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Synthesis of five- and six-membered 2-trimethylsilyl-1,3,3--trimethylcycloalkenes: a novel preparation of alkyl/alkenyl/aryl-(1′,3′,3′-trimethylcyclopentenyl)ketones

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Abstract: 2-Trimethylsilyl-1,3,3-trimethylcyclopentene and 2-trimethylsilyl-1,3,3-trimethylcyclohexene were prepared in good yields by the Wurtz–Fittig coupling reaction of the corresponding 2-iodo-1,3,3-trimethylcyclopentene and 2-chloro-1,3,3-trimethylcyclohexene with metallic sodium and chlorotrimethylsilane in anhydrous ether solvent. The Friedel–Crafts acylation reaction of 2-trimethylsilyl-1,3,3-trimethylcyclopentene with six different acid chlorides and the novel preparation of six alkyl/alkenyl/aryl-(1′,3′,3′-trimethylcyclopentenyl)ketones is reported.

Keywords: cyclic vinylsilanes; anionic synthons; Wurtz–Fittig reaction; Friedel–Crafts acylation; *β*-silyl effect.

INTRODUCTION

Cyclic vinylsilanes are an important class of compounds in synthetic organic chemistry.[1] The compounds are anionic synthons with the trimethylsilyl– group behaving as a masking agent.[2] The silicon in these compounds is capable of directing a reaction in a highly regio- and stereo-specific manner. Several methods have been reported in the literature for the preparation of cyclic vinylsilanes.[3]

Our laboratory is primarily involved in preparation of cyclic vinylsilanes by employing the Wurtz–Fittig type coupling reaction of cyclic vinyl halides with sodium and chlorotrimethylsilane in suitable anhydrous solvent. The method is simple, and employing this reaction we have been successful in preparing a number of simple and substituted cyclic vinyl silanes. Various novel reactions of the prepared simple and substituted cyclic vinylsilanes discovered in our laboratory have also been reported.[4]

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In further studies and in attempts to prepare some important substituted cyclic vinylsilanes, we chose to synthesize 2-trimethylsilyl-1,3,3-trimethylcyclopentene (**1**) and 2-trimethylsilyl-1,3,3-trimethylcyclohexene (**2**). The compounds **1** and **2** would serve as potential synthons to several terpenes, the Vitamin-A and related group of compounds.[5] In particular, it may be noted that the 1,3,3-trimethylcycloalkanyl- group is a common functionality present in the capnellane,[6a] taiwaniaquinoid,[6b] actinidiolide,[6c] heydechenone,[6d] and labdane diterpene[6e] group of compounds. Paquette has reported the preparation of **1** by the tosyl hydrazone route, and isolation using preparative VPC.[7] To our knowledge, the compound **2** has not been reported, but its corresponding vinyl stannane has been synthesized.[8]

In this article we wish to report the successful preparation of **1** and **2** by Wurtz–Fittig coupling reaction. The Friedel–Crafts acylation of **1** with six different acid chlorides gave some novel alkyl/alkenyl/aryl-(1′,3′,3′-trimethylcyclopentenyl)ketones.

RESULTS AND DISCUSSION

Chemistry

Preparation of five- and six-membered α,α,α′-trimethylcycloalkanones. We are hereby reporting a new route for the synthesis of *α,α,α′*-trimethylcyclopentanone.[9a] Diethyl adipate (**3**) upon Dieckmann cyclisation with sodium/toluene afforded 2-carbethoxycyclopentanone (**4**).[9b] Total methylation of **4** using methyl iodide (6 equivalents) and sodium hydride (4 equivalents), gave 2-carbethoxy-2,5,5-trimethylcyclopentanone (**5**) in 71% yield. Subsequent hydrochloric acid catalyzed hydrolysis and decarboxylation gave the pure five-membered 2,2,5-trimethylcyclopentanone (**6**) in 58% isolated yield from **5**.

The *α,α,α′*-trimethylcyclohexanone was prepared according to reported literature procedure.[10] Reaction of cyclohexanone (**7**) with diethyl oxalate in presence of sodium ethoxide followed by pyrolysis with a catalytic amount of ground iron powder/glass-wool at 175 ^{o}C gave 2-carbethoxycyclohexanone (**8**) in 45% yield. Total methylation of **8** using 4 equivalents of sodium hydride and 6 equivalents of methyl iodide gave 2-carbethoxy-2,6,6-trimethylcyclohexanone (**9**) in 78% yield. Hydrochloric acid catalyzed hydrolysis and decarboxylation yielded pure 2,2,6-trimethylcyclohexanone (**10**) in 77% yield (Scheme 1).

Conversion to cyclic vinyl halides. A number of procedures have been developed for the conversion of ketones to vinyl halides. This is due to the growing use of metal catalyzed coupling reactions of alky/alkenyl/aryl halides in organic synthesis. Some of the recently developed reagents used to perform the transformation include $(PhO)_3P/X_2$,[11a] CH_3COX/CF_3COOH,[11b] WCl_6,[11c] $(EtO)_2P(O)Cl/P(Ph_3)/X_2$,[11d] along with the traditional halogenating agents such as thionyl chloride and phosphorous pentachloride.[11e-g]

We explored some of the reagents reported for the conversion of cyclic ketones to cycloalkenyl halides. Our investigations have shown Takeda's general method for preparation of *gem*-halides most useful.[12] The method involves the conversion of the carbonyl compounds to their corresponding hydrazones, followed by reaction with cupric halide/Et_3N.

