# The Michael Reaction of Silyl Enol Ethers with α,β-Unsaturated Ketones and Acetals in the Presence of Titanium Tetraalkoxide and Titanium Tetrachloride

Koichi NARASAKA, Kenso SOAI, Yukiko AIKAWA, and Teruaki MUKAIYAMA

*Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

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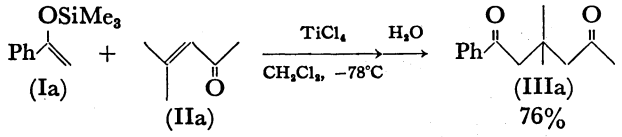
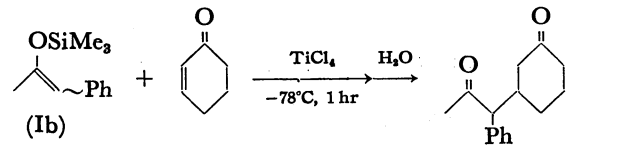
Silyl enol ethers react with α,β-unsaturated ketones and esters in the presence of $TiCl_4$ or in the coexistence of $TiCl_4$ and $Ti(O^i\text{-}Pr)_4$ to give 1,5-dicarbonyl compounds in good yields. The reactions of acetals derived from α,β-unsaturated ketones with silyl enol ethers in the coexistence of $TiCl_4$ and $Ti(O^i\text{-}Pr)_4$, followed by successive addition of 1,2-ethanedithiol, give the Michael products, δ-keto ethylene thioacetal, in good yields. The reaction of silyl enol ethers with acetals derived from α,β-unsaturated aldehydes also gives the Michael products when $Ti(OCEt_3)_4$ is employed instead of $Ti(O^i\text{-}Pr)_4$ in the above experiment and is successfully applied to the simple synthesis of dihydro rose oxide.

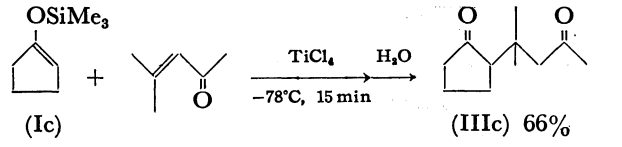
The Michael reaction of silyl enol ethers with various α,β-unsaturated ketones was briefly reported in the previous paper.[1] In this report, the reaction is explained in detail with additional results.

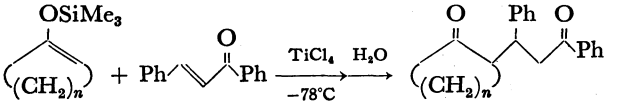
During the investigation on the cross-aldol reaction of silyl enol ethers with carbonyl compounds,[2] it was found that $TiCl_4$-promoted reaction of α,β-unsaturated ketones with silyl enol ethers results in the formation of 1,5-dicarbonyl compounds (the Michael products) instead of aldol products. For example, equimolar amounts of mesityl oxide (IIa) and α-trimethylsiloxystyrene (Ia) were treated with an equimolar amount of $TiCl_4$ in methylene chloride at −78 °C, and the mixture was quenched with aqueous $K_2CO_3$ after 2 min. Following purification by preparative tlc(silica gel), the Michael product, 3,3-dimethyl-1-phenyl-1,5-hexanedione (IIIa), was isolated in 76% yield.



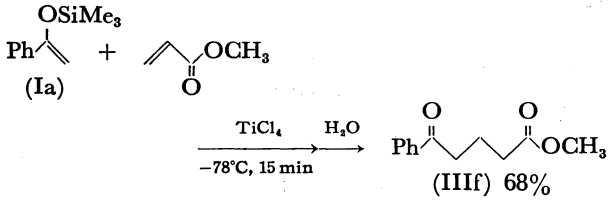

The reactions of various silyl enol ethers with a variety of α,β-unsaturated carbonyl compounds were tried in the presence of an equimolar amount of $TiCl_4$ and the corresponding Michael products were obtained in good yields as shown in the following equations.



