Convenient Synthesis of Jasmonoid Compounds from γ-(Trimethylsiloxy)butyronitrile

Isamu Matsuda,* Shizuaki Murata, and Yusuke Izumi

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya, 464 Japan

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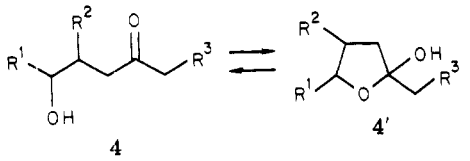
1,4-Dioxygenated compounds **4** are constructed by the addition of a Grignard reagent to γ-(trimethylsiloxy)nitriles **1**, **2**, and **3** and subsequent hydrolysis. Oxidation of **4** with pyridinium chlorochromate or Jones reagent yields compounds **5** which are used to produce cyclopentenones **6**. Methyl jasmonate and methyl dihydrojasmonate are made by the conjugate addition of silylated ketene acetal **9** to **6a** and **6b**, respectively, and subsequent protodesilylation. γ-Jasmolactone is also derived from **4a** by oxidation with pyridinium dichromate in DMF followed by reduction with $NaBH_4$ in ethanol.

γ-(Trimethylsiloxy)nitrile derivatives are attractive compounds as 1,4-bifunctional units.[1,2] For example, the addition of a Grignard reagent to the cyano group can result in 1,4-dioxygenated compounds after subsequent hydrolysis. While the most popular acetate synthon is diethyl malonate, this compound requires relatively tedious procedures, saponification, decarboxylation, and esterification, after the homologation. Therefore, it is advantageous to exploit a more straightforward reagent than diethyl malonate.

We previously reported a facile synthesis of *cis*-jasmone and dihydrojasmone via 1,4-diketones constructed from γ-(trimethylsiloxy)valeronitrile (**2**) and *cis*-1-bromo-3-hexene or 1-bromohexane.[3] In order to demonstrate the versatility of this method, the present paper will report a convenient synthesis of γ-jasmolactone (**8**), methyl jasmonate (**13a**), and methyl dihydrojasmonate (**13b**) starting from γ-(trimethylsiloxy)butyronitrile (**1**), coupled with exploitation of *O*-methyl-*C*,*O*-bis(trimethylsilyl)ketene acetal (**9**) as a methyl acetate anion equivalent.

Acetonitrile anion generated from acetonitrile and lithium diisopropylamide (LDA) reacted with 1 equiv of ethylene oxide, propylene oxide, and cyclohexene oxide in THF to give **1**, **2**, and **3**, after quenching with an excess of chlorotrimethylsilane, in good yields as shown in Scheme I.

The general sequence for the preparation of cyclopentenones **6** is outlined in Scheme II, which includes the addition of a Grignard reagent to the cyano group as the homologation step. Since γ-hydroxy ketones **4** are in an equilibrium with hemiacetal **4'**,[4] the separation of both comounds was not carried out.

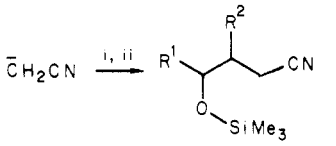


4 **4'**

Crude compounds **4** were oxidized with pyridinium chlorochromate[5] (for **4a** and **4b**) or with Jones reagent (for **4c**, **4d**, and **4e**), giving 1,4-dicarbonyl compounds **5** in yields of 36–77% from γ-(trimethylsiloxy)nitriles. The intramolecular aldol condensation of **5** gave cyclopentenones **6** under basic conditions.

On the other hand, primary γ-keto alcohol **4a** was oxidized to γ-keto carboxylic acid **7** with pyridinium dichromate in *N*,*N*-dimethylformamide.[6] The γ-keto acid **7** was transformed to γ-jasmolactone (**8**) in a good yield by the reduction of the carbonyl group with sodium borohydride in ethanol and subsequent acidification.

Scheme I[a]



1, R^1 = H; R^2 = H
2, R^1 = Me; R^2 = H
3, R^1, R^2 = -$(CH_2)_4$-

[a] (i) $R^1CH{-}CHR^2$ (ii) Me_3SiCl.

