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TETRACYCLOHEXYLSILANE: THE RESOLUTION OF AN ENIGMA*

LEONARD SPIALTER, GLEN R. BUELL, CHARLES W. HARRIS AND J. DUDLEY AUSTIN**
Chemistry Research Laboratory, Aerospace Research Laboratories, Office of Aerospace Research, Wright-Patterson AFB, Ohio (U.S.A.)

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INTRODUCTION

The objective of this paper is the resolution of a state of confusion in the literature resulting from conflicting published reports on the synthesis of tetracyclohexylsilane, (I)***. In 1954, Petrov and Chernysheva[1] described the preparation of this compound, of melting point 198, [labelled (I – P) in reaction (1)], from the condensation reaction of cyclohexyllithium with either tetrafluorosilane or with dicyclohexyldifluorosilane.

$$C_6H_{11}Cl+Li \xrightarrow[\text{pet. ether}]{Et_2O\text{ or}} C_6H_{11}Li \xrightarrow[(C_6H_{11})_2SiF_2]{SiF_4\text{ or}} \underset{\text{(I–P)}}{(C_6H_{11})_4Si} \qquad (?,\text{ m.p. }198^\circ) \qquad (1)$$

$$Ph_4Si+H_2 \xrightarrow{Ni} \underset{\text{(I–K)}}{(C_6H_{11})_4Si} \qquad (?,\text{ m.p. }281^\circ) \qquad (2)$$

where C_6H_{11} = cyclohexyl; Ph = Phenyl.

Structure proof was based on the method of synthesis and analyses for only silicon (7.41 and 7.87% compared to the theoretical 7.77%). Simultaneously and independently, Kanazashi and Takakusa[2] reported the nickel-catalyzed hydrogenation, with difficulty, of tetraphenylsilane to tetracyclohexylsilane, melting at 281°, [labelled (I–K) in reaction (2)]. Molecular identity was based on the nature of the reaction, on similarities among the infrared absorption bands compared to those for other cyclohexylsilanes, and on analyses for carbon and hydrogen only. They also predicted that steric hindrance should preclude synthesis of the compound by organometallic condensation, supporting an earlier unsuccessful attempt by Nebergall and Johnson[3]. It was also postulated, from the study of molecular models, that there was no free rotation nor "inverted isomerism involving *p*-bond" (*sic*). Gilman and Mills[4] subsequently rationalized the existence of the two "tetracyclohexylsilanes" as being due to rotational isomerism analogous to that evoked to explain the two tetra-*o*-tolylsilanes[5]. Recently, Takakusa[6] was unable to confirm the results of Petrov and Cher-

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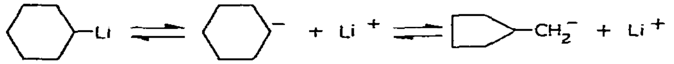
*** A synthesis of tetracyclohexylsilane by the heating of silicon powder, sodium tetracyclohexylaluminate, and cyclohexyl iodide in toluene is claimed in a patent by G. C. ROBINSON, U.S. 3,057,894 (Oct. 9, 1962), but no physical properties are described.

nysheva[1] and he suggested[7] that their product might actually be tricyclohexyl(cyclohexyloxy)silane (II), which has a closely agreeing silicon analysis (7.42%). He could not isolate this latter molecule from the reaction of cyclohexyllithium with fluorosilanes, the Petrov–Chernysheva conditions, (no reaction occurred even at 150–160° for 12 hours), but with chlorosilanes, some of it was isolated. Eaborn[8], earlier, had also obtained this oxygen-containing compound from treatment of dicyclohexylfluorosilane with cyclohexylmagnesium bromide. However, neither Eaborn[8] nor Takakusa[6] reproduced the Petrov–Chernysheva reaction exactly and neither explained the origin of the oxygen in their proposed structures.

An alternative explanation for the existence of two (or more) isomeric forms of tetracyclohexylsilane is the possibility of differing combinations of frozen boat-chair conformers for the cyclohexyl substituents. In view of the large steric requirements of cyclohexyl and the compact nature of the silane (I), (as evidenced in Stuart–Briegleb scale molecular models), separate isolable crystal modifications, such as one with one boat and three chair cyclohexyls, or another with two boat and two chair conformations, as well as others, for its substituents, might possibly exist.

