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## Synthesis of five- and six-membered 1,3,3-trimethyl-2-(trimethylsilyl)cycloalkenes: a novel preparation of alkyl/alkenyl/aryl 2,5,5-trimethyl-1-cyclopentenyl ketones

MANJUNATHA A. VENKATESHA and HARIPRASAD SURESH\*

*Department of Chemistry, Central College Campus, Palace Road, Bangalore University,  
Bangalore – 560001, India*

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**Abstract:** 1,3,3-trimethyl-2-(trimethylsilyl)cyclopentene and 1,3,3-trimethyl-2-(trimethylsilyl)cyclohexene 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 1,3,3-trimethyl-2-(trimethylsilyl)cyclopentene with six different acid chlorides and the novel preparation of six alkyl/alkenyl/aryl 2,5,5-trimethyl-1-cyclopentenyl ketones are reported.

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

### INTRODUCTION

Cyclic vinylsilanes are an important class of compounds in synthetic organic chemistry.<sup>1</sup> The compounds are anionic synthons with the trimethylsilyl group behaving as a masking agent.<sup>2</sup> 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.<sup>3</sup>

Our laboratory is primarily involved in the preparation of cyclic vinylsilanes by employing the Wurtz–Fittig-type coupling reaction of cyclic vinyl halides with sodium and chlorotrimethylsilane in a suitable anhydrous solvent. The method is simple, and employing this reaction, a number of simple and substituted cyclic vinylsilanes have been successfully prepared. Various novel reactions of the prepared simple and substituted cyclic vinylsilanes have also been reported.<sup>4</sup>

\* Corresponding author. E-mail: hariprasad@bub.ernet.in  
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In further studies and in attempts to prepare some important substituted cyclic vinylsilanes, the synthesis of 1,3,3-trimethyl-2-(trimethylsilyl)cyclopentene (**1**) and 1,3,3-trimethyl-2-(trimethylsilyl)cyclohexene (**2**) were chosen. Compounds **1** and **2** would serve as potential synthons to several terpenes, vitamin A and related compounds.<sup>5</sup> In particular, it may be noted that the 1,3,3-trimethylcycloalkanyl- group is a common functionality present in capnellane,<sup>6a</sup> taiwaniaquinoid,<sup>6b</sup> actinidiolide,<sup>6c</sup> hedychenone<sup>6d</sup> and labdane diterpene<sup>6e</sup> group of compounds. Paquette reported the preparation of **1** by the tosyl hydrazone route, and isolation using preparative vapour-phase chromatography (VPC).<sup>7</sup> To the best of our knowledge, compound **2** has not been reported, but its corresponding vinyl stannane has been synthesized.<sup>8</sup>

In this article, the successful preparation of **1** and **2** by the Wurtz–Fittig coupling reaction are reported. The Friedel–Crafts acylation of **1** with six different acid chlorides gave some novel alkyl/alkenyl/aryl 2,5,5-trimethyl-1-cyclopentenyl ketones.

