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Investigation of 1,4-elimination reactions of γ-trimethylsilyl alcohols via ionic and radical processes

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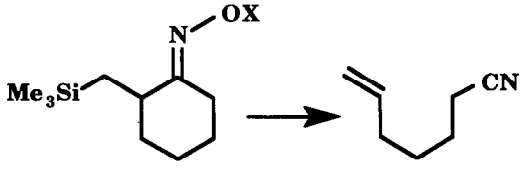
Abstract

Oxidative fragmentation of γ-trimethylsilyl alcohols with cerium ammonium nitrate occurs rapidly via a radical process to provide keto olefins. Attempts to obtain the same products via an ionic-type 1,4-elimination with the trimethylsilyl group as the directing moiety proved unsuccessful, even under a variety of harsh experimental conditions. Instead, dehydration products were produced in certain cases.

Introduction

Silyl-directed 1,*n*-elimination reactions have been studied extensively [1]. In general, 1,2-eliminations can be performed under mild conditions and have even been successfully applied to the synthesis of unstable cyclopropene derivatives [2]. In contrast, 1,4-eliminations are relatively difficult in cases involving the breakage of two σ bonds that link the initiator and the terminator [3]. However, exceptions published recently include the Beckmann fragmentation of β-(trimethylsilyl)ketoxime acetates (**1a**) by Itoh et al. [4] and β-(trimethylsilyl)ketoxime sulfonates (**1b**) by Hudrlik et al. [5] (eq. 1). These examples suggest that the trimethylsilyl group directs the 1,4-elimination.



(1)

(**1a**, X = COMe ;
1b, X = SO_3H)

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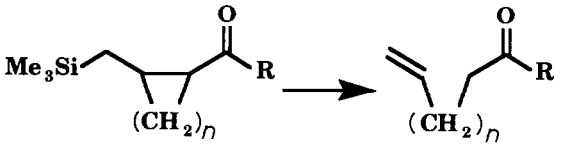
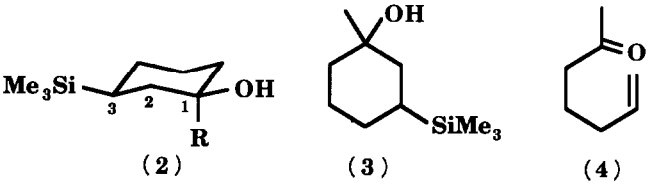
Fragmentations in a 1,4-fashion of substrates in which a trimethylsilyl group acts as the terminator can be facilitated by activating the C–C single bond that is to be cleaved. Fujita et al. have shown that γ-(trimethylsilyl)cyclopropyl- or γ-(trimethylsilyl)cyclobutyl ketones can be smoothly converted to nonconjugated enones upon treatment with boron trifluoride [6] (eq. 2). We have been interested in the silyl-directed 1,4-elimination reaction of substrates in which all the connecting units between the initiator and the terminator are unactivated single bonds.



(n = 1 or 2) (2)

Marshall et al. have developed a novel 1,4-solvolytic fragmentation of a decalylboronate system [7]. They utilized a boronate moiety to initiate the elimination reaction. We have selected silylcyclohexanol **2** as a substrate for the 1,4-fragmentation in order to investigate the suitability of the trimethylsilyl functionality as the directing group. Compound **2** possesses several unique properties: 1. the hydroxyl group can be easily activated as an initiator or a terminator; 2. the silicon atom can react with a fluoride ion to form a strong Si–F bond that may offer an extra "pushing force" for the fragmentation; 3. the cyclohexane nucleus provides an ideal



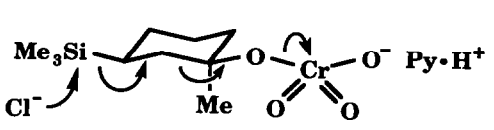
(2) (3) (4)

alignment of bonds involved in the fragmentation, but does not possess an activated C–C bond (i.e. C(1)–C(2)); 4. the product resulting from the 1,4-elimination would contain a C=O double bond (179 kcal/mol) [8], providing a strong driving force for the reaction.

