Five- and six–membered cyclic α-acylvinyl anionic synthons: Synthesis of α-trimethylsilyl-α,*β*-unsaturated cycloalkenones and their conversion into 2-(hydroxydimethylsilyl)cycloalk-2-enones through carbon–silicon bond scission [1]

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Dedicated to Prof. G. Nagendrappa, Retired Professor of Organic Chemistry, Bangalore University, Bangalore, India, on his 70th birthday

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Abstract

Five- and six-membered α-trimethylsilyl-α,β-unsaturated cycloalkenones were prepared by the Wurtz-Fittig coupling reaction of the corresponding 6-bromo-1,4-dioxaspiro[4,n]cycloalk-6-enes with sodium and chlorotrimethylsilane. Upon treatment with anhydrous $AlCl_3$, the compounds underwent carbon-silicon bond scission to yield a novel class of compounds: the 2-(hydroxydimethylsilyl)cycloalk-2-enones.

Keywords: α-Trimethylsilyl-α,β-unsaturated cycloalkenones, Wurtz-Fittig reaction, Lewis acid, 2-(hydroxydimethylsilyl)cycloalk-2-enones, carbon-silicon bond scission

Introduction

α-Trimethylsilyl-α,β-unsaturated cycloalkenones form an important class of compounds in synthetic organic chemistry. The compounds are cyclic α-acylvinyl anionic synthons.[2] There are only a few reports for preparation of cyclic α- or β-acylvinyl anionic synthons. The synthons bearing either the silyl- or the stannyl-[3] group act as a masking agent for the anions. The most common route reported in literature for the preparation of α-trimethylsilyl-α,β-unsaturated cycloalkenones is the reaction of *n*-butyl lithium with the corresponding 6-halo-1,4-dioxaspiro[4,n]cycloalk-6-enes at -78 ºC, followed by quenching of the resulting anion with

chlorotrimethylsilane. Subsequent workup yields α-trimethylsilyl-α,β-unsaturated cycloalkenone.[4-8]

We had earlier reported the preparation of a wide variety of simple and substituted cyclic vinyl silanes, by the simple Wurtz–Fittig coupling reaction of the corresponding halocycloalkene with sodium and chlorotrimethylsilane in different anhydrous solvents.[9-11]

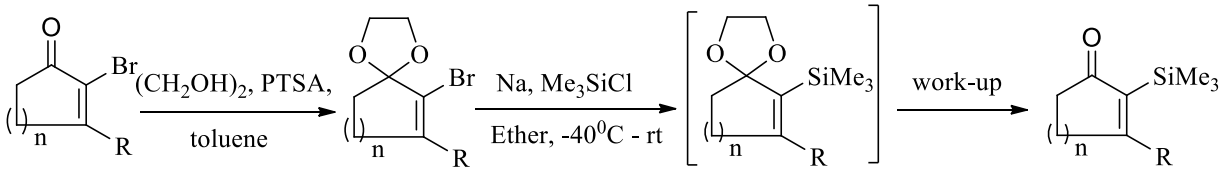
In this article we report the synthesis of some α-trimethylsilyl-*α,β*-unsaturated cycloalkenones employing the Wurtz–Fittig coupling reaction, and their conversion to novel 2-(hydroxydimethylsilyl)cycloalk-2-enones through carbon–silicon bond scission.

Results and Discussion

In continuation of our studies for the preparation of some novel cyclic vinyl silanes, and further expansion of the Wurtz–Fittig coupling reaction, we explored the preparation of some silyl-substituted cyclic α,β-unsaturated enones. The compounds are cyclic α-acylvinyl anionic synthons with trimethylsilyl-group behaving as a masking agent.

In this study, we report the successful synthesis of the five- and six-membered 2-trimethylsilylcycloalkenones **4a** to **4d** using the Wurtz–Fittig coupling reactions.

