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Diastereoselective Alkylation of Chiral Derivatives of Acetoacetic Acid

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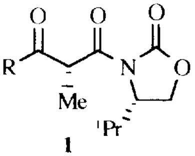
Abstract. *N*-acetoacetyl-(*S*)-4-benzyloxazolidin-2-one and *N*-acetoacetyl-(*R*)-bornane-10,2-sultam are alkylated at the C-α of the acetoacetyl moiety with significant diastereoisomeric excesses. The diastereoisomers are in general easily separable and configurationally fairly stable.

INTRODUCTION

In 1984 Evans and coworkers reported the preparation of compounds **1** and **2** by acylation of the corresponding *N*-propionyloxazolidinones.[1,2] Compounds of types **1** and **2**, having low kinetic acidity, are configurationally fairly stable in spite of having an intercarbonylic proton. Similar results have been further reported by others,[3] with these and similar compounds that are amenable to further transformations.[2,3]



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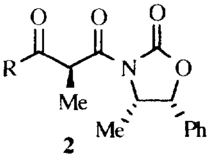

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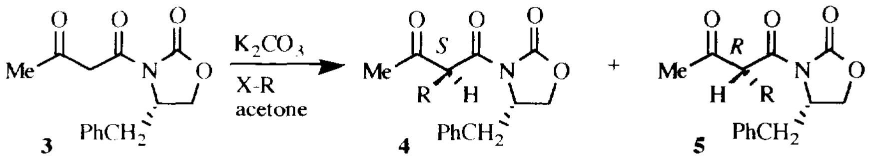
At the best of our knowledge the alkylation of *N*-acetoacetyl derivatives such as **3** and **6** (acac-X_c) featuring either an oxazolidinone or a bornanesultam[4] as chiral auxiliaries has never been reported.

RESULTS

We present now our results on this subject. *N*-Acetoacetyl-(4*S*)-4-benzyloxazolidin-2-one, **3** and *N*-acetoacetyl-(2*R*)-bornane-10,2-sultam, **6**, were prepared as previously described.[5]

Since the final products are sensitive to basic media we chose as mild reaction conditions as possible; potassium carbonate (1.1 eq) suspended in acetone was used to generate the conjugate bases of **3** and **6** (Scheme). When the reactions were fast enough, useful diastereoisomeric excesses (de) were achieved (Table). Thus, reactions of **6** with cinnamyl bromide (run 14) and with 4-bromophenacyl bromide (run 15) took 5 and 10 days to be completed and afforded de's of 46 and 24 %, lower that the excesses at 24 h of reaction time (de ca. 60%). In general the diastereoisomeric products (**4** and **5** from **3** and **7** and **8** from **6**) were easily separated by crystallization or by column chromatography. Only in run 9, when isolating products **4f** and **5f**, was a decrease of the diastereoisomeric excess noticed. X-Ray diffraction studies of the major diastereoisomer from run 10 and the only diastereoisomer from run 13 showed sterochemistries *S* and *R* at the new stereogenic centers (Products **4g** and **7b**, see Fig). We assume that the new stereogenic centers in the major diastereoisomers correspond to the same chirality as in **4g** and **7b**. In summary, the alkylation of **3** and **6** with K_2CO_3 and an alkyl halide in acetone is a general method affording from modest to good diastereomeric excesses of products **4** and **7**, which are easily isolable from their diastereoisomers **5** and **8**.



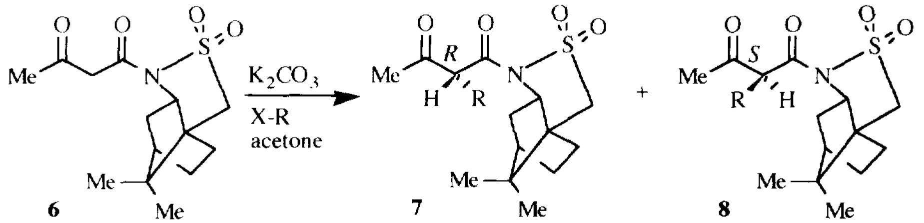


TABLE. Substituents R, Yields and Diastereoisomeric Excesses for Compounds 4,5,7 and 8.