Results and discussion

We have investigated a variety of methods for the oxidative 1,4-fragmentation of silylcyclohexanol **3**. The methylcarbinols **3a** and **3b** were prepared by the addition of methylmagnesium bromide to 3-(trimethylsilyl)cyclohexanone [5]. These tertiary alcohols were obtained as a diastereomeric mixture (5.0/1) in 96% yield and were easily separated by medium pressure liquid chromatography. Their structural assignment was based on two analogous reactions: the reduction of 3-(trimethylsilyl)cyclohexanone with lithium aluminium hydride [9], and the nucleophilic addition of methylmagnesium bromide to substituted cyclohexanones [10]. Both of these reactions occur with a preference for axial attack. Similarly, the phenylcarbinols **14a** and **14b** were prepared by the phenylation of 3-(trimethylsilyl)cyclohexanone with phenylmagnesium bromide in 52% and 27% yields, respectively.

Adopting Dauben's methodology of converting tertiary allylic alcohols to β-alkyl-α,β-unsaturated ketones [11], we treated a diastereomeric mixture of **3** with 1.2 equivalents of pyridinium chlorochromate in dichloromethane in order to generate the chromate intermediate **5**. Both the chromate moiety and trimethylsilyl group in **5** can reside at equatorial positions, providing an ideal geometry for 1,4-elimination. On the other hand, **5** could equilibrate with its conformer **6**. Decomposition of **6** via



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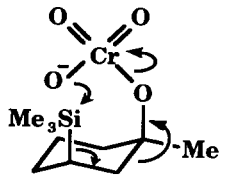
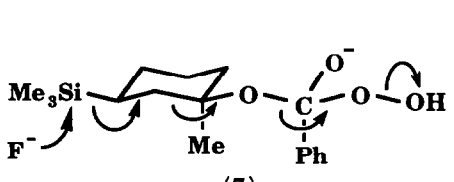


(6)

an intramolecular anionic silyl rearrangement might occur to yield the desired unsaturated ketone **4**. We carried out this reaction at room temperature for 2 h and only recovered the parent alcohol **3**, indicating that neither pathway was favorable.

Following the same concept, we intended to obtain **4** by reacting **3** with *m*-chloroperoxybenzoic acid (*m*-CPBA) under the reaction conditions reported by Saigo et al. [12]. We were not able to decompose either intermediate **7** or **8**. We also



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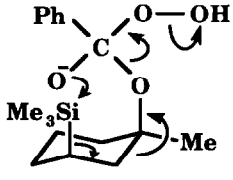
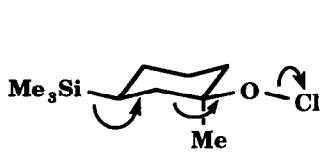


(8)

Ph = *m*-chlorophenyl

added cesium fluoride in order to provide a pushing force. However, we did not detect any of the desired product **4**. Further attempts were not successful even when *m*-CPBA was replaced by 1,1′-(azodicarbonyl)dipiperidine and the reaction mixture was heated to reflux [12]. Furthermore the silylhypochlorite **9**, prepared in situ from **3** and *N*-chlorosuccinimide [12], was also resistant to decomposition under refluxing conditions.



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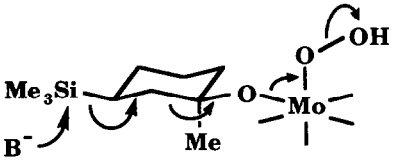


(10)

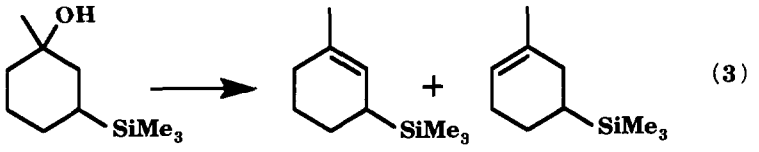
Hydrogen peroxide in the presence of ammonium molybdate(VI) tetrahydrate and potassium carbonate can efficiently oxidize hindered alcohols [13]. A molybdenum alkoxide intermediate has been suggested. However, extension of this approach to silicon-directed fragmentation of **10** failed.

