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CARBON-CARBON BOND FORMATION BETWEEN ENONE AND ESTER CARBONYL GROUP INDUCED BY SAMARIUM DIIODIDE

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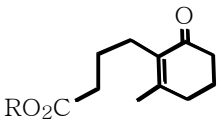
Abstract – Reductive cyclization of methyl, TBDMS, pentafluorophenyl, trichloroethyl, or MOM ester of 4-(2-methyl-6-oxocyclohex-1-enyl)butanoic acid was attempted by treating with SmI_2, with or without additive (MeOH, H_2O, HMPA, NiI_2), to establish whether Claisen-type carbon-carbon bond formation occurred. Methyl ester afforded dimeric products, while trichloroethyl and MOM ester yielded hexahydronaphthalenediones. Pentafluorophenyl ester gave a spiro compound. It is thought that all these products were formed through an anionic intermediate produced by two-electron reduction of the enone moiety by SmI_2.

This paper is dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday.

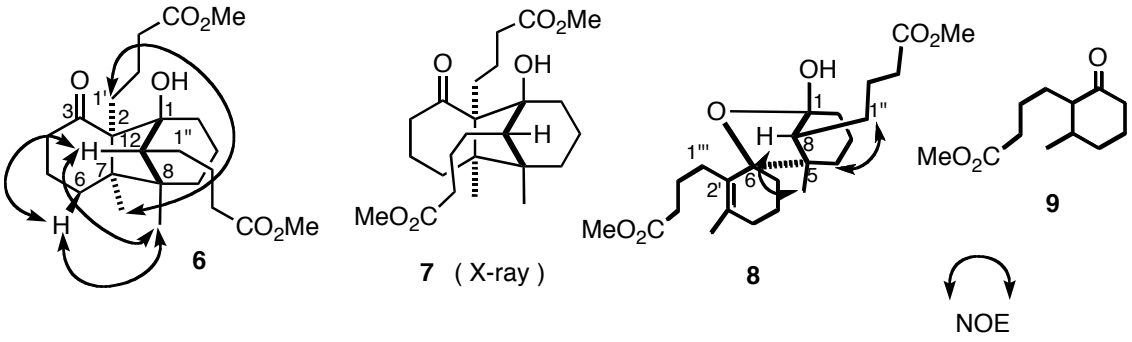
One-electron reduction using SmI_2 or electrolysis is an interesting reaction via a radical intermediate.[1-4] Electrolysis has been studied by many groups,[5-7] because it is completely benign to the surrounding circumstances, nowadays generally accepted as green chemistry. We have been investigating one-electron reducing reactions applied to the construction of perhydronaphthalenones,[8] hydrindanones,[9-11] and perhydroguaianes.[12] In these compounds, carbon-carbon bonds are formed between enones and ketones or aldehydes. It is assumed that one-electron reduction occurs first in the enone system to form a radical at the β-position of the enone carbonyl group.[13-15] This radical attacks the ketone (or aldehyde) carbonyl group to form a ring with a hydroxy group.[8-12] Alternatively, aldehyde is reduced to form a radical, which attacks the β-position of the enone group to yield a ring. This reaction mechanism has not yet been fully demonstrated spectroscopically.[4,11,13,16] Since a radical can not attack a carbonyl group of ester function, this type of reaction does not occur. However, if this reaction proceeds through an anion produced by

two-electron reduction, the anion at the β-position of the enone carbonyl group can attack the ester carbonyl group through a Claisen-type reaction to form a ring. We have therefore prepared esters (**1**)-(**5**) and attempted their ring forming reactions. We now report details of our results on the reactions of compounds (**1**)-(**5**), between enones and esters induced by SmI_2.



