanecarboxylate in 25 ml. of anhydrous ether was added 0.12 g. (0.0031 mole) of lithium aluminum hydride. After stirring for 3.5 hours, wet ether and then water were cautiously added, and the mixture was acidified with dilute hydrochloric acid. The ether layer was removed, dried with sodium sulfate, and evaporated to dryness under reduced pressure. The solid obtained was recrystallized from 15 ml. of petroleum ether (b.p. 60–70°) and the 0.75 g. (69%) of solid obtained melted at 109–111°. A mixed melting point with authentic triphenylhydroxymethylsilane, m.p. 109–111°, prepared by addition of triphenylsilylpotassium to formaldehyde,[9] was not depressed.

TORONTO, CANADA
AMES, IOWA

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[9] H. Gilman and T. C. Wu, THIS JOURNAL, **76**, 2502 (1954).

[CONTRIBUTION FROM FULMER LABORATORY, DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

A Carbon-14 Tracer Study of the Alkaline Rearrangement of Chlorophenanthraquinones[1,2]

BY DONALD G. OTT[3] AND GRANT GILL SMITH

RECEIVED JANUARY 26, 1954

The percentages of migration of the substituted rings in the alkaline rearrangements of 2-, 3- and 7-chlorophenanthraquinone-9-C^{14} were found to be 83.1, 66.8 and 79.8, respectively. A mechanism for the benzilic acid rearrangement is advanced based on the proposal that the migratory preferences are determined by the initial point of attack by hydroxide ion and not by the intrinsic migratory aptitudes of the aryl groups. Isotope effects of 1.09 and 1.12 were observed in the rearrangements of phenanthraquinones-9-C^{14} and of 2- and 7-chlorophenanthraquinone-9-C^{14}, respectively.

Although a number of substituted phenanthraquinones have been prepared and subjected to alkaline rearrangement since Baeyer[4] first reported the rearrangement of phenanthraquinone, no study of the migratory preferences in this rearrangement has been reported.

The migratory preferences of the chloro substituted rings with respect to the unsubstituted ring in the alkaline rearrangement of 2-, 3- and 7-chlorophenanthraquinone-9-C^{14} have been determined. These values are shown in Table I. The values 4.93 and 2.01 for the migratory preference ratios in 2- and 3-chlorophenanthraquinone-C^{14}, respectively, parallel the values obtained by Neville[5] for the analogous chlorobenzils: *m*-chlorobenzil, 4.10, and *p*-chlorobenzil, 2.05.[6] A study of the migratory preferences in the rearrangement of 1-chlorophenanthraquinone-9-C^{14} is reported elsewhere.[7]

The value of 1.09 ± 0.01 for migration of the identical unsubstituted rings in phenanthraquinone-9-C^{14} is a consequence of the isotope effect. The migration ratios in the rearrangements of 2- and 7-chlorophenanthraquinone-9-C^{14} indicate an isotope effect of 1.12 ± 0.03.

TABLE I

MIGRATORY PREFERENCES IN THE ALKALINE REARRANGEMENT CHLOROPHENANTHRAQUINONES

Compound	Counts/min., $BaCO_3$ plate[a]	Migratory preference[b] Migration ratio subst./unsubst.	Migration, % substd. ring
2-Chlorophenanthraquinone-9-C^{14}	2411 ± 11	4.93 ± 0.23	83.1
2-Chlorofluorenone-9-C^{14}	2158 ± 3	....	..
3-Chlorophenanthraquinone-C^{14}	756 ± 6	2.01 ± .03	66.8
3-Chlorofluorenone-9-C^{14}	543 ± 7	....	..
7-Chlorophenanthraquinone-9-C^{14}	1447 ± 11	3.95 ± .04	79.8
2-Chlorofluorenone-9-C^{14}[c]	315 ± 1	....	..
Phenanthraquinone-9-C^{14}	1112 ± 3	1.09 ± .01[d]	52.1[d]
Fluorenone-9-C^{14}	624 ± 3	....	..

[a] Plates of infinite thickness having an area of 2.4 cm.^{2}. [b] Ratio of the activity per labeled position of the fluorenone to the difference of the activities per labeled position of the phenanthraquinone and the fluorenone. Includes isotope effect. [c] Obtained from 7-chlorophenanthraquinone-9-C^{14}. [d] Isotope effect only.

The syntheses of the carbon-14 labeled chlorophenanthraquinones involved in this study were accomplished by methods such that the position of the chlorine substituents and the positions of the radioactive carbon atoms were unequivocably known.

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[1] Presented in part before the Division of Organic Chemistry, 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March 15, 1953.

[2] Abstracted from a thesis presented to the Graduate Faculty of the State College of Washington by Donald G. Ott in partial fulfillment of the requirements for the degree of Doctor of Philosophy, August, 1953. Supported in part by a grant from the State College of Washington Isotopes Research Fund.

[3] Atomic Energy Commission Predoctoral Fellow, 1951–1953.

[4] A. Baeyer, *Ber.*, **10**, 123 (1877).

[5] M. T. Clark, E. C. Hendley and O. K. Neville, THIS JOURNAL, in press.

[6] The additional bond present in the phenanthraquinones appears to have little effect in determining the course of the rearrangement of these isomers.

[7] G. G. Smith and Donald G. Ott, THIS JOURNAL, **76**, 2342 (1954).