Swern has shown that dimethyl sulfoxide (DMSO), activated by oxalyl chloride, can rapidly oxidize hindered alcohols [14]. We applied these conditions to alcohol **3**,

in order to generate sulfonium salt **11**, and added one equivalent of triethylamine to

(11)

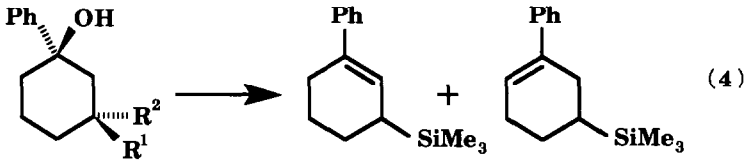
neutralize the resulting hydrogen chloride. The intermediate **11** contains a highly electron-deficient $O-S^+Me_2$ moiety; cleavage of the $O-S^+$ "pseudo" σ bond may initiate a 1,4-elimination. However, **11** did not decompose in dichloromethane or chloroform. Addition of cesium fluoride to the solution of **11** in acetonitrile [15], in order to facilitate a Grob fragmentation, still did not give ketone **4**. Instead, we obtained a mixture of dehydrated products **12** and **13** in 22% yield (eq. 3). Under



(3)

(3) (12) (13)

similar conditions, but without triethylamine and fluoride ion, phenylcarbinol **14a** gave regioisomers **15** and **16** in 57% yield; **14b** provided **15** and **16** in 50% yield (eq. 4). These examples show that dehydration of tertiary alcohols overrides the Grob fragmentation under Swern conditions.

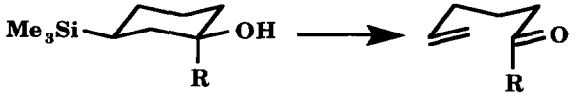


(4)

(14a, R^1 = $SiMe_3$, R^2 = H; (15) (16)

14b, R^1 = H, R^2 = $SiMe_3$)

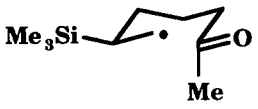
Since **5–11** resisted an ionic-type elimination under the harsh experimental conditions described above, we considered a radical process as an alternative for the fragmentation of **3** to **4**. In general organotin compounds are more amenable to radical reactions than organosilicon materials. For example, γ-hydroxyalkyl stannanes react readily with lead tetraacetate to give keto olefins, yet γ-hydroxyalkyl silanes remain inert [3]. However, the pioneering work of Trahanovsky has shown that the rapid oxidative cleavage of β-(trimethylsilylethyl)phenylmethanol to benzaldehyde and ethylene by ceric ammonium nitrate (CAN) occurs via a radical process [16]. Consequently we treated *cis*-1-methyl-3-(trimethylsilyl)cyclohexan-1-ol (**3a**), in which the trimethylsilyl group is *syn* to the hydroxyl moiety, with 2.0 equivalents of CAN in 50% aqueous acetonitrile at 85 °C to provide keto olefin **4** in 88% yield in 5 min (eq. 5). Under the same conditions, we converted phenylcarbinol **14a** to **17** in 75% yield.



(5)

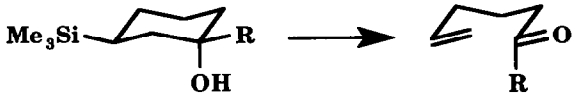
(3a, R = Me ; (4, R = Me ;
14a, R = Ph) 17, R = Ph)

Previous work published by Wilson et al. has clearly indicated that the oxidative fragmentation of γ-silyl alcohols by CAN is not stereospecific with respect to the C=C bond formed in the reaction product [17]. This can be illustrated by a stepwise mechanism originally proposed by Trahanovsky [16]. Note that this mechanism is in contrast to that of the oxidative fragmentation of γ-hydroxyalkyl stannanes by lead tetraacetate [3]. In silylcyclohexanol **3b**, the C–Si and the C–O bonds are not coplanar. However, we still should be able to convert **3b** to **4**, via the intermediate **18**. Indeed we found that both compounds **3b** and **14b** underwent oxidative cleavage



(18)

with CAN to provide **4** and **17** in 93% and 82% yields, respectively (eq. 6).



