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SYNTHESIS AND MONOCHLORINATION OF 1-CHLORO-1-SILABICYCLO[2.2.2]OCTANE

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Summary

A new synthetic route is described for the preparation of 1-chloro-1-silabicyclo[2.2.2]octane. Chlorination of this material afforded the α-, β- and γ-monochlorinated isomers which were isolated and characterized.

Introduction

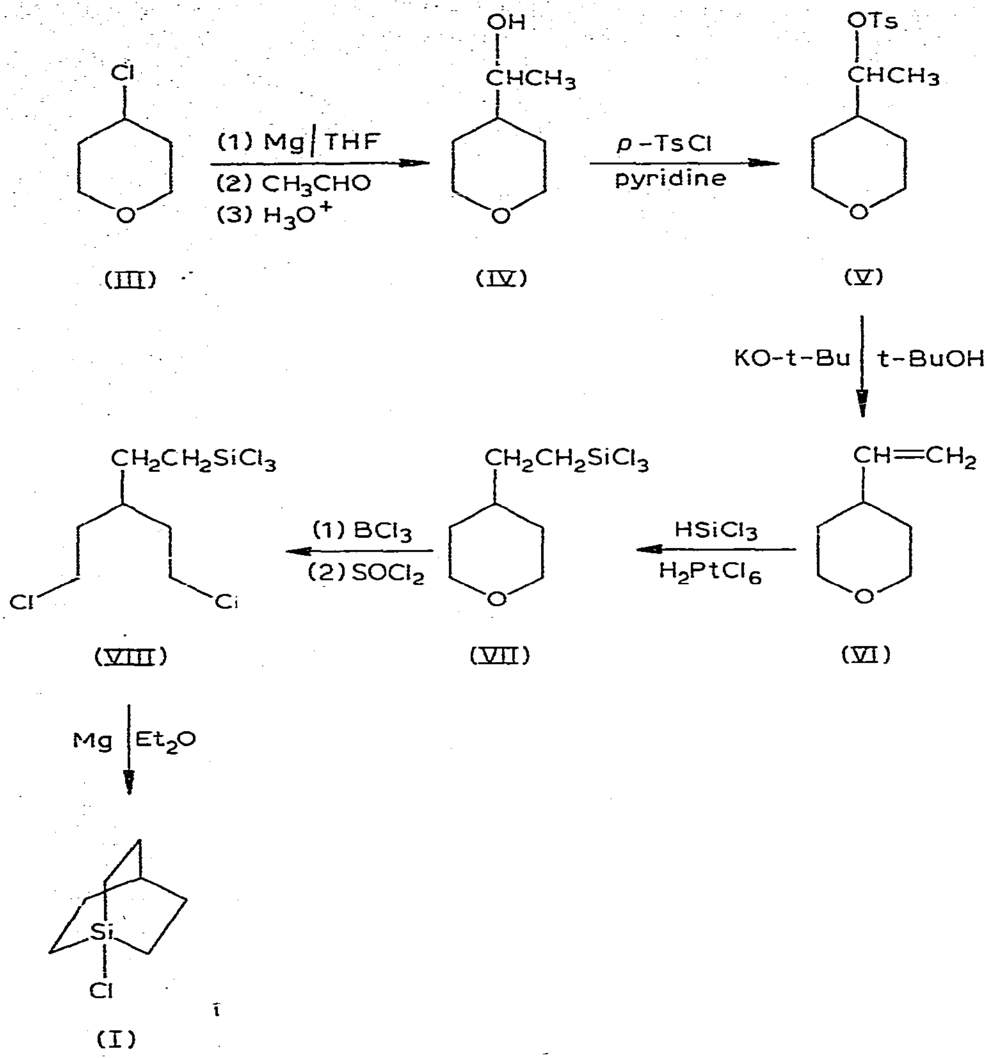
In contrast to its all-carbon analogue, little is known about the chemistry of the 1-silabicyclo[2.2.2]octane ring system. Sommer and Bennett were the first to prepare 1-chloro-1-silabicyclo[2.2.2]octane (I) and also reported its reduction to the parent 1-silabicyclo[2.2.2]octane (II) [1]. To our knowledge, the only subsequent report concerning transformations of this ring system details the conversion of II back to I [2]. It was thus of interest to examine the chemistry of the carbon skeleton of this system.