α-Bromo-α,β-unsaturated cycloalkenones[12] **1a** to **1d** were converted into the corresponding 6-bromo-1,4-dioxaspiro[4,n]alk-6-enes **2a** to **2d** by the azeotropic removal of water using ethylene glycol, *p*-TsOH/toluene. The acetals **2a** to **2d** upon Wurtz–Fittig coupling reaction with sodium and chlorotrimethylsilane in anhydrous ether solvent gave the corresponding 6-trimethylsilyl-1,4-dioxaspiro[4,n]alk-6-enes **3a** to **3d**, when followed by GC. The 6-trimethylsilyl-1,4-dioxaspiro[4,n]alk-6-enes however were found to be highly unstable even to the mildest acidic medium. The 2-trimethylsilylcycloalkenones **4a** to **4d** were formed through HCl acid catalyzed cleavage and removal of the ethylene glycol (Scheme 1).



1a: n=1, R=H
1b: n=1, R=CH_3
1c: n=2, R=H
1d: n=2, R=CH_3

2a: n=1, R=H
2b: n=1, R=CH_3
2c: n=2, R=H
2d: n=2, R=CH_3

3a: n=1, R=H
3b: n=1, R=CH_3
3c: n=2, R=H
3d: n=2, R=CH_3

4a: n=1, R=H
4b: n=1, R=CH_3
4c: n=2, R=H
4d: n=2, R=CH_3

Scheme 1. Synthesis of some 2-trimethylsilylcycloalkenones.

To the best of our knowledge, the only other report of using alkali metal for such reactions has been reported by Yus, who used metallic lithium for the preparation of 6-trimethylsilyl-1,4-dioxaspiro[4,5]dec-6-ene (**3c**)**.** However, he has reported that the treatment of **3c** with oxalic acid failed to produce 2-trimethylsilylcyclohexenone **4c**.[13]

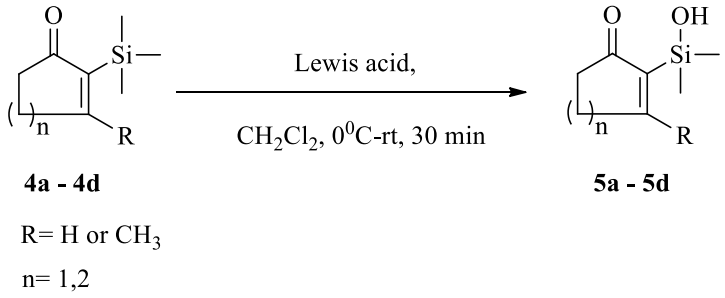
Therefore, our procedure which employs the Wurtz–Fittig coupling reaction using sodium and chlorotrimethylsilane is a simple method for the preparation of 2-trimethylsilylcycloalkenones **4a** to **4d**. The conditions for the formation of the compounds **4a** to **4d** have been standardized and the optimized isolated yields reported.

Conversion to novel 2-(hydroxydimethylsilyl)cycloalk-2-enones

The compounds **4a** to **4d** were subjected to the Friedel–Crafts acylation reaction in an attempt to prepare some novel cycloalkenyl-β-diketones.[14] This reaction was expected to employ the β-silyl effect.[15]

Reaction of 2-trimethylsilylcycloalkenones **3a to 3d** with several acid chlorides and anhydrous $AlCl_3$ in anhydrous dichloromethane solvent in the ratio 1:3:3[16a] did not yield the expected cycloalkenyl-β-diketones when monitored by GC and TLC.

As a further alteration from the standard 1:3:3 reaction conditions as given by Fleming,[16b] several experiments were conducted and the reaction conditions modified. As a test candidate 3-methyl-2-trimethylsilylcyclohexenone (**4d**) was chosen for further reactions. Some of the parameters that changed with **4d** were: (1) when the molar equivalent quantity of Lewis acid was raised from three to five equivalents, the TLC showed only trace amounts of disappearance of the starting material. When the concentration of Lewis acid was raised to seven molar equivalents, a new spot was observed on TLC at Rf value ~ 0.3. The extent of conversion of the starting vinylsilane was still only 30% after half an hour. (2) However, with the use of ten molar equivalents of the Lewis acid (anhydrous $AlCl_3$), the starting material disappeared completely within 30 minutes giving a single spot on the TLC plate with Rf value ~ 0.3. The compound was isolated after regular work-up and was found to be 2-(hydroxydimethylsilyl)-3-methylcyclohex-2-enone: (**5d**), formed by the carbon–silicon bond scission in the trimethylsilyl-group (Scheme 2).



