the above-mentioned modes by which π-electron density on the ring can be altered are operative but that the inductive effect determines the order. The effect must, in fact, be very strong to overshadow the steric factor so important in the alkyl series. These values do not at all approach a reasonable Hammett σ-plot.[25]

It is interesting that values in the 1-series are greater than those in the 2-series. This order of difference, which is the reverse of that expected on the basis of steric considerations, is best interpreted on the basis of a greater facility for electron transmission through the 1-position than the 2-position. This is a capacity for double bond formation or a resonance phenomenon. An examination of the various contributing resonance structures for each series leads one to the same conclusion. The difference between these two series parallels that observed in molecular polarization as reflected in molar Kerr constants; values for the 1-series are one-third to one-half of those for the 2-series.[26]

A comparison of the acidities of α- ($K_a = 2.0 \times 10^{-4}$) and β-naphthoic acid ($K_a = 6.9 \times 10^{-5}$) does not support this, but the carboxyl group of the α-isomer is somewhat hindered by the 8-position, and the difference in acidities is perhaps better explained in terms of an "*ortho* effect."[27]

Alkoxynaphthalenes.–The 1-alkoxynaphthalene complexes are significantly more stable than those of the 2-series. Here again it is apparent that the difference between the two series is best explained in terms of a greater facility for double bond formation at the 1-position; resonance effects here, as in the halogenonaphthalenes, dictate the relative series difference. Values within each series, however, do not follow any reasonable order and as yet are unexplained.

Acetonaphthones.–The association constant for the 1-acetonaphthone complex is seen to be greater than that of the 2-isomer, but both values are significantly higher than might be anticipated. The presence of the acetyl group in either position should effectively diminish the π-electron density on the ring and thereby weaken the complex binding. The fact that these values are comparable with those of the ethylnaphthalenes, which have a similar steric requirement in the substituent, suggests that other factors are involved in the acetonaphthones. It is possible, for example, that the carbonyl group behaves as a "localized" donor as appears to be the case with aryl amines,[1] and possibly with the alkoxynaphthalenes considered above and the association constants reflect both types of complexation. This explanation is supported by the higher value for the 1-isomer; resonance effects, transmitted through the 1-position more readily than the 2-position, should permit greater polarization of the carbonyl group in the 1-isomer. In this regard, it should be noted that even 1-nitronaphthalene has an appreciable tendency to complex with picric acid.

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[25] This is perhaps apparent from a cursory inspection of the σ-values (*meta* or *para*) in the halogen series. The order of electron-withdrawing power is the reverse of that observed here.

[26] C. H. LeFevre and R. J. W. LeFevre, *J. Chem. Soc.*, 1641 (1955).

[27] J. F. J. ippy, *Chem. Revs.*, **25**, 151 (1939).

[CONTRIBUTION NO. 752 FROM THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY]

Formation of the Silicon–Hydrogen Bond by the Reducing Action of Certain Sterically Hindered Grignard Reagents on Phenyltrichlorosilane

BY MACK C. HARVEY, WILLIAM H. NEBERGALL AND JOHN S. PEAKE

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Certain sterically hindered Grignard reagents have been found to react with phenyltrichlorosilane, $C_6H_5SiCl_3$, to form dialkylphenylsilanes, $R_2C_6H_5SiH$, and unsaturated hydrocarbons. By such reactions dicyclohexylphenylsilane and cyclohexene, dicyclopentylphenylsilane and cyclopentene, diisopropylphenylsilane and propene and di-*t*-butylphenylsilane and isobutylene have been obtained. Attempts to prepare di-*o*-tolylphenylsilane by this method were unsuccessful.