Results and discussion

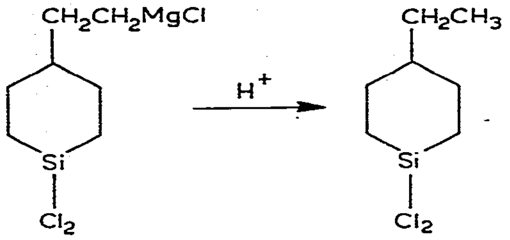
The existing synthesis of I from readily available starting materials is laborious and of low overall yield. The alternative approach shown in Scheme 1 was therefore explored in which the last two steps are identical with the original sequence.

4-Chlorotetrahydropyran (III) was readily obtained in large quantities by the condensation of propylene and paraformaldehyde in the presence of hydrogen chloride [3]. Although the alcohol IV could be formed from the Grignard of III [4] prepared in THF at reflux, better yields of IV were realized by forming the Grignard reagent at 30°C with 1,2-dibromoethane entrainment. Conversion of IV into the tosylate V was followed by elimination with potassium t-butoxide in order to favor [5] formation of the Hofmann olefin VI. Hydrosilylation with trichlorosilane then afforded VII which was ring-opened to VIII.

SCHEME 1



Cyclization of this material to I remained the weak link in the sequence. In an attempt to circumvent the long reaction time and poor yield inherent to the original procedure [1,6], more active metal was employed. However, attempted cyclization using 325 mesh magnesium (magnesium prepared from $MgCl_2$ reduction [7]) or lithium wire (1% Na) failed to afford I. The successful procedure employed 325 mesh magnesium with 1,2-dibromoethane entrainment and consistently yielded a product mixture containing I and IX in a 3/1 ratio. The latter may arise via proton abstraction by the half-cyclized di-Grignard from adventitious moisture, but the constancy of product composition over a number of runs suggests the involvement of other processes. A measure of purification could be effected by recrystallization of this product mixture and afforded, for the cyclization step, a 24% absolute yield of 87% pure I. In comparison with the original sequence [1,6], the present approach represents a reduction

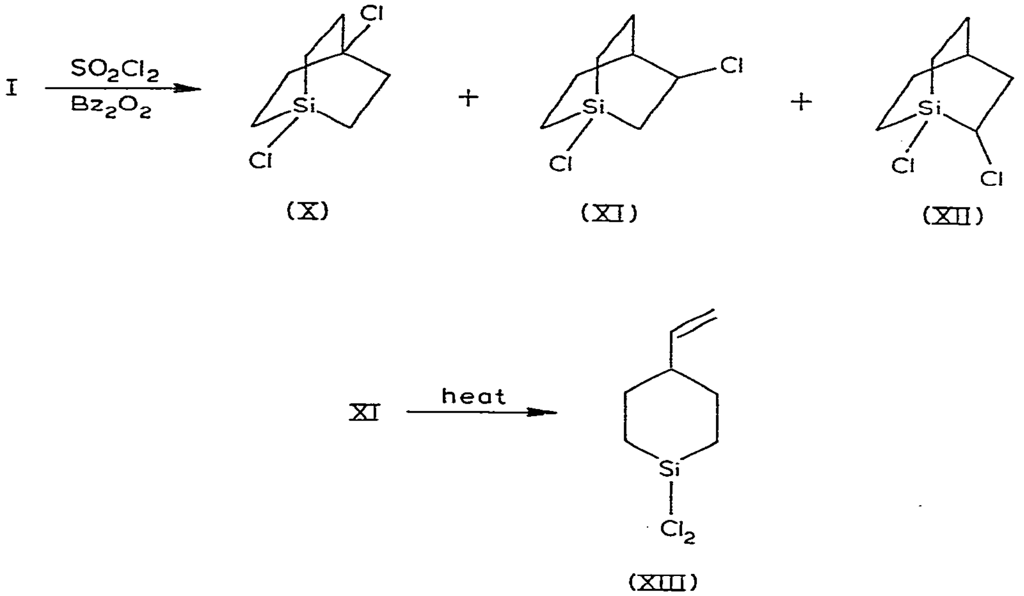


(IX)

by a third in the number of required steps from readily available materials and a doubling of overall yield. However, the low yield of the cyclization step and the co-formation of IX remain severe obstacles to production of synthetically useful quantities of pure I.

Introduction of functionality into the carbon framework of I was carried out by chlorination with sulfuryl chloride. Under these conditions, the monochlorinated isomers X—XII were produced in maximum respective yields of 7, 32 and 12% (Scheme 2). Isomer XI exhibited thermal instability towards ring cleavage to XIII, a known characteristic of other β-haloorganosilanes [8]. Further exploration of the chemistry of these interesting compounds was precluded by the overall low yields and difficulty in separating the isomer mixture.

