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Thioalkylation of Enolates, IV[1]

α-Alkylidenecyclopentanones by α-Alkylidation of Methyl 2-Oxocyclopentanecarboxylate

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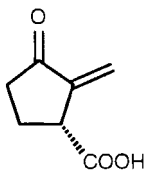
An α-alkylidation of cyclopentanone was achieved in two reaction steps in an overall yield of 20 to 79% via a zinc chloride-catalyzed thioalkylation of the zinc enolate of methyl 2-oxocyclopentanecarboxylate (**3**) and subsequent saponification/desulfurization of the β-(phenylthio) ketone intermediates **5**. For the saponification/desulfurization step DABCO proved to be the reagent of choice and superior to the use of alkali or magnesium halides.

The preparation of α,β-unsaturated exocyclic cycloalkanones and lactones like sarcomycine (**1**)[2], xanthocidine[3], methylenomycine[4] and confertine (**2**)[5] represents a challenging target in organic synthesis due to their pharmaceutical properties which may be utilized in the construction of anticancer drugs.



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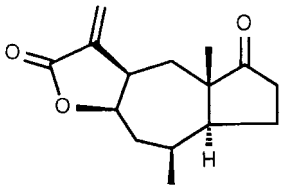

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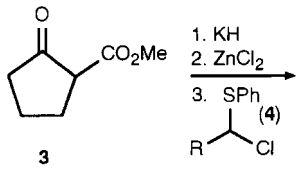

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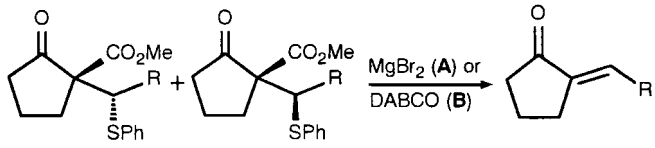

***u*-5** ***l*-5** **6**

Usually, an exocyclic double bond in α-position to a carbonyl group can be introduced by dehydration of the corresponding aldol adducts[6] or sulfinate elimination from β-sulfonyl ketones[7] but due to the harsh reaction conditions severe side reactions like isomerization or polymerization cannot be avoided. Whereas special methods for the preparation of α-methylenecycloalkanones have already been developed[8,9] a general method for the preparation of α-alkylidenecarbonyl compounds is still lacking.

Recently, we described the thioalkylation of zinc enolates which allows the regioselective attachment of primary side chains to a tertiary carbon atom[10]. Encouraged by these results, the thioalkylation of zinc enolates derived from β-keto esters was investigated. The thioalkylation products such as **5** should yield upon saponification and subsequent desulfurization the desired α-alkylidenecarbonyl compounds **6**.

The potassium salt of methyl 2-oxocyclopentanecarboxylate (**3**) was transmetalated into its corresponding zinc enolate with 1.2 equivalents of zinc chloride used as an ethereal solution. Since only 1 equivalent of zinc chloride was consumed for this transmetalation step an excess of 0.2 equivalents of zinc chloride was sufficient as a catalyst for the subsequent S_N1-type thioalkylation. Treatment of this zinc enolate, prepared from methyl 2-oxocyclopentanecarboxylate (**3**), and 0.2 equivalents of zinc chloride with 1.1 equivalents of the α-chloroalkyl phenyl sulfides **4** furnished in 70–90% yield the β-phenylthio keto derivatives **5a–d** and **5f**. Only the *tert*-butyl derivative **5e** was obtained in a significantly lower yield of 35% which might be the result of a zinc chloride-catalyzed rearrangement process. In all cases *u*-diastereomers[11] were predominantly formed[12]. However, this is not important since the stereogenic center

4 - 6	R	Yield (%) of **5**	Diastereomeric ratio *u* : *l*	Yield (%) of **6** Method **A**	Method **B**
a	CH_3	90	2.0 : 1	75	88
b	C_2H_5	87	1.7 : 1	69	85
c	n-C_3H_7	70	1.9 : 1	62	80
d	C_6H_5	86	2.6 : 1	43	82
e	t-C_4H_9	35	3.7 : 1	50	55
f	HC≡C	78	1.5 : 1		

at C-1 is subsequently destroyed in the saponification/desulfurization step.