In considering the Petrov–Chernysheva condensation procedure, it appeared that yet another rationale for the apparent occurrence of different tetracyclohexylsilanes might be molecular rearrangement of the cyclohexyllithium reagent, used in the Petrov–Chernysheva condensation, to cyclopentylmethyllithium. Any rearrangement would not alter the analytical results, but would produce the isomeric tricyclohexyl(cyclopentylmethyl)silane (III). The alkyl group in the lithium reagent should have substantial carbanion character and an equilibrium between cyclohexyl and cyclopentylmethyl species (Reaction 3) could exist. An analogous equilibrium for the corresponding carbonium ions is known to exist[9]. It is also responsible for an erroneous literature citation[10] to the preparation of cyclopentylmethyl chloride from cyclopentylcarbinol and phosphorus pentachloride, which actually gave cyclohexyl chloride based on the cited physical properties and our own repetition of the synthesis, as detailed in the experimental section below.



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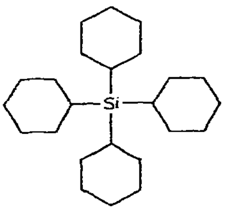
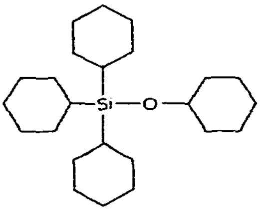


(I)



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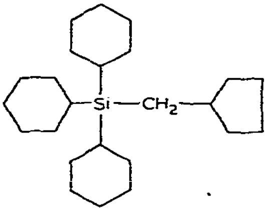

(III)

RESULTS AND DISCUSSION

The catalytic hydrogenation of tetraphenylsilane gave the same product as that reported by Kanazashi and Takakusa[2]. Although intermediate products, such as the various mixed phenyl, cyclohexylsilanes, were found under partial reaction conditions and identified by gas chromatographic comparison with authentic samples produced by condensation reactions[11], no stereoisomeric forms of tetracyclohexylsilane were detected. This confirms Takakusa's negative results in this direction[7]. The search for stereoisomers was extended to studies on the more sterically hindered carbon analog, tetracyclohexylmethane. This previously unreported compound proved to be preparable, contrary to the prediction of Kanazashi and Takakusa, by catalytic hydrogenation of tetraphenylmethane*. Here, too, however, no evidence was found for the existence of stereoisomers.

Additional evidence for the correct structural assignments to hydrogenation-produced tetracyclohexylsilane and tetracyclohexylmethane were obtained from their successful dehydrogenation to the respective parent tetraphenyl compound[11,12] and their appropriate retention times in a vapor phase chromatography when compared to those of other closely related compounds. It was found that on a DC 550 silicone capillary column, the cyclohexyl group contributed a significantly lower retention than did a phenyl group.

It therefore appeared that Kanazashi and Takakusa[2] indeed had tetracyclohexylsilane, and that the occurrence of stereoisomers was not likely. However, the identity of the Petrov–Chernysheva compound (I–P) remained to be determined. To check out the possibility of rearrangement of cyclohexyllithium to cyclopentylmethyllithium, it was deemed most expeditious to synthesize tricyclohexyl(cyclopentylmethyl)silane (III) by an unequivocal route and to compare its physical properties with those of (I–P). The final successful route is given in Fig. 1.