## RESULTS AND DISCUSSION

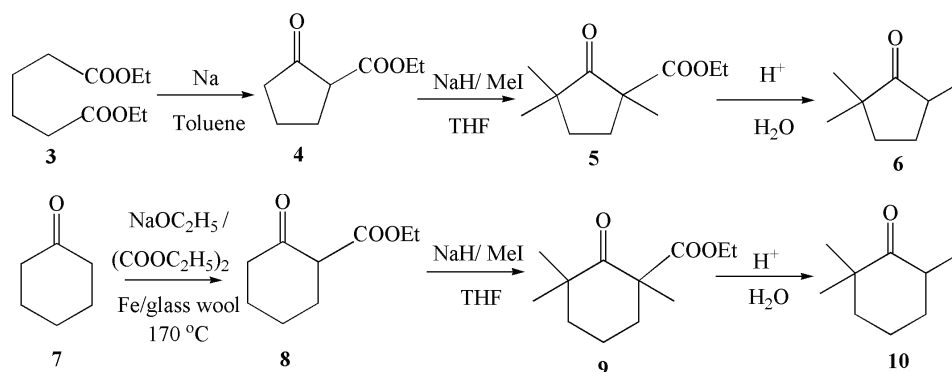
### Chemistry

*Preparation of five- and six-membered  $\alpha,\alpha,\alpha'$ -trimethylcycloalkanones.* Hereby a new route for the synthesis of 2,5,5-trimethylcyclopentanone is reported.<sup>9a</sup> Diethyl adipate (**3**) upon Dieckmann cyclisation with sodium/toluene afforded ethyl 2-oxocyclopentanecarboxylate (**4**).<sup>9b</sup> Total methylation of **4** using methyl iodide (6 equivalents) and sodium hydride (4 equivalents) gave ethyl 1,3,3-trimethyl-2-oxocyclopentanecarboxylate (**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**.

2,2,6-Trimethylcyclohexanone was prepared according to a reported literature procedure.<sup>10</sup> 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 °C gave ethyl 2-oxocyclohexanecarboxylate (**8**) in 45 % yield. Total methylation of **8** using 4 equivalents of sodium hydride and 6 equivalents of methyl iodide gave 1,3,3-trimethyl-2-oxocyclohexanecarboxylate (**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 alkyl/alkenyl/aryl halides in organic synthesis. Some of the recently developed reagents used to perform the transformation include  $(\text{PhO})_3\text{P}/\text{X}_2$ ,<sup>11a</sup>  $\text{CH}_3\text{COX}/\text{CF}_3\text{COOH}$ ,<sup>11b</sup>  $\text{WCl}_6$ ,<sup>11c</sup>  $(\text{EtO})_2\text{P}(\text{O})\text{Cl}$

$/P(Ph_3)/X_2$ ,<sup>11d</sup> along with traditional halogenating agents such as thionyl chloride and phosphorus pentachloride.<sup>11e-g</sup>



Scheme 1. Synthesis of five- and six-membered  $\alpha, \alpha, \alpha'$ -trimethylcycloalkanones (**6** and **10**).

Some of the reagents reported for the conversion of cyclic ketones to cycloalkenyl halides were explored in the present study. The investigations showed that the Takeda general method for preparation of *gem*-halides was most useful.<sup>12</sup> The method involves the conversion of the carbonyl compounds to their corresponding hydrazones, followed by reaction with cupric halide/Et<sub>3</sub>N.

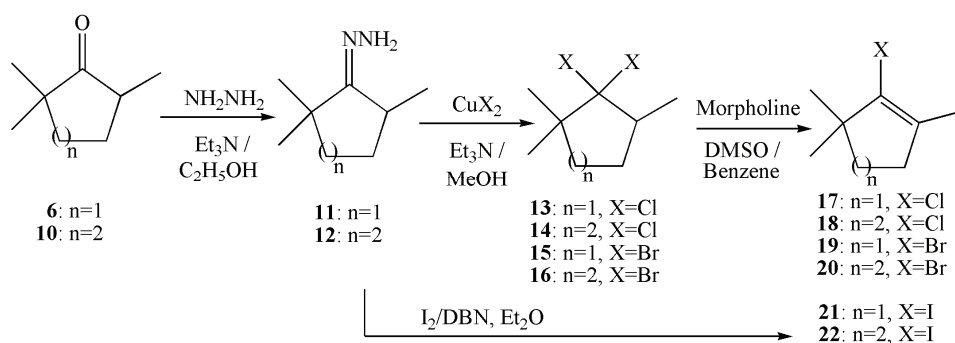
The compounds **6** and **10** were converted to their corresponding hydrazones 2,2,5-trimethylcyclopentanone hydrazone (**11**) in 75 % yield and 2,2,6-trimethylcyclohexanone hydrazone (**12**)<sup>6d</sup> in 78 % yield, respectively.

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<sup>13</sup> gave 2-chloro-1,3,3-trimethylcyclopentene (**17**) in 31 % yield and 2-chloro-1,3,3-trimethylcyclohexene (**18**)<sup>5c</sup> in 40 % yield, respectively.