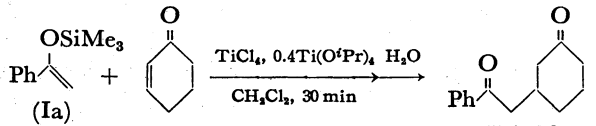



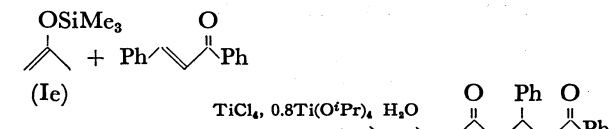



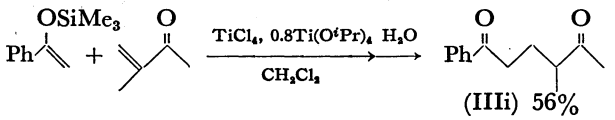

$n=2$ (Ic) $n=2$, 45 min 85% (IIId)
$n=3$ (Id) $n=3$, 60 min 95% (IIIe)




As shown in the above equations, 1,5-dicarbonyl compounds were generally obtained in good yields by the $TiCl_4$-promoted reaction of silyl enol ethers with α,β-unsaturated ketones. When $TiCl_4$-sensitive compounds such as isopropenyl trimethylsilyl ether (Ie) or 2-cyclohexen-1-one and isopropenyl methyl ketone were employed as a nucleophile or the Michael acceptors, the yields of the products became vary low. However, when the same reaction was carried out at −78 °C in the coexistence of $TiCl_4$ and $Ti(O^iPr)_4$, 1,5-diketones (IIIg, h, i) were obtained in fairly good yields.



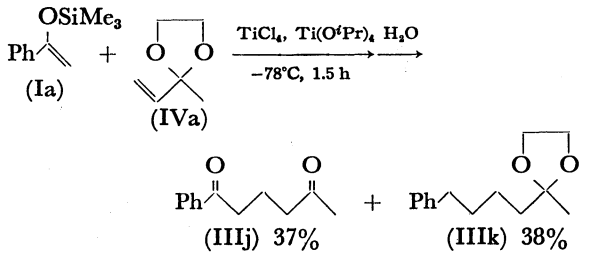



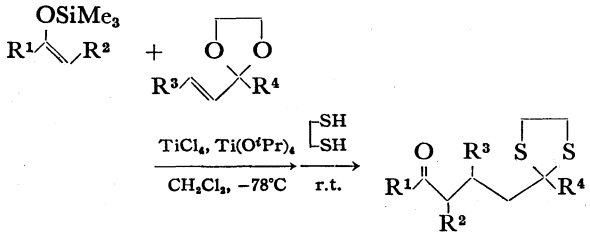

In general, the Michael reaction of an α,β-unsaturated carbonyl compound with a ketone is carried out under basic conditions and the product, a 1,5-dicarbonyl compound, frequently tends to undergo further transformation in the presence of a base.[3] Furthermore, when α,β-unsaturated ketones are used as the Michael acceptors, there are many possibilities leading to a variety of side reactions such as self-condensation reactions and the Michael reaction followed by aldol reaction.[4] On the other hand, a few examples are known concerning the acid catalyzed Michael reaction,

but in these cases, none of the 1,5-dicarbonyl compounds can be isolated bacause of further transformations of initially formed 1,5-dicarbonyl compounds.[5] In contrast to these known methods, the present Michael reaction proceeds under a very mild condition (−78 °C) to afford 1,5-dicarbonyl compounds exclusively without accompanying any by-product.

In addition, an advantage of this acid catalyzed Michael reaction is that an α,β-unsaturated acetal is able to be used as the Michael acceptor. When methyl vinyl ketone ethylene acetal (IVa)[6] was treated with α-trimethylsiloxystyrene (Ia) in the presence of equimolar amounts of $TiCl_4$ and $Ti(O^i\text{-}Pr)_4$ in methylene chloride at −78 °C, 1-phenyl-1,5-hexanedione (IIIj) and its monoacetal (IIIk) were isolated in 37% and 38% yields, respectively, after hydrolysis with aqueous $K_2CO_3$.