SCHEME 2



Experimental

General

Infrared data were obtained on neat films using a Beckman IR-8 spectrometer. NMR spectra were obtained on Varian A-60A or JEOL PFT-100 spectrometers;

chemical shift values are assigned from the center of a multiplet relative to TMS or chloroform (taken as δ 7.27 ppm) as internal standard. GLPC columns were conditioned by injections of ethyltrichlorosilane before analyses of chlorosilanes were performed.

4-(1-Hydroxyethyl)tetrahydropyran (IV)

A flask equipped with mechanical stirrer, condenser, addition funnel and thermometer was flamed out under nitrogen and charged with 80.8 g (3.33 mol) of 50 mesh magnesium powder and sufficient tetrahydrofuran (THF) to cover the metal. A mixture of 200 g (1.65 mol) of 4-chlorotetrahydropyran [3], 71.5 g (0.38 mol) 1,2-dibromomethane and 200 ml THF was then added dropwise over a 3.5 h period. The internal temperature was maintained at 30—36°C over the addition period by application of an ice bath. After an additional hour of stirring at 25°C, acetaldehyde was distilled into the Grignard solution through a sintered glass addition tube. The addition was accompanied by evolution of heat, but the mixture was maintained at 34—38°C by an ice bath. Hydrolysis was effected by pouring the reaction mixture into dilute HCl and ice. The product displayed considerable water solubility and was isolated by multiple ether extraction of the NaCl-saturated aqueous solution; total recovery was achieved by continuous ether extraction. After drying ($MgSO_4$), fractionation (6 in. Vigreux) afforded 145 g (68%) of IV, b.p. 65—67°C/0.7 mmHg. IR: 2.9 s, 3.4s, 3.5s, 6.95m, 7.3m, 8.1m, 9.2s, 9.9m, 10.2m, 10.6m, 11.4m, 11.8m, 12.35w μm. ^{1}H NMR (CCl_4, TMS): δ (ppm) 1.1 (d, J 6 Hz, 3H), 1.2—2.0 (br, m, 5H), 3.0—4.3 (m, 6H). Found: C, 64.56; H, 10.82. $C_7H_{14}O_2$ calcd.: C, 64.58; H, 10.84%.

Omission of 1,2-dibromoethane entrainment required that the Grignard preparation be run at the reflux temperature of the mixture (cooling terminated reaction) and resulted in yields of IV in the region of 50%.

4-[1-(p-Toluenesulfonyloxy)ethyl]tetrahydropyran (V)

A mixture of 145 g (1.11 mol) IV and 362 ml of pyridine was cooled to 10°C, and 234 g (1.23 mol) *p*-toluenesulfonyl chloride added in portions with mechanical stirring over 0.5 h. After stirring an additional 2 h, the thick mixture was poured into 6 *N* HCl, whereupon the tosylate layer settled to the bottom and crystallized. The supernatant liquid was decanted and the solid washed with water and collected (m.p. 50—60°C). The decanted layer was worked-up by ether extraction, solvent removed, and the residual oil seeded to afford material of m.p. 58—63°C. All crystalline material was combined for a total yield of 303 g (96%) of crude V. This material could be used without further purification in the subsequent step. Recrystallization from ether/pentane afforded the analytical sample, m.p. 62—64°C (Found: C, 58.99; H, 7.10. $C_{14}H_{20}O_4Si$ calcd.: C, 59.13; H, 7.09%). IR: 3.4m, 3.5m, 6.3m, 6.9m, 7.4s, 8.1m, 8.5s, 9.2m, 9.7m, 11.2s, 11.7m, 12.3m, 12.9m, 15.1s μm. ^{1}H NMR ($CDCl_3$, TMS): δ (ppm) 1.27 (d, J 6, 3H), 1.3—2.2 (m, 5H), 2.48 (s, 3H), 3.1—4.2 (m, 4H), 4.2—4.7 (m, 1H), 7.62 (AA′BB′ pattern, 4H).