Run	acac-X_C	R-X	T (°C)	Time	% (a)	Maj.(%) (b)	Min. (%) (b)	de (%)
1	**3**	CH_3I	40	5.5h	92	**4a** (48) (c)	**5a** (44)	6
2	**3**	$PhCH_2Br$	40	24h	ca. 100	**4b** (31) (c)	**5b** (29)	0
3	**3**	$PhCH_2Br$	-15	4d	ca. 100	**4b** (40) (c)	**5b** (25)	30
4	**3**	$PhCH_2Br$	-40	15d	50	(d)	(d)	37
5	**3**	4-$ClPhCH_2Cl$	40	5d	79	(d)	(d)	44
6	**3**	4-$ClPhCH_2Cl$	Refl.	5d	94	**4c** (e)	**5c** (15)	20
7	**3**	CH_2=$CHCH_2Br$	40	24h	ca. 100	**4d** (41)	**5d** (e)	6
8	**3**	PhCH=$CHCH_2Br$	40	48h	ca. 100	**4e** (45) (c)	**5e** (30)	26
9	**3**	4-$BrPhCOCH_2Br$	40	48h	ca. 100	**4f** (23)	**5f** (e)	39 (f)
10	**3**	$EtOCOCH_2I$	-15	72h	ca. 100	**4g** (45) (g)	**5g** (e)	20
11	**6**	$PhCH_2CH_2I$	40	4d	(h)	**4h** (43) (c)	**5h** (22)	32
12	**6**	CH_3I	40	30h	92	**7a** (29)	**8a** (e)	20
13	**6**	$PhCH_2Br$	rt	24h	ca. 100	**7b** (91) (g)		>95
14	**6**	PhCH=$CHCH_2Br$	rt	5d	73	**7e** (45)	**8e** (17)	46 (i)
15	**6**	4-$BrPhCOCH_2Br$	rt	10d	89	**7f** (31)	**8f** (e)	24 (j)

(a) Overall yield before separation; (b) Isolated yield as pure compd; (c) The other diastereoisomer (ca. 10%) was present; (d) No isolation was performed; (e) No isolation was achieved; (f) Upon column chromatography the de was reduced to 9%; (g) Structure determined by X-ray diffraction; (h) Complicated reaction crude; (i) 60 % at 24 h; (j) 62 % at 24 h.

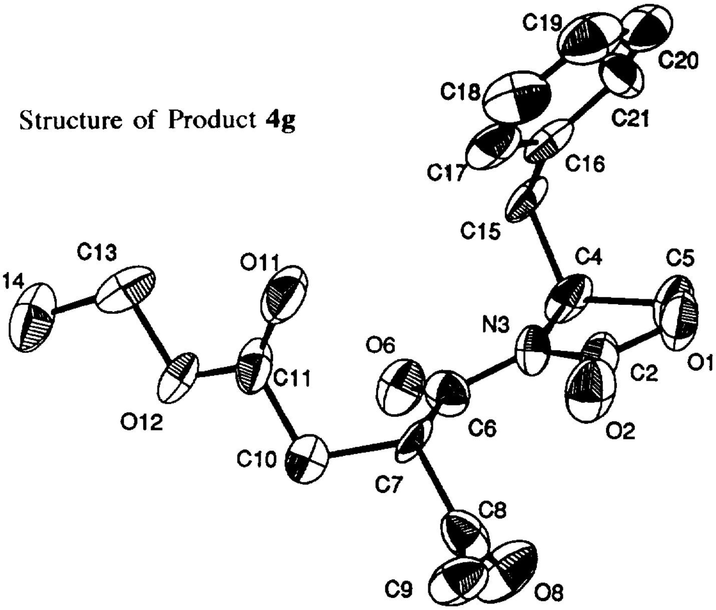
EXPERIMENTAL

^1H (^{13}C) NMR spectra were registered at 250 (62.5) MHz. Specific rotations were measured at room temp.