Similar bromination of **11** and **12** with 6 equivalents of copper(II) bromide and 3 equivalents of triethylamine gave a mixture of *gem*-dibromides **15** and **16** and vinyl bromides **19** and **20** in a 1:1 ratio due to the elimination of HBr under the employed reaction conditions. Without isolation of 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**)<sup>6d</sup> were prepared by adopting the Barton vinyl iodination procedure. Reaction of **11** and **12** with iodine and 2,3,4,6,7,8-hexahydropyrrolo[1,2-*a*]pyrimidine (DBN)<sup>6d,14</sup> 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.



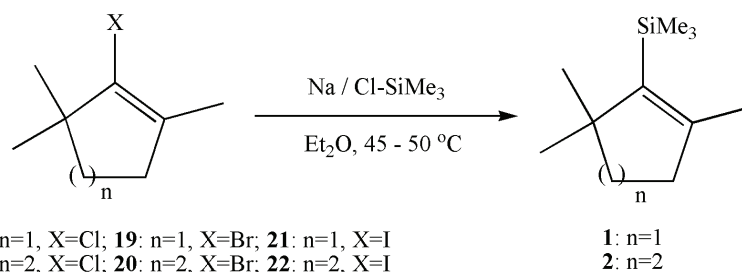
Scheme 2. Synthesis of five- and six-membered 2-halo-1,3,3-trimethylcycloalkenes (**17–22**).

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	<b>11</b>	CuCl <sub>2</sub> /Et <sub>3</sub> N/MeOH	5	<b>17</b>	31
2	<b>12</b>	CuCl <sub>2</sub> /Et <sub>3</sub> N/MeOH	6	<b>18</b>	40
3	<b>11</b>	CuBr <sub>2</sub> /Et <sub>3</sub> N/MeOH	5	<b>19</b>	64
4	<b>12</b>	CuBr <sub>2</sub> /Et <sub>3</sub> N/MeOH	6	<b>20</b>	69
5	<b>11</b>	I <sub>2</sub> /DBN/Et <sub>2</sub> O	5	<b>21</b>	79
6	<b>12</b> <sup>6d</sup>	I <sub>2</sub> /DBN/Et <sub>2</sub> O	6	<b>22</b> <sup>6d</sup>	82

#### Wurtz–Fittig coupling reaction to the five- and six-membered 1,3,3-trimethyl-2-(trimethylsilyl)cycloalkenes

The cyclic vinyl halides **17–22** were subjected to the Wurtz–Fittig coupling reaction with sodium and chlorotrimethylsilane in anhydrous ether solvent, using well established protocols.<sup>4</sup> 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).



Scheme 3. Wurtz–Fittig coupling to 1,3,3-trimethyl-2-(trimethylsilyl)cycloalkenes (**1** and **2**).

Each reaction was performed a minimum of five times for each cyclic vinyl halide substrate (**17–22**) and the yields of the products **1** and **2** were averaged and are given in Table II.

TABLE II. Synthesis of 1,3,3-trimethyl-2-(trimethylsilyl)cycloalkenes **1** and **2** by Wurtz–Fittig coupling of **17–22** with sodium and chlorotrimethylsilane in anhydrous diethyl ether as solvent

Entry	Substrate	Halogen	Ring size	Product	Yield, %
1	<b>17</b>	Cl	5	<b>1</b>	73–76
2	<b>18</b> <sup>5c</sup>	Cl	6	<b>2</b>	75–77
3	<b>19</b>	Br	5	<b>1</b>	72–74
4	<b>20</b>	Br	6	<b>2</b>	<10
5	<b>21</b>	I	5	<b>1</b>	81–83
6	<b>22</b> <sup>6d</sup>	I	6	<b>2</b>	<10

The hindered cyclic vinyl halides **17–22** exhibited different 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 1,3,3-trimethyl-2-(trimethylsilyl)cyclopentene (**1**), with the highest isolated yield of 81–83 %.