Initially, the saponification, decarboxylation and spontaneous thiophenolate elimination of **5** furnishing the α-alkylidenecyclopentanones **6** were investigated by using sodium chloride, lithium bromide and diethyl ether–magnesium bromide. The latter turned out to be the most appropiate of all reagents for this purpose due to the formation of a magnesium chelate complex which coordinates with the ester and the keto carbonyl group. Unfortunately, high reaction temperatures of 130–170°C and reaction times of about 4 hours were necessary for the completion of this reaction. Therefore, severe side reactions were unavoidable such as a Lewis acid-promoted polymerization of the formed α-alkylidenecyclopentanones **6**. The demethoxycarbonylation of β-keto esters **5** followed by elimination of thiophenolate was best achieved by using 1,4-diazabicyclo[2.2.2]octane (DABCO) for this reaction[13]. At significantly lower reaction temperatures and a reaction period of only 30 min the α-alkylidenecyclopentanones **6a–e** could be obtained in 55–88% yield after aqueous work-up and chromatographic purification of the crude product.

An *E*/*Z* mixture of α-alkylidenecyclopentanones **6** should have been formed initially since a diastereomeric mixture of *u*-**5** and *l*-**5** was used for this process. Obviously, under the influence of sunlight an isomerization of the *Z* isomers of **6** to the more stable *E* isomers took place completely[14].

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Experimental

Infrared (IR) spectra: Perkin-Elmer 298 spectrometer. – NMR spectra: Varian XL 200 or a VXR 200 spectrometer for ^1H and ^{13}C NMR. Chemical shifts are given in δ values by using tetramethylsilane as an internal standard. – Mass spectra: Varian MAT 731 or 311 A. – TLC analyses: Polygram Sil G/UV_{254} silica gel plates. Silica gel (0.030–0.060 mm) from Baker was used for flash chromatography. – Combustion analyses: Microanalytical laboratory of the University of Göttingen. – All reactions were carried out under argon. All reagents were purified and dried if necessary before use. THF was freshly distilled from $LiAlH_4$ prior to use. CCl_4 was distilled from P_4O_{10}. The ethereal $ZnCl_2$ solution was purchased from Aldrich. The phenyl sulfides were prepared by reaction of the corresponding halides or mesylates with thiophenol and K_2CO_3 in acetone.

α-Chlorosulfides **4a–f**. – *General Procedure: N*-Chlorosuccinimide (1.47 g, 11 mmol) was added in a single portion to a stirred solution of the corresponding alkyl phenyl sulfide (10 mmol) in CCl_4 (20 ml) at 2°C, and stirring was continued at this temp. for 16 h. The succinimide was filtered off and the filtrate was concentrated in vacuo to afford the moisture-sensitive α-chlorosulfides in almost quantitative yield. These chlorosulfides **4a–f** were used after drying in vacuo (0°C/0.1 Torr) without further purification.

Thioalkylation of Methyl 2-Oxocyclopentanecarboxylate (**3**) *to the β-Keto Esters* **5**. – *General Procedure:* Potassium hydride (5.33 g of a 30% suspension in mineral oil, 40 mmol) was washed three times with THF (20 ml each) and suspended in THF (100 ml). A solution of **3** (5.68 g, 40 mmol) in THF (10 ml) was added at room temp. with stirring, and stirring was continued until the evolution of hydrogen had ceased (10–20 min). A solution of zinc chloride in diethyl ether (1.0 M, 48 ml, 48 mmol) was slowly added at −50°C and stirring was continued for 15 min. After addition of a solution of the α-chlorosulfides **4** (44 mmol) in THF (10 ml) the solution was allowed to warm up to −30°C within 1 h, kept for 3 h at this temp. and allowed to warm up to room temp. within 2 h. The solvent was removed in vacuo (0°C/20 Torr), diethyl ether (150 ml) was added to the residue, then 1 N HCl was added until the inorganic salts had completely dissolved. The layers were separated, the aqueous layer was extracted three times with diethyl ether (50 ml each), and the combined organic layers were reextracted with H_2O (30 ml), a saturated aqueous $NaHCO_3$ solution (50 ml) and again with H_2O (50 ml). The ethereal solution was dried with $MgSO_4$, and the solvent was removed in vacuo (10°C/12 Torr). The residue – the crude products **5a–f** – was purified by chromatography on silica gel (deactivated by addition of 10% of H_2O). The NMR δ values of the minor *l* diastereomers are given in brackets.

