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SIMPLIFIED APPROACH TO SILAANTHRONES AND DISILAANTHRACENES *

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Summary

An improved synthesis of bis(*o*-chlorophenyl)methylsilane is reported from reaction of a mixture of *o*-BrC_6H_4Cl and $MeSiHCl_2$ with Mg shavings in THF. The diarylsilanes, (*o*-$ClC_6H_4)_2SiMeR$ (R = H, Me) could be converted to diGrignard reagents with Mg prepared by the Rieke method but not from commercial Mg (shavings or mesh). The diorganometallic reagents generated from (*o*-$XC_6H_4)_2SiMeR$ (R = H, Me) are used to prepare disilaanthracenes or silaanthrones. A new spiro derivative, bis(dimethyl-*o*,*o*′-diphenylsilyl)spirosilane, is obtained on addition of $HSiCl_3$ to the diGrignard reagent generated from (*o*-$ClC_6H_4)_2SiMe_2$. When gaseous CO_2 is added to the dilithio reagent formed from (*o*-$BrC_6H_4)_2SiMe_2$, silaanthrone is produced which provides a new route to the silanthracene framework. Aspects of this new ring closure route are described.

Introduction

Several years ago a route to dihydrosilaanthracene and silaanthrone derivatives (I and II respectively) was developed by Jutzi [1] through a sequence of steps shown as 1a through 1d in Scheme 1. In part because dihydrosilaanthracenes are precursors to silaanthracenes which are derivatives of theoretical interest, a detailed study of other precursors to the silaanthracene framework was made by Bickelhaupt and coworkers [2]. The final conclusion of this investigation was that bis(*o*-chlorophenyl)methane is the precursor of choice to I and II even though chloroaromatics are often difficult to convert to organometallic reagents. The single improvement in the sequence 1a to 1d is in the reduction of the carbinol formed in 1b which originally involved gaseous HI. We modified this step for aqueous HI by using HOAc and Ac_2O as cosolvents. Without Ac_2O the yields of bis(*o*-chlorophenyl)methane were irratic and often an

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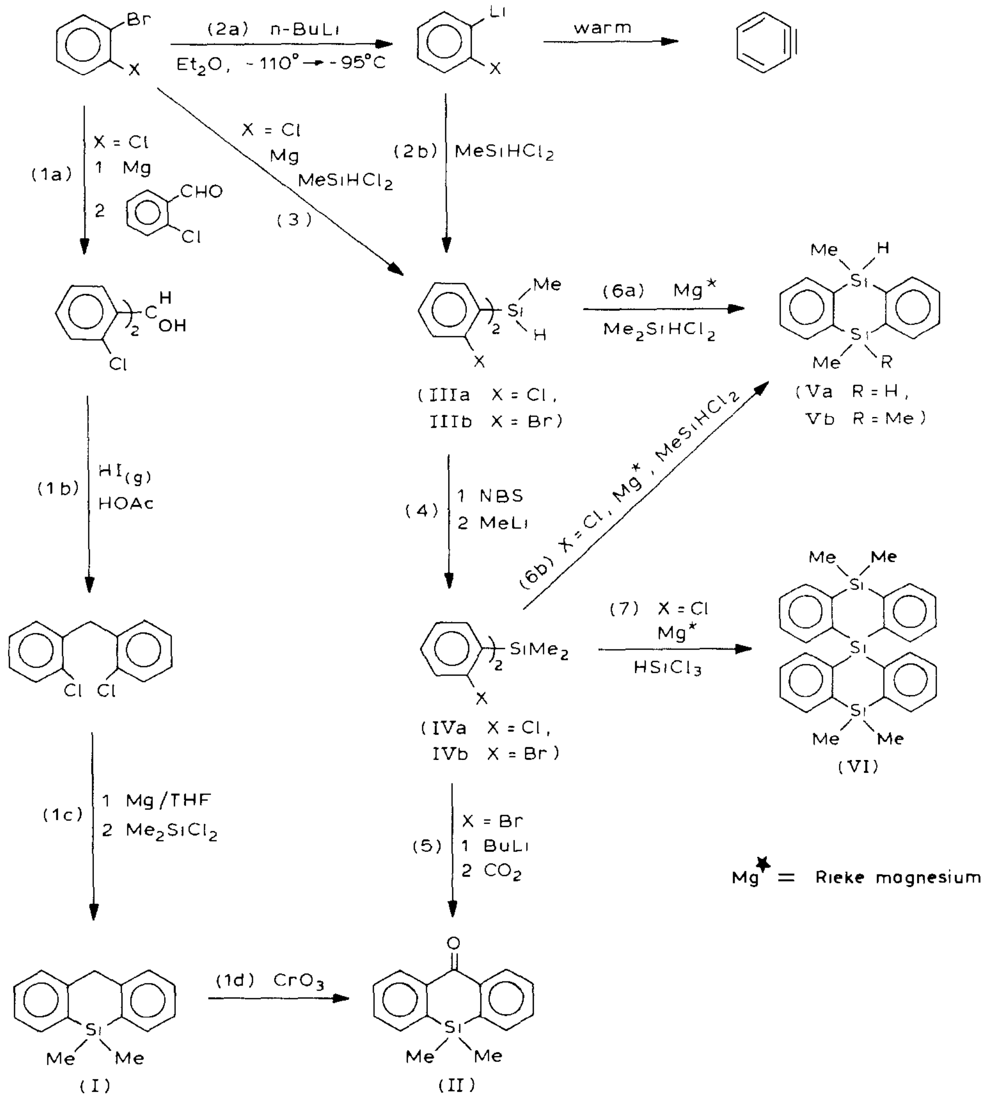
* Dedicated to Professor M. Kumada on the occasion of his retirement.

