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1-OXA-2-SILACYCLOHEXANES: MECHANISM OF FORMATION FROM MAGNESIUM HALIDE CATALYZED REACTIONS OF SOME DICHLOROSILANES AND MAGNESIUM METAL IN TETRAHYDROFURAN

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Summary

Details are provided for the preparation of three 1-oxa-2-silacyclohexanes; namely, 1-oxa-2,2-diphenyl-2-silacyclohexane, 1-oxa-2,2-dimethyl-2-silacyclohexane and 1-oxa-2-methyl-2-silacyclohexane from magnesium halide-catalyzed reactions of some dichlorosilanes and magnesium metal in tetrahydrofuran. A thorough discussion of their mechanism of formation is also presented and syntheses of the following compounds are reported for the first time: 1-oxa-2-methyl-2-silacyclohexane (the first reported compound of this type containing a chiral silicon), (4-bromobutoxy)chlorodimethylsilane and (4-bromobutoxy)-chloromethylsilane.

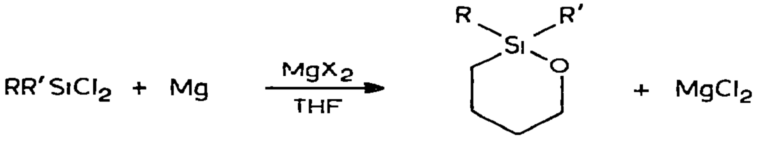
Introduction

Reactions between dichlorodiphenylsilane and some metals yielding octaphenylcyclotetrasilane and decaphenylcyclopentasilane are well documented [1]. Dodecamethylcyclohexasilane has also been prepared by similar procedures from dichlorodimethylsilane [2,3]. In 1963, Anderson found that when reactions of dichlorodiphenylsilane and magnesium metal in tetrahydrofuran (THF) were catalyzed with iodine crystals, 1-oxa-2,2-diphenyl-2-silacyclohexane (I) was isolated, and reactions of dichlorodimethylsilane and magnesium metal, catalyzed with ethyl iodide in THF yielded 1-oxa-2,2-dimethyl-2-silacyclohexane (II) [4]. We now report in some detail preparations and the mechanism of formation of some 1-oxa-2-silacyclohexanes from magnesium halide-catalyzed reactions of diorganodichlorosilanes and magnesium metal in THF.

Results and discussion

Formation of some 1-oxa-2-silacyclohexanes

We have found that when reactions of dichlorodiphenylsilane and magnesium metal were catalyzed with anhydrous magnesium iodide in THF, compound I was was formed (ca. 45%) in addition to a viscous oil:



(I-II)

I, R=R′=Ph, X=I
II, R=R′=CH_3, X=Br
III, R=CH_3, R′=H, X=Br

Unexpectedly, under similar conditions employing magnesium bromide instead of magnesium iodide, octaphenylcyclotetrasilane (IV) was isolated in a 44% yield and the formation of I was not observed.

$$Ph_2SiCl_2 + Mg \xrightarrow[THF]{MgBr_2} [Ph_2Si]_4 + MgCl_2$$

(IV)

Magnesium bromide-catalyzed reactions of dichlorodimethylsilane and magnesium metal in THF gave only II (ca. 65%) and no cyclopolysilanes (e.g. dodecamethylcyclohexasilane) were detected. In a similar manner, compound III, which contains a chiral silicon, was formed as a racemic modification from dichloromethylsilane, magnesium bromide and magnesium metal in THF.

Reactions between trichlorophenylsilane or silicon tetrachloride and magnesium metal in the presence of magnesium bromide have yielded only polymers and intractable oils

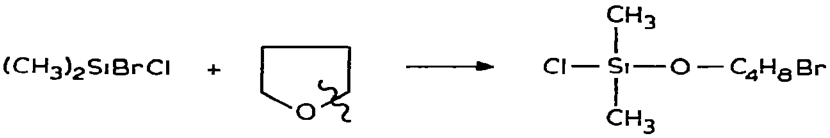
Mechanism of formation of II

The synthesis of II was thoroughly investigated and its mechanism of formation is postulated as follows:

Step 1. Halide exchange between dichlorodimethylsilane and magnesium bromide undoubtedly occurs [5].