1 R=Me
2 R=TBDMS
3 R=C_6F_5
4 R=CH_2CCl_3
5 R=MOM

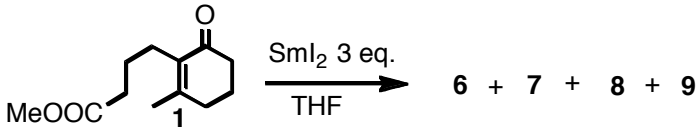
Methyl ester **1** was treated with SmI_2 (3 equiv.) in THF with or without additive as shown in Table 1 to afford compounds (**6**)-(**9**). At low temperature (entries 1, 4, 10, and 13), no reaction occurred or a small amount of a dihydro-derivative was formed. Addition of HMPA or NiI_2[17] gave similar results. However, without additive at rt and 0 °C (entries 2 and 3) or in the presence of MeOH (entries 5-8),[18] dimerization occurred to give two major dimers (**6**) and (**7**), with a small amount of **8**. Compound (**7**) crystallized and the structure was solved by X-ray analysis. The ORTEP drawing of compound (**7**) is shown in Figure 1. In compound (**7**), the four-carbon side chain was inside the bicyclic system (endo). Compound (**6**) was thought to be a stereoisomer of **7**, because both ^{1}H- and ^{13}C-NMR data of **6** were similar to those of **7**. The NOESY spectrum showed NOEs as depicted in the formula. In particular, the NOE between the methyl group at C-7 and the methylene proton attached to the side chain (H-1') indicated the cis fused ring. The proton at C-12 had NOE to H-6 and the methyl group at C-8. Therefore, the structure of compound (**6**) was established to be the stereoisomer of the side chain attached to C-12 (exo isomer). Compound (**8**) had the same molecular formula and showed very similar spectral data. However, it had two ester carbonyl groups (δ 174.1, 175.2) and one double bond (δ 131.0, 136.7) as well as an acetal (δ 106.3). It was assumed that radicals at the β-position of one enone group and the ketyl of the other enone coupled followed by acetalization. Therefore, two structures, **8** and **8'** were considered and their global minimum conformations were calculated by CONFLEX (Figure 2).[19-21] Since NOEs between H-8/C5-Me and H-4/H-1" were observed, the structure was determined to be **8**.



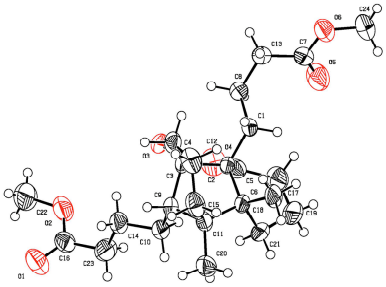
Thus, compounds (**6**) and (**7**) were dimers produced by carbon-carbon bond formation at the β-positions of both units followed by aldol cyclization. A similar dimerization reaction was reported by Inanaga *et al.*[22] and is the frequently encountered reaction by a radical coupling between β-carbons of enones followed by aldol-type cyclization.[13,15,23] However, compound (**8**) was formed by coupling between α-

and β-carbons of the carbonyl groups. We suspect that this was due to the poor leaving ability of the methoxyl group.

Table 1. SmI_2-induced reaction of compound **1**.



entry	additive (equiv.)	temp. (˚C)	recovery (%)	yield (%) 6	7	8	9
1	none	-78	79	-	-	-	-
2		0	39	8	8	-	9
3		rt	24	12	12	-	21
4	MeOH (2)	-78	87	-	-	-	5
5		0	26	7	13	trace	24
6		rt	0	4	7	trace	22
7	MeOH (10)	-78	11	11	0	-	20
8		0	0	8	8	trace	22
9		rt	0	-	-	trace	18
10	HMPA (12)	-78	70	-	-	-	-
11		0	44	-	-	-	26
12		rt	38	-	-	-	3
13	NiI_2 (0.1)	-78	87	-	-	-	3
14		0	47	-	-	-	31
15		rt	29	-	-	-	30



Fifgure 1. ORTEP drawing of compound **7**.

