

## The Wurtz-Fittig coupling reaction of 2,3-dichloronorbornene with sodium and chlorotrimethylsilane

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Manuscript received 28 July 2010, revised 12 May 2011, accepted 20 June 2011

**Abstract :** The Wurtz-Fittig coupling reaction of 2,3-dichloronorbornene (1) with sodium and chlorotrimethylsilane in anhydrous THF solvent is reported. The novel reaction affords 2,3-bis(trimethylsilyl)norbornene (2), along with a small amount of reductive carbon-carbon ring cleaved product (3'-trimethylsilylcyclopentanyl)-1-trimethylsilylacetylene (3).

**Keywords :** Cyclic dianions, dianionic synthons, 2,3-bis(trimethylsilyl)norbornene, Wurtz-Fittig coupling reaction, reductive carbon-carbon bond cleavage.

### Introduction

The chemistry of cyclic vinylsilanes is enormous and well documented<sup>1</sup>. The compounds are cyclic vinyl anionic synthons. The trimethylsilyl- group acts as a masking agent for the anion. In contrast, however, the chemistry of 1,2-bis(trimethylsilyl)cycloalkenes is relatively less reported. The 1,2-bis(trimethylsilyl)cycloalkenes are cyclic vinyl 1,2-dianionic synthons<sup>2</sup>. Their unmasked equivalents the 1,2-cyclic dianions are implicated in cycloalkyne chemistry<sup>3-5</sup>.

Several groups of investigators have reported the preparation of a few cyclic bis(trimethylsilyl)- substituted compounds. These include 1,2-bis(trimethylsilyl)-cyclopropene<sup>6</sup>, substituted 1,2-bis(trimethylsilyl)-cyclobutenes<sup>7</sup>, 1,2-bis(trimethylsilyl)acenaphthylene<sup>8</sup> and 2,3-bis(trimethylsilyl)norbornene<sup>3,4</sup>. The compounds have been prepared by the reaction of butyl-lithiums with the corresponding dihalocycloalkene, followed by quenching with chlorotrimethylsilane in THF solvent in a stepwise manner. 2,3-Bis(trimethylsilyl)bicyclo[2.2.2]octadiene and 1,2-bis(trimethylsilyl)benzene have been synthesized by the Diels-Alder cycloaddition reaction of bis(trimethylsilyl)acetylene to 1,3-cyclohexadiene<sup>9</sup>.

Our laboratory is primarily interested in the synthesis and reactions of some novel cyclic vinylsilanes, by using the Wurtz-Fittig coupling reaction. Towards achieving

this goal, 1,2-bis(trimethylsilyl)cyclopentene<sup>10</sup> and some novel substituted monocarbocyclic vinylsilanes<sup>11-13</sup> have been synthesized by us. During the course of studies on 1,2-dihalocyclopentenes, we reported an unusual reductive carbon-carbon bond cleavage of 1,2-dihalocyclopentenes using sodium and chlorotrimethylsilane in various solvents<sup>10</sup>.

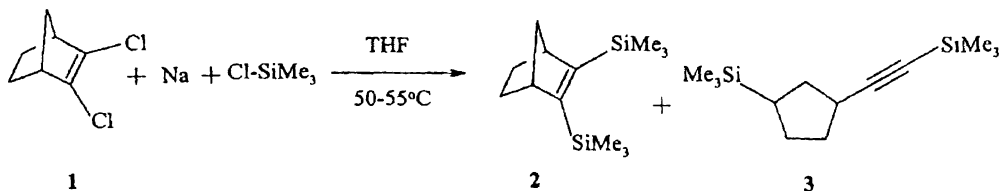
With this experience, the Wurtz-Fittig reaction appeared to be an attractive route for the synthesis of the bicarbocyclic 2,3-bis(trimethylsilyl)norbornene (2)<sup>3</sup>.

Therefore, the Wurtz-Fittig reaction was subsequently extended to the bicyclic compound : 2,3-dichloronorbornene (1)<sup>14</sup> for the preparation of 2,3-bis(trimethylsilyl)norbornene (2)<sup>3</sup>.

### Results and discussion

When 2,3-dichloronorbornene (1) was reacted with sodium and chlorotrimethylsilane in anhydrous THF solvent at 55 °C, all the starting compound disappeared completely in 20 h when followed by GLC. The GLC also indicated the formation of two products in the ratio 9 : 1. The GC-MS analysis indicated the mixture to be 2,3-bis(trimethylsilyl)norbornene (2) and another minor product (3'-trimethylsilylcyclopentanyl)-trimethylsilylacetylene (3) as shown in Scheme 1.

The mixture was subjected to repeated fractional distillation using a Vigreux fractionating column to individually isolate the products 2 and 3.



### Scheme 1

The formation of the ring opened product is important from the mechanistic aspect of organic chemistry. The only other reported instances of ring cleavage are those of hexachloro- and hexabromo-benzenes by Gilman. Hexachlorobenzene on reaction with lithium and chlorotrimethylsilane produced tetrakis(trimethylsilyl)-allene<sup>15,16</sup>. Hexabromobenzene on reaction with magnesium and chlorotrimethylsilane produced a small amount of 1,1,3,4,6,6-hexakis(trimethylsilyl)-1,2,4,5-hexatetraene, formed by the ring opening of benzene<sup>17,18</sup>. Among the mechanisms then considered by Gilman for the ring opening involved benzyne, dibenzyne, carbenoid types and radical anions. However, Gilman did not attempt to establish the exact mechanism for the ring cleavage reactions<sup>19-21</sup>.