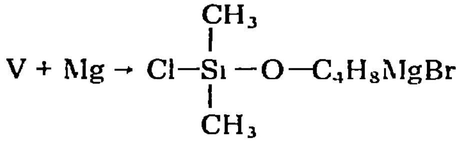
$$(CH_3)_2SiCl_2 + MgBr_2 \rightarrow (CH_3)_2SiBrCl + MgBrCl$$

Step 2 Ring opening of THF via cleavage of its carbon—oxygen bond by the silyl bromide gave (4-bromobutoxy)chlorodimethylsilane (V) which was isolated in a 95% yield. Its structure was confirmed by chemical and spectral methods.



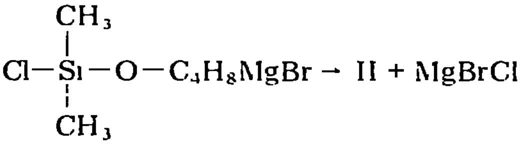
(V)

Step 3 Formation of a Grignard reagent by reaction of magnesium metal with the C—Br bond of V is proposed



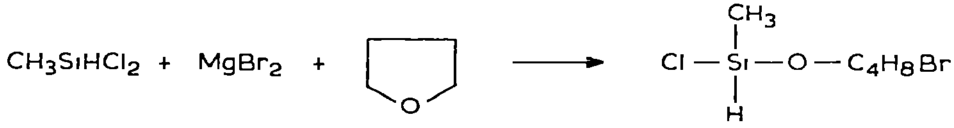
$$\mathrm{V + Mg \rightarrow Cl{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}C_4H_8MgBr}$$

Step 4 Ring closure by intramolecular cyclization between the Grignard reagent and the silyl chloride would yield II.



$$\mathrm{Cl{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}C_4H_8MgBr \rightarrow II + MgBrCl}$$

In a similar manner, (4-bromobutoxy)chloromethylsilane (VI) was isolated in a 40% yield from a reaction of dichloromethylsilane and magnesium bromide in THF.



(VI)

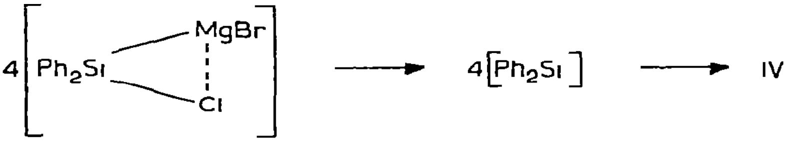
Treatment of VI with magnesium metal afforded III in 21% yield We believe that the mechanism of formation of I, although not investigated, from dichlorodiphenylsilane, magnesium iodide and magnesium metal in THF also proceeds via a similar pathway, with the intermediate formation of (4-iodobutoxy)chlorodiphenylsilane [$\mathrm{ClSiPh_2{-}O{-}(CH_2)_4I}$]. The fact that the presence of I was not observed when magnesium bromide was used in the place of magnesium iodide may very well reflect the low order of reactivity of bromochlorodiphenylsilane relative to chloroiododiphenylsilane (presumably formed by halide exchanges between dichlorodiphenylsilane and respective magnesium halides) towards cleavage of ethers. This seems to be a very reasonable assumption since the rate of cleavage of ethers by different silyl halides has been found to be governed markedly by both the type of organic groups and halogens bonded to a silicon atom [7—9]: $\equiv$Si—I > $\equiv$Si—Br > $\equiv$Si—Cl and $\equiv\mathrm{Si{-}CH_3}$ > $\equiv$Si—Ph Such a procedure, involving reactions of related dichlorosilanes with magnesium halides in the presence of cyclic ethers of varying ring size, has great potential as a general method for the preparation of a wide variety of heretofore inacessible compounds having the structure, $\mathrm{ClSi(RR')_2{-}O{-}(CH_2)_nX}$. It is quite conceivable that these novel types may be difficult to prepare, especially in high yields, by conventional methods, owing to the well established propensity of mixed silyl halides towards facile disproportionation [10].

$$2\,\equiv\mathrm{SiXCl} \rightleftharpoons \equiv\mathrm{SiCl_2} + \equiv\mathrm{SiX_2}$$

Mechanism of formation of IV

The mechanism of formation of IV from reactions of dichlorodiphenylsilane and magnesium metal in the presence of magnesium bromide is still questionable: A halide exchange reaction is expected to occur between dichlorodiphenylsilane and magnesium bromide affording bromochlorodiphenylsilane (vide supra) Reaction of this intermediate with magnesium metal could yield species with some silylene-like character (a silicon analog of carbenoids) or a free silylene (a silicon analog of carbenes) which may couple affording IV.