(6)

(**3b**, **R** = **Me** ; **14b**, **R** = **Ph**)

(**4**, **R** = **Me** ; **17**, **R** = **Ph**)

Our results indicate that ionic 1,4-elimination of γ-silyl alcohols with the trimethylsilyl group as a directing moiety (see intermediates **5–11**) is not feasible under the harsh reaction conditions we applied. A radical process, initiated by cerium ammonium nitrate, can rapidly lead such alcohols to keto olefins in good to excellent yields. The relative stereochemistry of the trimethylsilyl and hydroxyl groups is not a factor in this oxidative cleavage process, providing the flexibility of applying this methodology even to the fragmentation of a diastereomeric mixture of γ-silyl alcohols.

Experimental

All reactions were carried out in oven-dried glassware (4 h, 120 °C) under an atmosphere of nitrogen. Acetonitrile, dichloromethane, ethyl acetate and triethylamine were dried and distilled over CaH_2. Diethyl ether was freshly distilled from Na/benzophenone. Anhydrous cesium fluoride was prepared according to Vedejs' procedure [15b]. For column chromatography, EM reagents silica gel 60 (particle size 0.063–0.0200 mm) was used. Analytical TLC was performed on precoated plates purchased from Analtech, Inc. (silica gel GHLF) using UV light and/or 2.5% phosphomolybdic acid in ethanol with heating for visualization. Mixtures of ethyl acetate and hexanes were used as eluants. Infrared spectra (IR) were measured on a Perkin–Elmer 599B or a 710B spectrophotometer. The wavenumbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. IR intensities are designated using the following abbreviations: s, strong; m, medium; w, weak. ^1H NMR were obtained on a Varian CFT-20 spectrometer using chloroform-*d* as solvent and tetramethylsilane as an internal standard. ^1H NMR multiplicities are recorded by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; *J*, coupling constant (hertz). High-resolution mass spectra were obtained with a VG analytical 70-S Mass spectrometer. Melting points were

determined on a Büchi 510K melting point apparatus and are uncorrected. Medium pressure liquid chromatography (MPLC) equipment [18] includes a metering pump (ISCO model 312), and a 15 mm × 300 mm glass column packed with EM reagents silica gel 60 (partical size 0.040–0.063 mm). Mixtures of ethyl acetate and hexanes were used as eluting solvents. GC analyses were performed on a Hewlett–Packard 5794A instrument equipped with a 12.5-m cross-linked methylsilicone gum capillary column (0.2-mm i.d.).

*1-Methyl-3-(trimethylsilyl)cyclohexan-1-ol (**3a** and **3b**)*

A solution of 3-(trimethylsilyl)cyclohexanone [5] (1.08 g, 6.38 mmol, 1.0 equiv) in ether (4 ml) was added to a mixture of methylmagnesium bromide (3.2 *M* in ether, 6.0 ml, 19 mmol, 3.0 equiv) in anhydrous ether (15 ml) at 0 °C. The solution was stirred at the same temperature for 15 min then slowly warmed to room temperature. The mixture was quenched with water (10 ml) and saturated aqueous NH_4Cl (25 ml), then extracted with ether (3 × 25 ml). The combined ether extracts were washed with water (1 × 10 ml), saturated aqueous NaCl (1 × 25 ml) and dried over anhydrous $MgSO_4$. Filtration and removal of the solvent in vacuo gave a white crystalline material. This material was purified by MPLC (2% EtOAc in hexanes) to afford *cis*-1-methyl-3-(trimethylsilyl)cyclohexan-1-ol (**3a**) as a solid (955 mg, 5.13 mmol, 80%) and *trans*-1-methyl-3-(trimethylsilyl)cyclohexan-1-ol (**3b**) as an oil (193 mg, 1.03 mmol, 16%). Compound **3a**: m.p. 62.5–63.0 °C; TLC R_f 0.17 (5% EtOAc in hexanes); ^1H NMR δ 1.90–0.91 (m, 9H), 1.20 (s, 3H, CH_3), −0.04 (s, 9H, $Si(CH_3)_3$; IR(CCl_4) 3605 (m, O–H), 1375 (m, CH_3), 1255 (m, Si–C), 1250 (s, C–O) cm^{-1}; exact mass calc for $C_{10}H_{22}OSi$: 186.1440; found: 186.1422 Compound **3b**: TLC R_f 0.09 (5% EtOAc in hexanes); ^1H NMR δ 1.92–0.84 (m, 9H), 1.23 (s, 3H, CH_3), −0.08 (s, 9H, $Si(CH_3)_3$); IR (neat) 3360 (m, O–H), 1370 (m, CH_3), 1255 (m, Si–C), 1245 (s, C–O) cm^{-1}.