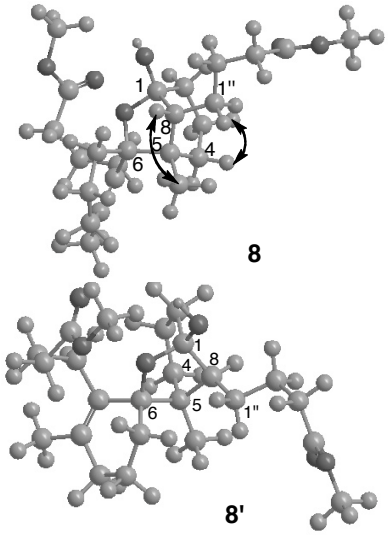
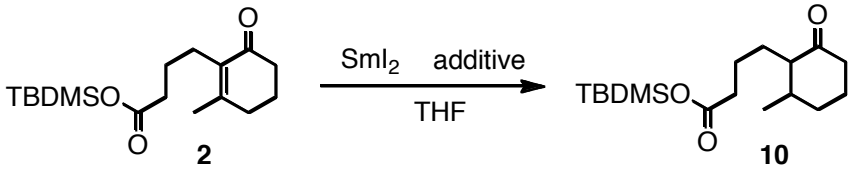


Figure 2. The conformation of **8** and its isomer **8'** (isomer at C-8) calculated by CONFLEX.

Silyl ester (**2**) was next treated with SmI_2 to afford dihydro compound (**10**) without additive. The addition of MeOH did not accelerate the reduction rate. No cyclized product was obtained.

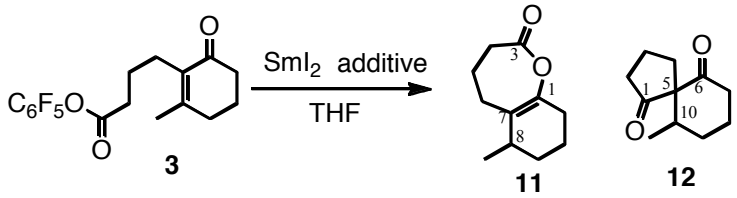
Table 2. SmI_2-induced reaction of compound **2**.



entry	SmI_2 (eq.)	additive (eq.)	time (h)	yield (%) 2	10
1	8.0	none	overnight	-	34
2	4.0	MeOH (1)	1.5	100	-
3	4.0	MeOH (12)	2.5	41	11

Pentafluorophenyl ester (**3**) was treated with SmI_2 in THF. In entries 1-3, the starting material was recovered. However, as in entry 4, when HMPA (12 equiv.) was added, enol lactone (**11**) and a spiro compound (**12**) were formed. Finally with NiI_2,[17] only a spiro compound (**12**) was formed. Compound (**11**) was formed by *O*-attack of the samarium-enolate to the ester carbonyl group and compound **12** was produced by a Claisen-type carbon-carbon bond formation of samarium enolate (*C*-attack).

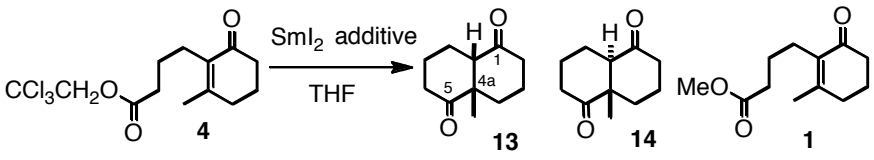
Table 3. SmI_2-induced reaction of compound **3**.



entry	SmI_2 (eq.)	additive (equiv.)	time (h)	yield (%)		
				3	**11**	**12**
1	3.7	none	3.5	51	-	-
2	3.7	MeOH (2)	3.5	32	-	-
3	3.7	MeOH (10)	3.2	30	-	-
4	5.0	HMPA (12)	2.5	-	33	45
5	8.0	NiI_2 (0.1)	4.0	-	-	30

In the case of trichloroethyl ester (**4**), when MeOH was added, the reactive trichloroethyl group was replaced by a methoxyl group. Addition of HMPA or NiI_2 afforded a complex mixture or recovery, respectively (entries 4 and 5). However, in the presence of water (entry 6) hexahydronaphthalenediones (**13**) and (**14**) were formed, in 12% and 6% yield, respectively. Because isomerization occurred between **13** and **14** under base treatment, these must have been isomers at the α-position of the carbonyl group (see EXPERIMENTAL). This probably arose from cyclization of the anion formed at the β-position to the ester carbonyl group followed by quenching of samarium enolate.