However, it was found that the subsequent treatment of the reaction mixture with 1,2-ethanedithiol gives the corresponding δ-keto thioacetal as the Michael product. For example, dropwise addition of a methylene chloride solution of equimolar amounts of Ia and IVa to a mixture of equimolar amounts of $TiCl_4$ and $Ti(O^i\text{Pr})_4$ in methylene chloride at −78 °C followed by stirring at −78 °C for 1 h. After addition of 1,2-ethanedithiol (1.1 molar amount) to the mixture, it was allowed to stand overnight at room temperature. δ-Keto thioacetal (Va) was isolated in 78% yield by preparative tlc (silica gel). Similarly, several δ-keto thioacetals were prepared and, in all cases, the carbonyl group originated from the starting acetal was selectively protected as an ethylene thioacetal.



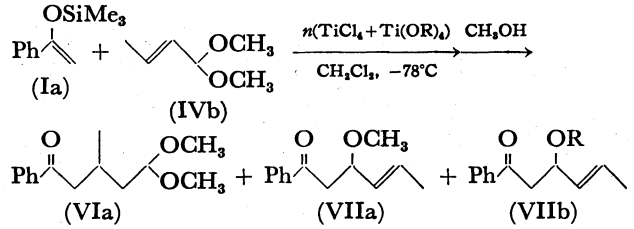

Va: $R^1$=Ph, $R^2$=H, $R^3$=H, $R^4$=Me 78%
Vb: $R^1$=Me, $R^2$=Ph, $R^3$=H, $R^4$=Me 61%
Vc: $R^1$=Ph, $R^2$=H, $R^3$, $R^4$=$-(CH_2)_3-$ 70%
Vd: $R^1$=Me, $R^2$=Ph, $R^3$, $R^4$=$-(CH_2)_3-$ 58%

Acetals derived from α,β-unsaturated aldehydes were also used as the Michael acceptors in order to prepare δ-ketoaldehyde derivatives. The reaction of crotonaldehyde dimethyl acetal (IVb) with α-trimethylsiloxystyrene (Ia) was carried out by using equimolar amounts of $TiCl_4$ and $Ti(O^i\text{Pr})_4$, but the desired Michael product (VIa) was not obtained and the β-alkoxyketones (VIIa, VIIb R=$^i$Pr) were isolated in 83% yield in total after quenching with methanol.

The preferential formation of β-alkoxyketones (VIIa, b) may be attributable to the decrease of steric hindrance around the acetal group as compared with that derived from ketones. According to this assumption, the formation of β-alkoxyketones (VIIa, b) may be suppressed by the use of aldehyde acetal having sterically large alkoxy groups instead of the methoxy group to result in the predominant formation of the Michael product (VIa).

On the other hand, it was found in our laboratory that on treatment with $Ti(O^i\text{Pr})_4$ and $TiCl_4$, 3-phenylpropionaldehyde dimethyl acetal is readily converted into the corresponding diisopropyl acetal at low tem-

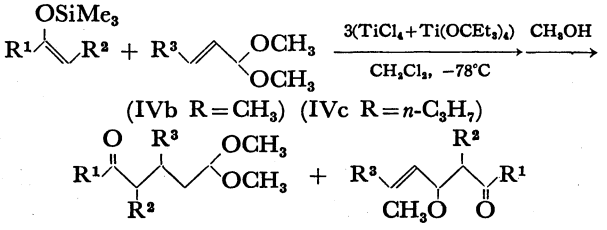
Table 1. Effect of titanium alkoxides

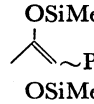
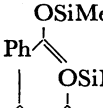



| $Ti(OR)_4$ | $n$ | Yield (%) VIa[a] | VIIa | VIIb |
|---|---|---|---|---|
| $Ti(O^i\text{Pr})_4$ | 1 | 0 | 33 | 50 |
| $Ti(O^t\text{Am})_4$ | 1 | 46 | 28 | 18 |
| | 3 | 59 | 10 | 19 |
| $Ti(OCEt_3)_4$ | 3 | 70 | — | — |

a) The Michael product was isolated as dimethyl acetal since the resulted mixture was quenched with a large amount of methanol.