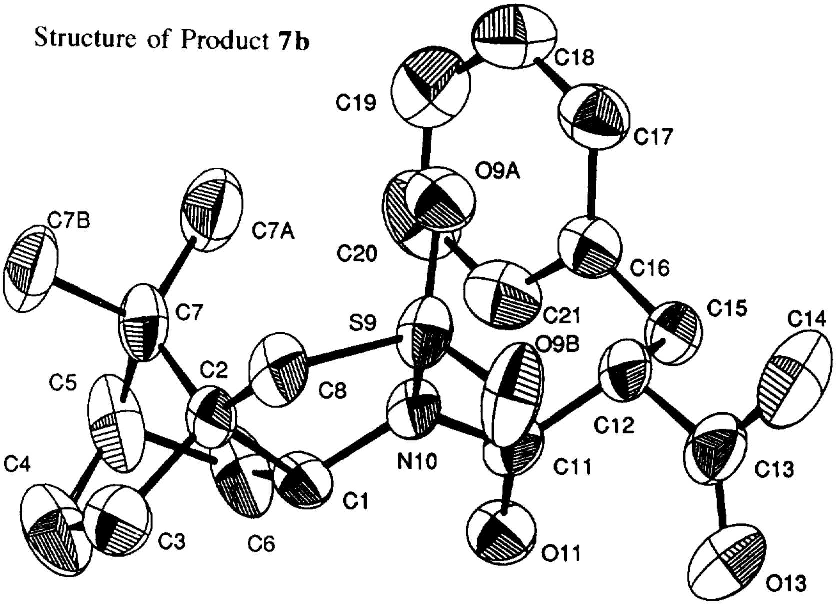
(4*S*)-4-Benzyl-*N*-(2-cinnamyl-1,3-dioxobutyl)oxazolidin-2-ones, **4e** and **5e**.

A mixture of oxazolidinone **3** (1.00g, 3.8 mmole), cinnamyl bromide (0.91g, 4.6 mmole), powdered potassium carbonate (0.58 g, 4.2 mmole) and anhydrous acetone (10 mL) was heated at 40°C under magnetic stirring for 48 h. The solid was filtered off and the solvent was evaporated. The residue was partitioned between dichloromethane and water. The organic layer was dried and evaporated to afford a mixture of **4e** and **5e** (1.50g, 100%) in a ratio ca. 63:27 (26% de) determined by integration of the signals of one of the CH_2-Ph protons at δ 3.24 and 3.42. The mixture was digested several times with diethyl ether to afford the minor diastereoisomer (4*S*)-4-Benzyl-*N*-((2*R*)-2-cinnamyl-1,3-dioxobutyl)oxazolidin-2-one, **5e**, in 30 % isolated yield. The solvent from the digestion was evaporated to afford the oily major diastereoisomer **4e** (45%).

Structure of Product **4g**



Structure of Product **7b**



(4*S*)-4-Benzyl-*N*-((2*S*)-2-cinnamyl-1,3-dioxobutyl)oxazolidin-2-one, **4e**: oil; IR(film) 1779, 1718, 1701, 970; ^{1}H NMR ($CDCl_3$) δ 2.37 (s, 3H), 2.70 (m, 1H), 2.76 (dd, J = 13.5 and 9.9 Hz, 1H), 2.84-2.97 (m, 1H), 3.42 (dd, J = 9.9 and 3.3 Hz, 1H), 4.17 (m, 2H), 4.64 (m, 1H), 4.71 (dd, J = 8.8 and 4.8, 1H), 6.23 (dd, J = 16.0 and 7.0 Hz, 1H), 6.52 (d, J = 16.0 Hz, 1H), 7.12-7.37 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 29.3, 31.0, 37.3, 55.3, 58.6, 66.3, 126.1, 132.9, 135.2, 136.8, 153.6, 168.5, 203.5.