Both **6a** and **6b** represent key intermediates in the jasmonic ester synthesis in which diethyl malonate[7] or a ketene *N*,*O*-acetal derivative[8] is used as a methyl acetate synthon. *O*-Methyl-*O*-(trimethylsilyl)ketene acetal is an ideal synthon for completion of the jasmonic ester synthesis, since it has been reported that O-silylated ketene acetal derivatives react with α,β-unsaturated carbonyl compounds to give 1,4-addition products.[9] However, the quenching of methyl acetate anion with chlorotrimethylsilane gave a mixture of C- and O-silylated products.[10] The product quenched with *tert*-butylchlorodimethylsilane could not be purified by distillation.[11] Therefore, a new compound, *O*-methyl-*C*,*O*-bis(trimethylsilyl)ketene acetal (**9**), was prepared as a desired methyl acetate synthon by quenching methyl (trimethylsilyl)acetate anion with chlorotrimethylsilane. The acetal **9** was a mixture of *E* and *Z* stereoisomers which were assigned and evaluated in the ratio of approximately 3:1 by the NMR spectrum. The formation of **9** was also confirmed by the combustion analysis.

Silylketene acetal **9** behaved as a highly reactive nucleophile toward α,β-unsaturated carbonyl compounds. 2-Cyclohexen-1-one was readily homologated to the acetate **11** by treatment with titanium tetrachloride and **9** (CH_2Cl_2, −78 °C, 2 h) in 70% yield followed by hydrolysis and protodesilylation.

Addition of silylketene acetal **9** to the cyclopentenone **6a** which was activated with titanium tetrachloride in

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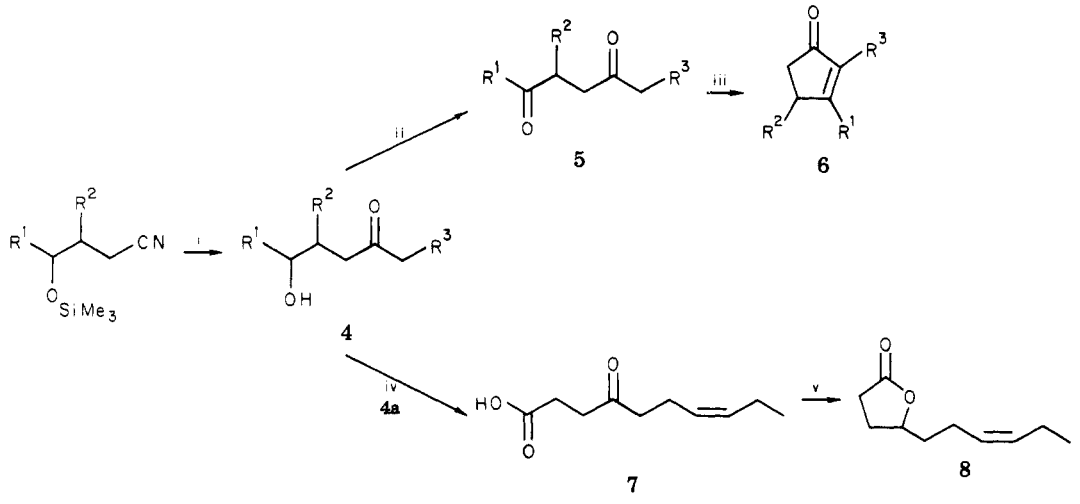
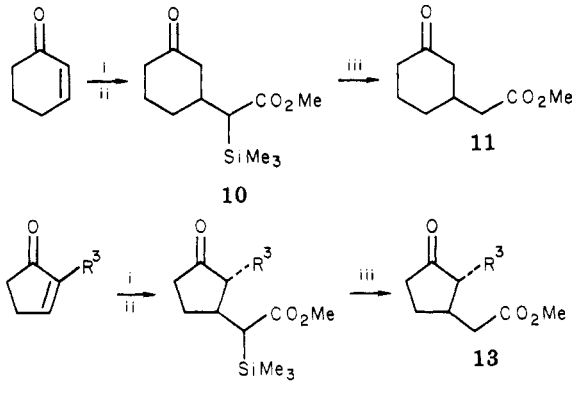
Scheme II[a]