Table 2. The reaction of silyl enol ethers with aldehyde acetals




| | Silyl enol ether | Acetal $R^3$ | Yield (%) VI | VII |
|---|---|---|---|---|
| b |  | $CH_3$ | 46 | trace |
| c |  | $CH_3$ | 42 | trace |
| d |  | $n$-$C_3H_7$ | 52 | 9 |
| e |  | $n$-$C_3H_7$ | 47[a] | trace |

a) In this case, the reaction mixture was quenched with water instead of methanol, and the product was isolated as aldehyde.

perature,[7] and this fact indicates that an acetal having sterically hindered alkoxy group would be readily prepared *in situ* by the reaction of the corresponding dimethyl acetal with titanium alkoxides such as $Ti(OCEt_3)_4$ and $Ti(O^tAm)_4$[8] derived from sterically hindered alcohols.

Based on this assumption, crotonaldehyde dimethyl acetal (IVb) was treated at −78 °C with $Ti(OCEt_3)_4$ or $Ti(O^tAm)_4$ and $TiCl_4$ prior to the addition of the silyl enol ether (Ia) in order to replace at least one of the methoxy group with sterically hindered alkoxy group originated in $Ti(OCEt_3)_4$ or $Ti(O^tAm)_4$. In fact, it was found that when Ia was added to the above reaction mixture, the Michael product (VIa) predominated over the formation of β-alkoxyketones (VIIa, b) as the steric hindrance of the alkoxy group increased. Especially, when 3 molar amounts of $Ti(OCEt_3)_4$ and $TiCl_4$ were employed, the Michael product (VIa) was isolated almost exclusively as summarized in Table 1.

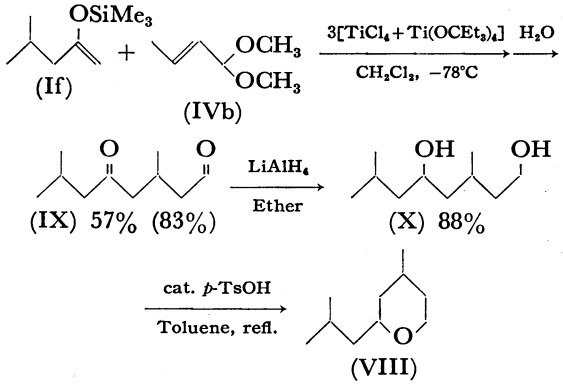
The reactions of crotonaldehyde dimethyl acetal (IVb) and (*E*)-2-hexenal dimethyl acetal (IVc) with several silyl enol ethers were tried using 3 molar amounts of $Ti(OCEt_3)_4$ and $TiCl_4$, and the results are shown in the Table 2.

The present method for the synthesis of δ-keto aldehyde acetal was successfully applied to the simple syn-

