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Regioselectivity in the trichlorosilylation of allylic halides. Synthesis of 1,1-dichloro-3-(methyldichlorosilyl)-1-silacyclopent-3-ene

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Abstract

Trichlorosilylation of *cis*-1,4-dichloro-2-(methyldichlorosilyl)but-2-ene (I) by reaction with a mixture of trichlorosilane, triethylamine, and a catalytic amount of copper(I) chloride yields *E*-4-chloro-1-trichlorosilyl-2-(methyldichlorosilyl)-2-butene (II) and 4-chloro-3-trichlorosilyl-2-(methyldichlorosilyl)but-1-ene (III) in a 3:1 ratio. The possible factors controlling the regioselectivity of this reaction are discussed. Treatment of II with magnesium leads to 1,1-dichloro-3-(methyldichlorosilyl)-1-silacyclopent-3-ene (XII) in 89% yield.

1. Introduction

The synthesis and the study of the chemical properties of 3-silyl-1-silacyclopent-3-enes have been important in our research programme. The carbon–carbon double bond in such compounds is part of both an allylic and a vinylic silane system. While alicyclic systems substituted by two silyl groups which possess this dual functionality are known, silacyclic systems have not been prepared previously. Such alicyclic systems react with electrophiles preferentially as allylic silanes [1,2]. Thus the carbon–carbon double bond of 3-silyl-1-silacyclopent-3-enes should be activated toward electrophilic attack due to its allylic relationship to the silyl centre of the heterocycle, while the regioselectivity of such reactions is expected to be controlled by the exocyclic α silyl group.

The reaction sequence that we used previously to prepare 1,1-dichloro-1-silacyclopent-3-ene has been adapted to prepare 3-silyl-1-silacyclopent-3-enes [3]. The first step involves a stereospecific H_2PtCl_6 catalysed *cis* hydrosilation reaction, in which the silicon–hydrogen bond of methyldichlorosilane adds across the carbon–carbon triple bond of 1,4-dichloro-2-butyne to give a quantitative yield of *cis*-1,4-dichloro-2-(methyldichlorosilyl)but-2-ene (I) [4,5]. Conversion of allylic chlorides to allyltrichlorosilanes was previously achieved by reaction of the allyl chloride with trichlorosilane, triethylamine and a catalytic amount of copper(I) chloride [6–8]. This reaction probably involves an intermediate trichlorosilyl anion. In fact, when trichlorosilane and triethylamine are mixed, the presence of an equilibrium concentration of trichlorosilyl anion has been demonstrated by ^1H NMR spectroscopy [9,10]. The role of copper(I) chloride in this reaction is uncertain. One possibility is that the trichlorosilyl anion reacts with the copper(I) ion to yield a trichlorosilylcuprate reagent. Alternatively, coordination of copper(I) by the chlorine atom of the allyl chloride may polarize the allylic carbon–chlorine bond, facilitating nucleophilic attack by the trichlorosilyl anion.

Using this procedure, I was allowed to react with a mixture of trichlorosilane, triethylamine, and a catalytic amount of copper(I) chloride in ether. After a non-aqueous work-up, an isomeric mixture of *E*-4-chloro-1-trichlorosilyl-2-(methyldichlorosilyl)but-2-ene (II) and 4-chloro-3-trichlorosilyl-2-(methyldichlorosilyl)but-1-ene (III) (3:1) was isolated by distillation under reduced pressure. Small amounts of 3-trichlorosilyl-2-methyldichlorosilyl-1,3-butadiene (IV) were also

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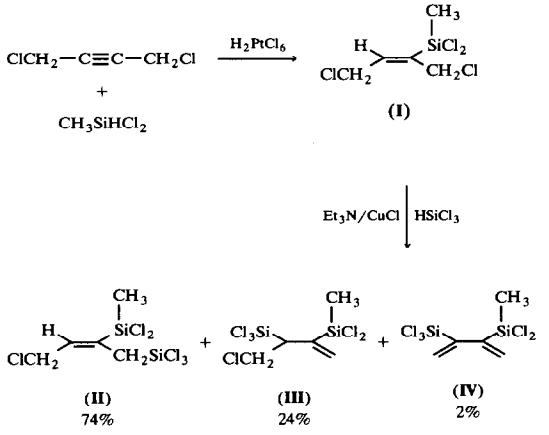
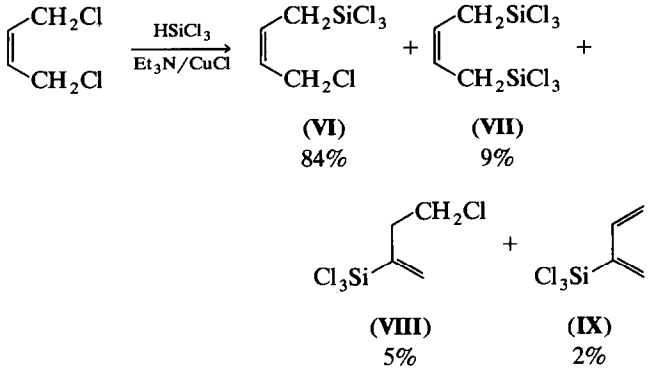
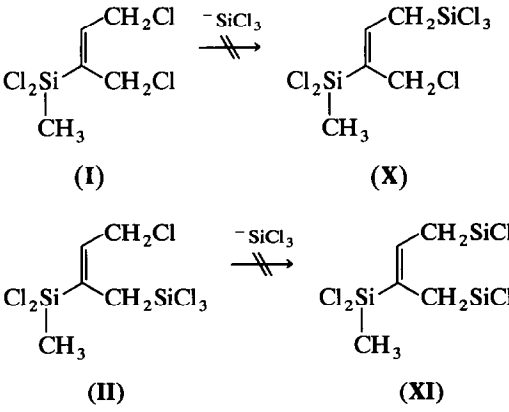
obtained. The structures of **II**, **III** and **IV** were determined by ^1H and ^{13}C NMR spectroscopy and GC/MS.