a, R^1 = H; R^2 = H; R^3 = *cis*-2-pentenyl
b, R^1 = H; R^2 = H; R^3 = pentyl
c, R^1 = Me; R^2 = H; R^3 = 2-propenyl
d, R^1 = Me; R^2 = H; R^3 = 3-chloropropyl
e, R^1, R^2 = $-(CH_2)_4-$; R^3 = H

[a] (i) R^3CH_2MgBr/Et_2O. (ii) PCC/CH_2Cl_2 (**4a** and **4b**) or Jones reagent (**4c**, **4d**, and **4e**). (iii) $KOH/H_2O/THF/Et_2O$ (**5a** and **5b**) or KOH/aqueous EtOH (**5c** and **5e**). (iv) PDC/DMF. (v) $NaBH_4$/EtOH.

Scheme III[a,b]



[a] a, R^3 = *cis*-2-pentenyl; b, R^3 = pentyl. [b] (i) $TiCl_4$, $9/CH_2Cl_2$, −78 °C. (ii) Aqueous K_2CO_3. (iii) KF/aqueous MeOH, room temperature.

methylene chloride afforded the keto ester **12a** in 94% yield after quenching the reaction mixture with aqueous potassium carbonate. An analogous reaction of **9** with **6b** gave **12b** in 95% yield. (Trimethylsilyl)acetate derivatives **12a** and **12b** were transformed to methyl jasmonate (**13a**, 90%) and methyl dihydrojasmonate (**13b**, 89%), respectively, by protodesilylation using potassium fluoride in aqueous methanol. The properties of **13a** and **13b** were identical with those reported.[7,12]

In conclusion, the present method offers a convenient synthetic route to γ-jasmolactone, methyl jasmonate, and methyl dihydrojasmonate through a relatively short reaction path from γ-(trimethylsiloxy)butyronitrile (**1**) under mild conditions. Especially, silylketene acetal **9** contributes to the simplification of the procedure and the increased yields in the synthesis of **13a** and **13b**.

Experimental Section

Boiling points are uncorrected. NMR spectra were recorded on a JEOL C-60HL instrument using tetramethylsilane as an internal standard. IR spectra were run on a JASCO IR-403G and IR-S instruments. 4-(Trimethylsiloxy)valeronitrile (**2**)[3] and *cis*-1-bromo-3-hexene[13] were prepared according to the literature.

4-(Trimethylsiloxy)butyronitrile (1). According to the previous paper,[3] 10.7 g (68%) of nitrile **1** was obtained as a colorless liquid from acetonitrile (4.10 g, 0.10 mol), ethylene oxide (5.2 mL), and chlorotrimethylsilane (17 g, 0.157 mol): bp 67–69 °C (10 mm); IR (CCl_4) 2270 (C≡N), 1249 cm^{-1} (SiC_3); NMR (CCl_4) δ 0.10 (s, 9 H, H_3CSi), 1.78 (quintet, J = 6.3 Hz, 2 H, CH_2CH_2CN), 2.35 (t, J = 6.8 Hz, 2 H, CH_2CN), 3.52 (t, J = 5.9 Hz, 2 H, CH_2O).

Anal. Calcd for $C_7H_{15}NOSi$: C, 53.45; H, 9.61; N, 8.91. Found: C, 53.60; H, 9.56; N, 8.99.