The compounds **6** and **10** were converted to their corresponding hydrazones 2,2,5-trimethylcyclopentanone hydrazone (**11)** in 75% yield and 2,2,6-trimethylcyclohexanone hydrazone (**12**)[6d] in 78% yield.

Treatment of the hydrazones **11** and **12** with 6 equivalents of copper (II) chloride and 3 equivalents of triethylamine gave 1,1-dichloro-2,2,5-trimethylcyclopentane (**13**) in 33% yield and 1,1-dichloro-2,2,6-trimethylcyclohexane (**14**) in 42% yield respectively. Subsequent dehydrochlorination of **13** and **14** employing morpholine/DMSO and benzene[13] gave 2-chloro-1,3,3-trimethylcyclopentene (**17**) in 31% yield and 2-chloro-1,3,3-trimethylcyclohexene (**18**)[5c] in 40% yield respectively.

Similar bromination of **11**/**12** with 6 equivalents of copper (II) bromide and 3 equivalents of triethylamine gave a mixture of *gem*-dibromides **15**/**16** and vinyl bromides **19**/**20** in 1:1 ratio due to the elimination of HBr under the reaction conditions employed. Without isolating the mixture of *gem*-dibromide and vinyl bromide, the mixture was subjected to dehydrobromination using morpholine/DMSO/benzene to isolate 2-bromo-1,3,3-trimethylcyclopentene (**19**) in 64% yield and 2-bromo-1,3,3-trimethylcyclohexene (**20**) in 69% yield.

The cyclic vinyl iodides 2-iodo-1,3,3-trimethylcyclopentene (**21**) and 2-iodo-1,3,3-trimethylcyclohexene (**22**)[6d] were prepared by adopting Barton's vinyl iodination procedure. Reaction of **11** and **12** with iodine and DBN[6d,14] gave **21** in 79% yield and **22** in 82% yield. (Scheme 2). The results for the preparation of the cyclic vinyl halides **17**-**22** are summarized in Table I.

Wurtz–Fittig coupling reaction to the five- and six-membered 2-trimethylsilyl-1,3,3-trimethylcycloalkenes

The cyclic vinyl halides **17**-**22** were subjected to the Wurtz–Fittig coupling reaction with sodium and chlorotrimethylsilane in anhydrous ether solvent, using protocols well established in our laboratory.[4] The reactions were followed using gas chromatography. After completion of reaction, as indicated by the chromatograms of aliquot samples, the mixtures were worked up and distilled to isolate pure **1** and **2** (Scheme 3).

Each reaction was carried out a minimum of five times for each cyclic vinyl halide substrate (**17**-**22**) and the yields of the products **1**/**2** are averaged and shown in Table II.

The hindered cyclic vinyl halides **17**-**22** showed difference in reactivity with sodium metal in the Wurtz–Fittig reaction. The five membered cyclic vinyl

halides 2-chloro-1,3,3-trimethylcyclopentene (**17**), 2-bromo-1,3,3-trimethylcyclopentene (**19**) and 2-iodo-1,3,3-trimethylcyclopentene (**21**) reacted with sodium smoothly to form **1** in > 70% yields (Table II). Among all the five-membered cyclic vinyl halides, the 2-iodo-1,3,3-trimethylcyclopentene (**21**) was found to be the best substrate for the preparation of 2-trimethylsilyl-1,3,3-trimethylcyclopentene (**1**), with the highest isolated yield of 81-83%.

In case of the six-membered ring system, the 2-chloro-1,3,3-trimethylcyclohexene (**18**)[5c] was found to be the best substrate with isolated yields of 2-trimethylsilyl-1,3,3-trimethylcyclohexene (**2**) in the range of 75-77% (Table II). The other six-membered cyclic vinyl halides **20** and **22** did not give satisfactory yields, under our reaction conditions. Change of metal to potassium, magnesium or lithium and use of solvents: THF, benzene or HMPA gave **2** in less than 10% yields.

We were not able to prepare **2** in large quantities (1 g scale). Although the vinyl halides **20** and **22** could be prepared in large quantities, their Wurtz–Fittig couplings proceeded in low and inconsistent yields. On the other hand, although the Wurtz–Fittig reaction of the vinyl chloride **18** took place in good yields, the preparation of **18** proved difficult because of low yields[5c] in both *gem*-chlorination (42% yield) and dehydrochlorination steps (40% yield).

In the light of preparation of the five-membered cyclic vinylsilane **1** in sufficient quantities (2 g scale), the Friedel–Crafts acylation reactions of the five membered cyclic vinyl silane **1** with six different acid chlorides were carried out.

Conversion to Novel Alkyl/alkenyl/aryl-(1',3',3'-trimethylcyclopentenyl) ketones. The Friedel–Crafts acylation reactions are some of the most widely studied and used reactions in organosilicon chemistry.[1-3] The reaction has been extended to several classes of organosilicon compounds like allylsilanes, arylsilanes, vinylsilanes etc. to obtain a wide variety of carbonyl moiety containing products. The conversions employ the *β*-silyl effect.[15] Using the Friedel–Crafts acylation reaction and employing standardized procedures, our laboratory had earlier reported the synthesis of a wide variety of novel products from cyclic vinylsilanes.[4]

The Friedel–Crafts reaction of **1** was carried out in 0.2 g scales with 3 molar equivalents each of anhydrous aluminium chloride and six different acid chlorides in dichloromethane solvent.

The reactions were found to be clean and afforded the novel alkyl/alkenyl/aryl-(1′,3′,3′-trimethylcyclopentenyl) ketones **23 a-f** (Scheme 4) in isolated yields ranging between 65-87 % in five trials for each substrate (Table III).