Methyl 2-Oxo-1-(1-phenylthioethyl)cyclopentanecarboxylate (**5a**): 1.19 g (30 mmol) of potassium hydride, 3.98 g (28 mmol) of **3**, 36 ml (36 mmol) of an ethereal 1 M zinc chloride solution and 5.18 g (30 mmol) of α-chloroethyl phenyl sulfide (**4a**) were used to afford after chromatographic purification on silica gel (200 g) with diethyl ether/petroleum ether (1:4) 7.10 g (90%) of **5a** as a colorless solid; diastereomeric ratio: 2.0:1, R_f = 0.37, m.p. 55°C. – IR (KBr): $\tilde{\nu}$ = 3040 (aromat. CH), 1740 (C=O), 1720 (O–C=O), 1540 (aromat. C=C), 1150 (C–O), 735 and 690 cm^{-1} (monosubst. aromat). – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.26 and [1.32] (2 d, *J* = 7.5 Hz; 3H, SCH–C*H*$_3$), 1.92–2.78 [m; 6H, C(CH_2)$_3$], [3.64] and 3.74 (2 s; 3H, OCH_3), 3.95 and [4.12] (2 q, *J* = 7.5 Hz; 1H, SC*H*–CH_3), 7.22–7.58 (m; 5H, C_6H_5). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 17.75 and [19.51] (SCH–*C*H_3), 19.69 and [20.05] (C-4), 27.78 and [28.82] (C-5), 39.06 (C-3), [48.32] and 49.51 (S*C*H–CH_3), 52.89 and [52.95] (OCH_3), [65.77] and 66.09 (C-1), 127.56, [127.63], [128.96], 129.06, 132.59 and [132.75] (aromat. CH), 134.33 and [134.78] (aromat. C), [168.92] and 169.25 (*C*O_2CH_3), 212.65 and [212.74] (C=O). – MS (70 eV): *m/z* (%) = 278 (11) [M^+], 169 (56) [$M^+ - SC_6H_5$], 137 (74) [$CH_3CHSC_6H_5^+$], 109 (100) [$SC_6H_5^+$]. – $C_{15}H_{18}O_3S$ (278.4): calcd. C 64.72, H 6.52; found C 64.70, H 6.51.

Methyl 2-Oxo-1-(1-phenylthiopropyl)cyclopentanecarboxylate (**5b**): 2.01 g (50 mmol) of potassium hydride, 6.39 g (45 mmol) of **3**, 60 ml (60 mmol) of a 1 M ethereal solution of zinc chloride and 9.33 g (50 mmol) of α-chloropropyl phenyl sulfide (**4b**) were used to afford after chromatographic purification on silica gel (300 g) with diethyl ether/petroleum ether (1:5) 11.40 g (87%) of **5b** as a colorless solid; diastereomeric ratio: 1.7:1, R_f = 0.26, m.p. 65°C. – IR (KBr): $\tilde{\nu}$ = 3060 and 3040 (aromat. CH), 1745 (C=O), 1720 (O–C=O), 1560 (aromat. C=C), 1200 (C–O), 740 and 685 cm^{-1} (monosubst. aromat.). – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.11 and [1.25] (2 t, *J* = 7 Hz; 3H, CH_2CH_3), 1.50 and [1.54] (2 dq, J_1 = 7 and J_2 = 6 Hz; 2H, CH_2CH_3), 1.94–2.80 [m; 6H, $(CH_2)_3$], [3.66] and 3.75 (2 s; 3H, OCH_3), 3.78 and [3.84] (2 t, *J* = 6 Hz; 1H, SCH), 7.18–7.52 (m; 5H, C_6H_5). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 12.01 and [12.84] (CH_2CH_3), 19.43 and [20.31] (C-4), 26.11 and [27.74] (CH_2CH_3), [28.61] and 29.39 (C-5), [38.99] and 39.17 (C-3), [52.36] and 52.89 (SCH–CH_2), 56.30 and [56.73] (OCH_3), 66.31 and [67.52] (C-1), 127.01, [128.78], [128.90], 128.98, 131.35 and [131.77] (aromat. CH), 135.86 and [136.37] (aromat. C), [168.68] and 169.36 (*C*O_2CH_3), 212.46 and [213.30] (C=O). – MS (70 eV): *m/z* (%) = 292 (18) [M^+], 183 (32) [$M^+ - SC_6H_5$], 151