***trans*-2-(Cyanomethyl)-1-(trimethylsiloxy)cyclohexane (3).** A crude product obtained from acetonitrile (1.20 g, 25.0 mmol), cyclohexene oxide (2.47 g, 25.3 mmol), and chlorotrimethylsilane (4 mL) was distilled to give 3.95 g (75%) of **3** as a colorless liquid: bp 83–85 °C (0.3 mm); IR (CCl_4) 2250 (C≡N), 1252 (SiC_3) cm^{-1}; NMR (CCl_4) δ 0.13 (s, 9 H, H_3Si), 1.0–2.0 (m, 10 H, cyclohexyl ring protons), 2.36 (d, J = 4.5 Hz, 2 H, CH_2CN), 3.3 (br, 1 H, CHO).

Anal. Calcd for $C_{11}H_{21}NOSi$: C, 59.77; H, 10.33; N, 4.10. Found: C, 59.67; H, 10.30; N, 4.33.

Methyl (Trimethylsilyl)acetate. Methyl bromoacetate (76.3 g, 0.50 mol), chlorotrimethylsilane (60 g, 0.56 mol), and zinc powder (35 g, 0.54 mol) gave 31 g (42%) of methyl (trimethylsilyl)acetate as a colorless liquid by the similar procedure to the case of ethyl (trimethylsilyl)acetate.[14] For methyl (trimethylsilyl)acetate: bp 65–68 °C (50 mm); IR (CCl_4) 1728 (C=O) cm^{-1}; NMR (CCl_4) δ 0.12 (s, 9 H, H_3CSi), 1.79 (s, 2 H, CH_2), 3.53 (s, 3 H, H_3CO).

Synthesis of 1,4-Diketones (5): 4-Oxo-*cis*-7-decenal (5a). To a solution of *cis*-3-hexenylmagnesium bromide (40.2 mmol), formed from magnesium (0.977 g, 40.2 mmol) and *cis*-1-bromo-3-hexene (6.84 g, 41.9 mmol) in 55 mL of ether, and 35 mL of benzene was added **1** (3.11 g, 19.8 mmol) in 8 mL of ether at room temperature. The reaction mixture was stirred for 22 h and

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hydrolyzed with 60 mL of 1 M HCl for 2 h at room temperature. The phases were separated, and the aqueous phase was extracted with dichloromethane (6 × 30 mL). The combined organic portions were washed with water (2 × 50 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to yield 3.03 g of crude **4a** (90%) as a colorless liquid: IR (CCl_4) 3610, 3400 (OH), 1720 (C=O) cm^{-1}.

To a suspension of pyridinium chlorochromate (5.75 g, 26.7 mmol) in 45 mL of dichloromethane was added crude **4a** (3.03 g) in 5 mL of dichloromethane in one portion. After being stirred for 1.5 h at room temperature, the black reaction mixture was diluted with 45 mL of anhydrous ether. The solvent was decanted, and the black solid was washed with ether (3 × 15 mL). The organic portions were filtered through a short pad of Florisil and concentrated under reduced pressure. The residual liquid was purified by column chromatography on silica gel using a mixed solvent (C_6H_6/hexane/EtOH, 40/40/1) as an eluent to give 2.39 g (72% from **1**) of **5a** as a colorless liquid: bp 62–65 °C (2 mm); spectral data were identical with those in the literature.[15]

1-Chloro-5,8-nonanedione (5d). To an acetone (18 mL) solution of crude **4d** (1.06 g, 66%) obtained from 4-chlorobutylmagnesium bromide (12.5 mmol) and **2** (1.72 g, 10.0 mmol) was added a slight excess of Jones reagent at 0 °C. The mixture was stirred for 15 min at room temperature, and the excess Jones reagent was decomposed with a few drops of 2-propanol. After neutralization of the mixture with saturated aqueous sodium carbonate, the phases were separated by decantation, and the residue was washed with acetone (3 × 20 mL). To the concentrated residue of the combined organic portions, water (50 mL) was added, and the solution was extracted with dichloromethane (7 × 20 mL). The combined extracts were washed with saturated brine (30 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual oil was chromatographed on silica gel by using a mixed solvent (C_6H_6/hexane/EtOH, 40/40/1) as an eluent to give 0.695 g (36% from **2**) of **5d** as a colorless oil: IR (CCl_4) 1720 (C=O) cm^{-1}; NMR (CCl_4) δ 1.72 (quintet, J = 4.5 Hz, 4 H, 2 methylenes), 2.12 (s, 3 H, H_3CC=O), 2.47 (t, J = 6.0 Hz, 2 H, H_2CC=O), 2.58 (s, 4 H, O=CCH_2CH_2C=O), 3.49 (t, J = 6.5 Hz, 2 H, H_2CCl).

