Cyclo- and hydrodimerization of α,β-unsaturated ketones promoted by samarium diiodide

Armando Cabrera,*[a] Ronan Le Lagadec,[a] Pankaj Sharma,[a] José Luis Arias,[b] Rubén Alfredo Toscano,[a] Luis Velasco,[a] Rubén Gaviño,[a] Cecilio Alvarez[a] and Manuel Salmón[a]

[a] *Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Coyoacán, 04720 México DF, Mexico*
[b] *Facultad de Estudios Superiores, Cuautitlán, Universidad Nacional Autónoma de México, Cuautitlán Izcalli, Estado de México, Mexico*

Received (in Cambridge) 5th June 1998, Accepted 2nd September 1998

Samarium(II) iodide is a strong one-electron transfer reducing agent, and is effective for the cyclo- and hydrodimerization of cyclic and non-cyclic α,β-unsaturated ketones. The title dimers can easily be prepared in good yields at room temperature under neutral conditions, using two-mole equivalent of SmI_2 per mole of starting substrate. The reaction is stereocontrolled. The absence of an alcohol as a proton source is essential in the process and the use of HMPA as a copromoter improves the yield of dimeric products, making the reaction regioselective over the competitive C=C double bond reduction. The crystal structures of some of the dimeric derivatives are reported. When η^2- or η^4-iron-coordinated α,β-unsaturated ketones are used as substrates, the reaction gives mainly the 1,4-reduced products.

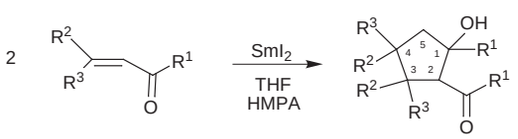
Introduction

From the pioneering studies by Kagan and co-workers[1] that demonstrated the use of samarium diiodide (SmI_2) as a homogeneous one-electron transfer agent, there have been several examples of the use of lanthanoid reagents in organic synthesis.[2] In a preliminary work, we reported that SmI_2 is effective for the coupling of α,β-unsaturated ketones.[3] However, to our knowledge, a general mechanism to explain the reductive behaviour of SmI_2 in α,β-unsaturated compounds has not yet been proposed. For example, Inanaga reported that the reaction of α,β-unsaturated esters with SmI_2 and an alcohol in THF gave 1,4-reduced products in the presence of *N*,*N*-dimethylacetamide as additive,[4] and that the system yielded only codimerization products in the presence of HMPA as copromoter.[5] On the other hand, we have shown that a similar system gives only the 1,4-reduced product in the presence of HMPA.[6] We found that the absence of alcohol, which was previously used as a proton source, is essential to observe behaviour different from Inanaga's results. When ketones were used as substrates several other differences were observed. Fukuzawa reported complex unidentified products for the intermolecular coupling of α,β-unsaturated esters with carbonyl compounds in the absence of alcohol,[7] while Otera found that some conjugated enones undergo reduction of the C=C double bond in the presence of an alcohol in the reaction.[8] Those results again show that the presence or absence of an alcohol as the proton source has a serious influence on the nature of the final products. Here we wish to report that the reaction of several α,β-unsaturated ketones with SmI_2, in the absence of alcohol, leads to a different pathway than that previously reported, producing reductive or cyclo-reductive stereocontrolled coupling reactions. In all cases, the use of HMPA as a copromoter increases the yield of dimer as Inanaga demonstrated with conjugated acid derivatives.[9]

Results and discussion

Reaction of α,β-unsaturated non-cyclic ketones

There appear to be only a few reports on the metal-promoted cyclodimerization of the title compounds. For instance, the Yb–THF–HMPA,[10] $NdCl_3$–lithium naphthalide[11] and tributyltin hydride[12] systems have been used, as well as some electro-assisted systems.[13] As shown in Scheme 1 and Table 1, SmI_2