Scheme 2. Synthesis of some novel 2-(hydroxydimethylsilyl)cycloalk-2-enones.

The formation of the novel cyclic ketovinylsilanol **5d** was highly serendipitous. To our knowledge, there are no reports of such a reaction which yields such novel cyclic ketovinylsilanols. The novel cyclic ketovinylsilanols form a new class of reagents in organosilicon chemistry. The formation of cyclic ketovinylsilanols indicated the prominent role of the anhydrous $AlCl_3$ as Lewis acid in the reaction.

To confirm the above conclusion we carried out the reaction of **4d** in the absence of benzoyl chloride and isolated **5d** in 96% isolated yield. This indicated that there was no role for the acid chlorides during the progress of the reaction.

Further reactions were carried out to study the efficacy of different Lewis acids. The other Lewis acids chosen for the study were $BiCl_3$, $SnCl_4$, $TiCl_4$ and $ZnCl_2$. Ten molar equivalents of the Lewis acid was taken for each reaction, with one molar equivalent of **4d**.

During these reactions, $BiCl_3$ did not produce any yield. $SnCl_4$ and $TiCl_4$ gave moderate yields in the range of 40–45%, whereas $ZnCl_2$ produced only 20% conversion to ketosilanol after 12 hours of reaction time. This indicated that the anhydrous $AlCl_3$ was the best Lewis acid for formation of the cyclic ketovinylsilanols under the conditions we have employed.

The reaction conditions were extended to the compounds **4a-4c**. We found that with the use of anhydrous $AlCl_3$, the resulting product was a single compound of high purity and yield in all the cases. The products that were formed in approximately 30 minutes yielded greater than 95%. The reactions were carried out for a minimum of three experiments in each case of **4a-4d**, and the results were consistent.