(100) [$CH_3CH_2CHSC_6H_5^+$], 109 (34) [$SC_6H_5^+$]. – $C_{16}H_{20}O_3S$ (292.4): calcd. C 65.72, H 6.89; found C 65.79, H 6.84.

Methyl 2-Oxo-1-(1-phenylthiobutyl)cyclopentanecarboxylate (**5c**): 0.68 g (17 mmol) of potassium hydride, 2.13 g (15 mmol) of **3**, 17 ml (17 mmol) of an ethereal 1 M zinc chloride solution and 3.41 g (17 mmol) of α-chlorobutyl phenyl sulfide (**4c**) were used to afford after chromatographic purification on silica gel (80 g) with diethyl ether/petroleum ether (1:10) 3.21 g (70%) of **5c** as a colorless solid; diastereomeric ratio: 1.9:1, R_f = 0.23, m.p. 88°C. – IR (KBr): $\tilde{\nu}$ = 3040 (aromat. CH), 1745 (C=O), 1720 (O–C=O), 1580 (aromat. C=C), 1170 (C–O), 740 and 690 cm^{-1} (monosubst. aromat.). – ^1H NMR (200 MHz, $CDCl_3$): δ = 0.81 and [0.89] (2 t, J = 7 Hz; 3H, CH_2CH_3), 1.90–2.78 [m; 10H, $(CH_2)_3$ and $CH_3CH_2CH_2$], [3.38] and 3.54 (2 s; 3H, OCH_3), 3.86 and [3.92] (2 t, J = 7 Hz; 1H, SCH), 7.15–7.50 (m; 5H, C_6H_5). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.63 and [13.73] (CH_2CH_3), 19.43 and [20.16] (C-4), 20.31 and [21.06] (CH_2CH_3), [28.55] and 29.32 (C-5), 35.19 and [36.89] (SCH–CH_2), [39.09] and 39.19 (C-3), 52.36 and [52.88] (SCH), [54.05] and 54.56 (OCH_3), 66.39 and [67.51] (C-1), 125.64, [126.96], [128.78], 128.91, 131.24 and [131.78] (aromat. CH), 135.77 and [136.32] (aromat. C), [168.66] and 169.35 (CO_2CH_3), 212.55 and [213.92] (C=O). – MS (70 eV): *m/z* (%) = 306 (34) [M^+], 197 (48) [$M^+ - SC_6H_5$], 109 (28) [$SC_6H_5^+$], 59 (8) [$CO_2CH_3^+$]. – $C_{17}H_{22}O_3S$ (306.4): calcd. C 66.64, H 7.24; found C 66.70, H 7.29.