*1-Phenyl-3-(trimethylsilyl)cyclohexan-1-ol (**14a** and **14b**)*

To a suspension of magnesium turnings (302 mg, 12.4 mmol, 5.1 equiv) in ether (10 ml) was added a solution of bromobenzene (1.25 ml, 11.8 mmol, 4.4 equiv) in ether (10 ml) at such a rate as to maintain a gentle reflux. The mixture was further refluxed for 15 min then cooled to 0 °C. To this cooled solution 3-(trimethylsilyl)cyclohexanone [5] (410 mg, 2.40 mmol, 1.0 equiv) in ether (1 ml) was added dropwise over a 5 min period. The solution was stirred at 0 °C for 15 min then warmed slowly to room temperature. The mixture was quenched with water (10 ml) and saturated aqueous NH_4Cl (10 ml), then extracted with ether (3 × 25 ml). The combined ethereal layers were washed with water (1 × 25 ml), saturated NaCl (1 × 25 ml) and dried over anhydrous $MgSO_4$. Filtration and removal of the solvent in vacuo gave a light yellow oil. This material was purified by MPLC (5% EtOAc in hexanes) to afford *cis*-1-phenyl-3-(trimethylsilyl)cyclohexan-1-ol (**14a**) (310 mg, 1.25 mmol, 52%) and *trans*-1-phenyl-3-(trimethylsilyl)cyclohexan-1-ol (**14b**) (160 mg, 0.65 mmol, 27%). Compound **14a**: m.p. 69.5–71.5 °C; TLC R_f 0.32 (5% EtOAc in hexanes); ^1H NMR δ 7.70–7.37 (m, 5H, ArH), 1.84–1.55 (m, 6H), 1.35–1.09 (m, 3H), 0.00 (s, 9H, $Si(CH_3)_3$; IR (CCl_4) 3590 (m, O–H), 3440 (w, O–H), 3050 (w, =CH), 1255 (m, Si–C), 1250 (s, C–O) cm^{-1}; exact mass calc for $C_{15}H_{24}OSi$: 248.1596; found: 248.1592. Compound **14b**: m.p. 71.5–73.5 °C; TLC R_f 0.17 (5% EtOAc in hexanes); ^1H NMR δ 7.49–7.26 (m, 5H, ArH), 2.59–2.40 (m, 2H, CH_2),

1.84–1.12 (m, 7H); 0.00 (s, 9H, $Si(CH_3)_3$); IR(CCl_4) 3600 (m, O–H), 3050 (w, =CH), 1255 (m, Si–C), 1250 (s, C–O) cm^{-1}.