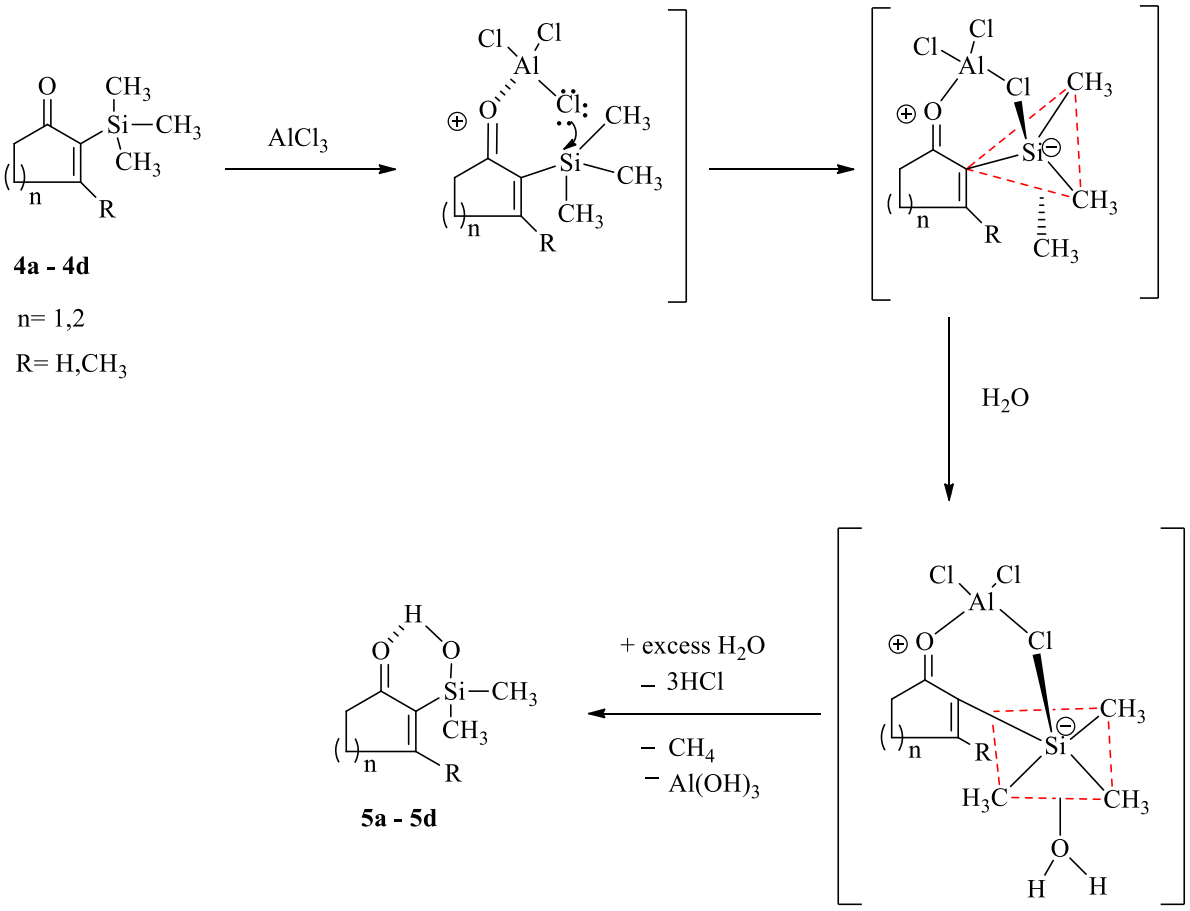
From the results obtained we concluded that these reactions are general for the formation of the novel cyclic ketovinylsilanols **5a to 5d**. The compounds **5a to 5d** are stable probably because of intramolecular hydrogen bonding between the keto-group and the hydroxyl-group of the silanol.

Some work was carried out to determine the mechanism for the formation of the novel cyclic ketovinylsilanols **5a to 5d**. We propose the mechanism for the formation of the novel cyclic ketovinylsilanols **5a-5d** as shown in Scheme 3.

It is reasoned that the addition of anhydrous $AlCl_3$ first leads to the formation of a tight complex with the oxygen of the keto-group. Due to the close proximity of chlorine and silicon, it is expected that the non-bonding electrons of chlorine first form a pentacoordinate intermediate with silicon exhibiting dsp^2 hybridization. Upon addition of water, we expect the hybridization of the silicon to change from dsp^2 to dsp^3 and formation of a hexacoordinated intermediate. Such penta- and hexa-coordinated silyl-compounds are well documented in literature.[17,18] Subsequent quenching with excess water leads to the elimination of HCl, CH_4 and $Al(OH)_3$ to yield the novel cyclic ketovinylsilanols **5a-5d**.

We have tried to isolate the pentacoordinated complex by freeze-evaporating the solvent. Vacuum stripping off the solvent resulted in a brown amorphous solid. The powder X-ray of sublimed anhydrous $AlCl_3$ shows a change of profile compared to the complex, indicating the complexation of $AlCl_3$ with the ketone. Unfortunately, we were unable to recrystallize the complex in crystalline form to obtain a single crystal X-ray.

Further, the brown amorphous complex was treated with water to identify the evolution of CH_4 gas. The evolution of CH_4 gas too was not observed, probably due to small scale (0.1 g) reaction.



Scheme 3. Proposed mechanism for the formation of 2-(hydroxydimethylsilyl)cycloalk-2-enones.