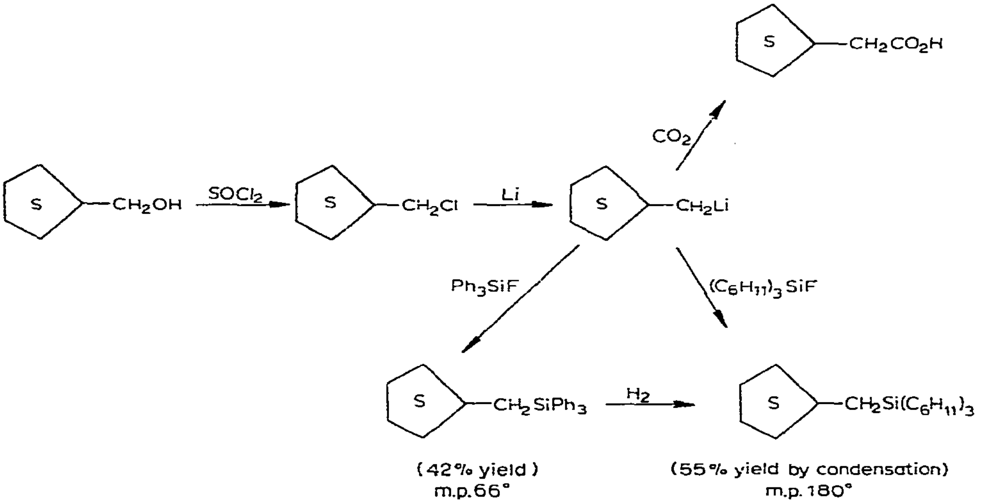

Fig. 1. Synthesis path for tricyclohexyl(cyclopentylmethyl)silane.

The non-occurrence of rearrangement or equilibrium (Reaction 3) at a fast rate was indicated by reacting cyclohexyl chloride and cyclopentylmethyl chloride with lithium, to give the corresponding organolithium compounds, and then carbonating them with carbon dioxide (a rapid reaction) to yield the separate expected carboxylic acids, naphthenic and cyclopentylacetic acid, respectively. However, it

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* The experimental details of tetracyclohexylmethane synthesis are reported in ref. 12.

remained conceivable that in a crowded condensation reaction, as with tricyclohexylfluorosilane, only the cyclopentylmethyllithium component (with lower steric requirement) of the proposed equilibrium mixture might react and thus drive the equilibrium in its direction over the long reaction times used. If this were the case —and no consideration had previously been given to this point— incorrect structures, not differentiated by any of the earlier studies, might have been assigned in the literature.

In stepwise studies of the Petrov–Chernysheva procedure[1] it was found, first of all, that cyclohexyllithium will condense with dicyclohexyldifluorosilane to give tricyclohexylfluorosilane in 62% yield. This product was identical in physical properties (melting point, infrared absorption, and vapor phase chromatogram) with that obtained in 87% yield by catalytic hydrogenation of triphenylfluorosilane*. On the reasonable assumption that no rearrangement occurs during hydrogenation of a phenyl group, the results of hydrogenation support the integrity of the six-membered rings in the molecule.

Tricyclohexylfluorosilane was then condensed with cyclopentylmethyllithium to ascertain whether the product tricyclohexyl(cyclopentylmethyl)silane, corresponded with the Petrov–Chernysheva compound. The silane had a melting point of 179–180°. Its structure was verified by both elemental analysis and residence time on a vapor phase chromatographic capillary silicone column (clearly distinguishable from that for hydrogenation-synthesized tetracyclohexylsilane), as well as independent synthesis by catalytic hydrogenation of triphenyl(cyclopentylmethyl)silane (from condensation of cyclopentylmethyllithium with triphenylfluorosilane) and comparison of physical properties. This compound did not coincide with that described by Petrov and Chernysheva.

The final check on the possibility of steric selectivity and its influence on the equilibrium system (Reaction 3) was the repetition of the Petrov–Chernysheva condensation, but with only one last substitution required. Authentic tricyclohexylfluorosilane was treated with cyclohexyllithium. No condensation reaction was discernible in solutions in diethyl ether, at $-10°$ or 20°, or in hexane at 60°**. After refluxing of the reagent in cyclohexane for 18 hours, or heating without solvent at 130° for 12 hours, more than half of the initial tricyclohexylfluorosilane was physically recovered unchanged, but, in addition, vapor phase chromatography disclosed the presence of tricyclohexylsilane, tricyclohexyl(cyclohexyloxy)silane, and tetracyclohexylsilane in the hydrolyzed reaction product mixture. The last-named compound was identical to that obtained by hydrogenation of tetraphenylsilane. The tricyclohexyl(cyclohexyloxy)silane, identified by comparison with an authentic sample, was the principal reaction product. Its occurrence and properties support Takakusa's suggestions[7] that this was also the compound obtained by Petrov and Chernysheva. The source of the oxygen appears to be cyclohexanol impurity in the cyclohexyl bromide or chloride used as the starting material for the preparation of cyclohexyllithium. Any such contaminant gives rise to a lithium cyclohexyloxide

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* The probability that triphenylfluorosilane can be hydrogenated readily and cleanly, whereas triphenylsilane cannot, was deduced from concepts introduced by ref. 11.

