ANOMALOUS REACTION OF STERICALLY HINDERED GRIGNARD REAGENTS

WITH 1-α-NAPHTHYL-1-CHLORO-1-SILACYCLOBUTANE

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In contrast to five- and six-member and acyclic analogs, there is a specific configuration of the bonds on the Si atom in silacyclobutanes which is extremely favorable for nucleophilic attack [1, 2]. For this reason, both Cl atoms in 1,1-dichloro-1-silacyclobutane can be substituted by bulky groups under the effect of Grignard reagents [3, 4]



$$\begin{split} \mathbf{R} &= \mathbf{R}' = \alpha - C_{10}\mathbf{H}_7, \ \text{cyclo} - C_6\mathbf{H}_{11}, \ C_6\mathbf{H}_5, \ p - C\mathbf{H}_3\mathbf{C}_6\mathbf{H}_4; \ \mathbf{R} &= \alpha - C_{10}\mathbf{H}_7; \ \mathbf{R}' = \text{cyclo} - C_6\mathbf{H}_{11}, \\ \mathbf{C}_6\mathbf{H}_5, \ p - \mathbf{H} \quad m - C\mathbf{H}_3\mathbf{C}_6\mathbf{H}_4, \ t - \mathbf{C}_4\mathbf{H}_9, \ \mathbf{C}_6\mathbf{H}_5\mathbf{C}\mathbf{H}_2. \end{split}$$

However, the yields of 1- α -naphthyl-1-cyclohexyl- (I), 1,1-di- α -naphthyl- and 1,1-dicyclohexyl-1-silacyclobutanes, for example, are 40-65% [3], and the yield of 1- α -naphthyl-1-tertbutyl-1-silacyclobutane (II) does not exceed 25% [4]. In addition to a significant excess of the Grignard reagent, prolonged (no less than 10 h) heating at 45-60°C after elimination of the ether is also required.

To increase the yield of silacyclobutanes with bulky substituents and to reduce the reaction time, the reaction of 1- α -naphthyl-1-chloro-1-silacyclobutane (III) with a four-fold excess of cyclohexyl- (IV) and tert-butylmagnesium chlorides (V) at 100-120°C (after elimination of ether, in an atmosphere of argon) was studied. The volatile products liberated during heating were condensed and analyzed by chromatography-mass spectrometry (CMS). The nonvolatile products of the reaction were analyzed by the same method after decomposition of the reaction mixture with water and elimination of the solvent (see Experimental). However, it was found that the yield of products (I) and (II) decreased, and the formation of a hydrosilane, 1- α -naphthyl-1-silacyclobutane (VI) (the product of reduction of the Si-Cl bond) and cyclohexene (VII) or isobutylene (VIII) (found in the distillate of the volatile products) was observed



The structure of (VI) was demonstrated by comparing its mass spectrum with the mass spectrum of a reference sample synthesized by an independent method and with the PMR and IR spectra (see Experimental)

(III)
$$\xrightarrow{\text{LIATH}_4}$$
 (VI) ether

In the case of $(cyclo-C_6H_{11})_3SiCl$, the introduction of a fourth cyclohexyl substituent by the organomagnesium method is generally impossible, and the yields of hydrosilane attain

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85% [5]. In the reaction examined, substitution and reduction compete, possibly due to the equilibrium of the associates: the solvated molecule of the organomagnesium compound, coordinated in some way with respect to the Si-Cl bond, is relatively stably held in the sphere of the complex



The rate of both processes increases with an increase in the temperature, but the rate of reduction is apparently stronger: at a temperature below 80°C, reduction generally does not take place, substitution takes place slowly, and at 120°C, approximately the same amounts of products of substitution and reduction are formed in the reaction mixture. $MgCl_2$ can split from the six-member complex with the formation of radical sites on the Si' and C atoms. Due to steric hindrances, recombination of these radicals with the formation of the normal product of substitution is difficult, and Si', located in a "cage," can separate the H atom from the β position of the organomagnesium compound* with the formation of hydrosilane and olefin (VII) or (VIII).

This representation of the anomalous reduction process is naturally simplified. Both the solvent, which enters the coordination sphere of the Grignard reagent (etherate) and the structure of the organomagnesium compound itself - symmetric or asymmetric - apparently play an important role. It is also possible that the solvated solvent is the source of the H atom or a Si-H bond is formed as a result of the reaction of HCl with a pseudo-organomagnesium compound.[†] The formation of the latter compound can be represented as a metal-halogen exchange within the complex, and stabilization can be explained by solvation and complexing

$$\equiv \operatorname{Si-Cl} + \operatorname{XMgR}(\mathbf{R}_{2}'\mathbf{O})_{n} \rightarrow \begin{bmatrix} \equiv \operatorname{Si-Cl} \\ \vdots \\ \mathbf{R} - \operatorname{MgX}(\mathbf{R}_{2}'\mathbf{O})_{n} \end{bmatrix} \rightarrow$$
$$\Rightarrow \begin{bmatrix} \equiv \operatorname{Si} - \operatorname{MgX}(\mathbf{R}_{2}'\mathbf{O})_{n} \\ \vdots \\ \mathbf{R} - \operatorname{Cl} \end{bmatrix} \xrightarrow{\operatorname{HCl}} \equiv \operatorname{Si} - \operatorname{H} + \operatorname{MgXCl} + n\operatorname{R}_{2}'\mathbf{O} + \operatorname{RCl}$$