Methyl 2-Oxo-1-(α-phenylthiobenzyl)cyclopentanecarboxylate (**5d**): 0.32 g (8 mmol) of potassium hydride, 0.99 g (7 mmol) of **3**, 9 ml (9 mmol) of an ethereal 1 M zinc chloride solution and 1.88 g (8 mmol) of α-chlorobenzyl phenyl sulfide (**4d**) were used to afford after chromatographic purification on silica gel (60 g) with diethyl ether/petroleum ether (1:5) 2.04 g (86%) of **5d** as a colorless solid; diastereomeric ratio: 2.6:1, R_f = 0.17, m.p. 92°C. – IR (KBr): $\tilde{\nu}$ = 3040 (aromat. CH), 1740 (C=O), 1730 (O–C=O), 1570 and 1560 (aromat. C=C), 1200 (C–O), 735 and 690 cm^{-1} (monosubst. aromat.). – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.74–2.86 [m; 6H, $(CH_2)_3$], [3.52] and 3.74 (2 s; 3H, CO_2CH_3), [4.86] and 5.24 (2 s; 1H, SCH), 7.14–7.52 (m; 10H, C_6H_5). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.62 and [19.93] (C-4), [27.40] and 29.86 (C-5), [38.74] and 38.80 (C-3), 52.69 and [53.13] (SCH), 57.16 and [58.43] (OCH_3), 66.73 and [66.96] (C-1), 128.15, [128.29], 128.37, [128.53], 128.75, [128.77], 128.82, [128.99], [130.39], 130.88, [131.04] and 131.31 (aromat. CH), [137.13], 137.92, [139.11] and 139.60 (aromat. C), [167.90] and 168.48 (CO_2CH_3), [211.43] and 211.87 (C=O). – $C_{20}H_{20}O_3S$ (340.2): calcd. C 70.54, H 5.93; found C 70.62, H 5.87.

Methyl 2-Oxo-1-(2,2-dimethyl-1-phenylthiopropyl)cyclopentanecarboxylate (**5e**): 0.40 g (10 mmol) of potassium hydride, 1.42 g (10 mmol) of **3**, 13 ml (13 mmol) of an ethereal 1 M zinc chloride solution and 2.11 g (10 mmol) of α-chloroneopentyl phenyl sulfide (**4e**) were used to afford after chromatographic purification on silica gel (50 g) with diethyl ether/petroleum ether (1:4) 1.12 g (35%) of **5e** as a colorless solid; diastereomeric ratio: 3.7:1, R_f = 0.23, m.p. 69°C. – IR (KBr): $\tilde{\nu}$ = 3040 (aromat. CH), 1730 (C=O), 1700 (O–C=O), 1565 (aromat. C=C), 1170 (C–O), 740 and 690 cm^{-1} (monosubst. aromat.). – ^1H NMR (200 MHz, $CDCl_3$): δ = [1.10] and 1.20 [2 s; 9H, $C(CH_3)_3$], 1.82–2.92 [m; 6H, $(CH_2)_3$], [3.16] and 3.30 (2 s; 3H, OCH_3), [4.04] and 4.14 (2 s; 1H, SCH), 7.08–7.30 (m; 5H, C_6H_5). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.39 and [20.07] (C-4), 28.68 and [29.11] (C-5), 29.57 and [30.26] [$C(CH_3)_3$], [36.42] and 37.86 [$C(CH_3)_3$], 38.03 and [38.31] (C-3), [52.01] and 52.13 (OCH_3), [59.24] and 60.68 (SCH), 68.45 and [69.02] (C-1), [125.70], 126.30, [127.99], 128.25, 129.45 and [129.89] (aromat. CH), [136.67] and 138.02 (aromat. C), [168.00] and 169.23 (CO_2CH_3), 211.77 and [212.84] (C=O). – MS (70 eV): *m/z* (%) = 320 (5) [M^+], 211 (6) [$M^+ - SC_6H_5$], 179 (100) [$(CH_3)_3CCHSC_6H_5^+$], 109 (8) [$SC_6H_5^+$], 59 (5) [$CO_2CH_3^+$]. – $C_{18}H_{24}O_3S$ (320.5): calcd. C 64.47, H 7.55; found C 64.50, H 7.62.