The isolation of the novel ketovinylsilanols **5a-5d** prompted us to do a literature survey. The only reported instance for such an unusual carbon–silicon scission has been given by Dubois *et al.*[19] Trimethylsilylcycloalkanes upon reaction with one equivalent of acetyl chloride and one equivalent of anhydrous $AlCl_3$ are reported to undergo C–Si bond scission to form chlorosilanes. Upon hydrolysis, the chlorosilanes form the corresponding silanols. The silanols being unstable were reported to undergo condensation to eliminate water to form the more stable disiloxanes.

In our reactions, it was found that the isolated novel cyclic ketovinylsilanols **5a-5d** are highly stable and can be stored by freezing for any period of time.

We reason this to be due to intramolecular hydrogen-bonding between the keto-group and the silanol as indicated for **5a-5d** in Scheme 3.

The driving force for the formation of the stable novel cyclic ketovinylsilanols may be due to the bond strengths between silicon and various other elements.

A comparison of the dissociation energies between silicon and oxygen shows the strength of the Si–O bond as 536 kJ mol^{-1} and for the Si–Cl bond as 472 kJ mol^{-1}.[20] This shows that silicon has more affinity for bonding with oxygen, when compared to chlorine. The formation of a pentacoordinated complex is due to the close proximity of chlorine with silicon, in the presence of $AlCl_3$, as depicted in **Scheme 3.** However, during work-up the chlorine is replaced by the hydroxyl-group of water through a fleeting hexacoordinated complex intermediate, to ultimately yield the stable keto-silanols **5a** to **5d.**

Conclusions

The synthesis of five- and six-membered α-trimethylsilyl-α,β-unsaturated cycloalkenones by the Wurtz–Fittig coupling reaction of the corresponding 6-halo-1,4-dioxaspiro[4,n]cycloalk-6-enes with sodium and chlorotrimethylsilane and their conversion to a new class of organosilyl-based reagents the 2-(hydroxydimethylsilyl)cycloalk-2-enones is reported.

Experimental Section

General. All the reactions were performed in oven dry apparatus. Reactions were monitored on Merck TLC plastic sheets of silica gel 60 F254 pre-coated plates, with elution solvent 1: 4 mixture of ethyl acetate: hexane (60–80º C). GC was run on SE-30 SS 2m × 1/8" column on Shimadzu 14-B / Mayura 9800 gas chromatographs. The yields refer to the optimum isolated products. Infrared spectra were recorded using a Nicolet 400D FT-IR and Perkin-Elmer 1310 IR spectrophotometer and the frequencies are reported in wave number (cm^{-1}). NMR spectra were recorded on 300 or 400 MHz AMX Bruker NMR spectrophotometer and the chemical shifts are relative to $CHCl_3$ for compounds with the trimethylsilyl-group, and to tetramethylsilane for those without the trimethylsilyl-group. Multiplicity is indicated using the following abbreviations: s (singlet), d (doublet), dd (double doublet), t (triplet), m (multiplet), bs (broad singlet) and br (broad). HR-MS spectra were recorded on a Q-TOF electro-spray instrument.

General procedure for preparation of 6-bromo-1,4-dioxaspiro[4,n]alk-6-enes

A mixture consisting of 30 mmol of α-bromo-α,β-unsaturated carbonyl compound (**1a-1d**), 250 mL of benzene, 4.2 mL of ethylene glycol, and 25 mg of *p*-toluenesulfonic acid were heated at reflux for azeotropic removal of water using the Dean-Stark apparatus. The resulting mixture was cooled and filtered through a filter cake consisting of 5g of $MgSO_4$ and 5g of silica gel. The filter cake was washed with 150 mL of CH_2C1_2. The filtrate and washings were combined and concentrated in-*vacuo* and subjected to distillation to obtain the pure product.

6-Bromo-l,4-dioxaspiro[4,4]non-6-ene (2a)[5]. Colourless oil, bp: bath 60 ºC (1.5 mm); IR (ν_{max}, cm^{-1}): 3075, 2980, 1635, 1340, 1175, 1050, 1035, 945, 920. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.16 (t, *J* = 2 Hz, 1H), 4.18 (m, 2H), 3.97 (m, 2H), 2.39 (m, 2H), 2.16 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.3, 119. 6, 122.8, 63.8, 30.2, 21.5.