The compound **23 a** is a known compound prepared earlier by Stille by the palladium catalysed coupling of (α-ethoxyvinyl)trimethylstannane with 1-trifluoromethanesulphonyl-1,3,3-trimethylcyclopentene.[16] All the other (1′,3′,3′-

trimethylcyclopentenyl)ketones **23 b-f** are not reported in the literature, and are being reported by us for the first time. Our procedure employs the Friedel–Crafts acylation reaction of **1** and utilizes the *β*-silyl effect. The compound **23 c** is the lower analogue of the naturally occurring *β*-damascone.[17] The compounds **23 a-f** maybe useful in the aroma and perfume industries.[18]

EXPERIMENTAL

All reactions were monitored using GC or TLC. TLC were run on Merck TLC Silica-gel 60 F_{254} pre-coated plates with elution solvent 1:20 ethyl acetate/hexane (60-80 ^{o}C fraction). GC was run on SE-30 SS 2m x 1/8" column Mayura 9800 Gas Chromatograph. IR spectra were recorded on Shimadzu FT-IR 8400S on NaCl flats as neat thin liquid film samples. NMR spectra were recorded in $CDCl_3$ with a Bruker AMX 400 spectrometer using tetramethylsilane (TMS) as an internal standard. GC-MS spectra were obtained using a Shimadzu GC-MS QP 5050A instrument equipped with a 30 m x 0.32 mm BP-5 capillary column. Elemental Analysis were obtained using Elementar Vario Microcube-15106062 instrument. All yields refer to the isolated yields of the products.

General procedure for the synthesis of five- and six-membered 2-chloro/bromo-1,3,3-trimethylcycloalkenes (17-20)

To a solution of copper (II) halide (6 molar equivalents) in 80 mL methanol was added triethylamine (3 molar equivalents) at 20 ^{o}C. The reaction mixture was stirred for 10 minutes and cooled to 0 ^{o}C. A methanolic solution of *α,α,α′*-trimethylcycloalkanone hydrazone **11**/**12** (3 g in 30 mL MeOH) was added drop wise over 20 minutes, and the mixture further stirred for 2 hours, simultaneously allowing the reaction mixture to attain ambient temperature. TLC indicated complete conversion of the hydrazone. The mixture was quenched by adding 50 mL of 3.5% aqueous NH_3 solution, and extracted with ether (3 x 30 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (2 x 30 mL), water (2 x 30 mL), saturated NaCl (2 x 30 mL) and dried (anhydrous $MgSO_4$). The solvent was removed on a rotavapor and the residue distilled under reduced pressure to isolate the halogenated products.

The mixture of halogenated products (2 g) was added to morpholine (10 molar equivalents)/DMSO (10 molar equivalents)/8 mL of benzene and refluxed at 100 °C for 24 hours. Gas chromatograms indicated complete conversion to the cyclic vinyl halides **17-20**. The mixture was cooled, added to ice cold 2N HCl (50 mL) and extracted with ether (3 x 40 mL). The combined organic extracts were washed with saturated $NaHCO_3$ (2 x 30 mL), water (2 x 30 mL), saturated NaCl (2 x 30 mL) and dried (an. $MgSO_4$). The solvent was removed on a rotavapor and the residue distilled under reduced pressure to isolate the pure 2-chloro/bromo-1,3,3-trimethylcycloalkenes (**17-20**).

General procedure for the synthesis of five- and six-membered 2-iodo-1,3,3-trimethylcycloalkenes (21/22):

To a suspension of 4 g of *α,α,α′*-trimethylcycloalkanone hydrazone **11/12** and 6 molar equivalents of 1,5–diazabicyclo[4.3.0]non-5-ene in 50 mL anhydrous ether was added dropwise a solution of 2.2 molar equivalents iodine in 100 mL anhydrous ether. The reaction mixture was stirred for 3.5 hours, when the GC indicated completion of reaction. The reaction mixture was washed with saturated sodium bicarbonate solution (20 mL). The ethereal layer was separated and the aqueous layer re-extracted with ether (3 x 40 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and evaporated *in-vacuo.*

The residue was chromatographed through silica gel using hexane as the solvent to afford the cyclic vinyl iodides **21**/**22**.

General procedure for the synthesis of 2-trimethylsilyl-1,3,3-trimethylcycloalkenes (1/2):

To a suspension of finely cut sodium pieces (5 molar equivalents) and chlorotrimethylsilane (3 molar equivalents) in 10 mL of dry ether was added 2-halo-1,3,3-trimethylcycloalkene [3.2g (13.5 mmol) of **21**; or 0.22g (1.3 mmol) of **18**] in 10 mL of anhydrous ether. The mixture was refluxed with efficient stirring on an oil bath at 45 – 50 °C, when a deep navy-blue coloration developed. Monitoring the reaction by GC indicated that the reactants required 6 hours for complete conversion to products. The mixture was cooled; the precipitated solids and remaining sodium were removed by filtering on a plug of glass wool and washed with ether (2 x 5 mL). Saturated sodium bicarbonate (15 mL) was added to the combined filtrate, the layers were separated, and the organic layer was successively washed with water (3 x 10 mL), saturated sodium chloride (15 mL), dried (anhydrous Na_2CO_3), concentrated and distilled under reduce pressure to isolate **1** and **2**. The yields of isolated products are given in Table II.