(4*S*)-4-Benzyl-*N*-((2*R*)-2-cinnamyl-1,3-dioxobutyl)oxazolidin-2-one, **5e**: mp 110-112°C (diethyl ether); IR (KBr) 1767, 1703, 980 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.38 (s, 3H), 2.74 (m, 2H), 2.92 (m, 1H), 3.24 (dd, J = 13.5 and 2.6 Hz, 1H), 4.16 (dd, J = 9.0 and 3.3 Hz, 1H), 4.23 (dd, J = 17.0 and 9.0 Hz, 1H), 4.78 (m, 2H), 6.27 (dt, J = 15.7 and 7.3 Hz, 2H), 6.54 (d,J = 15.7 Hz, 1H), 7.23 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 29.3, 31.0, 37.7, 55.0, 58.9, 66.3, 125.9-132.8 (12C), 134.8, 136.8, 153.7, 168.8, 203.7; $[\alpha]_D$ = +157° (c= 1.53, $CHCl_3$). Anal. Calcd for $C_{23}H_{23}NO_4$: C, 73.19; H, 6.14; N, 3.71. Found: C, 73.00 and 73.16; H, 6.18 and 6.20; N, 3.64 and 3.74.

(4*S*)-4-Benzyl-*N*-((2*S*)-2-acetyl-4-ethoxy-1,4-dioxobutyl)oxazolidin-2-one, **4g**.

A mixture of **3** (1.00 g, 3.8 mmole), ethyl iodoacetate (1.00 g, 4.6 mmole), powdered potassium carbonate (0.58g, 4.2 mmole) and anhydrous acetone (10 mL) was magnetically stirred at -15°C for 72 h. The solid was filtered and the solvent was evaporated. The residue was partitioned between dichloromethane and water. The organic layer was dried and evaporated to afford a mixture of **4g** and **5g** (1.27g, 100%) in a ratio 60:40 (20% de, by integration of the NMR signals of one $C\underline{H}_2$-Ph proton at δ 3.26 and 3.39). Recrystallizations from diethyl ether permitted the isolation of the major diastereoisomer **4g** (45%) (X-ray diffraction): mp 123-125°C; IR (KBr) 1767, 1722, 1702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28 (t, J = 7.1 Hz, 3H), 2.32 (s, 3H), 2.75 (dd, J = 17.2 and 4.0 Hz, 1H), 2.81 (dd, J = 13.4 and 9.3 Hz, 1H), 3.09 (dd, J = 10.6 and 17.2 Hz, 1H), 3.26 (dd, J = 13.4 and 3.3 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 4.22 (m, 2H), 4.76 (m, 1H), 5.09 (dd, J = 10.6 and 4.0 Hz, 1H), 7.19-7.39 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.0, 28.6, 31.9, 37.4, 54.9, 55.1, 61.2, 66.3, 127.3-134.9 (6C), 153.6, 168.4, 170.7, 202.9; $[\alpha]_D$ = +136° (c = 1.73, $CHCl_3$). Anal. Calcd for $C_{18}H_{21}NO_6$: C, 62.24; H, 6.09; N: 4.03. Found: C, 62.19 and 62.29; H, 5.76 and 5.83; N, 3.96 and 4.01.

Other products **4** and **5** were prepared by the same method (See Table).

(4*S*)-4-Benzyl-*N*-(2-methyl-1,3-dioxobutyl)oxazolidin-2-ones, **4a** and **5a**

(4*S*)-4-Benzyl-*N*-((2*R*)-2-methyl-1,3-dioxobutyl)oxazolidin-2-one **5a**: mp 88-91°C; IR (KBr) 1776, 1715, 1701 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.43 (d, J = 7.3 Hz, 3H), 2.33 (s, 3H), 2.77 (dd, J = 13.5 and 9.9 Hz, 1H), 3.42 (dd, J = 13.5 and 3.3 Hz, 1H), 4.16 (m, 2H), 4.54 (q, J = 7.3 Hz, 1H), 4.67 (m, 1H), 7.13-7.33 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 12.3, 28.3, 37.3, 52.9, 55.2, 66.3, 127.1, 128.8, 128.7, 129.2, 129.4, 135.3, 154.0, 169.7, 205.1; $[\alpha]_D$ = -29 (c = 1.19, $CHCl_3$). Anal. Calcd for $C_{15}H_{17}NO_4$: C, 65.44; H, 6.22; N, 5.09. Found: C, 64.99 and 65.12; H, 5.84 and 5.90; N, 4.91 and 4.91.