Methyl 2-Oxo-1-(phenylthiopropynyl)cyclopentanecarboxylate (**5f**): 0.53 g (13 mmol) of potassium hydride, 1.56 g (11 mmol) of **3**, 13 ml (13 mmol) of an ethereal 1 M zinc chloride solution and 2.02 g (11 mmol) of α-chloropropargyl phenyl sulfide (**4f**) were used to afford after chromatographic purification on silica gel (50 g) with diethyl ether/petroleum ether (1:4) 2.47 g (78%) of **5f** as a yellow oil; diastereomeric ratio 1.5:1, R_f = 0.19. – IR (neat): $\tilde{\nu}$ = 3280 (HC≡C), 3060 and 3040 (aromat. CH), 1750 (C=O), 1720 (O–C=O), 1560 (aromat. C=C), 1150 (C–O), 750 and 680 cm^{-1} (monosubst. aromat.). – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.80 and [1.82] (2 s; 1H, HC≡C), 1.90–2.82 [m; 6H, $(CH_2)_3$], [3.70] and 3.78 (2 s, 3H, OCH_3), 4.48 and [4.74] (2 s; 1H, SCH), 7.18–7.62 (m; 5H, C_6H_5). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.77 and [19.95] (C-4), [28.87] and 30.23 (C-5), [38.29] and 38.99 (C-3), 53.08 and [53.16] (SCH), 53.45 and [53.99] (OCH_3), [63.13] and 64.75 (HC≡C), 65.28 and [66.11] (C-1), 73.71 and [74.77] (HC≡*C*), [128.37], 128.98, 129.08, [129.14], 130.65 and [132.83] (aromat. CH), [136.66] and 137.77 (aromat. C), 167.25 and [168.52] (CO_2CH_3), 210.69 and [210.87] (C=O). – MS (70 eV): *m/z* (%) = 288 (14) [M^+], 179 (70) [$M^+ - SC_6H_5$], 109 (100) [$SC_6H_5^+$]. – $C_{16}H_{16}O_3S$ (288.4): calcd. C 66.72, H 5.59; found C 66.65, H 5.60.

Demethoxycarbonylation of β-Keto Esters **5** *with Diethyl Ether–Magnesium Bromide. – Method A. – General Procedure:* Diethyl ether–magnesium bromide (2.58 g, 10 mmol) was suspended in DMSO (10 ml), and the mixture was stirred at 140°C until the magnesium bromide had completely dissolved (ca. 10 min). A solution of β-keto ester **5** (3 mmol) in DMSO (3 ml) was added dropwise with stirring, and stirring was continued at 130–170°C for 4 h. After cooling down to room temp. pentane (50 ml) and H_2O (25 ml) were added to the reaction mixture and then 1 N HCl was added until the inorganic salts had completely dissolved. The layers were separated, the aqueous layer was extracted twice with pentane (40 ml each), and the combined organic layers were reextracted with a saturated aqueous NH_4Cl solution (25 ml), dried with $MgSO_4$, and the solvent was removed first at 40°C/760 Torr and then at –10°C/20 Torr. The residue – the crude products **6a–e** – was purified by chromatography on silica gel (deactivated by addition of 10% of H_2O) with diethyl ether/petroleum ether (1:4).

Demethoxycarbonylation of β-Keto Esters **5** *with 1,4-Diazabicyclo[2.2.2]octane (DABCO). – Method B. – General Procedure:* DABCO (2.24 g, 20 mmol) was dissolved in DMSO (20 ml) and a solution of β-keto ester **5** (3 mmol) in DMSO (3 ml) was added dropwise with stirring at 100°C and stirring was continued at 100–130°C for 30 min. After cooling down to room temp. pentane (50 ml), H_2O (25 ml) and 1 N HCl (5 ml) were added to the reaction mixture. The layers were separated, the aqueous layer was extracted twice with pentane (40 ml each) and the combined organic layers were reextracted with a saturated aqueous NH_4Cl solution (30 ml), dried with $MgSO_4$ and the solvent was removed first at 40°C/760 Torr and then at –10°C/20 Torr. The residue – the crude products **6a–e** – was purified by chromatography on silica gel (deactivated by addition of 5% of H_2O).