SCHEME 1



unidentified, high-melting solid was obtained as the major product.

Since we are interested in tricyclic derivatives with central six-membered rings that contain silicon heteroatoms as models for central nervous system agents we sought a more direct and less tedious route to the structural class which includes derivatives such as I or II. The route described in the sequence 1a to 1c incorporates the silicon grouping into the framework of the tricycle in the ring closure step. We chose to reverse the synthetic sequence by adding the aromatic rings to the silicon center in the initial step to form diarylsilanes, III and IV (X = Cl, Br) followed by a reaction which would lead to ring-closure. This approach led to a new synthesis of disilaanthracenes in essentially two or three steps (Scheme 1) and which allowed for the incorporation of functionality at both silicon centers (Va) or at one silicon center

(Vb) (Scheme 1, steps 6a and 6b, respectively) [3]. Specifically directed functionality in disilaanthracenes is not possible through previously published routes. We have now developed a more convenient method of synthesis of bis(*o*-chlorophenyl)methylsilane, IIIa, and the use of this reagent in the synthesis of a spirodisilaanthracene is described. In addition, this general approach has been successfully extended to the synthesis of silaanthrones, II.

Discussion

The original route to III (Scheme, steps 2a and 2b) utilized commercially available *o*-halobromobenzenes which were lithiated at -110 and $-95\,^{\circ}$C for the bromo and chloro derivatives respectively. Warming of the *o*-halolithiobenzene results in decomposition, probably to benzyne, and thus the reaction temperature must be carefully monitored. A simpler route to III ($X = Cl$) could involve a Grignard reagent which may be generated at room temperature. Indeed, when a mixture of *o*-chlorobromobenzene and methyldichlorosilane (ratio of 2/1) are added to either magnesium mesh or magnesium shavings [4] in ether, IIa is formed in 70 to 80% yields. Normal Grignard grade magnesium gave irratic results in ether, although a change to THF as solvent resolves this problem. When III (or IV) is treated with commercial Mg in THF until starting material is consumed, quenching reactions (water or Me_2SiCl_2) showed a complex mixture of products including Ph_2SiMeR ($R = H$, Me) and dibenzosilole. The best conditions found for formation of the diGrignard of IIa was with Rieke magnesium [3]. Thus IIIa may now be converted to 9,10-difunctional-9,10-dihydrodisilaanthracenes as shown in step 6a of Scheme 1 in a two-step process from commercial reagents without requiring the low temperatures necessary for sequence 2a–2b. An attempt to convert IIIb to Va by adding a mixture of IIIb and $MeSiHCl_2$ in THF to magnesium mesh was only moderately successful since a slightly impure sample of disilaanthracene, Va, was produced in only 36% yield. To further illustrate the versatility of this synthetic route, IIIa was converted to IVa. When IVa is treated with Rieke Mg followed by addition of half an equivalent of trichlorosilane, a new spiro-compound, VI, was obtained. An ESR study of the radical anion of VI is in progress to determine whether there is any delocalization of spin between the two rings as is observed in the disilacyclohexadiene analog of VI [5]. The spiro derivative also exhibits a singlet SiMe in the NMR spectrum (ratio of aryl/Me = 4/3) which could imply two orthogonal planar ring systems joined by the central silicon atom, although rapid inversion of both rings is not precluded. A crystal structure is in progress to determine if VI contains planar rings in the solid state.