1-Methyl-3-(trimethylsilyl)cyclohex-1-ene (12) and 1-methyl-5-(trimethylsilyl)cyclohex-1-ene (13)

To a solution of oxalyl chloride (160 mg, 1.26 mmol, 2.3 equiv) in dichloromethane (1 ml) at −78 °C was added dimethyl sulfoxide (231 mg, 2.95 mmol, 5.4 equiv). After 5 min a mixture of methylcarbinols **3a** and **3b** (101 mg, 0.54 mmol, 1.0 equiv) in dichloromethane (1 ml) was injected, followed by the addition of triethylamine (65.3 mg, 0.64 mmol, 1.1 equiv). The mixture was warmed to room temperature and the solvent was removed under a stream of nitrogen. Dry acetonitrile (10 ml) was then added and the solution was transferred via a cannula under nitrogen pressure into a flask containing anhydrous powdered CsF [15b] (296.0 mg, 1.90 mmol, 3.5 equiv). The mixture was stirred at room temperature for 13 h, quenched with water (30 ml), and then extracted with ether (3 × 20 ml). The combined ether extracts were washed with water (3 × 20 ml), saturated NaCl (2 × 20 ml), and dried over anhydrous $MgSO_4$. Filtration and removal of the solvent in vacuo provided a yellow oil. The oil was purified by column chromatography (5% EtOAc in hexanes) to give a mixture of cyclohexenylsilanes **12** and **13** (20.0 mg, 0.12 mmol, 22%) as a colorless oil. GC analysis indicates that the ratio of these two compounds is 4.2/1. Compounds **12** and **13**: ^1H NMR δ 5.50–5.10 (br, =CH), 4.80–4.65 (m, =CH), 1.58 (s, 3H, CH_3); 2.30–0.50 (m, 7H), −0.02 (s, 9H, $Si(CH_3)_3$); IR(CCl_4) 3050 (w, =CH), 1440 (w, C=C), 1255 (m, Si–C), 840 (w, =C–H) cm^{-1}; exact mass calc for $C_{10}H_{20}Si$: 168.1335; found: 168.1337.

*1-Phenyl-3-(trimethylsilyl)cyclohex-1-ene (15) and 1-phenyl-5-(trimethylsilyl)cyclohex-1-ene (16) from **14a***

To a solution of oxalyl chloride (72.7 mg, 0.57 mmol, 2.2 equiv) in dichloromethane (2 ml) at −78 °C was added dimethyl sulfoxide (110 mg, 1.40 mmol, 5.4 equiv). After 5 min phenylcarbinol **14a** (66.8 mg, 0.26 mmol, 1.0 equiv) in dichloromethane (1 ml) was injected and the reaction mixture was slowly warmed to room temperature. The reaction mixture was then diluted with dichloromethane (30 ml), washed with water (3 × 20 ml), and dried over anhydrous $MgSO_4$. Filtration and removal of the solvent in vacuo provided a colorless oil. The oil was purified by column chromatography (5% EtOAc in hexanes) to give a mixture of cyclohexenylsilanes **15** and **16** (36.0 mg, 0.15 mmol, 57%) as a colorless oil. GC analysis indicates that the ratio of these two compounds is 3.7/1. Compounds **15** and **16**: TLC R_f 0.87 (5% EtOAc in hexanes); ^1H NMR δ 7.37–7.31 (m, 5H, ArH), 6.20–6.10 (br, 1H, =CH), 2.4–0.50 (m, 7H), 0.03 (s, 9H, $Si(CH_3)_3$); IR(CCl_4) 2990 (w, =CH), 1465 (w, C=C), cm^{-1}; exact mass calc for $C_{15}H_{22}Si$: 230.1491; found: 230.1492.

*1-Phenyl-3-(trimethylsilyl)cyclohex-1-ene (15) and 1-phenyl-5-(trimethylsilyl)cyclohex-1-ene (16) from **14b***

Phenylcarbinol **14b** (40.0 mg, 0.16 mmol, 1.0 equiv), oxalyl chloride (43.6 mg, 0.34 mmol, 2.1 equiv), and dimethyl sulfoxide (66.0 mg, 0.84 mmol, 5.3 equiv) were used in the procedure described above. Purification of the resulting oil by column chromatography (5% EtOAc in hexanes) gave a mixture of cyclohexenylsilanes **15**

and **16** (17.9 mg, 0.08 mmol, 50%) as a colorless oil that exhibited the same ^{1}H NMR and IR behavior as a mixture of **15** and **16** prepared above.