(E)-2-Ethylidenecyclopentanone (**6a**): 2.24 g (20 mmol) of DABCO, 20 ml of DMSO and 0.84 g (3 mmol) of **u,l-5a** were allowed to react at 120–130°C for 30 min to yield after chromatographic purification on silica gel (8 g) with diethyl ether/pentane (1:4) 0.29 g (88%) of **6a** as a colorless oil; R_f = 0.29. – IR (neat): $\tilde{\nu}$ = 1705 (C=O), 1650 cm^{-1} (C=C). – ^1H NMR (200 MHz, $CDCl_3$): δ = 1.82 (d, J = 7 Hz; 3H, CH_3), 1.94 (tt, J = 7.5 Hz and

7.5 Hz; 2H, CH_2CH_2C=C), 2.35 (t, J = 7.5 Hz; 2H, CH_2C=O), 2.54–2.70 (m; 2H, CH_2C=C), 6.60 (qt, ^3J = 7 Hz, ^4J = 2 Hz; 1H, C=CH). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.14 (CH_3), 20.13 (C-4), 26.88 (C-3), 38.95 (C-5), 132.96 (*C*=CH), 138.90 (C=*C*H), 206.69 (C=O). – MS (70 eV): *m/z* (%) = 110 (100) [M^+], 95 (52) [$M^+ - CH_3$]. – $C_7H_{10}O$ (110.1): calcd. C 76.31, H 9.16; found C 76.17, H 8.93.

(E)-2-Propylidenecyclopentanone (**6b**): 2.24 g (20 mmol) of DABCO, 25 ml of DMSO and 1.46 g (5 mmol) of **u,l-5b** were allowed to react at 115–120°C for 30 min to yield after chromatographic purification on silica gel (10 g) with diethyl ether/pentane (1:5) 0.53 g (85%) of **6b** as a colorless oil; R_f = 0.18. – IR (neat): $\tilde{\nu}$ = 1700 (C=O), 1640 cm^{-1} (C=C). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.07 (t, J = 8 Hz; 3H, CH_3), 1.84–2.05 (m; 2H, CH_2CH_2C=C), 2.16 (tt, J = 7.5 and 7.5 Hz; 2H, CH_2CH_2C=C), 2.34 (t, J = 7.5 Hz; 2H, CH_2C=O), 2.52–2.64 (m; 2H, CH_2CH_3), 6.53 (tt, J = 7.5 Hz, ^4J = 2.5 Hz; 1H, C=CH). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 12.97 (CH_3), 19.83 (C-4), 23.00 (CH_2CH_3), 26.59 (C-3), 38.61 (C-5), 136.68 (*C*=CH), 137.50 (C=*C*H), 207.29 (C=O). – MS (70 eV): *m/z* (%) = 124 (100) [M^+], 109 (16) [$M^+ - CH_3$], 95 (78) [$M^+ - C_2H_5$]. – $C_8H_{12}O$ (124.1): calcd. C 77.36, H 9.75; found C 77.43, H 9.61.