$Ph_2SiBrCl + Mg \rightarrow Ph_2Si(MgBr)Cl$



Since the presence of silylenes have been invoked in many reactions of some dichlorosilanes with metals [11], we were prompted to investigate the importance of such reactive species in our system. In an effort to determine the intermediacy of these species, several reactions of dichlorodiphenylsilane, magnesium bromide and magnesium metal were carried out in the presence of cyclohexene and diphenylacetylene, common "trapping agents" of divalent species In both cases, IV was isolated and no products reflecting addition across the carbon—carbon multiple bonds were detected.

Some reactions of 1-oxa-2-silacyclohexanes

Treatment of I with phenyllithium resulted in an exothermic reaction which after acid hydrolysis gave 4-triphenylsilyl-1-butanol (VII) in an 80% yield.

$$I + PhLi \rightarrow Ph_3SiCH_2CH_2CH_2CH_2OH$$

(VII)

The physical and spectral properties of VII were in excellent agreement with those of VII obtained from a reaction between triphenylsilyllithium and THF [12].

When acid hydrolysis was used in the work-up of reactions involving dichlorodimethylsilane, magnesium bromide and magnesium metal, 5,5,7,7-tetramethyl-6-oxa-5,7-disilaundecan-1,11-diol (VIII) was obtained and the formation of II was not observed. A reaction of pure II with 20% aqueous hydrochloric acid at room temperature for 2 h affording VIII in an 87% yield confirms the direct formation of VIII from II

$$II + H_2O \xrightarrow{HCl} [HOCH_2CH_2CH_2CH_2(CH_3)_2Si]_2O$$

(VIII)

The formation of the aforementioned compounds served to further establish the structure of I and II

Experimental

All reactions were carried out under an atmosphere of oxygen-free dry nitrogen Tetrahydrofuran was freshly distilled from sodium under nitrogen prior to use. Chemicals were obtained from commercial sources and used without further purification.

Gas-liquid chromatographic (GLC) analyses were carried out using a 6 ft × 1/4 in. stainless steel column packed with 20% silicone rubber gum on Chromosorb W The instrument used was a Varian Model 202 B gas chromatograph Infrared spectra were determined on a Beckmann IR-10 and proton magnetic resonance spectra were carried out on a Varian A 60 spectrophotometer using carbon tetrachloride as the solvent and tetramethylsilane as an internal standard Molecular weights were determined in benzene with a Mechrolab Vapor Pressure Osmometer, Model 301 A. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee

All melting and boiling points are uncorrected

General procedure for the preparation of anhydrous salts

Anhydrous magnesium bromide and iodide were prepared by reactions between 1,2-dibromoethane and methyl iodide with magnesium metal in THF, respectively In general, the appropriate alkyl halide, dissolved in ca. 100 ml of THF, was added dropwise to a suspension of magnesium turnings in THF with rapid stirring. Upon completed addition, the presence of salts was observed and the reaction mixture was stirred at room temperature until the exothermic reaction subsided. Gilman's Color Test 1 of aliquots of these mixtures were negative at this stage, indicating the absence of any organometallic species, such as Grignard reagents [13]. In some cases excess THF was removed by distillation under nitrogen prior to the addition of the silyl chlorides.

Preparation of 1-oxa-2,2-diphenyl-2-silacyclohexane (I)

To ca. 0.1 mol of magnesium iodide (prepared from 28.4 g of methyl iodide and 7.2 g of magnesium turnings in 125 ml of THF) was added dropwise at room temperature with rapid stirring a solution of 25.3 g (0 1 mol) of dichlorodiphenylsilane dissolved in 125 ml of THF over a 2 h period. After the mixture was heated at reflux for 24 h, 200 ml of ether was added prior to removal of salts and excess magnesium metal by filtration The filtrate was hydrolyzed with 100 ml of 10 % HCl subsequent to washing the organic layer several times with 10% aqueous sodium bisulfite then distilled water. After drying the organic layer, the solvent was removed and the residue was distilled under reduced pressure affording 11.2 g (45%) of I, b.p. 128—132°/0.3 mm (Lit [4] b.p. 215—216°/34—38 mm). (Found C, 75.13, H, 7 05, Si, 11.15, mol. wt , 250. $C_{16}H_{18}OSi$ calcd · C, 75.59; H, 7.05, Si, 11.05%, mol wt 254.)