In 1933, Cusa and Kipping[1] reported that when no precautions were taken to exclude atmospheric oxygen, cyclohexoxydicyclohexylphenylsilane, $(C_6H_{11})_2C_6H_5SiOC_6H_{11}$, was formed when the product of the reaction of phenyltrichlorosilane with an excess of cyclohexylmagnesium bromide was hydrolyzed. When the reaction was carried out under nitrogen, however, the principal reaction product was found to be dicyclohexylphenylsilane, $(C_6H_{11})_2C_6H_5SiH$. These investigators suggested that $(C_6H_{11})_2C_6H_5SiMgBr$ was formed as an intermediate, which upon hydrolysis gave $(C_6H_{11})_2C_6H_5SiH$.

$$C_6H_5SiCl_3 + 2C_6H_{11}MgBr \longrightarrow (C_6H_{11})_2C_6H_5SiCl + 2MgBrCl$$

$$(C_6H_{11})_2C_6H_5SiCl + C_6H_{11}MgBr \longrightarrow (C_6H_{11})_2C_6H_5SiMgBr + C_6H_{11}Cl$$

$$(C_6H_{11})_2C_6H_5SiMgBr + H_2O \longrightarrow (C_6H_{11})_2C_6H_5SiH + Mg(OH)Br$$

It should be noted that tricyclohexylphenylsilane is not formed here due to the steric effects of the cyclohexyl group.[1,2]

Because various workers[3,4] have been unsuccessful in attempts to prepare stable Grignard type silicon–magnesium compounds, it was decided to repeat the work of Cusa and Kipping in an effort to determine the mechanism of the formation of

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[1] N. W. Cusa and F. C. Kipping, *J. Chem. Soc.*, 1040 (1933).

[2] W. H. Nebergall and O. H. Johnson, THIS JOURNAL, **71**, 4022 (1949).

[3] E. R. Van Artsdalen and J. Gavis, *ibid.*, **74**, 3196 (1952).

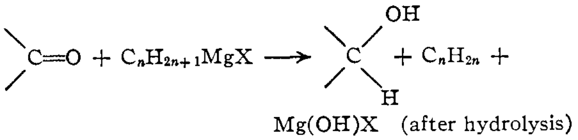
[4] R. A Benkeser and R. G. Severson, *ibid.*, **73**, 1424 (1951).

the silicon–hydrogen bond in dicyclohexylphenylsilane.

In the present investigation it was found that dicyclohexylphenylsilane is formed prior to the hydrolysis of the reaction mixture, which shows that the mechanism proposed by Cusa and Kipping[1] cannot be correct. It was also found that cyclohexene is a reaction product, an important fact that apparently was overlooked by the previous workers.

Because the steric effect of the cyclohexyl group is important in determining the course of the reaction, it was decided to try the action of other sterically hindered Grignard reagents upon phenyltrichlorosilane. Thus, it has been found that Grignard reagents containing the cyclopentyl, isopropyl and *t*-butyl groups react with phenyltrichlorosilane to form dicyclopentyl-, diisopropyl- and di-*t*-butyl-phenylsilane, respectively. The corresponding unsaturated hydrocarbons cyclopentene, propene and isobutylene were also identified as reaction products.

There are many reports in the literature concerning the reducing action of Grignard reagents toward carbonyl compounds. In these reactions the carbonyl compound is reduced to an alcohol and the alkyl group of the Grignard reagent is changed to an alkene.



$$>C{=}O + C_nH_{2n+1}MgX \longrightarrow >C(OH)(H) + C_nH_{2n} + Mg(OH)X \text{ (after hydrolysis)}$$

Generally, the reduction of carbonyl compounds by Grignard reagents has been observed in instances in which the normal addition reaction may be hindered sterically. Furthermore, reduction is observed usually with Grignard reagents which possess a hydrogen atom beta to the magnesium atom. According to mechanisms proposed by Whitmore[5] and by Wiberg and Bauer[6] for reactions of this type, the β-hydrogen shifts to the carbon atom of the carbonyl group and an alkene is formed.