(E)-2-Butylidenecyclopentanone (**6c**), *cf. Ref.*[15]: 1.68 g (15 mmol) of DABCO, 20 ml of DMSO and 0.92 g (3 mmol) of **u,l-5c** were allowed to react at 100–120°C for 30 min to yield after chromatographic purification on silica gel (8 g) with diethyl ether/pentane (1:4) 0.33 g (80%) of **6c** as a colorless oil; R_f = 0.27. – IR (neat): $\tilde{\nu}$ = 1695 (C=O), 1645 cm^{-1} (C=C). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.94 (t, J = 8 Hz; 3H, CH_3), 1.50 (qt, J = 8 Hz and 7.5 Hz; 2H, CH_2CH_3), 1.93 (dt, J = 7.5 Hz, ^4J = 2.5 Hz; 2H, $CH_2CH_2CH_2C$=C), 2.02–2.21 (m; 2H, C=C$CH_2CH_2CH_3$), 2.36 (t, J = 7.5 Hz; 2H, CH_2C=O), 2.53–2.65 (m; 2H, $CH_2CH_2CH_2C$=C), 6.55 (tt, J = 7.5 Hz, ^4J = 2.5 Hz; 1H, C=CH). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 13.91 (CH_3), 19.84 (C-4), 21.72 (CH_2CH_3), 26.77 (C-3), 31.70 ($CH_3CH_2CH_2C$=C), 38.64 (C-5), 136.05 (C=*C*H), 137.40 (*C*=CH), 207.20 (C=O). – MS (70 eV): *m/z* (%) = 138 (11) [M^+], 123 (54) [$M^+ - CH_3$], 109 (16) [$M^+ - C_2H_5$], 95 (100) [$M^+ - C_3H_7$]. – $C_9H_{14}O$ (138.1): calcd. C 78.20, H 10.22; found C 78.03, H 9.98.

(E)-2-Benzylidenecyclopentanone (**6d**): 4.48 g (40 mmol) of DABCO, 50 ml of DMSO and 3.40 g (10 mmol) of **u,l-5d** were allowed to react at 120–130°C for 30 min to yield after chromatographic purification on silica gel (10 g) with diethyl ether/pentane (1:4) 1.41 g (82%) of **6d** as a colorless oil; R_f = 0.22. – IR (neat): $\tilde{\nu}$ = 3040 and 3020 (aromat. CH), 1700 (C=O), 1635 (C=C), 1580 cm^{-1} (aromat. C=C). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.04 (tt, J = 7.5 and 7.5 Hz; 2H, CH_2CH_2C=O), 2.42 (t, J = 7.5 Hz; 2H, CH_2C=O), 2.98 (dt, J = 7.5 Hz, ^4J = 2 Hz; 2H, CH_2C=C), 6.32 (t, ^4J = 2 Hz; 1H, C=CH), 7.29–7.60 (m; 5H, C_6H_5). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 20.18 (C-4), 29.33 (C-3), 37.76 (C-5), 128.68, 129.29 and 130.73 (aromat. CH), 132.23 (C=*C*H), 135.53 (aromat. C), 136.06 (*C*=CH), 207.23 (C=O). – MS (70 eV): *m/z* (%) = 172 (100) [M^+], 95 (42) [$M^+ - C_6H_5$]. – $C_{12}H_{12}O$ (172.1): calcd. C 83.68, H 7.03; found C 83.42, H 6.88.

(E)-2-(2,2-Dimethylpropylidene)cyclopentanone (**6e**): 1.12 g (10 mmol) of DABCO, 15 ml of DMSO and 0.96 g (3 mmol) of **u,l-5e** were allowed to react at 115–135°C for 30 min to yield after chromatographic purification on silica gel (11 g) with diethyl ether/pentane (1:5) 0.25 g (55%) of **6e** as a colorless oil; R_f = 0.31. – IR (neat): $\tilde{\nu}$ = 1705 (C=O), 1640 cm^{-1} (C=C). – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.14 [s; 9H, $C(CH_3)_3$], 2.10 (tt, J = 7.5 Hz and 7.5 Hz; 2H, CH_2CH_2C=C), 2.40 (t, J = 7.5 Hz; 2H, CH_2C=O), 2.90 (dt, J = 7.5 Hz, ^4J = 2 Hz; 2H, CH_2C=C), 6.50 (t, ^4J = 2 Hz; 1H, C=CH). – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 19.88 (C-4), 24.40 [$C(CH_3)_3$], 26.59 (C-3), 36.71 [$C(CH_3)_3$], 38.66 (C-5), 136.70 (C=*C*H) 139.50 (*C*=CH), 207.17 (C=O). – MS (70 eV): *m/z* (%) = 152 (100) [M^+], 137 (52) [$M^+ - CH_3$]. – $C_{10}H_{16}O$ (152.1): calcd. C 78.88, H 10.60; found C 78.69, H 10.32.

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