In case of the six-membered ring system, the 1,3,3-trimethyl-2-(trimethylsilyl)cyclohexene (**18**)<sup>5c</sup> 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 the employed reaction conditions. Change of metal to potassium, magnesium or lithium and use of solvents: THF, benzene or hexamethylphosphoramide (HMPA) gave **2** in less than 10 % yields.

It was not possible 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 to give low and inconsistent yields. On the other hand, although the Wurtz–Fittig reaction of the vinyl chloride **18** occurred in good yields, the preparation of **18** proved difficult because of low yields<sup>5c</sup> in both the *gem*-chlorination (42 % yield) and dehydrochlorination steps (40 % yield).

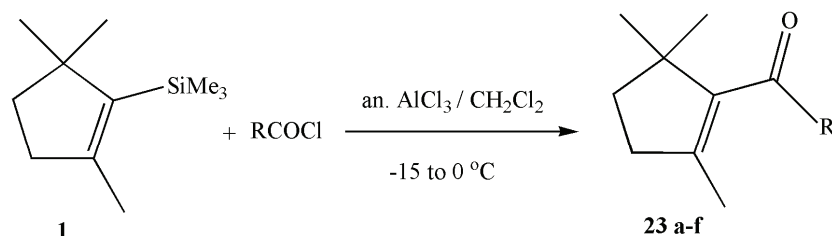
In the light of the preparation of the five-membered cyclic vinyl silane **1** in sufficient quantities (2 g scale), Friedel–Crafts acylation reactions of the five-membered cyclic vinyl silane **1** with six different acid chlorides were performed.

*Conversion to novel alkyl/alkenyl/aryl 2,5,5-trimethyl-1-cyclopentenyl ketones.* The Friedel–Crafts acylation reactions are some of the most widely studied

and used reactions in organosilicon chemistry.<sup>1-3</sup> The reaction has been extended to several classes of organosilicon compounds, such as allylsilanes, arylsilanes, vinylsilanes, *etc.*, to obtain a wide variety of carbonyl moiety-containing products. The conversions employ the  $\beta$ -silyl effect.<sup>15</sup> Using the Friedel–Crafts acylation reaction and employing standardized procedures, the synthesis of a wide variety of novel products from cyclic vinylsilanes was previously reported.<sup>4</sup>

The Friedel–Crafts reaction of **1** was performed on the 0.2 g scale with 3 molar equivalents each of anhydrous aluminium chloride and six different acid chlorides in dichloromethane as solvent.

The reactions were found to be clean and afforded the novel alkyl/alkenyl/aryl 2,5,5-trimethyl-1-cyclopentenyl ketones **23a–f** (Scheme 4) in isolated yields ranging between 65–87 % in five trials for each substrate (Table III).



(a) R: -CH<sub>3</sub> (b) R: -CH<sub>2</sub>CH<sub>3</sub> (c) R: *trans*-CH=CH-CH<sub>3</sub> (d) R: *n*-C<sub>4</sub>H<sub>9</sub> (e) R: *n*-C<sub>5</sub>H<sub>11</sub> (f) R: -C<sub>6</sub>H<sub>5</sub>  
 Scheme 4. Facile route for the synthesis of alkyl/alkenyl/aryl 2,5,5-trimethyl-1-cyclopentenyl ketones (**23a–f**).

TABLE III. Synthesis of some novel alkyl/alkenyl/aryl 2,5,5-trimethyl-1-cyclopentenyl ketones (**23a–f**)

Entry	Product	R	Yield, %	B.p. / °C (1 mm)
1	<b>23a</b> <sup>16</sup>	-CH <sub>3</sub>	65	53–57
2	<b>23b</b>	-C <sub>2</sub> H <sub>5</sub>	71	64–67
3	<b>23c</b>	-( <i>E</i> )-C <sub>3</sub> H <sub>5</sub>	78	69–73
4	<b>23d</b>	<i>n</i> -C <sub>4</sub> H <sub>9</sub>	83	68–72
5	<b>23e</b>	<i>n</i> -C <sub>5</sub> H <sub>11</sub>	87	71–74
6	<b>23f</b>	-C <sub>6</sub> H <sub>5</sub>	86	82–84