General procedure for the synthesis of alkyl/alkenyl/aryl-(1′,3′,3′-trimethylcyclopentenyl)ketones (23 a-f):

To a magnetically stirred mixture of anhydrous $AlCl_3$ (3 molar equivalents) and acid chloride (3 molar equivalents) in dry CH_2Cl_2 (20 mL), cooled to – 15 °C on an ice- salt bath, was added 0.2 g of **1** in 5 ml of dry CH_2Cl_2 drop wise over a period of 5 minutes. After three hours of stirring, the gas chromatogram of aliquot indicated complete disappearance of the reactant **1**. Saturated $NaHCO_3$ solution (20 mL) was added to the mixture and stirred for 30 minutes, simultaneously allowing the reaction to attain room temperature. The organic layer was separated, washed with $NaHCO_3$ solution (2 x 20 mL), water (25 mL) and saturated NaCl solution (20 mL). The pale yellow organic extract was dried (anhydrous Na_2SO_4) concentrated and finally subjected to bulb to bulb distillation under reduced pressure to isolate individually the alkyl/alkenyl/aryl-(1′,3′,3′-trimethylcyclopentenyl)ketones (**23 a-f**).

CONCLUSIONS

The simple synthesis of 2-trimethylsilyl-1,3,3-trimethylcyclopentene and 2-trimethylsilyl-1,3,3-trimethylcyclohexene is reported. The Friedel–Crafts acylations of 2-trimethylsilyl-1,3,3-trimethylcyclopentene gave a series of six alkyl/alkenyl/aryl-(1′,3′,3′-trimethylcyclopentenyl)ketones.

SUPPLEMENTARY DATA

The spectral characterization data is available as supplementary material.

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И З В О Д

СИНТЕЗА ПЕТО- И ШЕСТОЧЛАНИХ ПРСТЕНОВА ДЕРИВАТА 2-ТРИМЕТИЛСИЛИЛ-1,3,3-ТРИМЕТИЛЦИКЛОАЛКАНА: НОВ ПОСТУПАК СИНТЕЗЕ АЛКИЛ/АЛКЕНИЛ/АРИЛ-(1′,3′,3′-ТРИМЕТИЛЦИКЛОПЕНТЕНИЛ)КЕТОНА

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2-триметилсилил-1,3,3-триметилциклопентан и 2-триметилсилил-1,3,3-триметилциклохексан добијени су, у добром приносу, Вурц-Фитиг-овим куповањем полазећи од одговарајућих 2-јод-1,3,3-триметилциклопентена и 2-хлор-1,3,3-триметилцикохексена са металним натријумом и хлортриметилсиланом у анхидрованом етру као растварачу. Приказано је Фридел-Крафцовим ацилование 2-триметилсилил-1,3,3-триметилциклопентена са шест различитих алканоилхлорида и нова синтеза шест алкил/алкенил/арил-(1′,3′,3′-триметилциклопентенил)кетона.

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Captions for Tables

TABLE I: Synthesis of five- and six-membered 2-halo-1,3,3-trimethylcycloalkenes **17-22**

TABLE II: Synthesis of 2-trimethylsilyl-1,3,3-trimethylcycloalkenes **1** and **2** by Wurtz-Fittig coupling of **17-22** with sodium and chlorotrimethylsilane in anhydrous ether solvent

TABLE III: Synthesis of some novel alkyl/alkenyl/aryl-(1′,3′,3′-trimethylcyclopentenyl) ketones **23 a-f**

TABLE I: Synthesis of five- and six-membered 2-halo-1,3,3-trimethylcycloalkenes **17-22**

Entry	Substrate	Reagent/Base/Solvent	Ring size	Product	Yield (%)
1	**11**	$CuCl_2/Et_3N/MeO$H	5	**17**	31
2	**12**	$CuCl_2/Et_3N/MeO$H	6	**18**	40
3	**11**	$CuBr_2/Et_3N/MeO$H	5	**19**	64
4	**12**	$CuBr_2/Et_3N/MeO$H	6	**20**	69
5	**11**	$I_2/DBN/Et_2O$	5	**21**	79
6	**12**[6d]	$I_2/DBN/Et_2O$	6	**22**[6d]	82

TABLE II: Synthesis of 2-trimethylsilyl-1,3,3-trimethylcycloalkenes **1** and **2** by Wurtz-Fittig coupling of **17-22** with sodium and chlorotrimethylsilane in anhydrous ether solvent

Entry	Substrate	Halogen	Ring size	Product	Yield (%)
1	**17**	Cl	5	**1**	73–76
2	**18**[5c]	Cl	6	**2**	75–77
3	**19**	Br	5	**1**	72–74
4	**20**	Br	6	**2**	<10
5	**21**	I	5	**1**	81–83
6	**22**[6d]	I	6	**2**	<10

TABLE III: Synthesis of some novel alkyl/alkenyl/aryl-(1′,3′,3′-trimethylcyclopentenyl)ketones **23 a-f**

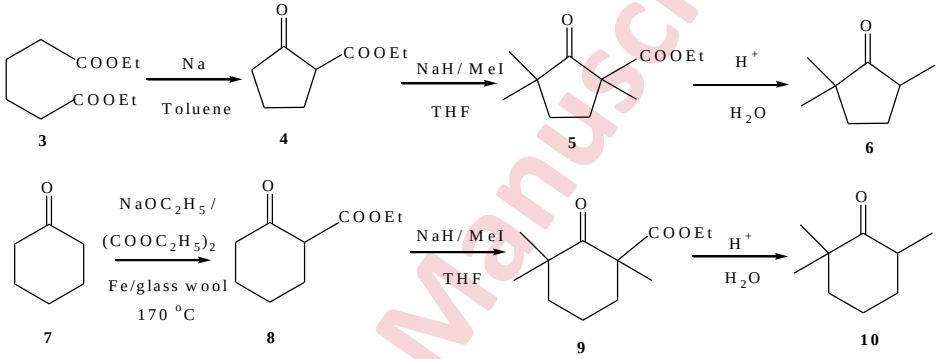
Entry	Product	R	Yield (%)	*b.p.* °C / 1mm
1	**23 a**[16]	-CH_3	65	53–57
2	**23 b**	-C_2H_5	71	64–67
3	**23 c**	-(*E*)-C_3H_5	78	69–73
4	**23 d**	*n*-C_4H_9	83	68–72
5	**23 e**	*n*-C_5H_{11}	87	71–74
6	**23 f**	-C_6H_5	86	82–84