4-Vinyltetrahydropyran (VI)

To a stirred solution of potassium t-butoxide prepared from 1060 ml t-butyl alcohol and 40.0 g (1.04 mol) potassium was added 140 g (0.49 mol) of V over 0.5 h. After a 5 h reflux period, the reaction was poured onto 400 ml of ice and the diluted mixture extracted with hexane. The organic layer was washed with water until the pH of the final wash was neutral, dried over $MgSO_4$, and solvent removed by distillation. Distillation of the residue afforded 36.9 g (67%) of VI, b.p. 130—134°C/760 mmHg (Found: C, 75.07; H, 10.93. $C_7H_{12}O$ calcd.: C, 74.95; H, 10.78%. IR: 3.22w, 3.39s, 3.50s, 3.61w, 3.70w, 6.10w, 6.92w, 7.21w, 7.40w, 7.74w, 8.09m, 8.64m, 8.88s, 9.2s, 9.89m, 10.05m, 10.21m, 10.59w, 10.97m, 11.68m, 12.34w μm. ^1H NMR (CCl_4, TMS): δ (ppm) 1.4—1.8 (m, 4H), (1.8—2.5 (m, 1H), 3.37 (t of d, *J* 11, *J* 3.5, 2H), 3.75—4.15 (m, 2H), 4.85—5.25 (m, 2H), 5.6—6.2 (m, 1H).

4-(2-Trichlorosilylethyl)tetrahydropyran (VII)

A one-neck flask with thermometer well was equipped with a Friedrich condenser leading to a mercury trap and charged with 7.78 g (0.069 mol) of VI and 6 drops of a 10% solution of chloroplatinic acid in 2-propanol. After cooling to 2°C, 9.42 g (0.069 mol) of trichlorosilane was added and the cooling bath removed. Upon warming to room temperature, the temperature of the mixture rose spontaneously to 60°C and then dropped. Heat was applied at 45°C until the internal temperature reached 85°C and then removed. The mixture was distilled to give 11.42 g (67%) of VII, b.p. 80—85°C/0.65 mmHg (Found: C, 34.19; H, 5.37. $C_7H_{13}OSiCl_3$ calcd.: C, 33.95; H, 5.29%). IR: 3.39s, 3.50s, 3.60w, 6.9m, 7.2m, 7.3m, 7.65w, 8.05m, 8.34m, 8.50m, 8.56m, 8.4s, 9.2s, 9.8s, 10.15m, 10.6w, 10.85w, 11.16m, 11.75m, 12.47m, 13.08s, 14.14s μm, ^1H NMR (CCl_4, TMS): δ (ppm) 1.38 (br, s, 9H) δ 2.80—3.35 (m, 2H), 3.35—3.85 (m, 2H).

1,5-Dichloro-3-(2-trichlorosilylethyl)pentane (VIII)

A flask fitted with a condenser leading to a bubbler and with a capillary tube for gas introduction was charged with 60.1 g (0.24 mol) of VII. Boron trichloride was then passed through the liquid at a rate which caused no gas to exit the bubbler. After 3 h, rapid gas evolution was noted at the exit and introduction of BCl_3 stopped; weighing the reaction mixture indicated that almost one equivalent of BCl_3 had been absorbed at this point. The mixture was then heated at 200°C for 1 h (heating another run at 275°C [6] resulted in a severe reduction in yield). When cool, 112 g (0.94 mol) of $SOCl_2$ and 1 ml quinoline were added, and the mixture was refluxed for 20 h. Thionyl chloride was removed under reduced pressure and the residue distilled to yield 58.7 g (80%) of VIII, b.p. 137.5—138.0°C/3.5 mmHg (lit. [1,6] b.p. 130—131°C/2.5 mmHg). (Found: C, 27.91; H, 4.35. $C_7H_{13}SiCl_5$ calcd.: C, 27.79; H, 4.33%). IR: 3.39s, 6.9s, 7.3w, 7.8s, 8.0w, 8.35m, 8.97m, 9.9m, 11.6m, 12.96s, 13.9s, 14.47vs, 15.2s μm. ^1H NMR ($CDCl_3$, $CHCl_3$): δ (ppm) 1.5—2.0 (m, 9H), 3.68 (t, *J* 6.5 Hz, 4H).

1-Chloro-1-silabicyclo[2.2.2]octane (I)

A three-neck flask equipped with mechanical stirrer, condenser, addition funnel and helium inlet was flame dried and charged with 60 ml of freshly distilled ethyl ether and 5.8 g (0.26 mol) of 325 mesh magnesium powder [9]. A mixture of 24 g (0.079 mol) VIII and 3.0 g (0.016 mol) of 1,2-dibromoethane in 160 ml ether was then added dropwise over 3 h with heating and stirring. After an additional 7 h reflux period, a large quantity of salts was present, together with unreacted magnesium. An additional 150 ml of ether was added, and reflux continued for 12 h longer. The mixture was then concentrated to a thick paste under vacuum, and dry pentane added. Salts were filtered off, the filtrate concentrated under vacuum to a thick liquid, and pentane added once more. Salts were again removed by filtration, and the filtrate concentrated and distilled. There was obtained 5.81 g of distillate, b.p. 62—68°C/6 mmHg which GLPC (5′ × 1/4″, 20% SE-30 on 60/80 Chromosorb W DMCS, 80°C) indicated contained 64% of I (Found: C, 52.31; H, 7.98. $C_7H_{13}SiCl$ calcd.: C, 52.31; H, 8.15%). IR: 3.41s, 3.48m, 6.93m, 7.12w, 7.51w, 8.59s, 9.02w, 10.12w, 10.87m, 11.57m, 12.81s, 14.95 μm. ^1H NMR ($CDCl_3$, TMS): δ (ppm) 0.9—1.1 (m, 6H), 1.50 (m, 5 lines resolved, J 3.4 Hz, 1H), 1.8—2.1 (m, 6H).