The reduction of the silicon–chlorine bond by sterically hindered Grignard reagents appears to be similar to that observed for the carbonyl group. Thus we may write the following equations for the reaction of phenyltrichlorosilane with an excess of cyclohexylmagnesium bromide

$$C_6H_5SiCl_3 + 2C_6H_{11}MgBr \longrightarrow (C_6H_{11})_2C_6H_5SiCl + 2MgBrCl$$

$$(C_6H_{11})_2C_6H_5SiCl + C_6H_{11}MgBr \longrightarrow (C_6H_{11})_2C_6H_5SiH + C_6H_{10} + MgBrCl$$

Similar equations can be written for the reactions involved when cyclopentyl-, isopropyl- and *t*-butylmagnesium halides were employed. Additional evidence that a β-hydrogen atom is involved in the mechanism is provided by the fact that *o*-tolylmagnesium bromide, which does not contain an easily removable β-hydrogen atom, failed to reduce the silicon–chlorine bond of phenyltrichlorosilane.

Experimental

All reactions involving a Grignard reagent were carried out in an atmosphere of oxygen-free, dry nitrogen. The ether used as a solvent was previously dried over sodium. All melting points and boiling points are uncorrected.

Dicyclohexylphenylsilane.—Magnesium turnings (37 g., 1.53 g. atoms) were placed in a one-liter, three-necked flask fitted with a motor-driven stirrer, reflux condenser, dropping funnel and nitrogen inlet. The magnesium was covered with anhydrous ethyl ether and nitrogen passed through the system to remove all air. The Grignard reagent was prepared by adding slowly a 30% solution of cyclohexyl bromide (253 g., 1.53 moles) in ether. After the addition of the cyclohexyl bromide was completed, the reaction mixture was refluxed for 2 hr. Phenyltrichlorosilane (25 g., 0.118 mole) in an equal volume of ether was added slowly to the Grignard reagent. The reaction mixture was then heated to 160–170° with all the volatile material being condensed and collected. Redistillation of the distillate gave 21 g. (0.25 mole) of cyclohexene, boiling at 81–82° (747 mm.). This compound was identified by its boiling point, unsaturation and infrared spectrum. A small portion of the residue in the distillation flask was extracted with ethyl ether and the ether removed by distillation. An infrared spectrum recorded for the residual liquid showed a strong Si–H bond.[7] This showed that dicyclohexylphenylsilane was produced prior to hydrolysis. The remainder of the residue in the distillation flask was hydrolyzed by a mixture of ice and dilute hydrochloric acid. The organic layer was extracted with ethyl ether, the ether solution dried over Drierite and the ether removed by distillation. Distillation of the residual liquid under reduced pressure gave 8.0 g. of dicyclohexyl (100–140° at 2.5 mm., and 236° at 737 mm.), 21 g. (0.078 mole) of dicyclohexylphenylsilane (124° at 0.03 mm.) and a small quantity of high-boiling polymeric material. The yield of $C_6H_5(C_6H_{11})_2SiH$ was 66%, $n^{25}D$ 1.538.

Anal. Calcd. for $C_{18}H_{28}Si$: C, 79.3; H, 10.3. Found: C, 79.3; H, 10.3.

Another experiment was conducted in which the above procedure was modified by holding the reaction mixture at the reflux temperature of the solvent for 30 hr. before hydrolysis. The yield of dicyclohexylphenylsilane in this experiment was only 2.0 g. (6%). This shows that the reduction of the silicon–chloride bond by the Grignard reagent is favored by higher temperatures.

Diisopropylphenylsilane.—Isopropylmagnesium chloride was prepared using 188 g. (1.53 moles) of isopropyl chloride and 37 g. (1.53 g. atoms) of magnesium. To the Grignard reagent was added 25 g. (0.118 mole) of phenyltrichlorosilane in an equal volume of ether. After the addition was completed, all volatile material was distilled into an ice-cooled chloroform solution of bromine, with the distillation flask being heated to 160–170°. The chloroform solution was then washed with a saturated aqueous solution of sodium sulfite to remove excess bromine, and, after drying the chloroform layer over Drierite, the chloroform was removed by distillation. The residual 1,2-dibromopropane distilled at 139–141° (747 mm.). This compound was identified by its boiling point and infrared spectrum; yield 61 g. (0.32 mole).

The residue in the distillation flask was worked up as described in the above experiment. The product obtained was diisopropylphenylsilane, which distilled at 58–60° (1.2 mm.), $n^{25}D$ 1.495, yield 24 g. (50%).