Scheme 1: Synthesis of five- and six-membered α, α, α′-trimethylcycloalkanones (**6**/**10**)

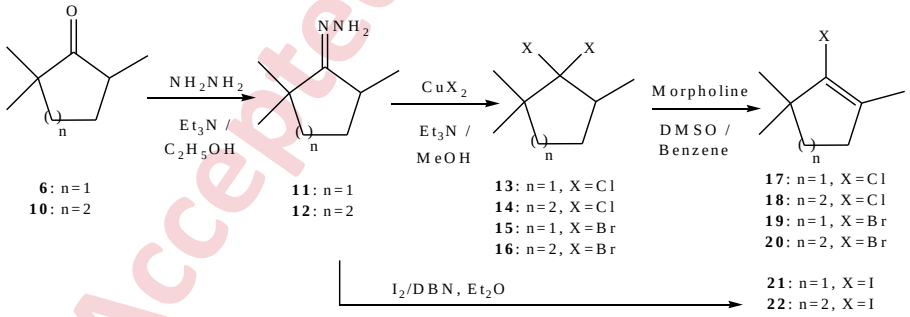
Scheme 2: Synthesis of five- and six-membered 2-halo-1,3,3-trimethylcycloalkenes (**17**-**22**)

Scheme 3: Wurtz–Fittig coupling to 2-trimethylsilyl-1,3,3-trimethylcycloalkenes (**1**/**2**)

Scheme 4: Facile route for the synthesis of alkyl/alkenyl/aryl-(1′,3′,3′-trimethylcycloalkenyl)ketones (**23a**–**f**)



Scheme 1: Synthesis of five- and six-membered α,α,α'-trimethylcycloalkanones (**6**/**10**)



6: n=1
10: n=2

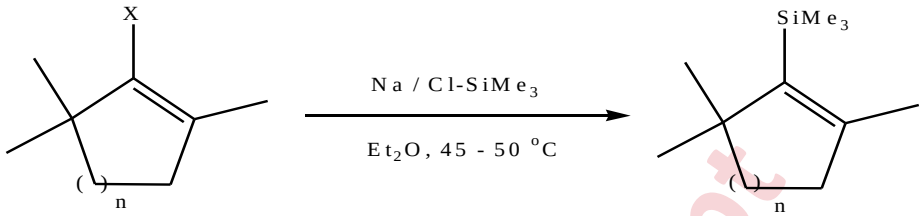
11: n=1
12: n=2

13: n=1, X=Cl
14: n=2, X=Cl
15: n=1, X=Br
16: n=2, X=Br

17: n=1, X=Cl
18: n=2, X=Cl
19: n=1, X=Br
20: n=2, X=Br

21: n=1, X=I
22: n=2, X=I

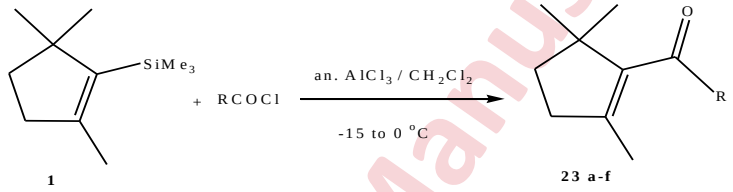
Scheme 2: Synthesis of five- and six-membered 2-halo-1,3,3-trimethylcycloalkenes (**17**-**22**)



17: n=1, X=Cl; **19**: n=1, X=Br; **21**: n=1, X=I
18: n=2, X=Cl; **20**: n=2, X=Br; **22**: n=2, X=I

1: n=1
2: n=2

Scheme 3: Wurtz-Fittig coupling to 2-trimethylsilyl-1,3,3-trimethylcycloalkenes (**1**/**2**).



1 **23 a-f**

(a) R: -CH_3 (b) R: -CH_2CH_3 (c) R: *trans*-CH=CH-CH_3 (d) R: n-C_4H_9 (e) R: n-C_5H_{11} (f) R: -C_6H_5

Scheme 4: Facile route for the synthesis of alkyl/alkenyl/aryl-(1′,3′,3′-trimethylcyclopentenyl)ketones (**23 a-f**)

SUPPLEMENTARY MATERIAL

SPECTRAL DATA OF THE PRODUCTS

2-Trimethylsilyl-1,3,3-trimethylcyclopentene ***(1)***.[7] Yield: 81-83 %; light yellow oil; *b. p.* 65–70 °C/4 mm. IR (film, cm^{-1}): 2958, 2866, 1647, 1458, 1377, 1261, 1095, 1016, 802. GC-MS: m/z (relative intensity): 182 (13, M^+), 167 (72), 108 (28), 93 (25), 73 (100%, base peak), 74 (46), 59 (58), 45 (62). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 0.08 (9H, *s*), 0.98 (6H, *s*), 1.48 – 1.51 (2H, *t*, *J* = 7.2 Hz), 1.70 (3H, *s*), 2.17 – 2.21 (2H, *t*, *J* = 7.2). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 1.5, 17.9, 28.7, 28.8, 39.0, 41.8, 51.7, 142.7, 149.6.