6-Hepten-2-one (4) from 3a

To a solution of methylcarbinol **3a** (65.2 mg, 0.35 mmol, 1.0 equiv) in 50% aqueous acetonitrile (2 ml) was added ceric ammonium nitrate (385 mg, 0.70 mmol, 2.0 equiv) in one portion. The mixture was placed in a pre-heated oil bath (85 °C) for 5 min and then allowed to cool to room temperature. The reaction mixture was extracted with ether (3 × 25 ml); the combined ether extracts were washed with saturated NaCl (1 × 10 ml), 10% aqueous Na_2CO_3 (3 × 10 ml) and dried over anhydrous $MgSO_4$. Filtration and removal of the solvent in vacuo gave a yellow oil. The oil was purified by column chromatography (5% EtOAc in hexanes) to give ketone **4** (34.7 mg, 0.31 mmol, 88%) as a colorless oil [19]: ^{1}H NMR δ 5.90–5.30 (m, 1H, =CH), 5.02–4.89 (m, 2H, $=CH_2$), 2.34 (t, J 6.5 Hz, 2H, CH_2CO), 2.12 (s, 3H, CH_3), 1.94–1.58 (m, 4H, CH_2CH_2); IR(CCl_4) 3065 (w, =CH), 1710 (s, C=O), 1640 (m, C=C), 1365 (m, CH_3), 995 (m, $CH=CH_2$), 915 (m, $CH=CH_2$) cm^{-1}.

6-Hepten-2-one (4) from 3b

Methylcarbinol **3b** (45.8 mg, 0.24 mmol, 1.0 equiv) and ceric ammonium nitrate (265 mg, 0.48 mmol, 2.0 equiv) were used in the procedure described above. The resulting oil was purified by column chromatography (5% EtOAc in hexanes) to give ketone **4** (25.0 mg, 0.22 mmol, 93%) as a colorless oil that exhibited the same ^{1}H NMR and IR behavior as sample **4** prepared above.

1-Phenyl-5-hexen-1-one (17) from 14a

Phenylcarbinol **14a** (41.0 mg, 0.16 mmol, 1.0 equiv) and ceric ammonium nitrate (185.0 mg, 0.33 mmol, 2.0 equiv) were used in the procedure described above. The resulting oil was purified by column chromatography (5% EtOAc in hexanes) to give pure ketone **17** (20.9 mg, 0.12 mmol, 75%) as an oil [20], and a mixture of cyclohexenylsilanes **15** and **16** (3.6 mg, 0.01 mmol, 10%). Compound **17**: TLC R_f 0.80 (5% EtOAc in hexanes); ^{1}H NMR δ 8.01–7.89 (m, 2H, *m*-ArH), 7.56–7.42 (m, 3H, *o,p*-ArH), 6.10–5.67 (m, 1H, =CH), 5.15–4.91 (m, 2H, $=CH_2$), 2.93 (t, J 6.5 Hz, 2H, CH_2CO), 2.21–1.55 (m, 4H, CH_2CH_2); IR(CCl_4) 3060 (w, =CH), 1685 (s, C=O), 1445 (m, C=C), 985 (m, $CH=CH_2$), 915 (m, $CH=CH_2$) cm^{-1}. Compounds **15** and **16** exhibited the same ^{1}H NMR, IR, and TLC behavior as samples of **15** and **16** prepared above.

1-Phenyl-5-hexen-1-one (17) from 14b

Phenylcarbinol **14b** (36.7 mg, 0.14 mmol, 1.0 equiv) and ceric ammonium nitrate (162 mg, 0.29 mmol, 2.0 equiv) were used in the procedure described above. The resulting oil was purified by column chromatography (5% EtOAc in hexanes) to give ketone **17** (21.1 mg, 0.12 mmol, 82%) as an oil, and a mixture of **15** and **16** (5.2 mg, 0.02 mmol, 15%). These compounds exhibited the same ^{1}H NMR, IR, and TLC behavior as samples of **15**, **16**, and **17** as described above.

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