The compound **23a** is a known compound prepared earlier by Stille in the palladium-catalysed coupling of ( $\alpha$ -ethoxyvinyl)trimethylstannane with 2,5,5-trimethyl-1-cyclopenten-1-yl trifluoromethanesulfonate.<sup>16</sup> All the other (2,5,5-trimethyl-1-cyclopentenyl)ketones **23b–f** are not reported in the literature and are reported herein for the first time. The procedure employs the Friedel–Crafts acylation reaction of **1** and utilizes the  $\beta$ -silyl effect. Compound **23c** is the lower analogue of the naturally occurring  $\beta$ -damascone.<sup>17</sup> Compounds **23a–f** may be useful in the aroma and perfume industries.<sup>18</sup>

## EXPERIMENTAL

All reactions were monitored using GC or TLC. The TLC was run on Merck TLC Silica-gel 60 F<sub>254</sub> pre-coated plates with elution solvent 1:20 ethyl acetate/hexane (60–80 °C fraction). The GC was run on an SE-30 SS 2 m×1/8" column in a Mayura 9800 gas chromatograph. The IR spectra were recorded on Shimadzu FT-IR 8400S on NaCl plates as neat thin liquid film samples. The NMR spectra were recorded in CDCl<sub>3</sub> on a Bruker AMX 400 spectrometer using tetramethylsilane (TMS) as an internal standard. The GC–MS spectra were obtained using a Shimadzu GC–MS QP 5050A instrument equipped with a 30 m×0.32 mm BP-5 capillary column. Elemental Analysis were realised using an Elementar Vario Microcube-15106062 instrument. All yields refer to the isolated yields of the products.

The spectral data of the products are given in the Supplementary material to this paper.

*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 °C. The reaction mixture was stirred for 10 min and cooled to 0 °C. A methanolic solution of  $\alpha,\alpha,\alpha'$ -trimethylcycloalkanone hydrazones **11** and **12** (3 g in 30 mL MeOH) was added dropwise over 20 min, and the mixture was further stirred for 2 h, simultaneously allowing the reaction mixture to attain ambient temperature. TLC indicated complete conversion of the hydrazone. The mixture was quenched by the addition of 50 mL of a 3.5 % aqueous NH<sub>3</sub> solution, and extracted with diethyl ether (3×30 mL). The combined organic extracts were washed with saturated NaHCO<sub>3</sub> (2×30 mL), water (2×30 mL), saturated NaCl (2×30 mL) and dried over anhydrous MgSO<sub>4</sub>. 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 h. Gas chromatography indicated complete conversion to the cyclic vinyl halides **17–20**. The mixture was cooled, added to ice cold 2M HCl (50 mL) and extracted with diethyl ether (3×40 mL). The combined organic extracts were washed with saturated NaHCO<sub>3</sub> (2×30 mL), water (2×30 mL), saturated NaCl (2×30 mL) and dried over anhydrous MgSO<sub>4</sub>. 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 and 22)*

To a suspension of 4 g of  $\alpha,\alpha,\alpha'$ -trimethylcycloalkanone hydrazones **11** and **12** and 6 molar equivalents of 1,5-diazabicyclo[4.3.0]non-5-ene in 50 mL anhydrous diethyl ether was added dropwise a solution of 2.2 molar equivalents iodine in 100 mL anhydrous diethyl ether. The reaction mixture was stirred for 3.5 h, when the GC indicated completion of the 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 diethyl ether (3×40 mL). The organic layers were combined, dried over anhydrous sodium sulphate, and evaporated *in vacuo*. The residue was chromatographed through silica gel using hexane as the solvent to afford the cyclic vinyl iodides **21** and **22**.