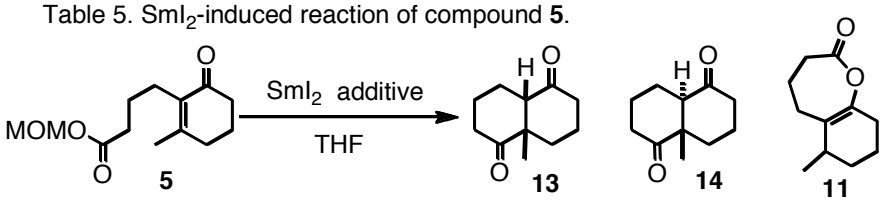
Table 4. SmI_2-induced reaction of compound **4**.



entry	SmI_2 (eq.)	additive (eq.)	time (h)	yield (%)			
				4	**13**	**14**	**1**
1	3.0	none	1.5	12	-	-	-
2	3.0	MeOH (2)	1.0	53	-	-	39
3	3.0	MeOH (20)	2.0	-	-	-	4
4	3.0	HMPA (12)	1.0	complex mixture			
5	6.0	NiI_2 (0.1)	1.5	85	-	-	-
6	5.0	H_2O (8)	0.5	-	12	6	-

The reaction with MOM ester (**5**) was next attempted. Bicyclic compounds (**13**) and (**14**) were formed in the presence of MeOH or water (entries 2, 3, and 4). However, without an additive, the reaction was messy (entry 1) and the addition of HMPA did not alter the reaction (entry 5). In entry 6, when TBDMSCl was added, the yield of compound (**13**) was increased to twice that in entry 2. It is assumed that the anion radical **5a** was silylated to **5b** followed by further reduction by SmI_2 to form an anion **5c**, which attacked the MOM ester carbonyl group. In the presence of TBDMSCl, cleavage of MOM ester group was accelerated to afford **13** or **14** (Figure 3). A similar cyclization reaction of unsaturated amide induced by triflic anhydride and SmI_2 has been reported.[24]

Table 5. SmI_2-induced reaction of compound **5**.



entry	SmI_2 (eq.)	additive (eq.)	time (h)	yield (%)		
				13	**14**	**11**
1	4.0	none	4	complex mixture		
2	4.0	MeOH (2)	2	27	9	-
3	4.0	MeOH (20)	2.5	12	4	-
4	3.0	H_2O (8)	0.5	8	3	-
5	6.0	HMPA (12)	3.0	-	-	trace
6	3.0	TBDMSCl (1)	2.0	53	11	-

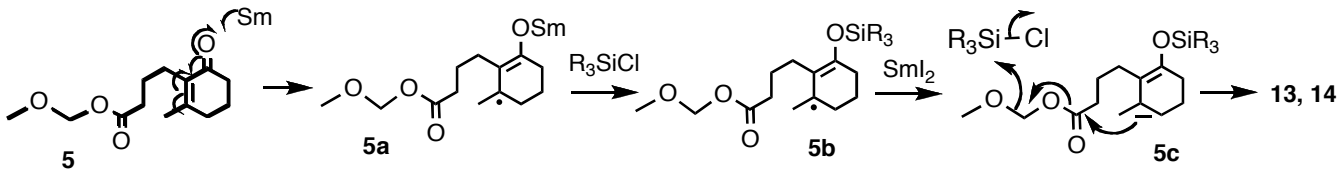


Figure 3. Possible mechanism for MOM ester

A methoxyl group is a poor leaving group and no cyclization occurred, instead dimerization was noted. Compound having a trichloroethyl group afforded hexahydronaphthalenediones, when the anion attacked the ester carbonyl group. In the case of compound having a more active leaving group, pentafluorophenyl, a spiro compound was obtained by attack of the samarium enolate to the ester carbonyl group followed by further reduction of the radical. SmI_2-promoted, ketone-ester coupling leading to the formation of hydroxy-ketones have been observed.[25,26] This is the first attempt, as far as we know, to form a carbon-carbon bond between an enone and an ester carbonyl group by two-electron reduction induced by SmI_2. We are currently studying the mechanism by trapping a radical or an anion intermediate.