2-Trimethylsilyl-1,3,3-trimethylcyclohexene ***(2)***. New compound. Yield: 75-77 %; light yellow oil; *b. p.* 77–80 °C/2 mm. Anal. Calcd. for $C_{12}H_{24}Si$: C, 73.38; H, 12.32 Found: C, 73.58; H, 12.42 %. IR (film, cm^{-1}): 2950, 2866, 1649, 1581, 1452, 1456, 1255, 1095, 1051, 840, 808, 761. GC-MS: m/z (relative intensity): 196 (3, M^+), 181(8), 123 (10), 122 (31), 107 (25), 73 (100%, base peak), 59 (15), 45 (24), 43 (15). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 0.22 (9H, *s*), 1.05 (6H, *s*), 1.33 – 1.36 (2H, *m*), 1.53 – 1.59 (2H, *m*), 1.75 (3H, *s*), 1.90 – 1.94 (2H, *t*, *J* = 8Hz). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 3.8, 19.3, 24.7, 29.5, 34.6, 35.5, 41.3, 139.1, 142.8.

2,2,5-Trimethylcyclopentanone hydrazone ***(11)***. New compound. Yield: 75 %; white needles. Anal. Calcd. for $C_8H_{16}N_2$: C, 68.52; H, 11.5; N, 19.98%. Found: C, 68.34; H, 11.65; N, 20.3 %. IR (film, cm^{-1}): 3357, 3211, 2962, 2871, 1737, 1461, 1380, 1361, 1255, 1080, 1006. GC-MS: m/z (relative intensity):140 (35, M^+), 125 (46), 124 (54), 109 (10), 108 (17), 95 (21), 81 (26), 69 (28), 67 (29), 55 (63), 41 (100%, base peak). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.07 (3H, *s*), 1.13 (3H, *s*), 1.16 – 1.18 (3H, *d*, *J* = 8), 1.46 – 1.56 (2H, *m*), 1.68 – 1.75 (1H, *m*), 1.93 – 2.00 (1H, *m*), 2.76 – 2.81 (1H, *m*), 4.8 (2H, *s*). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 15.9, 27.2, 27.6, 30.2, 32.8, 38.2, 42.1, 168.6.

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2,2,6-Trimethylcyclohexanone hydrazone ***(12)***.[6d] Yield: 78%; White needles. GC-MS: m/z (relative intensity):154 (5, M^+), 139 (3), 122 (5), 109 (4), 95 (5), 81 (10), 67 (14), 56 (31), 41 (100%, base peak). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.12 (6H, *s*), 1.16 (3H, *d*, *J* = 8), 1.53 – 1.58(2H, *m*), 1.59 – 1.63 (2H, *m*), `1.72-1.77(2H, m), 2.95-2.99 (1H, *m*), 4.69 (2H, *s*). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 17.6, 17.8, 26.9, 29.3, 29.9, 32.1, 38.06, 40.8, 163.02.

1,1-Dichloro-2,2,5-trimethylcyclopentane ***(13)***. New compound. Yield: 33 %; Yellow oil; *b. p.* 60-63 °C/4mm. Anal. Calcd for $C_8H_{14}Cl_2$: C, 53.06; H, 7.79 %. Found: C, 53.47; H, 7.29 %. IR (film, cm^{-1}): 2966, 2939, 2875, 1506, 1455, 1371, 1217, 1105, 1002, 973, 914, 848, 784, and 761. GC-MS: m/z (relative intensity): 184 (1, M+4), 182 (3, M+2), 180 (1, M^+), 144 (1), 131 (2), 129 (7),

109 (29), 104 (16), 97 (22), 77 (9), 70 (23), 69 (100%, base peak), 56 (19), 55 (9), 42 (14), 41 (30). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.17 (3H, *s*), 1.22-1.24 (3H, *d*, *J* = 8 Hz), 1.27 (3H, *s*), 1.36-1.43 (1H, *m*), 1.55-1.62 (1H, *m*), 1.73-1.78 (1H, *m*), 1.81-1.93 (1H, *m*), 2.65-2.71 (1H, *m*). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 15.0, 24.0, 27.0, 27.3, 35.0, 46.8, 50.5, 106.9.

1,1-Dichloro-2,2,6-trimethylcyclohexane (***14***). New compound. Yield: 42 %; Yellow oil; *b. p.* 72-75 °C /4mm. Anal. Calcd for $C_9H_{16}Cl_2$: C, 55.40; H, 8.26 %. Found: C, 55.12; H, 8.45 %. IR (film, cm^{-1}): 2987, 2937, 2864, 1456, 1373, 1326, 1278, 1242, 1215, 1175, 1122, 1058, 989. GC-MS: m/z (relative intensity): 198 (1, M+4), 196 (3 M+2), 194 (1, M^+), 145 (4), 143 (2), 123 (20), 109 (6), 107 (21), 93 (6), 91 (16), 81 (32), 69 (34), 53 (39), 41 (100, base peak). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.21-1.23 (3H, *d*, *J* = 8 Hz), 1.24 (3H, *s*), 1.28 (3H, *s*), 1.36 – 1.41 (1H, *m*), 1.46 – 1.61 (4H, *m*), 1.82 – 1.85 (1H, *m*), 2.36 – 2.37 (1H, *m*) ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 18.0, 20.6, 24.8, 27.3, 32.0, 36.5, 42.6, 44.8, 108.6.