(4*S*)-4-Benzyl-*N*-((2*S*)-2-methyl-1,3-dioxobutyl)oxazolidin-2-one **4a**: oil; IR (film) 1776, 1719, 1702; ^{1}H NMR ($CDCl_3$) δ 1.44 (d, J = 7.3 Hz, 3H), 2.29 (s, 3H), 2.80 (dd, J = 13.2 and 9.1 Hz, 1H), 3.29 (dd, J = 13.2 and 3.3 Hz, 1H), 4.10-4.27 (m, 2H), 4.61 (q, J = 7.3 Hz, 1H), 4.73 (m, 1H), 7.16-7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 28.1, 37.7, 53.2, 55.1, 66.4, 126.9-135.2 (6C), 153.7, 169.7, 205.2.

(4*S*)-4-Benzyl-*N*-(2-benzyl-1,3-dioxobutyl)oxazolidin-2-ones, **4b** and **5b**

(4*S*)-4-Benzyl-*N*-((2*S*)-2-benzyl-1,3-dioxobutyl)oxazolidin-2-one, **4b**

Oil; IR (film) 1778, 1772, 1720, 1717, 1703, 1700; ^{1}H NMR ($CDCl_3$) δ 2.25 (s, 3H), 2.74 (dd, J = 13.5 and 9.5 Hz, 1H), 3.09 (dd, J = 13.9 and 5.5 Hz, 1H), 3.32 (dd, J = 14.3 and 9.5 Hz, 1H), 3.37 (m, 1H), 4.01 (dd, J = 16.8 and 9.1 Hz, 1H), 4.09 (dd, J = 9.1 and 2.6 Hz, 1H), 4.53 (m, 1H), 4.95 (dd, J = 9.2 and 5.5 Hz, 1H), 7.17-7.39 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 29.4, 33.5, 37.2, 55.1, 60.1, 66.3, 126.5-138.2 (12C), 153.5, 168.3, 203.6.

(4*S*)-4-Benzyl-*N*-((2*R*)-2-benzyl-1,3-dioxobutyl)oxazolidin-2-one, **5b**

Mp 122-123°C; IR (KBr) 1768, 1711, 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3H), 2.64 (dd, J = 13.6 and 8.6 Hz, 1H), 3.02 (dd, J = 13.6 and 2.9 Hz, 1H), 3.13 (dd, J = 13.9 and 5.3 Hz, 1H), 3.37 (dd, J = 13.9 and 9.5 Hz, 1H), 4.12 (dd, J = 9.1 and 3.3 Hz, 1H), 4.22 (apparent t, J ca. 8.6 Hz, 1H), 4.74 (m, 1H), 5.05 (dd, J = 9.5 and 5.3 Hz, 1H), 7.19-7.38 (m, 10H); ^{13}C NMR (CDCl$_3$) δ 29.8, 33.8, 37.2, 54.7, 60.7, 66.1, 126-132 (12C), 153.6, 168.5, 203.7; $[\alpha]_D$ = +153 (c = 1.6, CHCl$_3$). Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99. Found: C, 70.93 and 71.43; H, 5.61 and 5.67; N, 3.90 and 3.92.

(4*S*)-4-Benzyl-*N*-((2*R*)-2-(4-chlorobenzyl)-1,3-dioxobutyl)oxazolidin-2-one, **5c**.

Mp 69-72°C; IR (KBr) 1778, 1717, 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.25 (s, 3H), 2.65 (dd, J = 13.5 and 8.8 Hz, 1H), 3.04 (dd, J = 13.5 and 3.3 Hz, 1H), 3.10 (dd, J = 14.1 and 5.1 Hz, 1H), 3.32 (dd, J = 14.1 and 9.1 Hz, 1H), 4.13 (dd, J = 9.1 and 3.3 Hz, 1H), 4.21 (dd, J = 17.2 and 9.1 Hz, 1H), 4.73 (m, 1H), 5.01 (dd, J = 9.1 and 5.1 Hz, 1H), 7.23-7.30 (m, 9H); ^{13}C NMR (CDCl$_3$) δ 29.4, 33.1, 37.4, 54.9, 60.6, 66.4, 127.3-130.6 (9C), 132.7, 134.6, 136.7, 153.6, 168.3, 203.3; $[\alpha]_D$ = +112° (c = 0.6, CHCl$_3$). Anal. Calcd for $C_{21}H_{20}ClNO_4$: C, 65.37; H, 5.22; N, 3.63. Found: C, 65.28 and 65.01; H, 5.22 and 5.22; N, 3.39 and 3.41.