The major contaminant in the product (21%) was identified as 1,1-dichloro-4-ethyl-1-silacyclohexane (Found: Cl, 36.15. $C_7H_{14}SiCl_2$ calcd.: Cl, 35.96%). IR: 3.36m, 3.39s, 3.48s, 6.87m, 7.16w, 7.26w, 8.35w, 8.51w, 10.35m, 11.03w, 11.71m, 12.0w, 12.92s, 13.57m, 14.54s μm. ^1H NMR ($CDCl_3$, $CHCl_3$): δ (ppm) 0.89 (t, J 6 Hz, 3H), 0.98—2.2 (m, 11H).

Low temperature recrystallization of crude I, above, from pentane afforded 3.5 g of material which GLPC indicated was 87% pure (24% yield of pure I). Material of this purity was used in subsequent chloration runs.

Chlorination of 1-chloro-1-silabicyclo[2.2.2]octane

A flask was fitted with condenser, magnetic stirrer and nitrogen line and charged with 1.1 g (0.068 mol) of I, 0.02 g (0.00008 mol) of benzoyl peroxide, 10 ml of benzene and 0.81 g (0.0068 mol) of sulfuryl chloride. After a 48 h reflux period, analysis and product isolation was carried out by GLPC (10′ × 1/4″ FFAP on 60/80 Chromosorb W, programmed at 0.5°C/min from 80—160°C). The γ- (X), β- (XI) and α- (XII) -monochlorinated isomers (order of elution) represented, respectively, 7, 32 and 12% of the volatiles; base line separation was not achieved for the last two isomers. A number of higher-boiling components accounted for 35% of the volatiles (dichlorinated isomers?) and eluted together.

X. Found: C, 43.34; H, 5.92. $C_7H_{12}SiCl_2$ calcd.: C, 43.08; H, 6.20%. IR: 3.39s, 3.47m, 6.97m, 7.13m, 8.71s, 11.2s, 12.9s, 14.87s μm. ^1H NMR (CCl_4, TMS): δ (ppm) 1.05—1.45 (m, 6H), 2.20—2.72 (m, 6H).

XI. Found: C, 43.14; H, 5.92. IR: 3.40s, 3.47m, 6.95w, 7.1w, 7.87m, 8.14w, 8.54s, 8.84m, 10.03m, 10.24w, 10.85w, 10.92w, 11.24w, 11.54m, 11.0m, 12.79s, 13.2m, 14.56s, 14.85s μm. ^1H NMR ($CDCl_3$, $CHCl_3$): δ (ppm) 0.9—2.1 (m, 10H), 2.1—2.7 (m, 1H), 4.52 (t, J 7 Hz, 1 H).

XII. Found: C, 43.10; H, 6.09. IR: 3.39s, 3.47m, 6.94m, 7.11w, 8.6s, 10.86m, 11.6m, 12.8s, 13.85m, 14.45s μm. ^1H NMR ($CDCl_3$, TMS): δ (ppm) 0.9—2.4 (m, 10H), 2.4—2.8 (m, 1H), 3.5—3.7 (m, 1H).

Preparative GLPC of XI with a detector temperature of 250°C afforded collected samples containing significant amounts of 4-vinyl-1,1-dichloro-1-silacyclohexane (XIII, Found: C, 43.21; H, 6.14. $C_7H_{12}SiCl_2$ calcd.: C, 43.08; H, 6.20%). IR: 3.22w, 3.39s, 3.47m, 6.11w, 6.92w, 7.20w, 8.35w, 10.11w, 10.25m, 10.95m, 11.70m, 12.39s, 13.15s, 14.52s μm. ^1H NMR ($CDCl_3$, $CHCl_3$): δ (ppm)

0.8—2.1 (m, 9H), 4.7—5.0 (m, 2H), 5.5—5.8 (m, 1H). Approximately 10% of XIII was present in samples of XI collected at a detector temperature of 100°C.

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