After elimination of the ether, the reaction mixture is a heterogeneous system, and for this reason (V) was heated with (III) in toluene. (V) is obtained with a yield of more than 90% in toluene according to [11], and THF is only used in the amount required for formation of the etherate. After addition of (III), the mixture was heated for 1 h at 45-50°C and then boiled for 24 h at the temperature of the reaction mixture of ~115°C. After the treatment described above and elimination of the solvents, the residue was analyzed by GLC. The yields found were: 18% for (VI), 58% for 1- α -naphthyl-1-benzyl-1-silacyclobutane (IX), and 19% for (IV). The yields of naphthalene and 1,1,3,3,-bis(trimethylene)-1,3,-di- α ,naphthyl-1,3-disiloxane were ~1.5%. The mass spectra of these compounds coincide with those reported in [4]. (VI) was eliminated by vacuum distillation (yield of 11%). (II) and (IX) were separated from the residue by chromatography in a column packed with Al₂O₃ (neutral. act. II, elution with n-hexane) with yields of ~10 and ~40%, respectively.

The reaction of normal substitution evidently takes place so slowly that (V) primarily metallizes the toluene and reduces the Si-Cl bond (76% consumption of (III) in these reactions). The benzyl substituent is less bulky than the tert-butyl substituent; for this reason,

*The hypothesis of the reducing character of the hydrogen in the β position to the magnesium in the molecule of an organomagnesium compound was again advanced in the study of the reactions of Ph₃SiCl with cyclo-C₆H₁₁MgCl [6] and PhSiCl₃ with different organomagnesium compounds with a β -H atom [7].

[†]For example, the mechanism of the formation of the Si-H bond in the reaction of $C_{6}H_{5}MgCl$ with trimethylchlorosilane [8], where there are neither any significant steric hindrances for substitution nor a β -H atom with respect to the Mg (the C-H binding energy in the aromatic nucleus is too high) is totally unclear. Pseudo-organomagnesium compounds are also apparently intermediate compounds in the reaction of Mg with chlorosilanes - with (III), for example [9] - and the reaction of cyclo- $C_{6}H_{11}MgBr$ with Ph₃SiCl [10]. The scheme in [10] explains the formation of cyclohexane.

the benzylmagnesium chloride formed basically reacts with (III) and forms (IX), and the yield of (II) also does not attain 20%. This can be represented as follows



In addition to nucleophilic substitution, $1-\alpha$ -naphthyl-1-chloro-1-silacyclobutane containing a bulky α -naphthyl substituent at Si undergoes reduction of the Si-Cl bond (apparently due to the β -H atom with respect to the Mg) with the formation of $1-\alpha$ -naphthyl-1-silacyclobutane in the reaction with sterically hindered Grignard reagents with a β -H atom with respect to Mg.

EXPERIMENTAL

The mass spectra were made on a LKB-2091 instrument (SE-30 column) with an ionization energy of 70 eV, the PMR spectra were made on a Varian T-60 spectrometer in CC1₄ from TMS (internal standard), and the IR spectra were made on Perkin-Elmer 577 and UR-20 spectrometers.

 $1-\alpha$ -Naphthyl-1-chloro-1-silacyclobutane (III) was synthesized according to [3]. Absolute ether, THF, pentane, and toluene were prepared by the usual methods.

<u>Reaction of (III) with Cyclo-C₆H₁₁MgCl (IV).</u> Here 0.025 mole of (III) was added to an ether solution of 0.1 mole of (IV) filtered in an atmosphere of dry argon and the ether was distilled off (over ~0.5 h) after 0.5 h of boiling. The mixture was then heated for 4 h at 100°C, absorbing the distilled volatile products (ether and cyclohexene with a small amount of cyclohexane). The ether was recovered during cooling and decomposed with 10% HCl. The organic layer was separated and the solvent was eliminated after the usual treatment. 30% (VI) and 33% (I) were found in the residue by CMS. The mass spectrum of the peak corresponding to (VI) coincided with the mass spectrum of (VI) prepared by reduction of (III) with lithium aluminum hydride (see below).

<u>Reaction of (III) with t-BuMgCl (V).</u> The reaction of 0.1 mole of (V) with 0.025 mole of (III) was conducted as above. The volatile products formed were collected with a condenser cooled with dry CO_2 . CMS analysis showed the presence of isobutylene and isobutane. The yield was 24% for (VI) and 20% for (II). The mass spectra of the corresponding peaks are similar to the mass spectra of known samples of (VI) and (II).