** An anomalous reaction involving cleavage of ether by cyclohexyllithium to give cyclohexylethyllithium under harsher conditions is described in a note by L. SPIALTER AND C. W. HARRIS submitted to *J. Org. Chem.*

which presumably reacts with tricyclohexylfluorosilane. The cyclohexanol is a likely impurity since even freshly distilled cyclohexyl chloride is readily hydrolyzed by atmospheric moisture and soon develops hydrogen chloride. When pure cyclohexyl halide, freshly prepared, was used, no oxygen-containing product was isolated, and tetracyclohexylsilane was obtained in 22% yield. This compound proved to be identical with that obtained by hydrogenation of tetraphenylsilane.

EXPERIMENTAL

General

Raw materials. Dicyclohexyldifluorosilane was supplied by Stauffer Chemical Co. Triphenylfluorosilane was obtained from Pierce Chemical Co. Lithium, in various forms and grades, came from the Lithium Corp. of America. Various hydrogenation catalysts, palladium, platinum, and rhodium were purchased from K & K Laboratories, Inc.

Equipment and apparatus. Density measurements were made with a Lipkin[17] pycnometer, and refractive indices determined with a Bausch & Lomb Abbe type refractometer, thermostatted with a constant temperature bath. Hydrogenation reactions were conducted on suitable equipment from both the American Instrument Co. and Autoclave Engineers, Inc. Liquid–gas chromatography was performed on silicone-coated capillary columns in Models 226 and 61-C instruments from the Perkin–Elmer Corp. and Barber–Colman Co., respectively. Infrared spectra were obtained on a Perkin–Elmer Model 521 Spectrophotometer and ultraviolet absorption data on a Cary Model 14 instrument.

Analyses. All microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of cyclohexyllithium

Ready and reproducible cyclohexyllithium formation was found to occur only if the lithium used contains at least 0.02% sodium, as is supplied by the Lithium Corporation of America in its "regular" grade or, even better, the "high sodium" (0.8%) lithium. The "low sodium" grade does not perform well*.

In a typical experiment, cyclohexyl chloride (43 g, 0.36 mole) reacted with "high sodium" lithium shot (5.4 g, 0.9 g-atom) in pentane (80 ml) to give cyclohexyllithium, assaying 85% by the double titration method[18].

Preparation of cyclopentylmethyl chloride

Cyclopentylcarbinol was synthesized from cyclopentylmagnesium chloride and paraformaldehyde by the method of Turkiewicz[10]. His results on direct product formation, as well as indirect isolation from the by-product bis[cyclopentylmethyl)-formal, were confirmed. However, although repetition of his procedure for conversion of the carbinol to the corresponding chloride, by reaction with phosphorus pentachloride (PCl_5), gave a product in similar yield (80%) and of the same physical properties (d_4^{22} 0.9938, n_D^{22} 1.4612; compared to Turkiewicz's d_4^{20} 0.993, n_D^{20}

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* C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, 25 (1960) 1807, also comment on the general utility of sodium in lithium.

1.4611), it was not the desired compound. The infrared absorption spectrum and physical properties checked with those determined on an authentic sample of cyclohexyl chloride.

The desired cyclopentylmethyl chloride, which had significantly different physical properties from its isomer above, was prepared from cyclopentylcarbinol, thionyl chloride, and pyridine according to the procedure* described for tetrahydrofuryl chloride[19]. The yield of cyclopentylmethyl chloride was 65%, b.p. 141–143° at 755 mm (lit.[15] b.p. 136–138 at 731 mm), d_4^{22} 0.9811, n_D^{22} 1.4612.

Carbonation of cyclopentylmethyllithium

Cyclopentylmethyllithium, prepared from lithium (0.14 g, 0.02 g-atom) and cyclopentylmethyl chloride (1.2 g, 0.01 mole) in tetrahydrofuran (10 ml) at −20°, was poured slowly over vigorously stirred, freshly powdered solid carbon dioxide. The resulting slush was allowed to stand until all of the carbon dioxide had evaporated. The residue was acidified with hydrochloric acid and extracted with ether. For purification, the acidic solute components were transformed into water-soluble salts by extraction with saturated aqueous sodium bicarbonate and then, after acidification, extracted with ether. There was isolated rancid-smelling liquid, cyclopentylacetic acid (0.6 g, 50% yield). Treatment with thionyl chloride and then ammonium hydroxide characterized the acid through its simple amide, m.p. 143–144° (lit. m.p.[20] 143–145°, m.p.[21] 145.5–146.5°.) The amide of the isomeric cyclohexylcarboxylic acid melts[22] at 188–189°.