A further illustration of the use of bis(*o*-halophenyl)silanes as precursors to silicon heterocycles is in the synthesis of silaanthrone. In this case the diorganometallic from III or IV must react with a suitable carbon source to obtain the tricyclic system. The carbon source must be able to react with two equivalents of RM ($M = Li$, MgX). Suitable organic reagents would be derived from carbonyl reagents such as carbamates, formates, amides or esters. It has been reported that *N*,*N*-disubstituted carbamates react with two moles of RM ($M = Li$, MgX) to yield symmetrical ketones in good yield [6]. When the diorganolithium reagent of IV was treated with $ClC(O)NMe_2$ and $EtOC(O)NMe_2$, II was obtained in about 10 to 31% yield (impure). Only reactions of the lithium organometallic were explored since if II is formed under conditions used to obtain the diGrignard with activated Mg (excess Mg) reductive coupling of the ketone would be expected as Rieke has described for benzophenone [7]. However, the Grignard route could be used if a ketone was not the direct product. When ethylformate was added to the diGrignard generated from IVa a product was obtained which when treated with pyridinium chlorochromate provided about 29% of impure II.

The route to II with highest conversion occurs in the reaction of CO_2 with the dilithium reagent of IVb. Gilman has shown that carbonation of PhLi leads to benzophenone in 86–88% yield when CO_2 is present in low concentration [8]. When CO_2 is bubbled into the diorganometallic reagent of IVb in refluxing ether, the silaanthrone II is obtained in 67% isolated yield. The product is identical in all respects to that prepared by Jutzi in the sequence la through ld [1]. From the same starting material, II is prepared in 40% yield overall by this new sequence (steps 3,4,5 in Scheme 1) as compared to 18% overall yield for the previous route (1a to 1d) [1]. An attempt to convert IIIb to II by the same method failed as the SiH bond of IIIb reacts under the lithiation conditions.

The synthesis of disilaanthracenes such as V from commercial *o*-bromochlorobenzene in two "one-pot" steps provides a series of new functional disilaanthracenes whose chemistry is currently under investigation. The most convenient sequence involves reaction of *o*-bromochlorobenzene with commercial magnesium in THF followed by Grignard formation of the bis(*o*-chlorophenyl)silane formed with activated Rieke magnesium. The more expensive *o*-dibromobenzene is the required precursor in the highest yield route to silaanthrone through two lithium exchange reactions the first of which requires a low temperature (−110 °C).

Experimental

Organometallic reactions were carried out in oven-dried glassware which was flamed under an inert atmosphere. Activated magnesium preparations were carried out under argon whereas N_2 was used for organolithium reactions.

Methyldichlorosilane, trichlorosilane, dimethylcarbamoyl chloride, ethyl formate (dried by distillation from P_2O_5), silica gel (100–200 mesh), CrO_3, $MgSO_4$ (anhydrous) and CO_2 (gas) were all commercial reagents and were used as supplied unless noted. Commercial magnesium shavings were obtained in prepackaged form from Reade Manufacturing Co.. Magnesium mesh (70–80) was purchased from Mallinckrodt.

o-Bromochlorobenzene was used as supplied or prepared by literature methods [9] as were pyridinium chlorochromate [10], *N,N*-dimethylethyl carbamate [6], 9,9-dimethyl-9,10-dihydro-9,10-disilaanthracene [3], bis(*o*-chlorophenyl)dimethylsilane [3], bis(*o*-bromophenyl)methylsilane [3,11], bis(*o*-bromophenyl)dimethylsilane [3] and diphenylmethyl- (or dimethyl-)silane [3].