The PMR (CCl_4) spectrum had the following resonances. δ 1.1 (t, 2 H), 1.7 (m, 4 H), 3.9 (t, 2 H) and 7.4 (m, 10 H). The IR (neat) spectrum showed bands at 3080 s, 2940 s, 1600 m, 1440 s, 1180—1010 s and 920 s cm^{-1}.

Preparation of 1-oxa-2,2-dimethyl-2-silacyclohexane (II)

To ca 0 1 mol of magnesium bromide (prepared from 18.8 g of 1,2-dibromoethane and 7.3 g of magnesium turnings in 125 ml of THF) was added dropwise at room temperature a solution of 12 9 g (0.1 mol) of dichlorodimethylsilane dissolved in 125 ml of THF. After the mixture was heated at reflux overnight, 200 ml of petroleum ether (b.p. 60—70°) was added followed by removal of salts and excess magnesium metal by filtration. Distillation of the filtrate yielded 8.5 g (65%) of II, b.p. 117–118°/760 mm (Lit. [4] b.p. 118–120°/760 mm). (Found: C, 55.30; H, 10.93; mol. wt. 532.* $C_6H_{14}OSi$ calcd.: C, 55.32; H, 10.83%; mol. wt. 130.)

The PMR (CCl_4) spectrum had the following resonances. 0 1 (s, 6 H), 0.6 (t 2 H), 1.6 (m, 4 H) and 4.8 (t, 2 H). The IR (neat) spectrum showed bands at 2950 s, 1440–10 m, 1260 s, 1180 m, 1160–1030 s, 840 s and 790 s cm^{-1}.

Preparation of (4-bromobutoxy)chlorodimethylsilane (V)

To ca. 0.1 mol of magnesium bromide (prepared from 2.4 g of magnesium turnings, 50.1 g of 1,2-dibromoethane and 125 ml of THF) was added dropwise at room temperature a solution of 25.6g (0.2 mol) of dichlorodimethylsilane dissolved in 125 ml of THF with rapid stirring. After heating the mixture at reflux overnight, the salts were removed by filtration and the solvent by distillation The residue was distilled under reduced pressure yielding 46.8 g (95%) of V (nc), b.p. 55–56°/0.3 mm. The equivalent weight, determined by titration of a H_2O/THF solution of an aliquot with standard 0.1 *N* NaOH, was found to be 241. ($C_6H_{14}BrClOSi$ calcd : 245.)

The PMR (CCl_4) spectrum had the following resonances δ 0 1 (s, 6 H), 1 4 (m, 4 H), 3.1 (t, 2 H) and 3.4 (t, 2 H).

Preparation of II from V

To 3.6 g of magnesium turnings was added dropwise over a 2 h period at room temperature, a solution of 24.5 g (0.1 mol) of V in 100 ml of THF. The reaction mixture was stirred afterwards at room temperature overnight. GLC analysis of an aliquot of this mixture indicated a greater than 90% yield of II A PMR spectrum of a purified portion of the mixture was identical with the spectrum of an authentic sample of II.

Preparation of (4-bromobutoxy)chloromethylsilane (VI)

To ca. 0.1 mol of magnesium bromide (prepared from 2.4 g of magnesium turnings and 50.1 g of 1,2-dibromoethane in 125 ml of THF) was added dropwise at room temperature 23.0 g (0.2 mol) of dichloromethylsilane dissolved in 125 ml of THF with rapid stirring. After heating the mixture at reflux overnight, the salts were removed by filtration and the solvents by distillation The residue was distilled under reduced pressure yielding 18 3 g (40%) of VI (nc), b.p 59–63°/0.8 mm

The PMR (CCl_4) spectrum had the following resonances. δ 0.1 (d, 3 H), 1.4 (m, 4 H), 3 0 (t, 2 H), 3.3 (t, 2 H) and 4.8 (q, 1 H)

Preparation of III from VI

To 2.4 g (0.1 mol) of magnesium turnings suspended in 50 ml of anhydrous

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[*] The unexpectedly high molecular weight, determined by vapor pressure osmometry in benzene, seems to indicate that II probably exists as a tetramer in that solvent A molecular weight determined by mass spectrometry was found to be 130 (calcd 130)

[**] A previous report mentions isolation of a small fraction presumably consisting of an unresolved mixture of V and (4-bromobutoxy)bromodimethylsilane [14]

ether was added dropwise a solution of 11.6 g (0.05 mol) of VI dissolved in 50 ml of anhydrous ether with rapid stirring. An exothermic reaction occurred After stirring for 2 h at room temperature, the mixture was filtered and the solvents were removed by distillation. The residue was distilled yielding 2.3 g (21%) of III, b.p. 75—83°/760 mm, and 4.3 g of a solid residue

The PMR (CCl_4) spectrum had the following resonances: δ 0.1 (d, 3 H), 0.6 (m, 2 H), 1.5 (m, 4 H), 3.7 (m, 2 H) and 4.5 (m, 1 H).