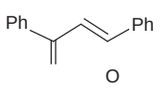
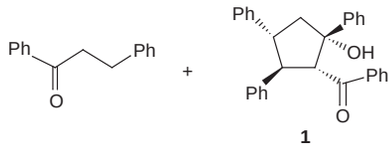
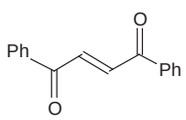
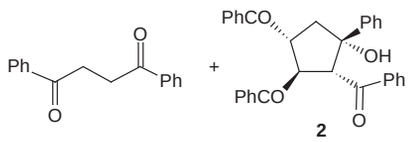
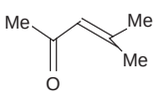
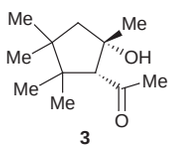
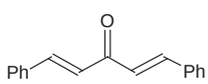
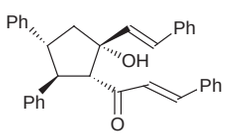
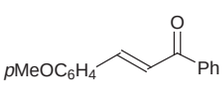
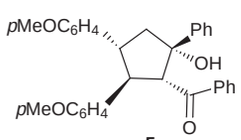
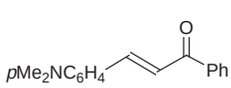
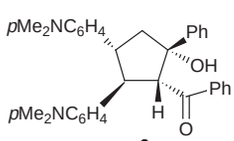
Scheme 1

induced the intramolecular cyclo-reductive coupling of α,β-unsaturated ketones to give cyclopentanol derivatives in higher yields, in shorter times than those reported for reactions with Yb, Nd and Sn. These results demonstrate that the reaction is not only applicable to aromatic ketones but also to aliphatic enones.

The relative stereochemistry of compound **3** was assigned by a 2D NMR study as shown in Fig. 1. The sample was carefully degassed and a NOESY experiment was performed, giving us clear evidence of the *cis*-position of the CH_3-11 and CH_3-8 groups. We observed a strong NOE effect between H-b and the hydrogen atoms of CH_3-6 and of CH_3-10. Additionally, double irradiation of the H-b signal caused enhancement (through a zigzag connection) of the CH_3-9 signal. These observations led us to assign a *trans*-relation between H-b and CH_3-9, and a *cis*-relation between both H-b and CH_3-6, and H-b and CH_3-10. Therefore we were able to establish that the configuration of C(1) was *SR* and that of C(2) was *RS*.

The structures of compounds **1**, **2**, **4**, **5** and **6** were determined by X-ray diffraction.[14] Fig. 2 shows the ORTEP diagram of compound **6** as a typical example of these structures. The regiocyclodimers were shown to be the racemic mixture (1*S*,2*R*,3*S*,4*R*) and (1*R*,2*S*,3*R*,4*S*) in agreement with our previous report for compound **1**,[3] and with the stereochemistry found for the same compound, prepared by Tataki[10] using the Yb–HMPA–THF system. However, Fournier reported that when the same substrate was cyclodimerized by electroreduction, with a mercury cathode in DMF, the observed stereochemistry was

Table 1 Reaction of non-cyclic α,β-unsaturated ketones with SmI_2

Entry	Substrate	Products[a]	Yield (%)
I		 **1**	15 + 85[b] 0 + 100[c,d]
II		 **2**	57 + 43[b] 0 + 100[c,d]
III		 **3**	61[c] 82[c,d]
IV		 **4**	40[c,d]
V		 **5**	55[c,d]
VI		 **6**	68[c,d]

[a] Only one (1*S*,2*R*,3*S*,4*R*) of the two enantiomers is shown for clarity. [b] Yield determined by ^{1}H NMR. [c] Isolated product. [d] Reaction in presence of HMPA.

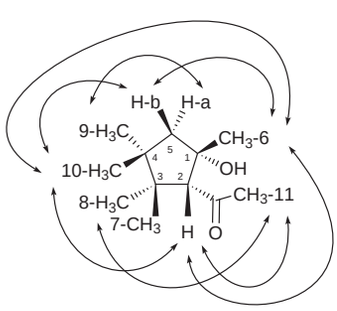


Fig. 1 Observed NOEs on compound **3**.