(4*S*)-4-Benzyl-*N*-((2*S*)-2-acetyl-1-oxo-4-penten-1-yl)oxazolidin-2-one, **4d**.

Mp 85-86°C; IR (KBr) 1772, 1716, 1696 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.33 (s, 3H), 2.56 (m, 1H), 2.76 (m, 2H), 3.42 (dd, J = 13.5 and 3.3 Hz, 1H), 4.19 (apparent d, 2H), 4.68 (m, 2H), 5.10 (dd, J = 11.3 and 1.5 Hz, 1H), 5.16 (dd, J = 17.1 and 1.5 Hz, 1H), 5.87 (ddt, J = 17.1, 10.2 and 6.9 Hz, 1H), 7.20-7.38 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 29.3, 31.6, 37.3, 55.2, 58.2, 66.3, 117.6, 127.2-129.4 (5C), 134.7, 135.2, 153.6, 168.5, 203.7; $[\alpha]_D$ = -35° (c = 1.49, CHCl$_3$). Anal. Calcd for $C_{17}H_{19}NO_4$: C, 67.74; H, 6.36; N, 4.65. Found: C, 67.37 and 67.39; H, 6.49 and 6.43; N, 4.57 and 4.60.

(4*S*)-4-Benzyl-*N*-((2*S*)-2-acetyl-1,4-dioxo-4-(4-bromophenyl)butyl)oxazolidin-2-one, **4f**.

Mp 46-48°C (EtOAc-hexanes); IR (KBr) 1777, 1722, 1689 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.36 (s, 3H), 2.74 (dd, J = 13.5 and 9.9 Hz, 1H), 3.18 (dd, J = 17.7 and 3.1 Hz, 1H), 3.35 (dd, J = 13.5 and 3.3 Hz, 1H), 3.85 (dd, J = 17.7 and 10.7 Hz, 1H), 4.12-4.27 (m, 2H), 4.64 (m, 1H), 5.20 (dd, J = 10.7 and 3.1 Hz, 1H), 7.17-7.32 (m, 5H), 7.60 (d, J = 8.7 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H); ^{13}C NMR (CDCl$_3$) δ 28.8, 36.1, 37.4, 54.0, 55.3, 66.4, 127.2-135.1 (12C), 153.6, 168.4, 195.5, 203.4; $[\alpha]_D$ = -45° (c = 1.5, CHCl$_3$). Anal. Calcd for $C_{22}H_{20}BrNO_5$: C, 57.66; H, 4.40; N, 3.06. Found: C, 57.46 and 57.48; H, 4.52 and 4.56; N, 2.93 and 3.03.

(4*S*)-4-Benzyl-*N*-(2-(2-phenylethyl)-1,3-dioxobutyl)oxazolidinones, **4h** and **5h**.

They were separated by column chromatography on silica gel.

(4*S*)-4-Benzyl-*N*-((2*S*)-2-(2-phenylethyl)-1,3-dioxobutyl)oxazolidinone, **4h**: ^{1}H NMR (CDCl$_3$) δ 2.02-2.12 (m, 1H), 2.28 (s, 3H), 2.28-2.44 (m, 1H), 2.62-2.83 (m, 3H), 3.41 (dd, J = 13.5 and 3.3 Hz, 1H), 4.06-4.15 (m, 2H), 4.55 (dd, J = 9.7 and 3.1 Hz, 1H), 4.62 (m, 1H), 7.18-7.35 (m, 10H)

(4*S*)-4-Benzyl-*N*-((2*R*)-2-(2-phenylethyl)-1,3-dioxobutyl)oxazolidinone, **5h**: Oil; IR (film) 1777, 1719, 1703 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.10 (m, 1H), 2.27 (s, 3H), 2.29-2.45 (m, 1H), 2.63-2.85 (m, 3H), 3.28 (dd, J = 13.3 and 3.5 Hz, 1H), 4.12-4.25 (m, 2H), 4.62 (dd, J = 9.3 and 3.5 Hz, 1H), 4.76 (m, 1H), 7.18-7.36 (m, 10H); ^{13}C NMR (CDCl$_3$) δ 28.7, 29.1, 34.0, 37.9, 55.0, 58.5, 66.3, 126.2-140.6 (12C), 153.6, 168.7, 204.2; $[\alpha]_D$ = + 114° (c = 1.28, CHCl$_3$). Anal. Calcd for $C_{22}H_{23}NO_4$: C, 72.31; H, 6.34; N, 3.83. Found: C, 72.04 and 71.93; H, 6.57 and 6.63; N, 3.74 and 3.59.