Preparation of octaphenylcyclotetrasilane (IV)

To ca. 0.1 mol of magnesium bromide [prepared from 18.8 g (0.1 mol) of 1,2-dibromoethane and 12 g of magnesium metal in ca. 125 ml of THF] was added dropwise over a 1 h period at room temperature with rapid stirring a solution of 25.3 g (0 1 mol) of dichlorodiphenylsilane dissolved in 200 ml of THF. The mixture was refluxed overnight prior to removal of salts and excess magnesium metal by filtration After stirring the salts in water, the white precipitate observed was collected by filtration, dried and soxhlet extraction using benzene as the solvent afforded 8 g (44%) of pure IV, m.p. 323—325°.

The original filtrate was hydrolyzed with dilute HCl. After drying of the organic layer and removal of the solvents a viscous residue was obtained. Attempts to isolate compounds from the latter by distillation and column chromatography were unsuccessful.

Preparation of IV in the presence of cyclohexene

A similar reaction, as described above, using the same quantity of reactants and solvent was carried out in the presence of 125 ml of freshly distilled cyclohexene Work-up in the same manner afforded 7.2 g (40%) of IV, m.p. 322—323° and a viscous residue. GLC analysis of the residue indicated the absence of any volatile material.

Preparation of IV in the presence of diphenylacetylene

A similar reaction, as described above, using the same quantities of reactants and solvent, was performed in the presence of 17.8 g (0.1 mol) of diphenylacetylene. Work-up of the reaction mixture in the usual manner afforded 7 5 g (45%) of IV, m.p. 325—328°, and a viscous residue. Chromatography of the residue on a column of alumina yielded 16.3 g, a 92% recovery of diphenylacetylene, m.p. 61—63°, after elution with petroleum ether/benzene (1/1).

Preparation of 5,5,7,7-tetramethyl-6-oxa-5,7-disilaundecan-1,11-diol (VIII)

From dichlorodimethylsilane, magnesium bromide and magnesium metal in THF A similar reaction as that described for the preparation of II, employing the same quantity of reactants and solvent, was carried out After heating the reaction mixture at reflux overnight, the salts and excess magnesium metal were removed by filtration. The filtrate was hydrolyzed with dilute HCl and the organic layer was dried. Removal of the solvent by distillation of the residue under reduced pressure afforded 16.2 g (59%) of VIII, b p. 68—72°/10 mm. (Found: C, 51.90; H, 10.78. $C_{12}H_{30}O_3Si_2$ calcd.: C, 51.74; H, 10.86%.)

The PMR (CCl_4) spectrum had the following resonances: δ 0.1 (s, 6 H), 0.6 (t, 2 H), 1.6 (m, 4 H), 3.7 (t, 2 H) and 6.1 (s, 1 H). The IR (neat) spectrum showed bands at 3310 s, 2950 s, 1420 w, 1260 s, 1180 w, 1080-1030 s, 920 m, 840 s and 790 s cm^{-1}.

From II and aqueous HCl. A mixture of 25 g (0.19 mol) of II, 50 ml of THF and 100 ml of 10% aqueous HCl was stirred at room temperature for 2 h. After several extractions with ether, the combined organic layers were dried over anhydrous sodium sulfate. Removal of ether, followed by distillation of the residue under reduced pressure afforded 22.6 g (87%) of VII, b.p. 68–72°/10 mm.

Reaction of I with phenyllithium

After stirring a mixture of 0.05 mol of phenyllithium and 12.5 g (0.05 mol) of I in 100 ml of THF/ether (1/1) at room temperature for 3 h, Color Test 1 was negative. The mixture was hydrolyzed by the addition of 100 ml of 10% HCl, prior to work-up in the usual manner affording 16 g (80%) of 4-triphenylsilyl-1-butanol, m.p. 109–110°, after recrystallization from benzene/petroleum ether.

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