Anal. Calcd for $C_9H_{15}O_2Cl$: C, 56.69; H, 7.93. Found: C, 56.63; H, 8.07.

4-Oxodecanal (5b,[15] 77%), 8-nonene-2,5-dione (5c, 47%), and 2-(2-oxopropyl)cyclohexan-1-one (5e,[4] 54%) were obtained by similar procedures. Spectral data were identical with those in the literature.

Anal. Calcd for $C_9H_{14}O_2$ (**5c**): C, 70.10; H, 9.15. Found: C, 69.85; H, 9.25. Calcd for $C_9H_{14}O_2$ (**5e**): C, 70.10; H, 9.15. Found: C, 70.03; H, 8.89.

Intramolecular Aldol Condensation of 1,4-Dicarbonyl Compounds 5. 2-(*cis*-2-Pentenyl)-2-cyclopenten-1-one (6a). To a solution of potassium hydroxide (1.09 g, 17.8 mmol) in 20 mL of water, 20 mL of THF, and 40 mL of ether was added **5a** (1.65 g, 9.78 mmol). The reaction mixture was refluxed for 10 h and then stirred for 36 h at room temperature. After neutralization with 1 M HCl (20 mL), the phases were separated, and the aqueous phase was extracted with ether (5 × 20 mL). The combined organic portions were washed with saturated brine (2 × 40 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual oil was chromatographed on silica gel by using a mixed solvent (C_6H_6/hexane/AcOEt, 46/46/6) as an eluent to give 1.26 g (86%) of **6a** as a colorless liquid. Spectral data were identical with those in the literature.[15]

Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 79.90; H, 9.62.

2-Pentyl-2-cyclopenten-1-one (6b,[12b] 71%), 3-methyl-2-(2-propenyl)cyclopenten-1-one (6c,[16] 81%), and 1,4,5,6,7,7a-hexahydro-2*H*-inden-2-one (6e,[4] 69%) were obtained by similar procedures. Spectral data were identical with those in the literature.

Anal. Calcd for $C_{10}H_{16}O$ (**6b**): C, 78.89; H, 10.59. Found: C, 78.65; H, 10.67. Calcd for $C_9H_{12}O$ (**6c**): C, 79.37; H, 8.88. Found: C, 79.48; H, 9.08. Calcd for $C_9H_{12}O$ (**6e**): C, 79.37; H, 8.88. Found: C, 79.30; H, 8.81.

Synthesis of (*Z*)-γ-Jasmolactone (8). To a solution of pyridinium dichromate (3.88 g, 10.3 mmol) in 9 mL of DMF was added **4a** (0.287 g, 1.69 mmol) at room temperature. After being stirred for 18 h at room temperature, the solution was poured into 70 mL of water. The organic materials were extracted with ether (5 × 20 mL). The combined extracts were washed with brine (2 × 20 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual crude **7** (0.290 g, 93%) was obtained as a colorless liquid: IR (CCl_4) 1723 (sh, C=O), 1714 (C=O) cm^{-1}.