The generation of dilithium intermediates and the general procedure for the preparation of diGrignard reagents from activated magnesium was previously reported [3].

Tetrahydrofuran and ether were purified by distillation from alkali metal benzophenone ketal.

Proton NMR data were recorded on a Varian T-60 spectrometer and a JEOL FX-100 Multinuclear spectrometer. Mass spectra were collected on an AEI MS-1201B mass spectrometer. Melting points were uncorrected and were obtained on a Thomas

Hoover capillary melting point apparatus. A Cole–Parmer Ultrasonic cleaner with heater was used.

Analyses were performed by Galbraith Laboratories, Inc.

Bis(o-chlorophenyl)methylsilane (IIIa)

A mixture of *o*-bromochlorobenzene (20 g, 105 mmol) and methyldichlorosilane (6.0 g, 52 mmol) in ether (50 ml) was added to a 2 molar excess of magnesium turnings (Reade) (5 g, 206 mmol) in ether (100 ml) and refluxed 5 h. The heat source was removed and the reaction mixture was stirred overnight. The slurry was filtered and the inorganic salts and excess magnesium were then dissolved in water and extracted with ether. The combined organic fractions were distilled by rotary evaporation to produce an oil. The oil was purified by Kugelrohr distillation to give impure IIIa (10.6 g, 76% yield) as a colorless oil, b.p. 96–160°C/0.07 mmHg, which could be used without further purification. A similar reaction on the same scale using commercial magnesium (70–80 mesh) gave IIIa in 71% yield.

When the reaction was performed with magnesium (shavings, commercial, Grignard grade) which had been stirred overnight and then a mixture of *o*-bromochlorobenzene (40 g) and methyldichlorosilane (12 g) in ether added, 2.5 g of Mg and 20 g of the starting aryl halide were recovered after 24 h along with 6.1 g of impure IIIa.

When a mixture of *o*-bromochlorobenzene (40 g, 98.5%) and freshly distilled methyldichlorosilane (12 g) in THF (225 ml) was added to Mg shavings (commercial, Grignard grade, 5.6 g) in THF (100 ml) at such a rate as to prevent refluxing of the solvent, 17.8 g (67%) of IIIa was obtained as an oil, b.p. 115-128°C/0.15 mmHg after workup with saturated, aqueous NH_4Cl.

Attempted preparation of the diGrignard of IIIa with commercial magnesium

A solution of IIIa (2.0 g, 7.5 mmol) in THF (ca. 100 ml) was refluxed for 48 h in the presence of magnesium (70–80 mesh, 1 g, 40 mmol). The filtered solution was treated with dimethyldichlorosilane (1.0 g, 7.7 mmol) by the method of simultaneous addition. After hydrolytic workup the product was a complex mixture which included 9,9,10-trimethyl-9,10-dihydro-9,10-disilaanthracene as well as 9-methyldibenzosilole and diphenylmethylsilane which were identified by comparison with authentic spectra. Starting material, IIIa, was absent.

Sonication of a mixture of IIIa and magnesium in THF at 55°C did not give a positive test for the presence of Grignard reagent after 20 h. After the usual workup and removal of the solvents an NMR spectrum of the residue showed it to be starting material.

Attempted preparation of the diGrignard of IVa from commercial magnesium

A solution of IVa (2 g, 7 mmol) in THF (150 ml) and magnesium (70–80 mesh, 3 g, 120 mmol) were refluxed for about 1 week. After hydrolytic workup a crude oil was obtained which contained the starting material, IVa, diphenyldimethylsilane and 9,9-dimethyldibenzosilole which were identified by comparison of R_f values and NMR spectra of those of authentic samples.

Reaction of IIIb with commercial magnesium

A solution of bis(*o*-bromophenyl)methylsilane, IIIb (1.0 g, 2.8 mmol) and magnesium (70–80 mesh, 1.0 g, 41 mmol) in ether (about 100 ml) was refluxed for 25 h.