<u>1- α -Naphthyl-1-silacyclobutane (VI)</u>. A suspension of 0.018 mole of LiAlH₄ in 20 ml of ether was added to a solution of 0.07 mole of (III) in 50 ml of ether (in an atmosphere of argon) in 0.5 h and mixed for 12 h. Then 100 ml of dry pentane were added, the mixture was filtered through a layer of dry powdered NaCl, and the salt was washed off with 50 ml of pentane. After elimination of the solvents, the residue was vacuum distilled. The yield of crude (VI) (containing naphthalene) was ~4.8 g (~35%). After slow sublimation of the naphthalene and repeated vacuum distillation, 2.35 g (17%) of (VI) were obtained, bp 51-55°C (0.014 mm), n_D^{20} 1.6109, d_4^{20} 1.030.

Mass spectrum, m/z (rel. intensity, %): M⁺ 198(42), 183(6.2), 170(100), 155(42), 141(5.1), 129(15), 128(2.1), 127(0.9), 117(1.4), 115(6.0), 105(2.3), 103(4.5), 91(1.9), 85(3.5), 79(2.5), 77(2.5), 70(5.7), 63(1.9), 55(2.2), 53(9.5), 43(6.5), 42(2.8), 41(5.2), 39(5.2). PMR spectrum (δ , ppm): 1.35 m (4H, α -CH₂), 2.17 m (2H, β -CH₂), 5.42 m (1H, SiH), 7.02-7.86 m (7H, aromat. H). IR spectrum (ν , cm⁻¹): 926 sh, 1120 and 1185 (silacyclobutane ring), 1145, 1400 (Si-naphthyl), 1650-1900 (characteristic of α -substituted naphthalene), 2115 (Si-H_{str}), 1498, 1583 (C=C_{str}), 2850, 2860, 2920, 2965 (C-H_{str} in the silacyclobutane ring), 3050 (C-H_{str}, atomat.).

In the volumetric determination of (VI) [reaction with an excess of moist piperidine, 40.8 mg ($2.06 \cdot 10^{-4}$ mole) weighed portion of (VI), 23°C, 744 mm], 5.9 ml of H₂ (theoretical 5.1 ml) were separated.

Reaction of (III) with Etherate of (V) in Toluene. Here 0.1 mole of (III) was added to a solution of 0.4 mole of (V) in toluene, prepared according to [11], and boiled for 24 h. After cooling, the mixture was decomposed with 10% HCl, the solvents were eliminated, and the residue was analyzed by CMS. The yields of (VI), (IX), and (II) were 18, 48, and 19%, respectively. (VI) was separated by vacuum rectification (~11%). (II) (10%) and (IX) (~40%) were separated by chromatography in a column packed with Al_2O_3 (neutral, act. II, elution with hexane). The constants corresponded to those reported in [4].

CONCLUSIONS

In the reaction of sterically hindered Grignard reagents with 1- α -naphthyl-1-chloro-1silacyclobutane, the Si-Cl bond is reduced to Si-H with the formation of 1- α -naphthyl-1silacyclobutane. When the reaction is conducted in toluene, metallization of the solvent is the basic transformation, resulting in the formation of 1- α -naphthyl-1-benzyl-1-silacyclobutane.

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SYNTHESIS AND STRUCTURE OF THE NEW BINUCLEAR COMPLEX

 $\eta^5 - C_5 H_5 (CO)_2 Fe - \eta^1 - C_5 H_4 (CO)_2 Fe - CH_3$

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Complexes of iron with the general formula $\eta^5-C_5H_5(CO)_2FeR$, where R is a σ -bonded alkyl or aryl, are metallated by n-butyllithium in THF at $-78^{\circ}C$ exclusively in the cyclopentadiene ring, and this reaction presents a convenient method for the synthesis of substituted complexes $\eta^5-R^*-C_5H_4(CO)_2Fe-\eta^{-1}-R$ [1, 2].

We have found that the dimeric complex $[\eta^5-C_5H_5(CO)_2Fe]_2$ is also metallated in the cyclopentadiene ring under these conditions, although the yield of the product from the decomposition of the lithium derivative with heavy water (the monodeuterated derivative) does not exceed 20%. During an attempt to use the metallation of $[\eta^5-C_5H_5(CO)_2Fe]_2$ to produce the methyl-substituted complex $\eta^5CH_3C_5H_4-\eta^5-C_5H_5(CO)_4Fe_2$ the binuclear complex $\eta^5-C_5H_5(CO)_2Fe-\eta^1-C_5H_4(CO)_2Fe-CH_3$ (I) was obtained instead of the expected product.

It can be supposed that the butyllithium used as metallating agent is capable of reducing the dimer with the formation of the $[\eta^5-C_5H_5(CO)_2Fe]^-$ anion. With the addition of the electrophilic agent methyl iodide this anion gives the σ -methyl derivative $\eta^5-C_5H_5(CO)_2Fe-$ CH₃, which is metallated in the cyclopentadiene ring by an excess of butyllithium. The obtained lithium derivative $\eta^5-LiC_5H_4(CO)_2Fe-CH_3$ reacts with $\eta^5-C_5H_5(CO)_2FeI$, which was also found among the reaction products, giving the binuclear complex (I).

In order to check this suggestion we realized the metallation of the authentic $\eta^5-C_5H_5-(CO)_2Fe-CH_3$ with butyllithium in THF at -78°C; with the subsequent addition of $\eta^5-C_5H_5(CO)_2-$

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