Table 3. Physical properties and analytical data of the products

| Product | Physical property Mp, °C | IR, $cm^{-1}$ | NMR, δ | *Anal.* (%) Found, (Calcd) C | H |
|---|---|---|---|---|---|
| IIIa | | 1680 (C=O)<br>1715 (C=O) | 8.00—7.10 (m, 5H, arylCH), 3.09 (s, 2H, $CH_2$), 2.63 (s, 2H, $CH_2$), 1.97 (s, 3H, $CH_3CO$), 1.08 (s, 6H, $CH_3$) | | |
| IIIb | | 1715 (C=O) | 7.25 (s, 5H, arylCH), 3.52 (d, 1H, CH), $J$=9.0 Hz | | |
| IIIc | | 1715 (C=O)<br>1735 (C=O) | 2.91 (d, 1H, $CH_2CO$), $J$=18.0 Hz, 2.33 (d, 1H, $CH_2CO$), $J$=18.0 Hz, 1.00 (s, 3H, $CH_3$), 0.93 (s, 3H, $CH_3$) | 72.38 (72.49) | 10.24 (9.96) |
| IIId | 85 | 1680 (C=O)<br>1735 (C=O) | 8.09—7.00 (m, 10H, arylCH) | 82.36 (82.15) | 6.89 (6.89) |
| IIIe | 128—132 | 1680 (C=O)<br>1710 (C=O) | 8.10—7.10 (m, 10H, arylCH) | 82.52 (82.32) | 7.42 (7.24) |
| IIIf | | 1685 (C=O)<br>1735 (C=O) | 8.12—7.00 (m, 5H, arylCH), 3.60 (s, 3H, $OCH_3$), 2.94 (t, 2H, $CH_2CO$), $J$=6.0 Hz, 2.55—1.55 (m, 4H, $CH_2$) | | |
| IIIg | 75—76 | 1680 (C=O)<br>1720 (C=O) | 8.00—7.40 (m, 5H, arylCH), 2.90 (d, 2H, CHCO), $J$=5.4 Hz | 77.64 (77.75) | 7.56 (7.46) |
| IIIh | 81—82 | 1690 (C=O)<br>1715 (C=O) | 8.00—6.80 (m, 10H, arylCH), 3.80 (m, 1H, CH), 2.00 (s, 3H, $CH_3$), 3.26 (d, 2H, $CH_2$), $J$=6.0 Hz, 2.90 (d, 2H, $CH_2$), $J$=6.0 Hz | 81.27 (81.17) | 7.01 (6.81) |
| IIIi | | 1685 (C=O)<br>1710 (C=O) | 8.00—7.15 (m, 5H, arylCH), 2.08 (s, 3H, $CH_3CO$), 1.08 (d, 3H, $CH_3$), $J$=6.6 Hz | | |
| IIIj | | 1680 (C=O)<br>1715 (C=O) | 8.00—7.10 (m, 5H, arylCH), 2.90 (t, 2H, $CH_2CO$), $J$=6.0 Hz, 2.05 (s, 3H, $CH_3$) | | |
| IIIk | | 1680 (C=O) | 8.00—7.10 (m, 5H, arylCH), 3.85 (s, 4H, $OCH_2CH_2O$), 1.25 (s, 3H, $CH_3$) | | |
| Va | 60—61 | 1690 (C=O) | 8.07—7.30 (m, 5H, arylCH), 3.32 (s, 4H), 1.78 (s, 3H) | | |
| Vb | | 1715 (C=O) | 7.20 (s, 5H, arylCH), 3.20 (s, 4H, $SCH_2CH_2S$), 2.05 (s, 3H, $CH_3CO$) | | |
| Vc | | 1690 (C=O) | 8.30—7.20 (m, 5H, arylCH), 3.30 (s, 4H, $CH_2CH_2$) | | |
| Vd | | 1715 (C=O) | 7.18 (s, 5H, arylCH), 2.00 (s, 3H, $CH_3$) | | |
| VIb | | 1735 (C=O)<br>2820 | 4.35 (m, 1H, CH), 3.22—3.14 (m, 6H, $OCH_3$) | 66.19 (65.97) | 10.20 (10.07) |
| VIc | | 1710 (C=O)<br>2820 | 7.22 (s, 5H, arylCH), 4.40 (t, 1H, CH), 3.25 (s, 6H, $OCH_3$), 1.97 (s, 3H, $CH_3CO$), 0.65 (d, 3H, $CH_3$), $J$=7.2 Hz | | |
| VId | | 1685 (C=O)<br>2820 | 8.01—7.08 (m, 5H, arylCH), 4.38 (t, 1H, CH), $J$=6.0 Hz, 3.18 (s, 3H, $OCH_3$), 3.12 (s, 3H, $OCH_3$), 2.86 (dd, 2H, $COCH_2$) | | |
| VIe | | 1720 (C=O)<br>2715 | 9.67 (t, 1H, CHO) | | |

thesis of dihydro rose oxide (VIII). The reaction of 4-methyl-2-trimethylsiloxy-1-pentene (If) with crotonaldehyde dimethyl acetal (IVb) was carried out using 3 molar amounts of $TiCl_4$ and $Ti(OCEt_3)_4$ at −78 °C in methylene chloride. After hydrolysis, the ketoaldehyde (IX) was obtained in 57% yield (83% when 2 molar amounts of If was employed). Reduction of IX with $LiAlH_4$ in ether readily afforded the corresponding diol (X) in 88% yield and the dehydration of the diol (X) according to literature[9] gave a *cis* and *trans* mixture of dihydro rose oxide (VIII), which was identical by glc analysis with the authentic sample prepared by the hydrogenation of a *cis* and *trans* mixture of rose oxide over palladium.