After hydrolytic workup a crude oil was obtained and distilled to give an oil (0.24 g), b.p. 80–120 °C/0.02 mmHg whose NMR spectrum corresponds to an authentic spectrum of methyldiphenylsilane.

When the reaction was repeated in THF on the same scale a 57% yield of methyldiphenylsilane was obtained after hydrolysis.

Reaction of IVb with commercial magnesium

A solution of bis(*o*-bromophenyl)dimethylsilane, IVb (0.75 g, 2.0 mmol), and an excess of magnesium (70–80 mesh, 1 g) in ether (125 ml) was refluxed for about 3 h. Hydrolytic workup provided an oil after removal of the solvent. An ^{1}H NMR spectrum of the oil corresponds to a spectrum of an authentic sample of dimethyldiphenylsilane.

Formation of Va from simultaneous reaction of IIIb and Me_2SiHCl_2 with magnesium

A mixture of IIIb (2 g, 5.6 mmol) and methyldichlorosilane (0.62 g, 5.5 mmol) in THF (50 ml) were added to a large excess of magnesium (70–80 mesh, 2 g, 82 mmol) and refluxed overnight. After the usual aqueous workup with NH_4Cl (sat. aq.) and extraction with ether, the solvent was removed by rotary evaporation to yield an oil. Kugelrohr distillation provided a sample of Va, 0.47 g (36%), b.p. up to 95 °C/0.04 mmHg. An NMR spectrum of the distilled product was identical to that of an authentic sample of Va but showed the presence of an impurity.

When the reaction was run with magnesium turnings (Reade) and ether as a solvent with an overnight reflux, only starting material was recovered.

Bis(dimethyl-o,o′-diphenylsilyl)spirosilane (VI)

To a slurry of activated magnesium generated from $MgCl_2$ (7.8 g, 82 mmol) in THF (150 ml) was added bis(*o*-chlorophenyl)dimethylsilane (5.0 g, 18 mmol) in THF (50 ml) and the mixture stirred overnight. The reaction vessel was cooled to 0 °C and trichlorosilane (1.2 g, 8.9 mmol) was added and the mixture stirred for 3 h followed by a 3 h reflux. After aqueous workup the crude oil was dissolved in hexanes/CH_2Cl_2 (1/1), dried over $MgSO_4$, filtered and stripped to obtain VI as an oil which crystallized on standing. Several recrystallizations of VI from hexanes/CH_2Cl_2 (1/1) produced an analytical sample, m.p. 201–202 °C (1.9 g, 47% yield). ^{1}H NMR ($CDCl_3$) δ (ppm) (internal TMS): 0.62 (s, 12, Si-C*H*$_3$); 7.07–7.46, 7.60–7.77 (m, 16, arom). Anal. Found: C, 74.80; H, 6.35. $C_{28}H_{28}Si_3$ calcd.: C, 74.95; H, 6.29%). $m/e = 448$ (M^+).

Formation of II from dimethylcarbamoyl chloride and IVb

A solution of IVb (1.8 g, 4.8 mmol) in ether (75 ml) was added to an excess of n-BuLi (8 ml of 1.6 *M* in hexanes, 13 mmol) which had been diluted with ether (50 ml) at 0 °C and stirred for 0.5 h. The solution was warmed to room temperature and stirred an additional 0.5 h before transferring the aryllithium to an addition funnel. A solution of dimethylcarbamoyl chloride (0.50 g, 4.8 mmol) in ether (50 ml) was added to a second addition funnel and both solutions were added simultaneously to the same reaction vessel. The resulting solution was stirred 0.5 h then refluxed for 2 h. The reaction mixture was hydrolyzed with HCl (3 *N*, 50 ml) followed by extraction with ether. The combined organic layers were dried over $MgSO_4$ and the solvent was removed by rotary evaporation to produce an oil. Kugelrohr distillation gave II (0.35 g, 31%) as an impure oil, b.p. 114–138 °C/0.03 mmHg (lit. [1], b.p. 110–111 °C/0.04 mmHg). The presence of II was verified by an NMR spectrum and TLC of the crude oil and comparison to an authentic sample.