6-Bromo-7-methyl-l,4-dioxaspiro[4,4]non-6-ene (2b)[5]. White solid; mp. 36-38 ºC; IR (ν_{max}, cm^{-1}): 2949, 2889, 1637, 1176, 1024, 948, 738. ^{1}H NMR: (400 MHz, $CDCl_3$): δ 4.20-4.14 (m, 2H), 4.02-3.96 (m, 2H), 2.37-2.33 (m, 2H), 2.19- 2.15 (m, 2H), 1.80 (s, 3H). ^{13}C NMR: (100 MHz, $CDCl_3$): δ 144.1, 118.9, 118.1, 65.6, 34.3, 32.7, 16.3.

6-Bromo-l,4-dioxaspiro[4,5]dec-6-ene (2c)[5]. Light yellow oil; bp 50-55 ºC (1 mm); IR (ν_{max}, cm^{-1}): 2949, 2890, 1637, 1437, 1352, 1176, 1156, 1110, 1070, 950 and 739. ^{1}H NMR: (400 MHz, $CDCl_3$): δ 6.34 (t, 1H, *J* = 5.4 Hz), 4.21-4.15 (m, 2H), 4.02-3.97 (m, 2H), 2.12-2.08 (m, 2H), 1.93-1.90 (m, 2H), 1.82-1.76 (m, 2H). ^{13}C NMR: (100 MHz, $CDCl_3$): δ 135.9, 124.4, 105.6, 65.6, 35.4, 27.3, 20.2.

6-Bromo-7-methyl-l,4-dioxaspiro[4,5]dec-6-ene (2d)[5]. White solid; mp. 55-56 ºC; IR (ν_{max}, cm^{-1}): 2949, 2889, 1637, 1176, 1024, 948, 738. ^{1}H NMR: (400 MHz, $CDCl_3$): δ 4.22-4.19 (m, 2H), 3.98-3.96 (m, 2H), 2.17-2.13 (m, 2H), 1.91-1.87 (m, 2H), 1.79 (s, 3H), 1.78-1.74 (m, 2H). ^{13}C NMR: (100 MHz, $CDCl_3$): δ 141.2, 124.5, 104.6, 53.5, 37.3, 24.5, 20.6.

General procedure for the Wurtz-Fittig coupling silylation reactions

Chlorotrimethylsilane (1.3mL, 1.113 g, 10 mmol) was added to a stirred solution of finely cut sodium pieces (0.15 g, 6.52×10^{-3} g atoms) suspended in 5 mL anhydrous diethyl ether. The reaction flask was cooled in a cryolator at -40 ºC. Ice cold starting material **2a-2d** (2.5 mmol) in 1 mL anhydrous ether was added to the mixture, and the stirring continued for another hour. The mixture was then allowed to attain room temperature overnight with continuous stirring, when a blue coloration developed. Monitoring by gas chromatography indicated complete disappearance of the starting material. The precipitated solids and unreacted sodium were filtered out on a plug of glass wool and washed with dry ether (2×5mL). The combined ethereal extracts were washed with ice-cold saturated $NaHCO_3$ solution (20 mL) and brine (20 mL) and then dried (an. $MgSO_4$). Vacuum concentration and distillation yielded the products **4a-4d**.

2-Trimethylsilylcyclopentenone (4a)[4]. Colourless liquid; bp: bath 60 ºC (5 mm**);** IR (ν_{max}, cm^{-1}) 2956, 2929, 2872, 1714, 1599, 1455, 1279, 1250, 1018, 868, 839, 756. ^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.78 (s, 1H), 2.65 (t, 2H, *J* = 2.04 Hz), 2.34 (t, 2H, *J* = 3.1Hz), 0.17 (s, 9H). ^{13}C NMR: (100 MHz, $CDCl_3$): δ 213.7, 172,1, 147.3, 35.1, 30.3, -1.8. HRMS: Calculated for $C_{10}H_{14}OSi$ $[M+Na]^+$= 177.0712 ; found = 177.0723