## Experimental

*Materials.* Commercially available $TiCl_4$ and $Ti(O^iPr)_4$ were distilled under an argon atmosphere before use. Trimethylsilyl enol ethers of carbonyl compounds, α-trimethylsiloxystyrene (Ia), 1-phenyl-2-trimethylsiloxy-1-propene (Ib), 1-trimethylsiloxy-1-cyclopentene (Ic), 1-trimethylsiloxy-1-cyclohexene (Id), were prepared according to the procedures described in the literature[10] and purified by distillation: Ia, bp 89—91 °C/12 mmHg (lit, bp 89—91 °C/12 mmHg); Ib, bp 103 °C/8 mmHg (lit, bp 106 °C/10 mmHg); Ic, bp 155 °C/760 mmHg (lit, bp 158—159 °C/760 mmHg); Id, bp 97—99 °C/65 mmHg (lit, 74—75 °C/20 mmHg). In a similar manner, isopropenyl trimethylsilyl ether (Ie) was prepared from acetone, trimethylsilyl chloride and triethylamine and 4-methyl-2-trimethylsiloxy-1-pentene (If) was prepared from the corresponding ketone, trimethylsilyl chloride and lithium diisopropylamide: Ie, bp 94.5—95.5 °C, NMR($CCl_4$); δ 3.96 (s, 2H, vinyl $CH_2$), δ 1.75 (s, 3H, $CH_3$), δ 0.19 (s, 9H, $Si(CH_3)_3$); If, bp 58—60 °C/35 mmHg, NMR($CCl_4$); δ 3.97(s, 2H, vinyl $CH_2$), δ 0.19(s, 9H, $Si(CH_3)_3$).

*Reaction of α-Trimethylsiloxystyrene (Ia) with Mesityl Oxide (IIa) in the Presence of $TiCl_4$.* A solution of $TiCl_4$ (2 mmol) in 8 ml of $CH_2Cl_2$ was cooled to −78 °C and stirred under an argon atmosphere. A solution of mesityl oxide (IIa, 2 mmol) in $CH_2Cl_2$ (3 ml) and a solution of α-trimethylsiloxystyrene (Ia, 2 mmol) in $CH_2Cl_2$ (3 ml) were added successively to the above solution. After stirring for 2 min at −78 °C, the mixture was quenched with aqueous $K_2CO_3$ (0.7 g in 15 ml of water), and resulting precipitate was filtered off. The filtrate was extracted with ether and the extract was washed with water and brine. After removal of the solvent, 3,3-dimethyl-1-phenyl-1,5-hexanedione (IIIa, 76%) was separated by preparative tlc (silica gel) using hexane–ether 2: 1) as eluent.

*Reaction of α-Trimethylsiloxystyrene (Ia) with 2-Cyclohexen-1-one in the Presence of $TiCl_4$ and $Ti(O^iPr)_4$.* To a $CH_2Cl_2$ (4 ml) solution of $TiCl_4$ (1.0 mmol) and $Ti(O^iPr)_4$ (0.4 mmol) [$TiCl_4$ and $Ti(O^iPr)_4$ must be mixed at −78 °C] was added a mixture of α-trimethylsiloxystyrene (Ia, 1.0 mmol) and 2-cyclohexen-1-one (1.0 mmol) in $CH_2Cl_2$ (6 ml) at −78 °C with stirring under an argon atmosphere. After being stirred for 30 min, the mixture was hydrolyzed with 12 ml of aqueous $K_2CO_3$ (0.75 g) and extracted with ether. The extract was washed with brine, dried over anhydrous $Na_2SO_4$ and condensed under reduced pressure. By preparative tlc (silica gel), 3-phenacylcyclohexan-1-one (IIIg) was isolated in 70% yield.