2-Chloro-1,3,3-trimethylcyclopentene (***17***). New compound. Yield: 31 %; Yellow oil; *b.p.* 60-63 °C/4mm. Anal. Calcd for $C_8H_{13}Cl$: C, 66.43; H, 9.06 %. Found: C, 66.23; H, 9.27 %. IR (film, cm^{-1}): 2960, 2867, 1664, 1461, 1363, 1259, 1006, 939. GC-MS: m/z (relative intensity): 146 (5, M+2), 144 (17, M^+), 131 (31), 129 (100%, base peak), 93 (59), 91 (31), 78 (43), 63 (67), 53 (14), 45 (30), 41 (22). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.04 (6H, *s*), 1.69 (3H, *s*), 1.76 (3H, *t*, *J* = 4.4 Hz), 2.26 (2H, *t*, *J* = 6 Hz), ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 14.2, 24.9, 26.4, 33.0, 34.8, 37.3, 130.9, 134.9.

2-Chloro-1,3,3-trimethylcyclohexene (***18***)[5c]: Yield: 40 %; Yellow oil; *b.p.* 72-75 °C/4mm. Anal. Calcd for $C_9H_{15}Cl$: C, 68.13; H, 9.53 %. Found: C, 68.23; H, 9.27 %. IR (film, cm^{-1}): 2964, 2933, 2870, 1654, 1458, 1361, 1161, 964. GC-MS: m/z (relative intensity): 160 (4, M+2), 158 (12, M^+), 145 (12), 143 (41), 123 (12), 109 (10), 107 (100, base peak), 91 (41), 81 (25), 79 (34), 77 (28), 53 (23), 41 (51). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.06 (6H, *s*), 1.55 – 1.58 (4H, *m*), 1.70 (3H, *s*), 2.03 – 2.04 (2H, *m*) ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 18.5, 20.4, 27.8, 32.5, 36.9, 38.8, 128.9, 135.1.

2-Bromo-1,3,3-trimethylcyclopentene (***19***). New compound. Yield: 64 %; brown oil; *b.p.* 69-71 °C/4mm. Anal. Calcd for $C_8H_{13}Br$: C, 50.81; H, 6.93 %. Found: C, 51.2; H, 7.23 %. IR (film, cm^{-1}): 2956, 2925, 2854, 1656, 1504, 1467, 1441, 1375, 1259, 1080, 1020, 860, 796. GC-MS: m/z (relative intensity): 190 (18, M+2), 188 (18, M^+), 175 (83), 173 (86), 94 (100%, base peak), 79 (44), 64 (14), 53 (16), 41 (20). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.06 (6H, *s*), 1.70 (3H, *s*), 1.79 – 1.82 (2H, *m*), 2.23 – 2.27 (2H, *m*). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 16.1, 27.1, 28.2, 34.1, 37.3, 128.3, 139.3.

2-Bromo-1,3,3-trimethylcyclohexene (***20***). New compound. Yield: 69 %; brown oil; *b. p.* 76-78 °C/4mm. Anal. Calcd for $C_9H_{15}Br$: C, 53.22; H, 7.44 %.

Found: C, 53.42; H, 7.13 %. IR (film, cm^{-1}): 2960, 2927, 2866, 1650, 1456, 1361, 1338, 1280, 1211, 1049, 939, 803, 815, 761. GC-MS: m/z (relative intensity): 204 (26, M+2), 202 (24, M^+), 188 (79), 186 (77), 123 (53), 107 (100), 91 (49), 81 (42), 67 (21), 52 (25), 41 (44). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.05 (6H, *s*), 1.53 – 1.58 (4H, *m*), 1.72 (3H, *s*), 1.98 – 2.01 (2H, *m*). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 19.2, 24.4, 29.3, 29.7, 33.8, 39.5, 131.8, 131.9.

2-Iodo-1,3,3-trimethylcyclopentene ***(21)***. New compound. Yield: 79 %; brown oil. *b. p.* 82-85 °C /4mm. Anal. Calcd for $C_8H_{13}I$: C, 40.70; H, 5.55 %. Found: C, 40.31; H, 5.71 %. IR (film, cm^{-1}): 2954, 2923, 2866, 1677, 1589, 1446, 1308, 1261, 1018, 802. GC-MS: m/z (relative intensity): 236 (31, M^+), 221 (100, base peak), 127(20), 109 (5), 94 (87), 79 (70), 65 (19), 53 (24), 41 (31). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 0.99 (6H, *s*), 1.75 (3H, *s*), 1.85 (2H, *t*, *J* = 6.96), 2.35 (2H, *t*, *J* = 7.44). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 19.5, 28.1, 35.6, 36.7, 49.3, 51.8, 109.4, 141.7.

2-Iodo-1,3,3-trimethylcyclohexene ***(22)***.[6d] Yield 82%; brown oil. GC-MS: m/z (relative intensity): 250 (52, M^+), 235 (21), 123(86), 108 (41), 93 (58), 81 (100), 67 (28), 53 (26), 41 (56). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.02 (6H, *s*), 1.54-1.67 (m, 4H), 1.79 (3H, *s*), 2.07-2.11 (2H, *t*, *J* = 7.76). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 19.4, 31.0, 31.5, 33.7, 37.9, 39.5, 117.3, 137.7.