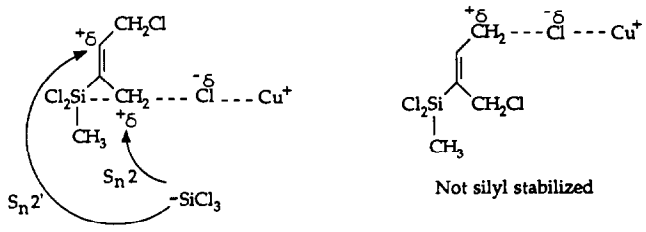
For comparison, we have reinvestigated the reaction of *cis*-1,4-dichlorobut-2-ene (**V**) with trichlorosilane, triethylamine, and a catalytic amount of copper(I) chloride [3]. In addition to *Z*-1-chloro-4-trichlorosilylbut-2-ene (**VI**) and *Z*-1,4-bis(trichlorosilyl)but-2-ene (**VII**) which we have already described [3], we have characterized by NMR spectroscopy and GC/MS small amounts of 4-chloro-2-trichlorosilyl-but-1-ene (**VIII**) and 2-trichlorosilylbuta-1,3-diene (**IX**) [4].



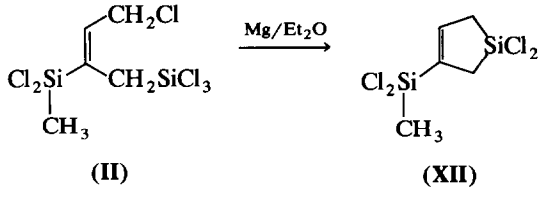
We believe that the formation of **II** and **VI** proceeds by analogous S_N2 nucleophilic pathways, while the formation of **III** and **VIII** apparently proceeds by similar S_N2' nucleophilic reactions. It is apparent that **IV** and **IX** result from dehydrohalogenation by triethylamine of **III** and **VIII** respectively. Of particular note, neither *E*-1-chloro-4-trichlorosilyl-2-(methyldichlorosilyl)but-2-ene (**X**) nor *E*-1,4-di(trichlorosilyl)-2-(methyldichlorosilyl)but-2-ene (**XI**), the expected products of S_N2 attack of the trichlorosilyl anion on allylic carbon-4–chlorine bond of **I** and **II**, are detected. Apparently, the 2-methyldichlorosilyl group controls the regioselectivity of S_N2 nucleophilic attack on the two allylic carbon–chlorine bonds of **I**.



We believe that the regioselectivity observed in the trichlorosilylation of **I** results from the well-known stabilization of positively charged carbocation centres β to silicon. Such partial positive charge probably results from coordination of copper(I) to the allylic chlorine atoms. Thus the formation of **II** and **III** can be accounted for by coordination of the copper(I) to the chlorine atom bonded to carbon-1 of **I**. This results in partial positive charge at carbon atoms 1 and 3, both of which are β to the methyldichlorosilyl group of **I**. S_N2 nucleophilic attack by the trichlorosilyl anion at carbon-1 then leads to **II**, while S_N2' attack at the partially positively charged carbon-3 leads to **III**. On the other hand, coordination of copper(I) to the chlorine atom bonded to carbon-4 causes less polarization because the partial positive charge is not stabilized by the methyldichlorosilyl group. Attack by the trichlorosilyl anion does not occur at carbon-4.



Reaction of **II** with magnesium in ether leads to the formation of 1,1-dichloro-3-(methyldichlorosilyl)-1-silacyclopent-3-ene (**XII**) in high yield. Studies on the chemical reactivity of **XII** are in progress.