*Reaction of α-Trimethylsiloxystyrene (Ia) with Methyl Vinyl Ketone Ethylene Acetal (IVa).* To a $CH_2Cl_2$ (4 ml) solution of $TiCl_4$ (1.0 mmol) and $Ti(O^iPr)_4$ (1.0 mmol) was added a mixture of α-trimethylsiloxystyrene (Ia, 1.0 mmol) and methyl vinyl ketone ethylene acetal (IVa, 1.0 mmol) in $CH_2Cl_2$ (6 ml) at −78 °C with stirring under an argon atmosphere. After stirring the mixture for 1 h, 1,2-ethanedithiol (1.1 molar amounts) was added to the mixture. After being allowed to stand overnight at room temperature, the mixture was quenched with aq. $K_2CO_3$ (0.7 g in 15 ml of water) and the resulting precipitate was filtered off. The filtrate was extracted with ether and the extract was washed with water and brine, dried over anhydrous $Na_2SO_4$. After removal of the solvent δ-keto thioacetal (Va, 78%) was isolated by preparative tlc (silica gel) using hexane–ether (2: 1) as eluent. The structure was also established by hydrolysis in the presence of $CuCl_2$[11] to 1-phenylhexane-1,5-dione.

*Reaction of α-Trimethylsiloxystyrene (Ia) with Crotonaldehyde Dimethyl Acetal (IVb).* To a mixture of $Ti(OCEt_3)_4$(3 mmol) and crotonaldehyde dimethyl acetal (1 mmol) in $CH_2Cl_2$ (6 ml) was added $TiCl_4$ (3 mmol) in 2 ml of $CH_2Cl_2$ under an argon atmosphere. After stirring the mixture for 6 min, α-trimethylsiloxystyrene (Ia, 1 mmol in 3 ml of $CH_2Cl_2$) was added. The mixture was stirred for 1 h, treated with 3 ml of MeOH at 0 °C for 30 min and worked-up in the usual manner. After separation by preparative TLC (silica gel), 5,5-dimethoxy-3-methyl-1-phenylpentan-1-one (VIa) was isolated in 70% yield. (VIa: NMR($CCl_4$): δ 0.98 (d, 3H), δ 3.17 (s, 3H), δ 3.20 (s, 3H), δ 4.41 (t, 1H): IR; 2820, 1685 $cm^{-1}$).

*3,5-Dimethyl-5-oxooctanal (IX).* To a mixture of 3 mmol of $Ti(OCEt_3)_4$ and crotonaldehyde dimethyl acetal (1 mmol) in $CH_2Cl_2$ (6 ml) was added $TiCl_4$ (3 mmol) in 2 ml of $CH_2Cl_2$ at −78 °C under an argon atmosphere. After stirring the mixture for 6 min 4-methyl-2-trimethylsiloxy-1-pentene (If, 1 mmol in 3 ml $CH_2Cl_2$) was added. The mixture was stirred for 1 h, followed by hydrolysis with aq. $K_2CO_3$ (0.75 g in 12 ml of water), and extracted with ether. The extract was washed with brine, dried over anhydrous $Na_2SO_4$ and condensed under reduced pressure. 3,7-Dimethyl-5-oxooctanal (IX) was isolated in 57% (83% when 2 equimolar amounts of If was employed) by preparative tlc (silica gel) using hexane–ether (2: 1) as eluent. (IX: NMR ($CCl_4$); δ 9.72 (t, 1H): IR; 2725, 1725, 1715 $cm^{-1}$).

*3,7-Dimethyl-1,5-octanediol (X).* To a suspension of $LiAlH_4$ (2.4 mmol) in $Et_2O$ (16 ml) was added a $Et_2O$ (12 ml) solution of 3,7-dimethyl-5-oxooctanal (IX, 1.19 mmol) in 7 min at 0 °C. After stirring the mixture for 1 h at room temperature, saturated aqueous solution of $Na_2SO_4$ was added into the mixture. The resulted precipitate was washed with THF (5 ml×3) by decantation. The THF–$Et_2O$ solution was dried over anhydrous $Na_2SO_4$. Distillation under reduced pressure gave 3,7-dimethyl-1,5-octanediol (X, 88%). (X: NMR ($CCl_4$); δ 4.49 (s (broad), 2H), δ 3.40—4.40 (m, 3H), δ 0.79—2.20 (m, 15H): IR; 3330, 1370, 1380 $cm^{-1}$).

*Dihydro Rose Oxide (VIII).* Dehydration of 3,7-dimethyl-1,5-octanediol (X) according to literature[9] method gave a *cis* and *trans* mixture of dihydro rose oxide (VIII), which was identical by glc analysis with the authentic sample prepared by the hydrogenation of a *cis* and *trans* mixture of rose oxide over palladium catalyst.

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