EXPERIMENTAL

General. All reactions were carried out under an argon atmosphere. Anhydrous solvents were purchased from Kanto Chemical Co., Inc. Reagents were purchased at the highest commercial quality and used without further purification. The IR spectra were measured on a JASCO FT/IR 500 spectrophotometer. Mass spectra, including high-resolution spectra, were recorded on a JEOL JMS-700 MStation. ^{1}H and ^{13}C NMR spectra were measured on a Varian Unity 600 (600 MHz and 150 MHz, respectively) and a Varian Unity 200 (200 MHz and 50 MHz, respectively) spectrometer. Silica gel 60 (70-230 mesh, Fuji Silysia) was used for column chromatography. Silica gel BW-300 (200-400 mesh, Fuji Silysia) was used for column chromatography, and silica-gel $60F_{254}$ plate (0.25mm, Merck) were used for TLC.

Synthesis of substrates.

3-Methyl-2-cyclohexenone (**16**, 220 mg, 2 mmol) was treated with *t*BuOK (4.8 mL, 4.8 mmol) in THF at rt for 30 min, then bromide **17** (798 mg, 3mmol) was added and the mixture was heated under reflux for 3 h. Work-up as usual and silica-gel column chromatography afforded **18** (300 mg, 51%). A solution of **18** (6.4 g, 20.6 mmol) in THF (50 mL) was treated with TBAF (56 mL, 56 mmol) at rt overnight. Work-up as usual and silica-gel column chromatography afforded **19** (2.36 g, 63%). To a stirred solution of **19** (2.36 g, 13 mmol) in acetone (15 mL) was added Jones reagent (25 mL) at 0°C and the mixture was stirred for 30 min. Work-up as usual gave a residue (2.79 g), which was treated with diazomethane to afford methyl ester (**1**) (1.94 g, 71% from **19**) after purification. Compounds (**2**) and (**3**) were prepared by esterification of **20** with corresponding alcohol and DCC, while compounds (**4**) and (**5**) were prepared by direct alkylation of **20** with each chloride and a base.

Methyl ester (1)

oil; MS (EI) *m/z* 210 $(M)^{+}$, 178, 150, 137 (base), 121, 108, 95; HRMS (EI) Found *m/z* 210.1237 (Calcd. for $C_{12}H_{18}O_3$ 210.1246); IR: 1705, 1735 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.55–1.75 (4H, m), 1.95 (3H, s), 2.22–2.45 (8H, m), 3.67 (3H, s).

TBDMS ester (2)

oil; MS (EI) *m/z* 310 (M^{+}), 295, 253 (base), 235, 225, 211, 195; HRMS (EI) Found *m/z* 310.1954 (Calcd. for $C_{17}H_{30}O_3Si$ 310.1964); IR: 1625, 1661, 1714 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.28 (6H, s), 0.95 (9H, s), 1.00–1.95 (6H, m), 1.95 (3H, s), 2.20–2.50 (6H, m); ^{13}C NMR (50MHz, $CDCl_3$) δ 17.6, 17.9, 21.2, 22.2, 23.9, 24.3, 24.4, 24.5, 32.8, 33.6, 35.7, 35.8, 135.0 (C), 156.6 (C), 177.7 (C), 198.8 (C).

