The Products from the Methyl Ketone.—The fractionation of the products was sufficient to isolate the tertiary alcohols from the other products. The analyses of the tertiary alcohols are given in the table. Weighed amounts of the lower boiling fractions in each case were treated with excess semicarbazide hydrochloride in pyridine for 48 hours. After dissolution in ether they were extracted with dilute hydrochloric acid until free of pyridine, washed with water and steam distilled to remove ether and secondary alcohol. The crude residual semicarbazones were filtered, dried and weighed. The weight of product checked within 5–10% of that predicted by the gas analysis.[5] No effort was made to isolate the secondary alcohol. In one case the lower boiling fractions were combined and the amount of ketone determined by measuring the amount of oxime produced.[6] The percentage ketone agreed within 5% of that predicted by the gas analysis.[5]

The Products from the Ethyl Ketones.—The ketones and secondary alcohols were easily separable by distillation from the tertiary alcohols. The analyses of the latter are in Table I. Qualitative tests showed the presence of both ketones and alcohols in the lower boiling fractions, but no effort at quantitative determinations was made.

The Products from the Isopropyl Ketones.—The products were distilled and divided into 3 major portions based on b.p. and refractive index. The intermediate fractions having a constant index of refraction and boiling point were taken as secondary alcohols. Their analyses are in the table. The highest boiling fractions having constant b.p. and refractive index were taken as tertiary alcohol and their analyses are also recorded. No attempt was made to establish the quantity of ketones produced.

The Products from the *t*-Butyl Ketones.—Although the gas analyses indicated a small amount of addition, only one product, having from first to last fraction an almost constant refractive index and b.p., could be found in each case. The amount of tarry residue was not noticeably greater than in the case of the other compounds. The analyses of these two secondary alcohols are recorded.

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(5) Computed on the basis that % ketone + % sec. alcohol = 100%, *e.g.*, the gas analysis indicate sthat in the case of acetophenone the lower fractions would be 92% ketone and 8% sec. alcohol.

(6) E. C. Suratt, J. R. Proffitt, Jr., and C. T. Lester, THIS JOURNAL, **72**, 1561 (1950).

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Some Long-chained Organosilicon Compounds

BY HELMUT MERTEN AND HENRY GILMAN

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As a result of the report of Kharasch and coworkers[1] of the addition of polyhalomethanes to olefins with terminal double bonds and the subsequent publications of several authors[2] of similar reactions of trichlorosilane, it was of interest to investigate the manner in which triphenylsilane, as an analog to triphenylmethane, reacts with olefins.

In the course of a current investigation of the preparation and properties of some long-chained organosilicon compounds, these compounds were synthesized employing the method used by Gadsby[3] for the synthesis of carboxyalkylsilanes. Triphenylsilane was found to add to the olefinic linkage in the presence of benzoyl peroxide to give fair yields of alkyltriphenylsilanes.

$$(C_6H_5)_3SiH + CH_2{=}CH(CH_2)_nCH_3 \xrightarrow{Bz_2O_2} (C_6H_5)_3SiCH_2(CH_2)_{n+1}CH_3$$

The authentic samples of these silanes were prepared by a more conventional method, the reaction of the corresponding organolithium compound with triphenylchlorosilane. The long-chained organolithium compounds were prepared from the corresponding bromides. The *n*-heptadecyl bromide was prepared in 84% yield by means of the silver salt reaction (Hunsdiecker reaction). It was found possible to improve the previously reported yield[4] by taking extreme care in the purification of the silver salt and by scrupulously excluding moisture from the reaction flask. This *n*-heptadecyl bromide was also used in a comparison of the yields of the corresponding organolithium and Grignard compounds. The yield of the Grignard reagent was somewhat lower than that of the corresponding organolithium compound. Since it was expected that the reactivities of the Grignard reagents would be lower than those of the organolithium compounds, only the latter were used for the reaction with triphenylchlorosilane.

Table II records the melting points observed for the *n*-alkyltriphenylsilanes as well as their mixed melting points. It is of particular interest to note that the melting points appear to increase monotonically with additional methylene groups and no al-

TABLE I

n-ALKYLTRIPHENYLSILANES

Triphenyl-silanes	Silicon, %[a] Calcd.	Silicon, %[a] Found	Yield, %[b] Method A	Yield, %[b] Method B	Organo-lithium cmpd. yield, %[c]
n-Dodecyl	6.5	6.5, 6.5	46	67	45
n-Tetradecyl	6.1	6.1, 6.1	52	50	70
n-Hexadecyl	5.8	5.6, 5.6	45	30	60
n-Heptadecyl	5.6	5.4, 5.3		43	75
n-Octadecyl	5.5	5.5, 5.6	40	70	48

[a] Silicon was determined as silica by the method of H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, THIS JOURNAL, **72**, 5767 (1950). [b] Method A represents the peroxide initiated reaction; method B, the reaction of triphenylchlorosilane with the corresponding *n*-alkyllithium compound. [c] The yield of the alkyllithium compound was determined by the "double titration" described by H. Gilman and A. H. Haubein, *ibid.*, **66**, 1515 (1944).