Earlier, in the reactions of 1,2-dihalogocyclopentenes carried out by us, no conclusive proof was established for the ring opening of the strained five membered rings. Therefore, it was concluded that the ring opening may be taking place after the formation of the vinylic anion<sup>10</sup>.

In the case of 2,3-dichloronorbornene (1) also, we expect the ring opening to occur due to the formation of the cyclic anion.

## Experimental

The reaction of 2,3-dichloronorbornene (1) with sodium and chlorotrimethylsilane in anhydrous THF was carried out more than five times, with consistent results. The reactions were carried out in an oven dried 50 mL round bottomed flask fitted with a Graham's water cooled condenser attached to a mercury trap/CaCl<sub>2</sub> guard tube. THF was dried and distilled over sodium-benzophenone ketyl radical. Chlorotrimethylsilane was freshly distilled twice over quinoline before use. Sodium metal was cut into approximately 1 mm<sup>3</sup> pieces, washed thoroughly with anhydrous THF and used. The reactions were monitored using a Vista Varian 6000 GC instrument with 10% OV

101 and 15% FFAP columns with temperature programs. NMR was recorded on a Bruker AC-250 spectrometer, and the chemical shifts are relative to  $\text{CHCl}_3$ . IR spectra were run on Beckmann IR-4260 and Carl Zeiss Specord-75 spectrophotometers with liquid films between NaCl plates. GC-MS were obtained on HP 5985 B system attached to HP 5840 A gas chromatograph.

*General procedure for the Wurtz-Fittig coupling reaction :*

In a typical reaction, a mixture of 0.60 g (26.1  $\mu$ mol) of finely cut sodium, 1.37 g (12.6  $\mu$ mol) of chlorotrimethylsilane and 0.51 g (3.1  $\mu$ mol) of 2,3-dichloronorbornene (**1**) in 10 mL of THF was heated on an oil bath at 50–55 °C. After 20 h of reflux, the gas-liquid chromatograms indicated complete conversion of the starting material. The mixture was cooled, excess sodium was filtered out on a plug of glass wool and the residual solid material washed with 2  $\times$  25 mL anhydrous ether. The combined ethereal extracts were washed with saturated NaHCO<sub>3</sub> solution (2  $\times$  10 mL), water (10 mL), saturated brine (5 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> crystals. The ethereal extract was concentrated under vacuo using a rotavapor and distilled under reduced pressure to obtain 0.44 g (59%) of a mixture of two products 2,3-bis(trimethylsilyl)norbornene (**2**) and (3'-trimethylsilylcyclopentanyl)-1-trimethylsilylacetylene (**3**) in the ratio 9 : 1. Further fractional distillation under reduced pressure using a six inch Vigreux column gave pure compounds **2** and **3** respectively.

**2,3-Bis(trimethylsilyl)-2-norbornene (2)<sup>3</sup>** : b.p. 65–70 °C/1.0 Torr : IR (neat) : 2952, 2868, 1412, 1250, 1060, 1025 and 805 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ : 3.06 (2H, narrow, m), 1.58–1.52 (2H, m), 1.15–1.00 (1H, m), 0.95–0.90 (1H, m), 0.85–0.73 (2H, m), 0.15 (18H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ : 158.5, 48.6, 47.6, 24.5 and 0.8; GC MS : *m/e* (relative intensity) : 238 (3.8) (M<sup>+</sup>), 223 (2.9),

210 (2.1), 197 (3.9), 179 (0.5), 164 (2.8), ( $M^+$ -SiMe<sub>3</sub>), 155 (7.2), 135 (3.7), 122 (18.3), 109 (20.6), 97 (5.6), 90 (4.9), 83 (6.0), 73 (100), 59 (15.3), 45 (35.4), 43 (18.6), 29 (2.0).

(3'-Trimethylsilylcyclopentanyl)-trimethylsilylacetylene (3) : b.p. 50–60 °C/4.0 Torr : IR (neat) : 2945, 2870, 2160, 1430, 1400, 1215 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ : 3.67 (1H, t, *J* = 7 Hz), 1.64–1.55 (2H, m), 1.45–1.36 (4H, m), 0.40–0.51 (1H, m), 0.12 (9H, s), 0.01 (9H, s); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ : 63.7, 62.8, 36.7, 34.0, 20.2, 16.6, 0.77, -1.62; GC MS : *m/e* (relative intensity) : 238 (4.6) ( $M^+$ ), 223 (5.7), 210 (2.1), 197 (9.9), 164 (13.7), 155 (43.0), 150 (17.7), 135 (13.9), 122 (8.0), 114 (41.9), 109 (100), 97 (12.3), 83 (16.3), 73 (99.2), 59 (10.3), 45 (7.7) (Found : C, 65.37; H, 10.82. C<sub>13</sub>H<sub>26</sub>Si<sub>2</sub> requires : C, 65.46; H, 10.99%).

### Acknowledgement

We thank the DST and UGC for financial assistance. We are grateful to the Chairman, Department of Organic Chemistry, IISc, Bangalore and Professor K. Griesbaum, Karlsruhe University, Karlsruhe, Germany, for furnishing spectral and analytical data.

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