Pentafluorophenyl ester (3)

oil; MS (EI) m/z 362 (M^{+}), 274, 179 (base), 161, 151, 133; HRMS (EI) Found *m/z* 362.0956 (Calcd. for $C_{17}H_{15}O_3F_5$ 362.0941); IR: 1790, 1660 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.71–1.88 (2H, m), 1.98 (3H, s), 2.34-2.46 (6H, m), 2.68 (2H, t, *J* = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.1 (CH_3), 22.2 (CH_2),

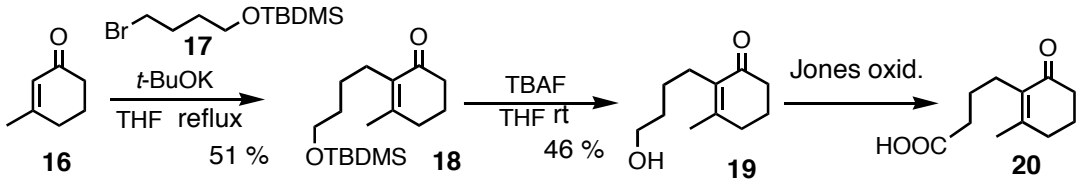
23.9 (CH_2), 24.3 (CH_2), 32.8 (CH_2), 33.0 (CH_2), 37.7 (CH_2), 134.4-141.9 (6C, not identified due to F-coupling), 143.8 (C), 156.6 (C), 169.5 (CO), 198.7 (CO).

Trichloroethyl ester (4)

oil; MS (EI) *m/z* 326 (M^+), 311, 292, 270, 255, 244, 230, 207, 195, 179, 150 (base); HRMS (EI) Found *m/z* 326.0254 (Calcd. for $C_{13}H_{17}O_3Cl_3$ 326.0243); IR: 1625, 1659, 1751 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.60–1.80 (6H, m), 1.99 (3H, s), 2.25–2.60 (6H, m), 4.78 (2H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.2 (CH_2), 23.8 (CH_2), 24.4 (CH_2), 32.8 (CH_2), 33.5 (CH_2), 33.9 (CH_2), 37.7 (CH_3), 73.9 (CH_2), 95.0 (C), 134.7 (C), 156.4 (C), 172.2 (C), 198.8 (C).

MOM ester (5)

oil; MS (EI) *m/z* 240 (M^+), 222, 208, 195, 179, 162, 149 (base); HRMS (EI) Found *m/z* 240.1354 (Calcd. for $C_{13}H_{20}O_3$ 240.1361); IR: 1625, 1657, 1737 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.60–1.80 (6H, m), 1.99 (3H, s), 2.30–2.55 (6H, m), 3.50 (3H, s), 5.23 (2H, s).



General procedure for SmI_2-induced reaction.

A solution of SmI_2 in THF was cooled to a fixed temperature. A substrate and an additive in THF were slowly added dropwise. The mixture was stirred at a specific temperature for a certain time. The reaction was quenched with a saturated aq. solution of Rochelle's salt. The organic materials were extracted with diethyl ether, washed with brine and dried over $MgSO_4$. The products were purified by silica-gel flash chromatography.

Compound (6)

oil; MS (CI) *m/z* 423 $[M+H]^+$, 405 (base), 391, 373, 211, 179; HRMS (CI) Found *m/z* 423.2750 (Calcd. for $C_{24}H_{39}O_6$ 423.2746); IR: 1672, 1736, 3390 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.72 (3H, s, 8-Me), 1.09 (3H, d, *J* = 0.5 Hz, 7-Me), 1.69 (1H, t, *J* = 5.7 Hz, H-12), 3.66 (3H, s, OMe), 3.67 (3H, s, OMe), 6.27 (1H, s, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 15.3 (7-Me), 18.4 (CH_2), 19.0 (CH_2), 21.3 (CH_2), 21.5 (8-Me), 23.4 (CH_2), 25.4 (CH_2), 28.4 (CH_2), 29.3 (C-9), 30.9 (CH_2), 34.2 (C-6), 34.3 (CH_2), 34.7 (CH_2), 36.4 (CH_2), 44.8 (C-8), 50.3 (C-7), 51.4 (OMe), 51.5 (OMe), 59.9 (C-2), 83.1 (C-12), 173.6 (CO), 174.3 (CO), 225.8 (C-3).