TABLE II

MELTING POINTS OF *n*-ALKYLTRIPHENYLSILANES AND THEIR MIXTURES

Triphenylsilanes	M.p.,[a] °C.	Mixed m.p. with deriv. immediately following in table, °C.
n-Dodecyl	64–65	56–58
n-Tetradecyl	66–67	61–64
n-Hexadecyl	68.5–69	67–69.5
n-Heptadecyl	71–71.5	69.5–71.5
n-Octadecyl	72–73	
n-Dodecyl		56–59
n-Hexadecyl		61.5–69
n-Octadecyl		

[a] All melting points are uncorrected.

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(1) M. S. Kharasch, E. V. Jensen and W. H. Urry, *Science*, **102**, 128 (1945); M. S. Kharasch, W. H. Urry and E. V. Jensen, THIS JOURNAL, **67**, 1626 (1945); M. S. Kharasch, E. V. Jensen and W. H. Urry, *ibid.*, **69**, 1100 (1947).

(2) C. A. Burkhard and R. H. Krieble, *ibid.*, **69**, 2887 (1947); A. J. Barry, L. DePree, J. Gilkey and D. E. Hook, *ibid.*, **69**, 2916 (1947); L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *ibid.*, **69**, 188 (1947); **70**, 484 (1948); R. Calas and E. Frainnet, *Bull. soc. chim. France*, 241 (1952); N. Duffant and R. Calas, *ibid.*, 241 (1952); E. Frainnet, *ibid.*, 792 (1953); R. Calas, E. Frainnet and J. Valade, *ibid.*, 792 (1953).

(3) G. N. Gadsby, *Research* (*London*), **3**, 338 (1950).

(4) J. W. H. Oldham, *J. Chem. Soc.*, 100 (1950).

ternation is observed in the melting points of the compounds containing sixteen, seventeen and eighteen carbon atoms in the chain.

The determination of mixed melting points between successive members of this series was undertaken to ascertain whether there would be significant depression in melting points. It was observed that the magnitude of depression decreases with an increase of chain length.[5]

Experimental[6]

The following experimental procedures are described below: the preparation of *n*-heptadecyl bromide and of *n*-heptadecyllithium and the reaction of triphenylsilane with *n*-hexadecyllithium and of tetradecene-1 with triphenylsilane. Similar procedures were used in the preparation and reactions of the homologs. The identity of the corresponding compounds prepared by the two methods was shown by infrared spectra.

***n*-Heptadecyl Bromide.**—To a solution of 56.8 g. (0.2 mole) of stearic acid, m.p. 69.5–70°, in 400 ml. of methanol (95%) in a 2-l. beaker or other appropriate container fitted with a mechanical stirrer was added a solution of 15 ml. (about 0.2 mole) of concd. ammonium hydroxide (C.P., sp. gr. 0.9) in 100 ml. of distilled water. The mixture developed a milky appearance and became clear when it was warmed to 45–50° with continuous stirring. A solution of 42 g. (0.25 mole) of silver nitrate in 200 ml. of distilled water was added over a 20-minute period. When the addition was complete, 300 ml. of distilled water was added and the mixture was allowed to cool to room temperature with continuous stirring.

The precipitated silver stearate was filtered on a 12-cm. büchner funnel, then placed in a 1-l. beaker and stirred with 500 ml. of distilled water for 20 minutes. The silver stearate was filtered again on a büchner funnel and washed with about 100 ml. of distilled water; a similar washing procedure was carried out with about 500 ml. of acetone. Finally the silver stearate was dried in a vacuum oven (1 mm. pressure) at 60–65° for 12 hours in the flask in which the degradation was to be performed. The yield was 62.0 g. (81%). A melting point taken in an evacuated sealed tube was 206° (lit. 208°).

Fifty-one grams (0.13 mole) of silver stearate was placed in a 1-l. four-necked flask. Dry carbon tetrachloride (400 ml.) was distilled from phosphorus pentoxide into this flask. A solution of 21 g. (about 0.13 mole) of bromine in 60 ml. of carbon tetrachloride was distilled from phosphorus pentoxide into a dropping funnel and then was added over a 40- to 50-minute period. When the addition was completed, the mixture was heated for one hour on a steam-bath with continuous stirring. It was then filtered hot and the silver bromide was washed thoroughly with 100 ml. of warm carbon tetrachloride. The reddish colored filtrate was concentrated under reduced pressure at steam-bath temperature. The residue was dissolved in 400 ml. of ether and washed once with 100 ml. of 10% sodium carbonate solution. The ether layer was separated and dried over anhydrous potassium carbonate. The solvent was removed and a white solid was obtained. The weight of this product melting between 27 and 29° was 35.3 g. The yield was 84% based on the weight of the silver stearate.