To a solution of crude **7** (0.283 g, 1.54 mmol) in 10 mL of ethanol was added sodium borohydride (0.117 g, 3.10 mmol). The mixture was stirred for 3 h at room temperature and then acidified with 10 mL of 1 M HCl. After being stirred for 1.5 h, the mixture was poured into 40 mL of water and extracted with ether (5 × 20 mL). The combined extracts were washed with saturated brine (2 × 20 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual colorless oil was chromatographed on silica gel by using a mixed solvent (C_6H_6/hexane/AcOEt, 47/47/5) as an eluent to give 0.185 g (71%) of **8** as a colorless oil: bp 120 °C (0.1 mm) (Kugelrohr distillation); IR (CCl_4)[17] 1787 (C=O) cm^{-1}; NMR (CCl_4)[17] δ 0.97 (t, J = 7.4 Hz, 3 H, H_3CC), 1.4–2.6 (m, 10 H), 4.40 (quintet, J = 6.0 Hz, 1 H, HCO), 5.05–5.65 (m, 2 H, olefinic protons).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.12; H, 9.70.

Preparation of *O*-Methyl-*C*,*O*-bis(trimethylsilyl)ketene Acetal (9). To a THF solution (260 mL) of lithium diisopropylamide generated from butyllithium (0.218 mol) and diisopropylamine (22.4 g, 0.222 mol) was added methyl (trimethylsilyl)acetate (23.0 g, 0.157 mol) at −78 °C. After being stirred for 3.5 h at −78 °C, the reaction mixture was quenched with an excess of chlorotrimethylsilane (28.3 g, 0.260 mol) at the same temperature. The mixture was stirred for 1.5 h at room temperature and concentrated under reduced pressure. Distillation of the residual liquid yielded 27.8 g (81%) of **9** as a colorless liquid: bp 40–41 °C (0.5 mm); IR (CCl_4) 1612 (C=C), 1252 (SiC_3) cm^{-1}; NMR (CCl_4) major isomer δ −0.01 (s, 9 H, H_3CSiO), 0.25 (s, 9 H, H_3CSiC), 2.95 (s, 1 H, HC=C), 3.46 (s, 3 H, H_3CO); minor isomer δ 0.01 (s, 9 H, H_3CSiO), 0.19 (s, 9 H, H_3CSiC), 2.86 (s, 1 H, HC=C), 3.51 (s, 3 H, H_3CO).

Anal. Calcd for $C_9H_{22}O_2Si_2$: C, 49.49; H, 10.15. Found: C, 49.25; H, 9.98.

1,4-Addition of 9 to α,β-Unsaturated Ketones. 3-[(Methoxycarbonyl)(trimethylsilyl)methyl]cyclohexan-1-one (10). To a solution of 2-cyclohexen-1-one (0.893 g, 9.29 mmol) in 23 mL of dichloromethane was added titanium tetrachloride (1.8 g, 9.52 mmol) at −78 °C. Three minutes later, **9** (2.09 g, 9.59 mmol) in 3 mL of dichloromethane was added to the mixture within 5 min at the same temperature. The dark red mixture was stirred for 2 h and hydrolyzed with aqueous potassium carbonate (15 mL of a 1.7 M solution) at −78 °C. The resultant mixture was stirred for 10 min at room temperature and extracted with ethyl acetate (4 × 30 mL). The combined extracts were washed with saturated brine (2 × 40 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual oily liquid was chromatographed on silica gel by using a mixed solvent (C_6H_6/hexane/AcOEt, 46/46/8) as an eluent to give 1.79 g (79%) of **10** as a colorless liquid: bp 105 °C (0.1 mm) (Kugelrohr distillation); IR (CCl_4) 1721 (C=O), 1252 (SiC_3) cm^{-1}; NMR (CCl_4) δ 0.11 (s, 9 H, H_3CSi), 1.4–2.3 (m, 10 H), 3.57 (s, 3 H, H_3CO).

Anal. Calcd for $C_{12}H_{22}O_3Si$: C, 59.46; H, 9.15. Found: C, 59.57; H, 9.04.

Protodesilylation of **10** was accomplished as follows. A 20% aqueous methanol solution (50 mL) of **10** (1.68 g, 6.91 mmol) and potassium fluoride (0.72 g, 12.4 mmol) was stirred for 6 h at room temperature. The resultant mixture was concentrated under reduced pressure and extracted with dichloromethane (5 × 30 mL). The combined extracts were washed with water (2 × 30 mL), dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residual oil was chromatographed on silica gel by

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using a mixed solvent (C_6H_6/hexane/AcOEt, 47/47/5) as an eluent to give 1.04 g (88%) of **11** as a colorless oil: IR (CCl_4) 1743 (C=O), 1720 (C=O) cm^{-1}; NMR (CCl_4) δ 1.3–2.4 (m, 11 H), 3.62 (s, 3 H, H_3CO).