Carbonation of cyclohexyllithium

Cyclohexyllithium, prepared from cyclohexyl chloride (4.3 g, 0.04 mole) and lithium shot (0.5 g, 0.09 g-atom) in pentane (10 ml) as described above, was poured onto well stirred, freshly pulverized, solid carbon dioxide. The remainder of the work-up was identical to that described for the carbonation of cyclopentylmethyllithium. Isolated in 50% yield was the odorous solid, cyclohexylcarboxylic acid, m.p. 30.5–31.5° (lit.[23] m.p. 30°).

Preparation of tricyclohexylfluorosilane (by condensation)

To cyclohexyllithium, prepared from cyclohexyl chloride (26.0 g, 0.22 mole) and lithium shot (3 g, 0.5 g-atom) in pentane (40 ml), was added dicyclohexyldifluorosilane (3 g, 13 mmole). The mixture was refluxed for 18 h, hydrolyzed with saturated aqueous ammonium chloride and filtered. The filtrate was extracted with ether and concentrated to give an oil. After distillation of all material boiling up to 120° at 0.5 mm, the still residue, upon being cooled, crystallized. Recrystallization from 1:1 pentane/isopropyl alcohol mixture gave tricyclohexylfluorosilane, m.p. 43–45° (2.4 g, 62%). This was identical with that prepared from tricyclohexylsilanol and hydrofluoric acid by the method of Eaborn[8], m.p. 42–44°.

Preparation of tricyclohexylfluorosilane (by hydrogenation)

Triphenylfluorosilane (50 g, 0.18 mole) was dissolved in methylcyclohexane (75 ml, spectro-quality) and a catalyst of 5% rhodium on charcoal (1 g) was added.

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* A similar procedure is implied in ref. 15. The authenticity of other preparations[14,16] has not been checked.

The mixture was subjected in a magnetically stirred high pressure reactor to 1500 psi of hydrogen at 100° for 12 h to yield, after recrystallization from pentane/isopropyl alcohol, tricyclohexylfluorosilane (44 g, 87%), m.p. 42–44°.

Preparation of tricyclohexyl(cyclohexyloxy)silane

This compound was prepared by the procedure of Eaborn[8] from the sodium salt of cyclohexanol and tricyclohexylchlorosilane. (The latter was synthesized by the method of Nebergall and Johnson[3], using high-sodium lithium.) Yields and physical properties checked closely: tricyclohexylchlorosilane, m.p. 101–102° (lit.[3] m.p. 101–102°); tricyclohexyl(cyclohexyloxy)silane, m.p. 203–204° lit.[8] m.p. 203–204°).

Preparation of tricyclohexyl(cyclopentylmethyl)silane (by condensation)

To cyclopentylmethyllithium, readily prepared under argon from cyclopentylmethyl chloride (5.9 g, 0.05 mole) and lithium wire (0.76 g, 0.11 g-atom) in freshly purified[19] tetrahydrofuran (10 ml) at −10°, was added tricyclohexylfluorosilane (2.97 g, 0.01 mole) in tetrahydrofuran solution (15 ml) at the same temperature. The resulting light brown solution was allowed to warm to room temperature and, about 20 min later, a white precipitate appeared with no appreciable exothermicity. The mixture was stirred for 16 h. The solvent was evaporated under reduced pressure and the residue extracted with pentane. Addition of isopropyl alcohol to the water-washed pentane solution and cooling gave crude product (2.0 g, 55% yield). Recrystallization from n-butyl alcohol yielded white needles, m.p. 178–180°. (Found: C, 79.73; H, 12.19; Si, 7.94; mol.wt. 355. $C_{24}H_{44}Si$ calcd.: C, 79.92; H, 12.30; Si, 7.79%; mol.wt. 360.)