Anal. Calcd. for $C_{12}H_{20}Si$: C, 75.0; H, 10.4. Found: C, 74.8; H, 10.5.

Dicyclopentylphenylsilane.—The procedure described above was repeated using the Grignard reagent prepared from 238 g. (1.53 moles) of cyclopentyl bromide and 25 g. (0.118 mole) of phenyltrichlorosilane. The volatile material produced by heating the reaction mixture to 160–170° was condensed and redistilled. The cyclopentene formed as a reaction product distilled at 43–44° (747 mm.), yield 8 g. (0.12 mole). This compound was identified by its boiling point, unsaturation and infrared spectrum.

The dicyclopentylphenylsilane, which was obtained upon working up the residue in the distillation flask, distilled at 100° (0.03 mm.), $n^{25}D$ 1.529, yield 14.3 g. (49%).

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(5) F. Whitmore and R. George, THIS JOURNAL, **64**, 1239 (1942).

(6) E. Wiberg and R. Bauer, *Z. Naturforsch.*, **7б**, 129 (1952).

(7) M. C. Harvey, W. H. Nebergall and John S. Peake, THIS JOURNAL, **76**, 4555 (1954).

Anal. Calcd. for $C_{16}H_{24}Si$: C, 78.6; H, 9.90. Found: C, 78.8; H, 9.96.

Di-*t*-butylphenylsilane.—The procedure described above was repeated using the *t*-butylmagnesium bromide prepared from 279 g. (1.53 moles) of *t*-butyl bromide and 25 g. (0.118 mole) of phenyltrichlorosilane. The volatile material produced by heating the reaction mixture to 160–170° was passed into an ice-cooled chloroform solution of bromine. The chloroform solution was washed with an aqueous saturated solution of sodium sulfite to remove the excess bromine. The chloroform layer was dried over Drierite and the chloroform removed by distillation. The residual isobutylene bromide distilled at 149° (747 mm.), yield 27 g. (0.128 mole). This compound was identified by its boiling point and infrared spectrum.

The di-*t*-butylphenylsilane, which was obtained upon working up the residue in the distillation flask, distilled at 46° (0.4 mm.), yield 5.5 g. (10%), $n^{25}D$ 1.489.

Anal. Calcd. for $C_{14}H_{24}Si$: C, 76.4; H, 10.96. Found: C, 76.6; H, 10.90.

Attempted Preparation of Di-*o*-tolylphenylsilane.—The procedure described above was repeated using the Grignard reagent prepared from 190 g. (1.1 moles) of *o*-tolyl bromide and 11 g. (0.077 mole) of phenyltrichlorosilane. Ether was the only volatile compound recovered when the reaction mixture was heated to 160–170°. Upon working up the residue in the distillation flask and distilling the organic layer, toluene and a high-boiling, semi-crystalline material were obtained. An infrared spectrum of this material did not show the Si–H bond. This material was dissolved in a hot solution of alcoholic sodium hydroxide, from which 4 g. of a white crystalline solid precipitated upon cooling. Recrystallization from absolute alcohol gave a product which melted at 87–89°. Infrared spectral analysis showed the solid to contain the following groups: C_6H_5–Si, *o*-$CH_3C_6H_4$–Si–OH and Si–O. This compound may be di-*o*-tolylphenylsilanol, (*o*-$CH_3C_6H_4)_2C_6H_5SiOH$.

Anal. Calcd. for $C_{20}H_{20}OSi$: C, 78.9; H, 6.60. Found: C, 79.0; H, 7.2.

Another experiment was conducted in which the above procedure was modified by holding the reaction mixture at the reflux temperature for 4 hr. Upon hydrolysis of the reaction mixture a white solid was precipitated. This solid was recrystallized from hot toluene, giving 1.6 g. (0.07 mole) of product, m.p. 103°; identified as being *o*-tolylphenylsilanediol, (*o*-$CH_3C_6H_4)C_6H_5Si(OH)_2$.

Anal. Calcd. for $C_{13}H_{14}O_2Si$: C, 67.8; H, 6.10. Found: C, 67.8; H, 6.3.