2-(1′,3′,3′-Trimethylcyclopent-2′-enyl)eth-2-one ***(23 a)***.[16] Yield 65%; light Yellow oil; 53-57 °C/1mm. GC-MS: m/z (relative intensity): 152 (27, M^+), 109 (100%, base peak), 91 (15), 81(28), 67(82), 55 (17),40 (92).

3-(1′,3′,3′-Trimethylcyclopent-2′-enyl)prop-3-one ***(23 b)***. New compound. Yield: 71 %; light yellow oil; *b. p.* 64-67 °C/1mm. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91%. Found: C, 78.98; H, 10.67 %. IR (film, cm^{-1}): 2881, 2857, 2830, 1718,1450, 1360, 1248, 1017. GC-MS: m/z (relative intensity): 166 (22, M^+), 151 (2), 137 (4), 123 (10), 109 (100%, base peak), 95 (7), 91 (14), 81 (20), 67 (59), 57 (43), 55 (19), 40 (73). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 0.96 (3H, *t*, 3H, *J* = 3.08 Hz), 0.96 (3H, *s*), 1.27 (3H, *s*), 1.26 – 1.38 (2H, *m*), 1.54 – 1.59 (2H, *m*), 1.67 (3H, *s*), 2.09 – 2.13 (2H, *m*), 2.14 – 2.35 (2H, *m*). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 15.2, 23.9, 28.8, 31.0, 35.6, 42.2, 46.6, 71.3, 126.5, 137.0, 212.0.

(E)-4-(1′,3′,3′-Trimethylcyclopent-2′-enyl)but-2-en-4-one ***(23 c)***. New compound. Yield: 78 %; light yellow oil; *b. p*. 69-73 °C/1mm. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18 %. Found: C, 80.36; H, 10.43 %. IR (film, cm^{-1}): 2950, 2890, 1755, 1708, 1635, 1442, 1301, 1075, 950. GC-MS: m/z (relative intensity): 178 (9, M+), 163 (6), 135 (3), 122 (4), 109 (33), 91 (9), 79 (14), 69 (100, base peak), 55 (12), 41 (55). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.08 (6H, *s*), 1.48 (3H, *s*), 1.75 – 1.85 (5H, *m*), 1.95 – 2.15 (2H, *m*), 6.18 – 6.23(1H, *m*), 6.84 – 6.93 (1H, *m*). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 15.2, 17.2, 24.2, 31.1, 42.2, 46.9, 126.5, 130.2, 137.2, 138.6, 141.6, 200.2.

5-(1′, 3′, 3′-Trimethylcyclopent-2′-enyl)pentan-5-one ***(23 d)***. New compound. Yield: 83 %; light yellow oil; *b. p*. 68-72 °C/1mm. Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41 %. Found: C, 80.56; H, 11.13 %. IR (film, cm^{-1}): 2880, 2855, 2830, 1720,1450, 1340, 1250, 1020. GC-MS: m/z (relative intensity): 194 (26, M^+), 179 (1), 151 (4), 137 (4), 109 (100%, base peak), 91 (10), 85 (74), 67 (52), 57 (70), 41 (43). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 0.93(3H, *t*, *J* = 3.08 Hz), 0.99 (3H, *s*), 1.28(3H, *s*), 1.29 – 1.36 (4H, *m*), 1.51 – 1.58 (2H, *m*), 1.65 (3H, *s*), 2.07 – 2.11 (2H, *m*), 2.1 – 2.39 (3H, *m*). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 12.9, 15.3, 21.4, 24.36, 24.5, 31.0, 42.3, 46.7, 71.3, 126.4, 137.1, 211.5.

6-(1′, 3′, 3′-Trimethylcyclopent-2′-enyl)-hexan-6-one ***(23 e)***. New compound. Yield: 87 %; light yellow oil; *b. p* 71-74 °C/1mm. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61 %. Found: C, 80.34; H, 11.45 %. IR (film, cm^{-1}): 2958**,** 2931, 1710, 1465, 1335, 12651073. GC-MS: m/z (relative intensity): 208 (24, M^+), 193 (2), 165 (2), 137 (4), 109 (100%, base peak), 99 (68), 81 (20), 71 (56) 67 (49), 55(19), 43 (73). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 0.87 (3H, *m*), 0.97 (3H, *s*), 1.25 (3H, *s*), 1.28 – 1.35 (6H, *m*), 1.53 – 1.68 (5H, *m*), 2.11 – 2.38 (4H, *m*). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 13.9, 16.3, 22.5, 23.1, 25.0, 29.7, 31.5, 32.1, 43.5, 47.7, 72.3, 127.4, 138.1.

(1,3,3-Trimethylcyclopent-2-enyl)phenylmethanone ***(23 f)***. New compound. Yield: 86 %; yellow oil; *b. p.* 82-84 °C /1mm. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47%. Found: C, 84.74; H, 8.45%. IR (film, cm^{-1}): 2846, 1681, 1600, 1454, 1415, 1323, 1026. GC-MS: m/z (relative intensity): 214 (16, M^+), 199 (38), 158 (9), 137 (1), 105 (100%, base peak), 91 (7), 77 (52), 67 (6), 51 (12), 41 (9). ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 1.22 (6H, *s*), 1.48 (3H, *s*), 1.80 (2H, *t*, *J* = 6.8 Hz), 2.41 – 2.48 (2H, *m*), 7.41 – 7.45 (3H, *m*), 7.80 – 7.87 (2H, *m*). ^{13}C-NMR (100, MHz, $CDCl_3$, δ / ppm): 16.0, 26.1, 29.3, 35.7, 39.1, 48.3, 124.4, 127.0, 127.2, 131.1, 138.5, 142.3, 143.5, 197.6.