2. Experimental details

^1H NMR spectra were obtained on a Bruker AC 80 spectrometer. ^{13}C NMR spectra were run on a Bruker

AC 200 with broad band proton decoupling. Ten per cent solutions in chloroform-d_3 were used to obtain NMR spectra. IR spectra were obtained on a Perkin–Elmer 1600 FT instrument of samples in KBr pellets. GC/MS were obtained at an ionizing voltage of 70 eV on a Hewlett Packard 5890 mass spectrometer. A Hewlett Packard 5890 gas chromatograph was coupled to the mass spectrometer and was used as the MS inlet.

All glassware was dried overnight in an oven at 120°C. The apparatus was assembled and was then flame-dried while being swept with argon. All reactions and transfers were conducted under purified argon. Ether was distilled immediately before use from sodium benzophenone ketyl. Triethylamine was dried over potassium hydroxide pellets.

2.1. 1,4-Dichloro-2-(methyldichlorosilyl)but-2-ene (I)

1,4-Dichlorobut-2-yne (13.0 g, 105 mmol), methyldichlorosilane (17.3 g, 150 mmol) and four drops of a 1% solution of $H_2PtCl_6 \cdot 6H_2O$ in THF were placed in a 100 ml autoclave. The hydrosilylation reaction mixture was heated to 85°C for 24 h. The product was purified by distillation through a 15 cm vacuum-jacketed Vigreux column. A fraction (b.p. 57°C/0.1 mmHg, 17.2 g, 89% yield) was isolated. Anal. Found: C, 25.80; H, 3.45. $C_5H_8Cl_4Si$ calc.: C, 25.23; H, 3.39%. IR: 2966, 1615, 1459, 1403, 1344, 1262, 1100, 1014, 795, 754, 700 cm^{-1}. ^1H NMR spectrum: 0.95 (s, 3H), 4.23 (d, 2H, $J = 7.1$ Hz), 4.27 (d, 2H, $J = 0.6$ Hz), 6.52 (tt, 1H, $J = 7.1$ and 0.7 Hz). ^{13}C NMR spectrum: 5.75, 37.55, 38.35, 136.29, 144.87. GC/MS *m/e* (rel. intensity): 238(1) $(M)^+$, 200(11) $(M-HCl)^+$, 165(1) $(M-HCl-Cl)^+$, 113(42) $(CH_3SiCl_2)^+$, 88(44) $(M-CH_3SiCl_3)^+$, 63(28) $(ClSi)^+$, 53(100) $(C_4H_5)^+$, 27(38).

2.2. E-4-Chloro-1-trichlorosilyl-2-(methyldichlorosilyl)-but-2-ene (II) and 4-chloro-3-trichlorosilyl-2-(methyldichlorosilyl)but-1-ene (III)

Copper(I) chloride (0.12 g), triethylamine (12.0 g, 119 mmol), and 100 ml of ether were placed in a two-necked round-bottomed flask equipped with a Teflon-covered magnetic stirring bar, a reflux condenser which was topped with a calcium chloride drying tube and a pressure-equalizing dropping funnel. 2-Methyldichlorosilyl-1,4-dichlorobut-2-ene (I) (21.5 g, 90 mmol), trichlorosilane (15.3 g, 113 mmol), and 60 ml of ether were placed in the dropping funnel. This mixture was added dropwise with stirring. Stirring was continued for 12 h at room temperature. The reaction mixture and precipitate were filtered under argon. The precipitate was washed with pentane. The organic layers were combined and the volatile solvents were removed by distillation through a 15 cm vacuum-jacketed Vigreux column. A fraction composed of a mixture of II and III, b.p. 70–75°C/0.1 mmHg, 17.9 g, 80% yield was obtained. Anal. Found: C, 17.55; H, 2.49. $C_5H_8Cl_6Si_2$ calc.: C, 17.82; H, 2.39%. IR: 2959, 2900, 1608, 1443, 1404, 1263, 986, 792, 738 cm^{-1}.

2.2.1. Spectral properties of II

^1H NMR spectrum: 0.94 (s, 3H), 2.74 (d, 2H, $J = 1.2$ Hz), 4.16 (d, 2H, $J = 7.1$ Hz), 6.43 (tt, 1H, $J = 7.1$ and 1.2 Hz). ^{13}C NMR spectrum: 5.27, 26.40, 39.66, 132.06, 142.51. GC/MS *m/e* (rel. intensity): 336(1) $(M)^+$, 301(1) $(M-Cl)^+$, 188(14) $(M-CH_3SiCl_3)^+$, 133(14) $(Cl_3Si)^+$, 113(28) $(CH_3SiCl_2)^+$, 63(26) $(ClSi)^+$, 53(100) $(C_4H_5)^+$, 27(17).