2-Trimethylsilyl-3-methylcyclopentenone (4b)[5]. Pale yellow liquid. bp: bath 50 ºC (1.0 mm); IR (ν_{max}, cm^{-1}): 2955, 2913, 1705, 1690, 1592, 1436, 1259, 1144, 840. ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.49 (t, 2H, *J* = 5.1 Hz), 2.26 (t, 2H, *J* = 5.1Hz), 2.10 (s, 3H), 0.14 (s, 9H). ^{13}C NMR: (100 MHz, $CDCl_3$): δ 214.2, 185.4, 139.4, 35.8, 35.5, 20.2, -0.6. GC-MS: *m/z* (%): 168 (12), 154 (15), 153 (100), 137 (4), 112 (4), 111 (23), 97 (10), 83 (8), 75 (28), 74 (9), 59 (7), 43 (10). HR-MS: Calculated for $C_9H_{16}OSi$ $[M+Na]^+$=191.0868; found =191.0869.

2-Trimethylsilylcyclohexenone (4c)[4]. White solid; mp: 39-40 ºC (mp 40 - 41.5 ºC); IR (ν_{max}, cm^{-1}): 2593, 2895, 1665, 1592, 1427, 1349, 1161, 1126, 862, 840. ^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.10 (t, 1H, *J* = 3.77 Hz), 2.32 (m, 2H), 2.27 (m, 2H), 1.91 (q, 2H, *J* = 6.5Hz), 0.05 (s, 9H). ^{13}C NMR: (100 MHz, $CDCl_3$): δ 202.6, 158.3, 141.7, 38.5, 27.1, 22.7, -1.51. HR-MS: Calculated for $C_9H_{16}OSi$ $[M+Na]^+$ =191.0868; found = 191.0866

2-Trimethylsilyl-3-methylcyclohexenone (4d)[5]. Pale yellow liquid**,** bp: bath 50 ºC (1.0 mm); IR (ν_{max}, cm^{-1}): 2952, 2870, 1656, 1584, 1246, 1270, 855, 844, 765. ^{1}H NMR: (400 MHz, $CDCl_3$): δ 2.33 (t, 2H, *J* = 6.4 Hz), 2.28 (t, 2H, *J* = 6.5 Hz), 1.99 (s, 3H), 1.89 (qn, 2H, *J* = 6.4 Hz), 0.19 (s, 9H). ^{13}C NMR: (100 MHz, $CDCl_3$): δ 201.4, 167.7, 134.8, 36.1, 32.9, 23.0, 20.4, 0.0. *m/z* (%): 182 (2.06), 167 (100), 154 (5.1), 139 (10.3), 111 (5.15), and 91 (4.1). HR-MS: Calculated for $C_{10}H_{18}OSi$ $[M+Na]^+$ 205.1025; found. 205.1026

General procedure for preparation of 2-(hydroxydimethylsilyl)cycloalk-2-enones (5a-5d)

To a magnetically stirred mixture of 10 mmol equivalents of anhydrous $AlCl_3$ in dry dichloromethane cooled to -15 ºC in an ice-salt bath was added 1 mmol equivalent of 2-trimethylsilylcycloalkenones (**4a-4d)** in 5 ml of dry dichloromethane dropwise over a period of 30 min. Then, saturated $NaHCO_3$ (20 mL) was added and stirred for another 30 minutes and the reaction mixture was simultaneously allowed to attain room temperature. The organic layer was separated and washed with saturated $NaHCO_3$ solution (2 × 20 mL) and brine (20 mL). The organic extract was dried (Na_2SO_4), concentrated and distilled (twice) under reduced pressure to obtain the pure 2-(hydroxyldimethylsilyl)cycloalk-2-enones **5a-5d**.