Compound (7)

crystal; MS (CI) *m/z* 423 $[M+H]^+$, 405 (base), 391, 373, 211, 179; HRMS (CI) Found *m/z* 423.2744 (Calcd. for $C_{24}H_{39}O_6$ 423.2747); IR: 1672, 1736, 3400 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.88 (3H, s, 8-Me), 1.08 (3H, d, *J* = 0.5 Hz, 7-Me), 3.66 (3H, s, OMe), 3.67 (3H, s, OMe), 7.05 (1H, s, OH); ^{13}C NMR

(150 MHz, $CDCl_3$) δ 18.1 (C-5), 19.9 (CH_2), 21.4 (CH_2), 26.9 (CH_2), 27.1 (CH_2), 31.2 (CH_2), 34.1 (CH_2), 34.5 (CH_2), 35.9 (C-6), 37.3 (C-4), 39.0 (C-11), 40.4 (C-9), 45.8 (C-8), 49.7 (C-7), 51.4 (OMe), 51.5 (OMe), 60.2 (C-2), 61.2 (C-12), 84.5 (C-1), 173.6 (CO), 174.2 (CO), 225.5 (C-3).

Compound (8)

oil: MS (FAB) *m/z* 445 $[M+Na]^+$, 423 $[M+H]^+$, 405; HRMS (FAB) Found *m/z* 445.2541 (Calcd. for $C_{24}H_{38}O_6Na$ 445.2566); IR: 1733, 3450 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.83 (3H, s, Me), 1.68 (3H, s, Me), 2.07 (1H, dd, J = 9.1, 5.2), 3.67 (6H, s, OMe ×2), 4.01 (1H, br s, OH); ^{13}C NMR (150 MHz, $CDCl_3$) δ 18.5 (CH_2), 18.9 (CH_2), 20.2 (CH_3), 22.9 (CH_3), 23.2 (CH_2), 24.9 (CH_2), 25.0 (CH_2), 27.7 (CH_2), 30.1 (CH_2), 30.5 (CH_2), 30.7 (CH_2), 32.9 (CH_2), 33.5 (CH_2), 34.5 (CH_2), 50.2 (C), 51.4 (CH_3), 51.7 (CH_3), 52.1 (CH), 85.8 (C), 106.3 (C), 131.0 (C), 136.7 (C), 174.1 (CO), 175.2 (CO).

Compound (9)

oil; MS (EI) *m/z* 212 (M^+), 197, 180, 165, 152, 135, 112, 97 (base); HRMS (EI) Found *m/z* 212.1396 (Calcd. for $C_{12}H_{20}O_3$ 212.1413); IR: 1711, 1738 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.05 (3H, d, *J* = 6.4 Hz), 1.40–1.79 (6H, m), 1.80–2.15 (4H, m), 2.25–2.50 (4H, m), 3.67 (3H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.4 (CH_3), 22.5 (CH_2), 25.5 (CH_2), 26.0 (CH_2), 33.4 (CH_2), 34.2 (CH_2), 38.3 (CH), 41.5 (CH_2), 51.4 (CH_3), 57.0 (CH), 174.2 (CO), 205.3 (CO).

Compound (10)

oil; MS (EI) *m/z* 312 (M^+) 297, 279, 255, 237, 145 (base), 135, 121; HRMS (CI) Found *m/z* 313.2198 (Calcd. For $C_{17}H_{33}O_3Si$ 313.2198); ^1H NMR (200 MHz, $CDCl_3$) δ 0.21 (6H, s), 0.84 (3H, br d, *J* = 7 Hz), 0.90 (9H, s), 2.36 (2H, br d, *J* = 6.9 Hz).