*General procedure for the synthesis of 1,3,3-trimethyl-2-(trimethylsilyl)cycloalkenes (1 and 2)*

To a suspension of finely cut sodium pieces (5 molar equivalents) and chlorotrimethylsilane (3 molar equivalents) in 10 mL of dry diethyl ether was added 2-halo-1,3,3-trimethylcycloalkene (3.2 g (13.5 mmol) of **21**, or 0.22 g (1.3 mmol) of **18**) in 10 mL of anhydrous



diethyl ether. The mixture was refluxed with efficient stirring on an oil bath at 45–50 °C, whereby a deep navy blue colouration developed. Monitoring the reaction by GC indicated that the reactants required 6 h for complete conversion to the products. The mixture was cooled; the precipitated solids and remaining sodium removed by filtration through a plug of glass wool and washed with diethyl ether (2×5 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 (3×10 mL), saturated sodium chloride (15 mL), dried over anhydrous Na<sub>2</sub>CO<sub>3</sub>, concentrated and distilled under reduce pressure to isolate **1** and **2**. The yields of the isolated products are given in Table II.

*General procedure for the synthesis of alkyl/alkenyl/aryl 2,5,5-trimethyl-1-cyclopentenyl ketones (23a–f)*

To a magnetically stirred mixture of anhydrous AlCl<sub>3</sub> (3 molar equivalents) and acid chloride (3 molar equivalents) in dry CH<sub>2</sub>Cl<sub>2</sub> (20 mL), cooled to –15 °C on an ice–salt bath, was added dropwise 0.2 g of **1** in 5 ml of dry CH<sub>2</sub>Cl<sub>2</sub> over a period of 5 min. After stirring for 3 h, the gas chromatogram of an aliquot indicated complete disappearance of the reactant **1**. Saturated NaHCO<sub>3</sub> solution (20 mL) was added to the mixture and stirred for 30 min, simultaneously allowing the reaction mixture to attain room temperature. The organic layer was separated, washed with NaHCO<sub>3</sub> solution (2×20 mL), water (25 mL) and saturated NaCl solution (20 mL). The pale yellow organic extract was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated and finally subjected to bulb-to-bulb distillation under reduced pressure to isolate individually the alkyl/alkenyl/aryl 2,5,5-trimethyl-1-cyclopentenyl ketones (**23a–f**).

### CONCLUSIONS

The simple synthesis of 1,3,3-trimethyl-2-(trimethylsilyl)cyclopentene and 1,3,3-trimethyl-2-(trimethylsilyl)cyclohexene is reported. The Friedel–Crafts acylations of 1,3,3-trimethyl-2-(trimethylsilyl)cyclopentene gave a series of six alkyl/alkenyl/aryl 2,5,5-trimethyl-1-cyclopentenyl ketones.

### SUPPLEMENTARY MATERIAL

Spectral data of the products are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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### ИЗВОД

СИНТЕЗА ПЕТО- И ШЕСТОЧЛАНИХ 2-(ТРИМЕТИЛСИЛИЛ)-1,3,3-ТРИМЕТИЛЦИКЛОАЛКАНА: НОВ ПОСТУПАК СИНТЕЗЕ АЛКИЛ/АЛКЕНИЛ/АРИЛ-(2,5,5-ТРИМЕТИЛЦИКЛОПЕНТЕНИЛ)-КЕТОНА

VENKATESHA M. ACHANNA и HARIPRASAD SURESH

Department of Chemistry, Central College Campus, Palace Road, Bangalore University,  
Bangalore – 560001, India

1,3,3-Триметил-2-(триметилсилил)-циклопентен и 1,3,3-триметил-2-(триметилсилил)-циклохексен добијени су, у добром приносу, Вурц–Фитиговим купловањем пола-



зећи од одговарајућих 2-јод-1,3,3-триметилциклопентена и 2-хлор-1,3,3-триметилциклопентена са металним натријумом и хлортриметилсиланом у анхидрованом етру као растварачу. Приказано је Фридел–Крафтсово ациловање 1,3,3-триметил-2-(триметилсил)-циклопентена са шест различитих алканоилхлорида и нова синтеза шест алкил/алкенил/арил-(2,5,5-триметил-1-циклопентенил)-кетона.

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