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.58; H, 8.36.

***trans*-2-(*cis*-2-Pentenyl)-3-[(methoxycarbonyl)(trimethylsilyl)methyl]cyclopentan-1-one (12a).** Analytically pure **12a** (1.08 g, 94%) was obtained as a colorless oil by an analogous reaction of **9** (1.31 g, 5.99 mmol) with **6a** (0.583 g, 3.89 mmol) activated by titanium tetrachloride (0.83 g, 4.35 mmol) in 20 mL of dichloromethane: bp 120 °C (0.1 mm) (Kugelrohr distillation); IR (CCl_4) 1744 (C=O), 1723 (C=O), 1252 (SiC_3) cm^{-1}; NMR (CCl_4) δ 0.12 (s, 9 H, H_3CSi), 0.95 (t, J = 7.7 Hz, 3 H, H_3CC), 1.8–2.3 (m, 11 H), 3.59 (s, 3 H, H_3CO), 5.29 (m, 2 H, vinyl protons).

Anal. Calcd for $C_{16}H_{28}O_3Si$: C, 64.82; H, 9.52. Found: C, 64.57; H, 9.66.

Protodesilylation of **12a** (0.585 g, 1.98 mmol) in a 20% aqueous methanol solution (20 mL) of potassium fluoride (0.255 g, 4.39 mmol) gave 0.398 g (90%) of methyl jasmonate (**13a**) as a colorless oil by a procedure analogous to that for **10**. For **13a**: IR (CCl_4) 1744 (C=O) cm^{-1}; NMR ($CDCl_3$) δ 0.96 (t, J = 7.2 Hz, 3 H, H_3CC), 1.8–3.0 (m, 12 H), 3.70 (s, 3 H, H_3CO), 5.38 (m, 2 H, vinyl protons).

Anal. Calcd for $C_{13}H_{20}O_3$: C, 69.61; H, 8.99. Found: C, 69.93; H, 9.21.

***trans*-2-Pentyl-3-[(methoxycarbonyl)(trimethylsilyl)methyl]cyclopentan-1-one (12b).** Analytically pure **12b** (0.746 g, 95%) was obtained as a colorless oil by an analogous reaction of **9** (0.807 g, 3.69 mmol) with **6b** (0.402 g, 2.64 mmol) activated by titanium tetrachloride (0.52 g, 2.74 mmol) in 15 mL of dichloromethane: bp 120 °C (0.1 mm) (Kugelrohr distillation); IR (CCl_4) 1743 (C=O), 1722 (C=O), 1252 (SiC_3) cm^{-1}; NMR (CCl_4) δ 0.14 (s, 9 H, H_3CSi), 0.89 (t, J = 5.3 Hz, 3 H, H_3CC), 1.2–2.8 (m, 15 H), 3.62 (s, 3 H, H_3CO).

Anal. Calcd for $C_{16}H_{30}O_3Si$: C, 64.38; H, 10.13. Found: C, 64.31; H, 10.06.

Protodesilylation of **12b** (0.287 g, 0.961 mmol) in 20% aqueous methanol solution (15 mL) of potassium fluoride (0.26 g, 4.47 mmol) gave 0.193 g (89%) of methyl dihydrojasmonate (**13b**) as a colorless oil by a procedure analogous to that for **10**.

When **12b** was immediately desilylated without purification, **13b** was obtained in quantitative yield: IR (CCl_4) 1744 (C=O) cm^{-1}; NMR (CCl_4) δ 0.86 (t, J = 4.5 Hz, 3 H, H_3CC), 1.1–2.5 (m, 16 H), 3.58 (s, 3 H, H_3CO).