Compound (11)

oil; MS (EI) *m/z* 180 (M^+), 162, 152, 137, 125 (base); HRMS (EI) Found *m/z* 180,1157 (Calcd. for $C_{11}H_{16}O_2$ 180.1151); IR: 1749 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 1.07 (3H, d, *J* = 7.1 Hz), 1.39 (1H, m), 1.65 (1H, m), 1.75 (1H, m), 1.78 (1H, m), 2.03 (1H, m), 2.09 (1H, m), 2.11 (1H, m), 2.12 (1H, m), 2.14 (1H, m), 2.26 (1H, m), 2.30 (1H, m), 2.51 (1H, m), 2.57 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 19.6 (CH_3), 19.7 (C-10), 25.6 (C-5), 27.0 (C-11), 27.4 (C-6), 30.6 (C-9), 32.1 (C-4), 33.0 (C-8), 123.9 (C-7), 146.5 (C-1), 173.2 (C-3).

Compound (12)

oil; MS (EI) *m/z* 180 (M^+) 162, 152, 137, 125 (base); HRMS (EI) Found *m/z* 180.1158 (Calcd. for $C_{11}H_{16}O_2$ 180.1150); IR: 1694, 1745 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 0.86 (3H, d, *J* = 7.2 Hz), 1.44 (1H, m), 1.80 (1H, m), 1.84 (1H, m), 1.89 (1H, m), 1.95 (1H, m), 1.99 (1H, m), 2.06 (1H, m), 2.16 (1H, m), 2.24 (1H, m), 2.32 (1H, m), 2.37 (1H, m), 2.43 (1H, m), 2.47 (1H, m); ^{13}C NMR (150 MHz, $CDCl_3$) δ 16.5 (CH_3), 19.2 (C-3), 23.8 (C-8), 29.0 (C-9), 29.1 (C-4), 37.3 (C-10), 38.4 (C-7), 39.1 (C-2), 68.7 (C-5), 210.2 (C-6), 217.1 (C-1).

Compound (13)

oil; MS (EI) *m/z* 180 (M^+) 152, 136, 124, 111 (base); HRMS (EI) Found *m/z* 180.1125 (Calcd. For $C_{11}H_{16}O_2$ 180.1150); IR: 1706 cm^{-1}; ^1H NMR (600 MHz,$CDCl_3$) δ 1.26 (3H, s, Me), 1.38 (1H, m), 1.82 (1H, m), 1.84 (1H, m), 1.88 (1H, m), 1.90 (1H, m), 2.00 (1H, m), 2.25 (1H, m), 2.29 (1H, m), 2.38 (1H, m), 2.40 (1H, m), 2.43 (1H, m), 2.47 (1H, m), 2.51 (1H, m, H-9a); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0 (CH_2), 22.7 (CH_2), 23.9 (CH_2), 25.0 (CH_3), 32.0 (C-4), 37.9 (CH_2), 39.5 (CH_2), 51.9 (C-4a), 58.1 (C-9a), 210.9 (C-1), 213.1 (C-5).

Isomerization of diketone (13)

A solution of **12** (8 mg) in MeOH (3 mL) was treated with K_2CO_3 (3.6 mg) under reflux for 3 days. Water was added and the mixture was extracted with ether. The organic layer was washed with brine and dried ($MgSO_4$) to afford a residue after evaporation. The residue was analyzed with GC-MS (**13**:**14** = 41:59).

X-Ray crystallographic analysis of compound 7

Program(s) used to refine structure: *SHELXL*-97 (Sheldrick, 1997). Mo *K*α radiation, λ = 0.71073Å, 3806 measured reflections, 3119 observed reflections, Data collection: DIP Image plate, Crystal data: monoclinic, C2/c, a = 26.347(5)Å, b = 19.605(4)Å, c = 9.0280(18)Å, α = 90.00°, β = 104.37(3)°, γ = 90.00°, V = 4517.4(16)$Å^3$, R = 0.0578, Crystallographic data (excluding structure factors) for the structure of this compound have been deposited with Cambridge Crystallographic Data Centre as supplementary publication **CCDC 676392**. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-(0)1223-336033 or e-mail:deposit@ccdc.cam.ac.UK).

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