different at the C(3) and C(4) atoms.[13] These observations suggest stereocontrol in the reaction promoted by SmI_2 since in all cases we found cyclopentanol derivatives with R^2 groups in *trans*-positions at C(3), C(4) atoms and *cis*-related carbonyl and OH groups at C(1), C(2) atoms. On two occasions, by-products crystallized and the X-ray structures of such compounds were determined. These compounds were present only as traces and therefore of insufficient quantity to obtain more analytical data (the yield of compounds **1** and **2** was determined by GC, therefore products **7** and **8** must be present in quantities lower than 1%). Attempts to isolate these by-products in the reactions with other substrates were unsuccessful. In the case of the reaction with dibenzoylethylene (Entry II, Table 1) the by-product isolated proved to be the *meso* open-dimer **7** (Fig. 3). More surprising was the presence of a C(5)-alkylated dimer **8** from the reaction with chalcone (Entry I, Table 1). The X-ray structure of **8** (Fig. 4) shows the stereochemistry at C(3) and C(4) atoms to be different from that of all compounds **1**–**6**. This observation suggests that compound **8** must arise from a small percentage of *cis*-R^2[C(3)]-R^2[C(4)] cyclodimer (not isolated), and the latter from a radical of the same type that produces the *meso* open-dimer **7**. Here, it is important to note that in the *cis*-R^1[C(3)]-R^2[C(4)] cyclodimers, there are two hydrogen atoms in position 5, one of them being far from the bulky substituents in the ring (Fig. 5) so its removal should generate compound **8**. In all cases, the proton source was THF, used as the solvent for the reaction, which has previously been reported by Kagan as

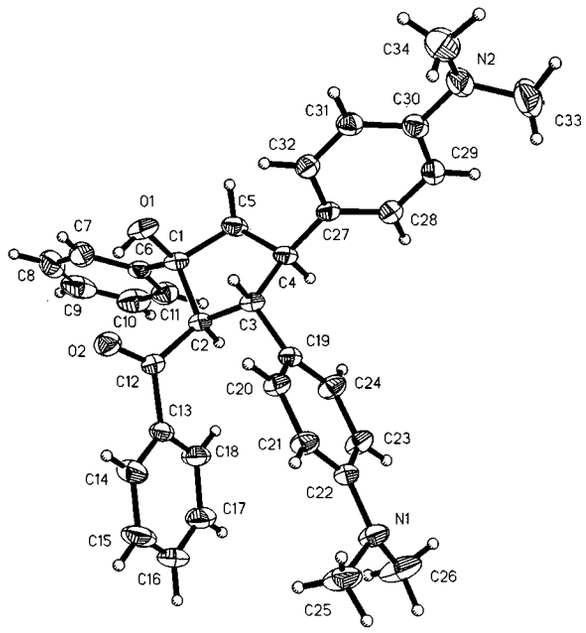


Fig. 2 ORTEP diagram of compound **6**.

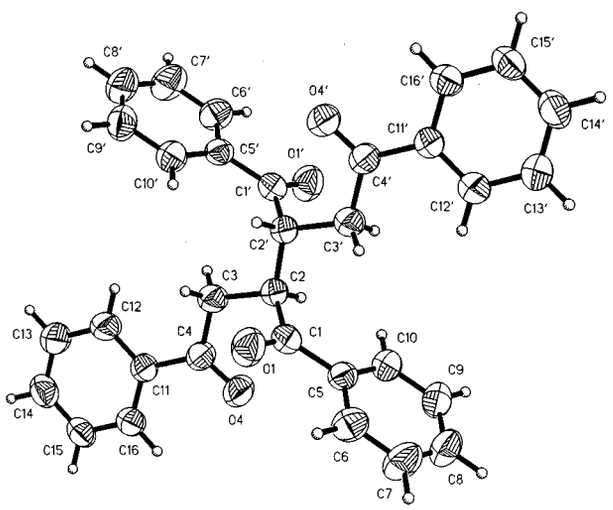


Fig. 3 ORTEP diagram of compound **7**.