2.2.2. Spectral properties of III

^1H NMR spectrum: 0.93 (s, 3H), 3.11 (ddt, 1H, $J = 9.0$, 5.9 and 0.6 Hz), 3.83 (dd, 1H, $J = 11.2$ and 9.0 Hz), 4.04 (dd, 1H, $J = 11.2$ and 5.9 Hz), 6.26 (dd, 2H, $J = 6.8$ and 0.6 Hz). ^{13}C NMR spectrum: 5.19, 40.60, 44.10, 134.64, 140.77. GC/MS *m/e* (rel. intensity): 188(22) $(M-CH_3SiCl_3)^+$, 133(16) $(Cl_3Si)^+$, 113(34) $(CH_3SiCl_2)^+$, 63(27) $(ClSi)^+$, 53(100) $(C_4H_5)^+$, 27(15).

2.3. 3-Trichlorosilyl-2-(methyldichlorosilyl)buta-1,3-diene (IV)

It was not possible to isolate IV as a pure compound. However, the spectra allowed an unambiguous characterization of this very minor component. ^1H NMR spectrum: 0.93 (s, 3H), 5.82 (d, 2H, $J = 1.5$ Hz), 5.96 (d, 2H, $J = 1.5$ Hz). GC/MS *m/e* (rel. intensity): 202(13) $(M-SiCl_2)^+$, 185(8) $(M-CH_3SiCl_2)^+$, 165(2) $(M-SiCl_3)^+$, 135(5) $(SiCl_3)^+$, 113(54) $(CH_3SiCl_2)^+$, 98(7) $(Cl_2Si)^+$, 63(40) $(ClSi)^+$, 52(100) $(C_4H_4)^+$, 51(61) $(C_4H_3)^+$, 26(9).

2.4. 1,1-Dichloro-3-methyldichlorosilyl-1-silacyclopent-3-ene (XII)

Magnesium powder (3.0 g, 123 mmol) and 20 ml of ether were placed in a 250 ml two-necked round-bottomed flask equipped with a Teflon-covered magnetic stirring bar, an efficient reflux condenser and a pressure equalizing dropping funnel. The flask and its contents were cooled to 0°C. An ether solution of II (17.5 g, 47 mmol) and 1,2-dibromoethane (0.8 g) was placed in the dropping funnel. This solution was added dropwise to the stirred ether suspension of magnesium powder. After the addition was complete the solution was heated under reflux for 48 h. After cooling to room temperature, the solution was filtered and the precipitate was rinsed with ether. The ether was removed by evaporation under reduced pressure. The product was purified by fractional distillation through a 15 cm vacuum-jacketed Vigreux column. Two fractions were obtained. The first, 9.25 g, b.p. 47–48°C/0.1

mmHg, was found to be **XII**. Anal. Found: C, 22.32; H, 3.12. $C_5H_8Cl_4Si_2$ calc.: C, 22.56; H, 3.03%. IR: 3017, 2903, 1575, 1404, 1388, 1288, 1261, 1193, 1154, 1100, 960, 790 cm^{-1}. ^1H NMR spectrum: 0.86 (s, 3H), 2.04 (m, 4H), 6.71 (m, 1H). ^{13}C NMR spectrum: 4.19, 22.77, 24.48, 137.95, 143.85. GC/MS *m/e* (rel. intensity): 266(24) $(M)^+$, 230(9) $(M-HCl)^+$, 151(7) $(M-CH_3SiCl_2)^+$, 133(12) $(Cl_3Si)^+$, 115(100) $(CH_3HSiCl_2)^+$, 113(43) $(CH_3SiCl_2)^+$, 98(14), 63(85), 53(31), 27(28). The second fraction, b.p. 52–65°C/0.1 mmHg, was a mixture of **XII** and **III**.

2.5. 4-Chloro-3-trichlorosilylbut-1-ene (VIII)

The compounds **VI** and **VII** in the mixture (**VI–IX**) have been isolated and described previously [3]. **IX** was prepared separately following reference 4 and identified by its spectra. The spectral properties of **VIII** are summarized here. ^1H NMR spectrum: 2.71 (m, 1H), 3.75 (dd, 1H, $J = 11.3$ and 10.6 Hz), 3.97 (dd, 1H, $J = 11.3$ and 3.6 Hz), 5.33 (ddd, 1H, $J = 17.0$ and 0.9 Hz), 5.42 (ddd, 1H, $J = 10.2$ and 0.9 Hz), 5.72 (m, 1H). ^{13}C NMR spectrum: 42.63, 43.96, 121.32, 129.95. GC/MS *m/e* (rel. intensity): 224(6) $(M)^+$, 189(47) $(M-Cl)^+$, 153(14) $(M-Cl-HCl)^+$, 133(54) $(Cl_3Si)^+$, 98(6) $(Cl_2Si)^+$, 63(18) $(ClSi)^+$, 54(100) $(C_4H_6)^+$, 39(40), 27(46).

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