N-((2*R*)-2-Benzyl-1,3-dioxobutyl)-(2*R*)-bornane-10,2-sultam, **7b**.

A mixture of sultam **6** (0.50g, 1.7 mmole), benzyl bromide (0.34g, 2.0 mmole), powdered potassium carbonate (0.25g, 1.8 mmole) and anhydrous acetone (10 mL) was magnetically stirred at room temperature for 24 h. The solid was filtered and the solution was evaporated. The residue was partitioned between dichloromethane and water. The organic layer was dried and evaporated to afford oily **7a** (**8a** was not detected) which crystallized (91%) upon digestion with diethyl ether: mp 149-150°C; IR (KBr) 1729, 1684, 1328 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 0.69 (s, 3H), 0.89 (s, 3H), 1.33 (m, 2H), 1.89 (m, 5H), 2.23 (s, 3H), 3.11 (dd, J = 14.0 and 8.8 Hz, 1H), 3.26 (dd, J = 14.0 and 6.2 Hz, 1H), 3.42 (AA' system, J ca. 14.5 Hz, 2H), 3.86 (m, 1H), 4.50 (dd, J = 8.8 and 6.2 Hz, 1H), 7.15-7.30 (m, 5H); ^{13}C NMR (CDCl$_3$) δ 19.7, 20.4, 26.3, 29.5, 32.7, 36.0, 38.1, 44.5, 47.5, 48.1, 52.9, 60.1, 65.3, 131.9, 168.0, 201.4; $[\alpha]_D$ = -22° (c = 1.47, CH$_3$CN). Anal. Calcd for $C_{21}H_{27}NO_4S$: C, 64.76; H, 6.99; N, 3.60. Found: C, 64.74 and 64.66; H, 6.57 and 6.53; N, 3.52 and 3.56.

N-(2-Cinnamyl-1,3-dioxobutyl)-(2*R*)-bornane-10,2-sultams, **7e** and **8e**.

A mixture of **6** (0.50g, 1.7 mmole), cinnamyl bromide (0.36g, 1.8 mmole), powdered potassium carbonate (0.25g, 1.8 mmole) and anhydrous acetone (10 mL) was stirred at room temperature for 5 days. The diastereoisomeric excess (60% at 24 h and 46% at 5 days) was monitored by integration of the methyl signals at δ 0.82 and 1.10. The solid was filtered off and the solvent was evaporated to afford a residue which was partitioned between dichloromethane and water. The organic layer was dried and evaporated to afford a residue (0.72g) which was chromatographed through a silica-gel column to separate both isomers.

N-((2*R*)-2-Cinnamyl-1,3-dioxobutyl)-(2*R*)-bornane-10,2-sultam, **7e**: mp 73-75°C; IR (film) 2959, 2917, 1728, 1684, 1326, 1117, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82 (s, 3H), 0.89 (s, 3H), 1.20-1.43 (m, 2H), 1.70-2.25 (m, 5H), 2.25 (s, 3H), 2.72-2.88 (m, 2H), 3.45 (d, J = 13.9 Hz, 1H), 3.52 (d, J = 13.9 Hz, 1H), 3.93 (dd, J = 7.7 and 5.1 Hz, 1H), 4.34 (dd, J = 8.6 and 5.7 Hz, 1H), 6.18 (ddd, J = ca. 15, 8.2 and 5 Hz, 1H), 6.42 (d, J = 15.4 Hz, 1H), 7.20-7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.8, 20.3, 26.3, 29.3, 31.3, 32.6, 37.8, 44.3, 47.7, 48.3, 52.9, 58.7, 65.0, 125.4-132.5 (6C), 132.6, 137.0, 166.7, 202.2; $[\alpha]_D$ = +8° (c = 0.48, $CHCl_3$). Anal. Calcd for $C_{23}H_{29}NO_4S$: C, 66.48; H, 7.03; N, 3.37. Found: C, 65.92, 66.52 and 65.76; H, 7.06, 7.12 and 7.07; N, 3.21, 3.26 and 3.18.