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.28; H, 10.07.

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Registry No. **1**, 72049-81-1; **2**, 66408-81-9; **3**, 72049-82-2; **4a**, 72049-83-3; **4d**, 72049-84-4; **5a**, 41031-87-2; **5b**, 43160-78-7; **5c**, 5312-86-7; **5d**, 72049-85-5; **5e**, 6126-53-0; **6a**, 41031-88-3; **6b**, 25564-22-1; **6c**, 3569-36-6; **6e**, 39163-29-6; **7**, 72049-86-6; **8**, 63095-33-0; **9**, 32583-40-7; **10**, 72049-87-7; **11**, 2808-12-0; **12a**, 72049-88-8; **12b**, 72049-89-9; **13a**, 1211-29-6; **13b**, 29852-02-6; *cis*-1-bromo-3-hexene, 5009-31-4; acetonitrile, 75-05-8; chlorotrimethylsilane, 75-77-4; ethylene oxide, 75-21-8; cyclohexene oxide, 286-20-4; methyl (trimethylsilyl)acetate, 2916-76-9; methyl bromoacetate, 96-32-2; 4-chlorobutyl bromide, 6940-78-9; lithium diisopropylamide, 4111-54-0; 2-cyclohexen-1-one, 930-68-7.

Arynic Condensations of Ketone Enolates. 15.[1] New Synthetic Applications of the Condensation of α,β-Unsaturated Ketone Enolates on Benzyne

Munir Essiz, Gérald Guillaumet, Jean-Jacques Brunet, and Paul Caubere*

Laboratoire de Chimie Organique I, ERA CNRS No. 476, Université de Nancy I, Case Officielle 140, 54037 Nancy Cédex, France

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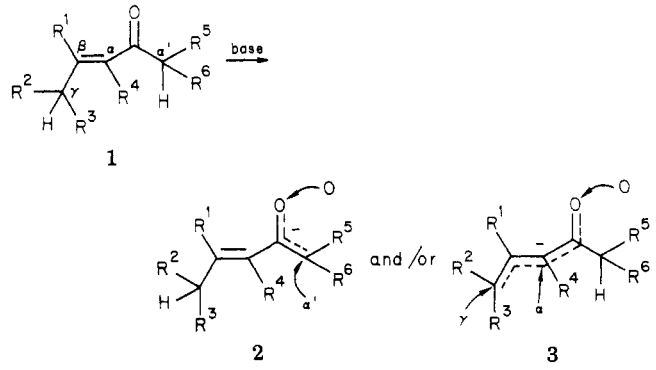
Arynic condensations of both cyclic and acyclic α,β-unsaturated ketone enolates are studied. First, condensation of substituted cyclohexenone enolates with benzyne leads to a new class of cyclobutanic alcohols **6**. Ring opening of **6** under basic conditions is described as a good means of synthesizing benzocyclooctadienones **10** and **19**, and, in appropriate cases, benzocyclooctenediones of type **12**. Thermal dehydration of **6** affords 1,3-disubstituted naphthalenes in good yields. Second, condensations of a few acyclic α,β-unsaturated ketone enolates with benzyne are shown to be of synthetic usefulness; depending on the substituents on both sides of the carbonyl group, these condensations may lead either to substituted naphthalenes or to phenyl ketones or tetralones.

$S_{RN}1$[2] and arynic[3] condensations of saturated ketone enolates on aryl halides have attracted much interest in view of their synthetic usefulness. Thus, numerous phenyl ketones,[2,4] benzocycloenones,[5] and benzocyclobutenols[6] may be easily obtained from inexpensive starting materials.

Scheme I



As far as arynic condensations are concerned, α,β-unsaturated ketone enolates have been much less studied than saturated ones. Of course, much more complex re-

(1) For part 14, see M. Essiz, G. Guillaumet, and P. Caubere, *Tetrahedron*, **35**, 1167 (1979). Parts 14 and 15 together with ref 11 and 12 represent part of the research work of M.E. for his Ph.D. Thesis.

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