Formation of II from N,N-dimethylethyl carbamate and IVb

A solution of IVb (1.9 g, 5.1 mmol) in ether (50 ml) was added to an excess of n-BuLi (8 ml of 1.6 *M* in hexanes, 13 mmol) in ether (25 ml) at 0 °C and stirred for 1 h. *N,N*-Dimethylethyl carbamate (0.60 g, 5.1 mmol) in ether was added and stirred at room temperature for 3 h. After hydrolysis with NH_4Cl (sat. aq.) and extraction with ether the volatiles were removed to give an oil residue. Kugelrohr distillation produced a fraction, b.p. 105–150 °C/0.03 mmHg which contained II. The estimated yield of II is less than 10% (NMR).

Formation of II from CO_2 and IVb

A solution of bis(*o*-bromophenyl)dimethylsilane (1.0 g, 2.7 mmol) in ether (50 ml) was added to n-BuLi (2.5 ml of 2.6 *M* in hexanes, 6.5 mmol) which had been added to ether (about 50 ml) during 0.3 h at 0 °C with stirring. The solution was then heated to reflux and a stream of CO_2 (gas) was passed over the solution for 1 h during which most of the solvent evaporated. The remaining material was hydrolyzed with NH_4Cl (sat. aq.) and extracted with ether. The combined organic extracts were dried with $MgSO_4$, filtered and the solvents removed to give an oil. Kugelrohr distillation gave II (0.43 g, 67% yield), b.p. 110–150 °C/0.1 mmHg. A sample was crystallized once from hexane, m.p. 83 °C (lit. m.p. 75 °C [1] and 83 °C [12]). Spectroscopic data and TLC characteristics were identical to an authentic sample prepared by the original route [1].

Attempted preparation of 10-oxo-9-methyl-9,10-dihydro-9-silaanthracene

A solution of IVb (3.0 g, 8.4 mmol) in ether (50 ml) was added to a 10% excess of n-BuLi (6.2 ml of 2.6 *M* in hexanes, 19 mmol) which had been added to ether (50 ml) at room temperature and stirred 0.3 h. The mixture was heated to reflux and a stream of CO_2 (gas) was passed over the solution for 1 h during which time most of the solvent evaporated. The remaining material was hydrolyzed with NH_4Cl (sat. aq.) and extracted with ether. The combined organic extracts were dried over $MgSO_4$, filtered and the solvent removed by rotary evaporation to produce an oil. An NMR spectrum of the oil failed to show the expected SiH resonance (about 5 ppm) or a resonance due to hydrogens peri to the 10-oxo group at 8.3–8.6 ppm.

Formation of II from IVa and ethyl formate followed by oxidation

To a slurry of activated magnesium prepared from $MgCl_2$ (7.5 g, 79 mmol) in THF (100 ml) was added IVa (5.2 g, 18 mmol) in THF (25 ml) and the mixture refluxed for 2 h. Ethyl formate (1.34 g, 18 mmol) was added and the mixture was stirred overnight. The usual workup with NH_4Cl (sat. aq.) was followed by extraction with ether and rotary evaporation of the solvents to produce an oil. Kugelrohr distillation provided the impure ketone, II (1.3 g, 29% yield), b.p. 110–140 °C/0.1 mmHg. When the reaction was conducted at 0 °C and at −35 °C the yields were not improved.

In an effort to isolate the alcohol which is presumed to be the direct product of the diGrignard and ethyl formate, the oil obtained after removal of the volatiles was eluted over silica gel. The fractions which were obtained from 50–60% hexane (50–40% CH_2Cl_2) contained an oil with the following spectroscopic characteristics: ^1H NMR (100 MHz) ($CDCl_3$) δ (ppm) (internal TMS): 0.50 and 0.53 (s, $Si(CH_3)(CH_3)$); 5.12 (s, AromC*H*(OH)Arom); 7.2–7.6 (m, arom). Attempts to obtain an analytical sample by crystallizations from alcohol or hexanes were not successful.

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4 The only commercial Mg shavings which were used successfully were those prepackaged in 25 gram lots and supplied by Reade Manufacturing Co. We thank them for the complimentary samples used in this study.

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