N-((2*S*)-2-Cinnamyl-1,3-dioxobutyl)-(2*R*)-bornane-10,2-sultam, **8e**: oil; IR (film) 2960, 2919, 1722, 1697, 1327, 1133, 970 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 3H), 1.10 (s, 3H), 1.18-1.42 (m, 2H), 1.88-2.28 (m, 5H), 2.28 (s, 3H), 2.72 (m, 1H), 2.82 (m, 1H), 3.42 (d, J = 13.9 Hz, 1H), 3.50 (d, J = 13.9 Hz, 1H), 3.89 (dd, J = 7.8 and 4.9 Hz, 1H), 4.37 (dd, J = 8.0 and 5.5 Hz, 1H), 6.29 (dt, J = 15.7 and 6.9 Hz, 1H), 6.48 (d, J = 15.7 Hz, 1H), 7.19-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 19.8, 20.4, 26.3, 29.5, 31.3, 32.7, 37.8, 44.4, 47.7, 48.4, 53.0, 59.1, 65.4, 125.4-132.5 (6C), 132.7, 137.0, 166.7, 202.2; $[\alpha]_D$ = -40° (c = 0.85, $CHCl_3$).

Other products **7** were obtained by the same method

N-((2*R*)-2-methyl-1,3-dioxobutyl)-(2*R*)-bornane-10,2-sultam, **7a**

Mp 153-155°C; IR (KBr) 1719, 1692, 1327 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (s, 3H), 1.06 (s, 3H), 1.23-1.41 (m, 2H), 1.32 (d, J = 6.9 Hz, 3H), 1.76-1.89 (m, 3H), 1.96-2.18 (m, 2H), 2.18 (s, 3H), 3.37 (d, J = 13.9 Hz, 1H), 3.44 (d, J = 13.9 Hz, 1H), 3.82 (dd, J = 7.6 and 4.7 Hz, 1H), 4.14 (q, J = 6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 12.6, 19.8, 20.2, 26.4, 28.1, 32.6, 37.9, 44.4, 47.7, 48.4, 52.8, 53.4, 65.0, 168.2, 202.5; $[\alpha]_D$ = -58° (c = 1.22, $CHCl_3$). Anal. Calcd for $C_{15}H_{23}NO_4S$: C, 57.48; H, 7.40; N, 4.47; S, 10.23. Found: C, 57.87 and 57.78; H, 7.24 and 7.17; N, 4.45 and 4.44; S, 10.11 and 10.15.

N-((2*R*)-2-acetyl-4-(4-bromophenyl)-1,4-dioxobutyl)-(2*R*)-bornane-10,2-sultam, **7f**

Mp 151-155°C (diethyl ether); IR (KBr) 1731, 1689, 1330 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.00 (s, 3H), 1.21 (s, 3H), 1.25-1.48 (m, 2H), 1.90-2.17 (m, 5H), 2.17 (s, 3H), 3.36-3.64 (m, 4H), 3.98 (dd, J = 7.5 and 4.9 Hz, 1H), 4.73 (t, J = 6.9 Hz, 1H), 7.60 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 19.8, 20.7, 26.3, 29.3, 32.7, 37.9, 38.3, 44.5, 47.7, 48.5, 52.9, 54.0, 65.3, 128.5-134.6 (6C), 168.0, 194.7, 201.3; $[\alpha]_D$ = -52° (c = 1.3, $CHCl_3$). Anal. Calcd for $C_{22}H_{26}BrNO_5S$: C, 53.33; H, 5.29; N, 2.83; S, 6.46. Found: C, 53.60 and 53.39; H, 5.33 and 5.35; N, 2.82 and 2.82; S, 6.29 and 6.31.

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