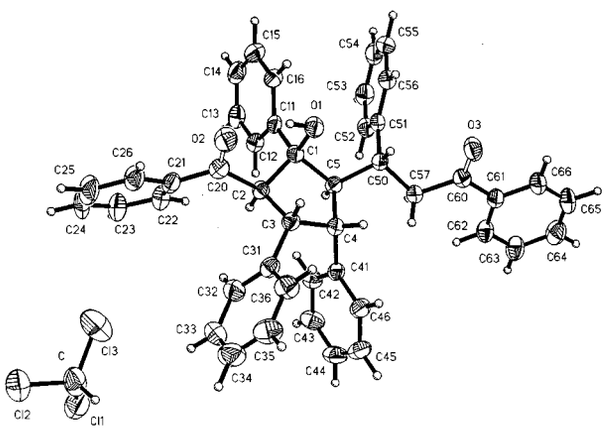


Fig. 4 ORTEP diagram of compound **8**.

a potential proton donor.[15] In order to clarify this point, we carried out the reaction to obtain compounds **1**, **3** and **6** in strictly anhydrous conditions, and without a hydrolytic step. In all cases the cyclodimers were detected, either by GC or mass spectroscopy, thus eliminating the hypothesis of protonation during the isolation process. Additionally, we conducted the

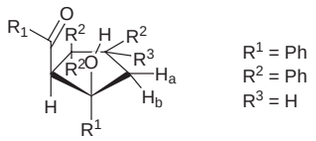
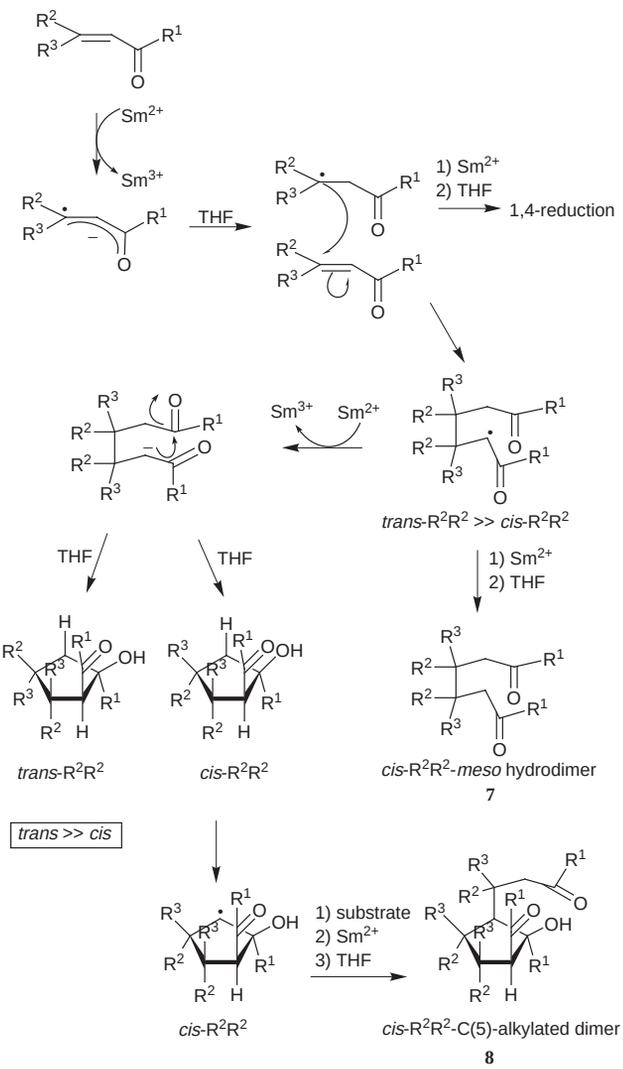


Fig. 5 Conformation of cyclopentanol derivatives.

reaction to obtain compound **6** in dry THF-d_8. At the end of the reaction, the crude product was analysed by mass spectroscopy, showing in the spectra both M + 1 and M + 2 peaks. Those experiments reinforced the theory that THF is the proton donor. As for the inorganic samarium products deriving from these reactions, we reported previously the isolation and characterization of two crystalline complexes $[Sm(HMPA)_3(H_2O)_4]^{3+}$ $3[I]^-$, and $[Sm(HMPA)_4I_2]^+$ $[I]^-$.[3,16] The isolation of the latter is additional proof of the absence of water in the medium. Our working hypothesis for the possible mechanism of the reaction is shown in Scheme 2.[17]