2-(Hydroxydimethylsilyl)cyclopent-2-enone (5a). Colourless liquid; bp: bath 40 ºC (1 mm**);** IR (ν_{max}, cm^{-1}): 3348, 2956, 2926, 2852, 1662, 1591, 1512, 1351, 1250, 1062. ^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.38 (t, 1H, *J* = 8 Hz), 3.16 (t, 2H, *J* = 8 Hz), 2.70 (t, 2H, *J* = 8 Hz), 1.25 (s, 1H), 0.00 (s, 6H). ^{13}C NMR: (100 MHz, $CDCl_3$): δ 213.7, 172,1, 147.3, 35.1, 30.3, -1.8. HR-MS: Calculated for $C_7H_{12}O_2Si$ $[M+Na]^+$ 179.0504; found: 179.0505

2-(Hydroxydimethylsilyl)-3-methylcyclopent-2-enone (5b). Colourless liquid; bp: bath 40 ºC (1 mm**);** IR (ν_{max}, cm^{-1}): 3416, 2958, 2924, 1686, 1592, 1258, 1047, 799. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26-2.23 (m, 4H), 2.16 (s, 1H), 2.08 (s, 3H), 0.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.2, 185.4, 139.4, 35.8, 35.5, 20.2, -0.6. HR-MS: Calculated for $C_8H_{14}O_2Si$ $[M+Na]^+$ 193.0661; found:193.0661

2-(Hydroxydimethylsilyl)cyclohex-2-enone (5c). Colourless liquid; bp: bath 40 ºC (1 mm**).** IR (ν_{max}, cm^{-1}): 3409, 2955, 2929, 1651, 1592, 1354, 1248, 1165, 885, 775, 666. ^{1}H NMR: (400 MHz, $CDCl_3$): δ 7.30 (t, 1 H, *J* = 3.8 Hz), 2.41-2.34 (m, 4 H), 2.02-1.95 (m, 2 H), 1.69 (s, br, 1H), 0.2184 (s, 6 H). ^{13}C NMR: (100 MHz, $CDCl_3$): δ 202.7, 159.3, 141.2, 136.5, 38.5, 27.1, 22.7, 1.0. HR-MS: Calculated for $C_7H_{14}O_2Si$ $[M+Na]^+$ 193.0661; found: 193.0656

2-(Hydroxydimethylsilyl)-3-methylcyclohex-2-enone (5d). Colourless liquid; bp: bath 40 ºC (1 mm**).** IR (ν_{max}, cm^{-1}): 3474, 2932, 2868, 1667, 1390, 1256, 1098, 661. ^{1}H NMR: (400 MHz, $CDCl_3$): δ 4.46 (s, 1H), 2.38-2.33 (m, 4 H), 2.03 (s, 3 H), 1.96-1.93 (m, 2 H), 0.32 (s, 6H).

^{13}C NMR: (100 MHz, $CDCl_3$): δ 205.9, 171.9, 134.5, 37.7, 34.1, 25.0, 21.9, 2.4. HR-MS: Calculated for $C_9H_{16}O_2Si$ $[M+Na]^+$ 207.0817; found: 207.0819.

Experiment to identify the evolution of CH_4 gas

To a magnetically stirred mixture of 10 mmol equivalents of anhydrous $AlCl_3$ in dry dichloromethane cooled to -15 ºC on an ice-salt bath was added 1 mmol equivalent of 2-trimethylsilylcycloalkenones in 5 ml of dry dichloromethane dropwise over a period of 30 min. Then, the solvent was freeze-evaporated using high vacuum to isolate a brown amorphous solid. The brown amorphous solid was taken in a two necked round bottom flask fitted with a dropping funnel and a rubber tube ending in an inverted glass tube for downward displacement of water. Water was added to the brown amorphous solid through the dropping funnel, to check for evolution of methane gas if any. In our reaction apparatus employed, there was found to be no evolution of methane gas.

Supplementary Material Available

Copies of the IR, ^{1}H NMR, ^{13}C NMR, and HR-MS for compounds **4a-5d** are attached.

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