Acknowledgments.—Analyses were by Miss J. Dickey of the Indiana University Microanalytical Laboratory. This paper is based upon work performed under contract Nonr-90802-Task NR 356-321 (Office of Naval Research).

BLOOMINGTON, IND.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Aliphatic Organo-functional Siloxanes. V. Synthesis of Monomers by Platinum-catalyzed Addition of Methyldichlorosilane to Unsaturated Esters and Nitriles[1]

BY L. H. SOMMER, F. P. MACKAY, O. W. STEWARD AND P. G. CAMPBELL

RECEIVED NOVEMBER 23, 1956

Extension of an important synthesis discovered by G. H. Wagner, which involves platinum-catalyzed addition of silicon hydrides to olefins, has resulted in simple synthetic routes to nine monomers for organo-functional siloxanes. The nitriles and esters being reported have a functionality of 2 at the silicon atom. Reaction of methyldichlorosilane with acrylate esters results in addition of the silyl group to the non-terminal olefinic carbon and thus gives products in which the ester group is readily cleaved from silicon. In important contrast, methacrylate esters give addition of the silyl group to the terminal olefinic carbon and yield adducts which are stable toward cleavage of the ester group from silicon. Olefins in which the functional group is not conjugated with the double bond give products resulting from addition of the silyl group to the terminal olefinic carbon.

Introduction.—If organosilicon chemistry is to progress appreciably beyond the point represented in organic chemistry by monomers and polymers in which the basic chain of atoms (C–C–C bonds in organic chemistry and Si–O–Si groupings in organosilicon chemistry) bears unsubstituted hydrocarbon substituents, it seems essential that simple synthetic procedures be developed for the preparation of monomers which can easily be converted to aliphatic organo-functional siloxanes.

Previous publications from this Laboratory have reported synthetic approaches to aliphatic organo-functional siloxanes involving selective cleavage of one methyl group from trimethylsilyl, Me_3Si, in a variety of organo-functional silanes through reaction with concd. sulfuric acid.[2a,b,c]

More recently, the direct synthesis of organosiloxane esters and acids from halomethylsiloxanes and halomethylethoxysilanes has been reported. These latter syntheses represented a definite improvement over the former method and involved reaction, in suitable solvents, of the halomethylsilanes with anions derived from ethyl malonate and ethyl cyanoacetate. Organofunctional monomers in which the silicon is mono- as well as difunctional can be made by this synthesis.[2d]

However, an even simpler and more direct synthetic route obviously was desirable. In the present paper we wish to record such a synthesis which leads easily to aliphatic organo-functional monomers in which the functionality at the silicon atom is 2.

The addition of trichlorosilane to simple olefins proceeds smoothly and in excellent yield in the presence of diacetyl peroxide or ultraviolet light.[3] Addition of compounds containing the Si–H bond

$$R\text{—}CH\text{=}CH_2 + HSiCl_3 \xrightarrow[\text{or u.v. light}]{(CH_3COO)_2} RCH_2CH_2SiCl_3$$

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[1] Paper 52 in a series on organosilicon chemistry. For Paper 51, see L. H. Sommer and O. F. Bennett, THIS JOURNAL, **79**, 1008 (1957).

[2] (a) L. H. Sommer, R. P. Pioch, N. S. Marans, G. M. Goldberg, J. Rockett and J. Kerlin, THIS JOURNAL, **75**, 2932 (1953); (b) L. H. Sommer, W. D. English, G. R. Ansul and D. N. Vivona, *ibid.*, **77**, 2485 (1955); (c) L. H. Sommer, G. M. Goldberg, G. H. Barnes and L. S. Stone, Jr., *ibid.*, **76**, 1609 (1954); (d) L. H. Sommer, J. M. Masterson, O. W. Steward and R. H. Leitheiser, *ibid.*, **78**, 2010 (1956).

[3] L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *ibid.*, **69**, 188 (1947); **70**, 484 (1948); C. A. Burkhard and R. H. Krieble, *ibid.*, **69**, 2687 (1947).