Preparation of triphenyl(cyclopentylmethyl)silane (by condensation)

To cyclopentylmethyllithium, prepared under argon from cyclopentylmethyl chloride (2.6 g, 0.02 mole) and lithium wire (0.8 g, 0.12 g-atom) in freshly purified[19] tetrahydrofuran (10 ml) at −20°, was added triphenylfluorosilane (2.5 g, 0.009 mole) in tetrahydrofuran (5 ml). After overnight stirring of the reaction mix, the solvent was evaporated and the residue recrystallized from pentane/isopropyl alcohol to give white crystalline product (1.3 g, 42% yield), m.p. 64–66°. A mixed melting point determination with triphenylfluorosilane (which also melts at 64°) showed a depression of 16 to 24°. Moreover, the product, unlike the fluoride, shows no infrared absorption band at 12.0 μ. (Found: C, 84.41; H, 7.35; Si, 8.15; mol. wt., 350. $C_{24}H_{26}Si$ calcd.: C, 84.17; H, 7.65; Si, 8.18%; mol.wt., 342.)

Preparation of tricyclohexyl(cyclopentylmethyl)silane (by hydrogenation)

A solution of triphenyl(cyclopentylmethyl)silane (0.50 g), prepared as above, in methylcyclohexane (200 ml) was hydrogenated in the presence of 5% rhodium on charcoal catalyst (0.25 g) at 100° for 12 h with 1500 psi of hydrogen. After evaporation of the solvent recrystallization of the residue from n-butyl alcohol gave the desired product (0.45 g, 90% yield), m.p. 177–180°. It was identical in infrared absorption spectrum and showed no mixed melting point depression with the sample of tricyclohexyl(cyclopentylmethyl)silane prepared by the condensation method above.

Preparation of tetracyclohexylsilane (by condensation)

Run 1. Cyclohexyllithium, prepared in pentane from lithium shot (0.9 g, 0.15 g-atom) and cyclohexyl chloride (6 g, 0.05 mole) which had not been freshly distilled, was added to tricyclohexylfluorosilane (7.5 g, 0.025 mole). After 18 h of refluxing, the reaction mixture was hydrolyzed and extracted with ether. After evaporation of the solvent, the resulting oil had a gas–liquid chromatogram indicating large quantities of tricyclohexylsilanol and tricyclohexylfluorosilane. The crude product was refluxed in aqueous/ethanolic potassium hydroxide for 30 min, precipitated with excess water and extracted with ether and benzene. The organic extract was passed over a column of activated alumina and eluted with pentane. Evaporation of the solvent from the eluate gave 0.2 g of a white, glassy solid. Gas–liquid chromatography showed the absence of any hydroxy or fluorosilane. However, there was a large peak corresponding to tricyclohexyl(cyclohexyloxy)silane and a considerably smaller peak identified as tetracyclohexylsilane, as evidenced by comparison with authentic samples. Recrystallization of the solid from hexane/isopropyl alcohol failed to raise the melting point of the solid above 195–200°. This latter value was not significantly affected by admixture with authentic tricyclohexyl(cyclohexyloxy)-silane, m.p. 203–204°.

Run 2. The procedure above was repeated, but with reaction maintained below −10°, tetrahydrofuran as reaction solvent, and freshly distilled cyclohexyl chloride. There was isolated a 22% yield of tetracyclohexylsilane, m.p. 279–280°, and with all physical characteristics, including melting point, infrared absorption spectrum, and vapor phase chromatographic behavior, identical with those of an authentic sample prepared by the catalytic hydrogenation of tetraphenylsilane. (Found: C, 79.51; H, 12.27; Si, 8.13; mol.wt., 352. $C_{24}H_{44}Si$ calcd.: C, 79.92; H, 12.30; Si, 7.79%; mol.wt., 360.)

SUMMARY

The conflicting experimental data and subsequent rationalizations in the literature on tetracyclohexylsilane are critically examined. It is established that the authentic compound, obtained by hydrogenation of tetraphenylsilane, can be synthesized by organolithium condensation, although a prior report mistakenly identified an impurity-caused product, tricyclohexyl(cyclohexyloxy)silane, as such. Studies on cyclohexyllithium and cyclopentylmethyllithium, as well as the synthesis of tricyclohexyl(cyclopentylmethyl)silane and its aromatic analog, demonstrate that the literature on the subject can be resolved without invoking isomerism due to rearrangement, restricted rotation, frozen conformation, or polymorphism.

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