The improvement of the yield depended not only on the scrupulous exclusion of moisture but also to a great extent on the purity of the silver salt. The presence of free acid in the silver salt reduced the yield significantly.

***n*-Hexadecyllithium.**—In a 500-ml. four-necked flask equipped with a stirrer, a low-temperature thermometer, and a dropping funnel was placed 100 ml. of anhydrous ether. After the apparatus was swept with dry, oxygen-free nitrogen, 1.08 g. (0.15 gram atom) of lithium wire (30 cm.) was cut into small pieces which were allowed to fall directly into the reaction flask in a stream of nitrogen. With the stirrer operating, about 2 ml. of a solution of 18.3 g. (0.06 mole) of *n*-hexadecyl bromide in 100 ml. of anhydrous ether was added from the dropping funnel. After a period of about 30 minutes the mixture became slightly cloudy. The reaction mixture then was cooled to −10° by immersing the flask in a Dry Ice–acetone-bath. The remainder of the *n*-hexadecyl bromide solution was added over a period of two hours while the internal temperature was maintained at −10°. After addition was completed the reaction mixture was kept at the same temperature for one hour and then was allowed to warm up to 0–10° with stirring. The reaction mixture was filtered under an atmosphere of nitrogen by decantation through glass wool into a graduated dropping funnel. The yield, determined by double titration, was 60%.

***n*-Hexadecyltriphenylsilane.**—In a 1-l. three-necked flask equipped with a stirrer, a reflux condenser and a dropping funnel, 10.3 g. (0.035 mole) of triphenylchlorosilane was dissolved in 200 ml. of anhydrous ether. After the apparatus had been swept with dry, oxygen-free nitrogen, the stirrer was started; a colorless solution resulted. Over a period of 30 minutes a solution of 8.06 g. (0.035 mole) of *n*-hexadecyllithium in 295 ml. of anhydrous ether was added. Since Color Test I[7] was still positive after ten hours, another 1.4 g. of triphenylchlorosilane was added. Color Test I was negative after ten minutes. Water (200 ml.) was added and the mixture was stirred for about 20 minutes. The two layers were separated, the water layer was washed with 100 ml. of ether, and the ether extracts were collected and dried over anhydrous sodium sulfate. After about three hours the ether solution was filtered and the ether evaporated. The residue (25.1 g.) was dissolved in 350 ml. of anhydrous petroleum ether (b.p. 60–90°) and was passed through an alumina column (20 × 180 mm.). The column was eluted with 200 ml. of petroleum ether, and the colorless eluate was concentrated on a steam-bath. This material was distilled in a modified molecular still. The main fraction, between 225–235° (0.005 mm.) (air-bath temperature), was recrystallized twice from glacial acetic acid and twice from absolute ethanol, giving 4.4 g. (30%) of *n*-hexadecyltriphenylsilane, m.p. 68.5–69.5°.[8]

***n*-Tetradecyltriphenylsilane.**—A 250-ml. three-necked flask equipped with a stirrer and a reflux condenser was flushed with dry oxygen-free nitrogen; 26.0 g. (0.10 mole) of triphenylsilane, 0.32 g. (0.0013 mole) of benzoyl peroxide, 3.2 g. (0.016 mole) of tetradecene-1 and 25 ml. of *n*-hexane were added and stirring commenced. The flask was heated with an oil-bath (70–75°). The reaction mixture was refluxed gently for 14 hours in a dry nitrogen atmosphere. The reaction product was transferred to a modified molecular still and distilled. After an initial fraction between 110–160° (0.005 mm.) (air-bath temperature) a colorless product was obtained between 180–220° (0.005 mm.). It was redistilled to give 4.2 g. of white crystals, m.p. 54–56° (59%). After repeated recrystallizations of this crude material from absolute ethanol and treatment with charcoal, 3.9 g. (52%, based on tetradecene-1) of *n*-tetradecyltriphenylsilane, m.p. 66–67°, was isolated.

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[5] The triphenyllead salts of lauric, myristic, palmitic and stearic acids exhibit the same behavior: H. Gilman and G. M. Ford, *Iowa State Coll. J. Sci.*, **13**, 135 (1939).

[6] All reactions involving organometallic compounds were carried out in a dry, oxygen-free nitrogen atmosphere. Melting points are uncorrected.

[7] H. Gilman and F. Schulze, THIS JOURNAL, **47**, 2002 (1925).

[8] The qualitative test for silicon described by H. Gilman, R. K. Ingham and R. D. Gorsich, *ibid.*, **76**, 918 (1954), was used successfully to characterize solid fractions obtained from a chromatogram of the product of the reaction of *n*-heptadecyllithium and triphenylchlorosilane.

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Preparation and NaBH$_4$ Reduction of 7-Ketocholanic Acid

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Studies on the metabolism of 7-ketocholesterol[1] made it desirable to have 7-ketocholanic and the

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[1] F. E. Kendall, E. H. Mosbach, L. L. Abell and W. Meyer, *Federation Proc.*, **12**, 449 (1953).