Scheme 2

At this point, we can discuss the observed selectivity of the reaction based on the existence of different conformations for the anions which undergo ring closure to form the final cyclopentanol derivative. Fig. 6 shows two important conformations **A** and **B** coming from the attack of the first radical species on the enone. As seen in the figure, the non-eclipsed form **A** may be favoured since the steric interactions are minimized (the R^2 groups being in *anti*-positions) and when the cycle is generated, *trans*-R^2[C(3)]-R^2[C(4)] groups are obtained regio- and stereo-specifically. In addition, the proximity of the carbonyl groups must stabilize the resulting Sm^{3+} species by

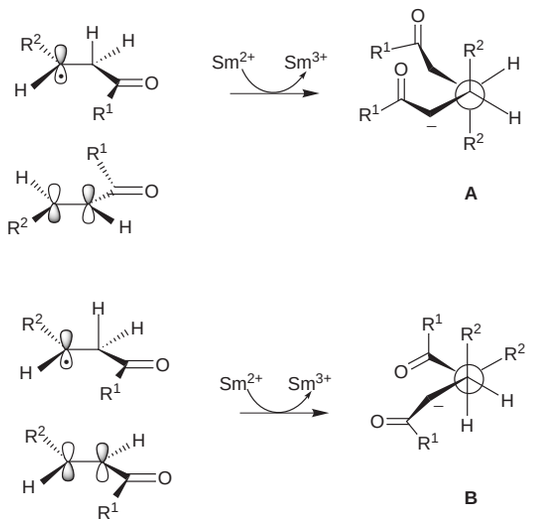
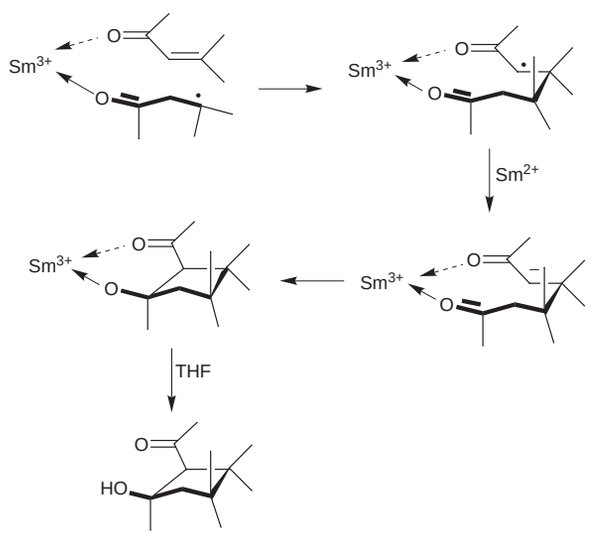


Fig. 6 Possible conformations for the cyclodimerization process.

coordination. In conformation **B**, the R^2 groups are in *syn*-positions, a less favourable arrangement, producing the *meso*-hydrodimer and ultimately the *cis*-R^2[C(3)]-R^2[C(4)] cyclodimer in low quantities. Scheme 3 suggests the possible



Scheme 3

pathway to cyclodimeric products through the coordination with a samarium ionic species.

Reaction of cyclic α,β-unsaturated ketones

As Table 2 shows, both SmI_2–THF and SmI_2–HMPA–THF systems promote the hydrodimerization of cyclic α,β-unsaturated ketones. It is interesting to note the absence of products resulting from the reduction of the monomer C=C double bond. When the reaction is carried out with the sterically hindered 4-*tert*-butylcyclohexen-2-one, the coupling at the double bond is impeded, yielding instead the selective reduction of the carbonyl group. The X-ray structure of compound **9** isolated from the reaction with isophorone was determined and previously reported.[18] The stereochemistry of this compound was found to be *meso* (5*R*,5′*S*). In this case, it seems that the favoured conformation is the one shown in Fig. 7, in which the sterically hindered alicyclic rings cannot occupy suitable positions for the carbanion attack on the carbonyl group. In addition, the carbonyl moieties are too far from one another to coordinate the samarium ionic species involved. In the case of the (*R*)-(+)-pulegone, possessing an exocyclic C=C double bond, the cyclodimer **14** was obtained. Its X-ray structure is

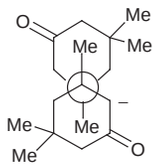


Fig. 7 Arrangement for isophorone-dimer precursor.

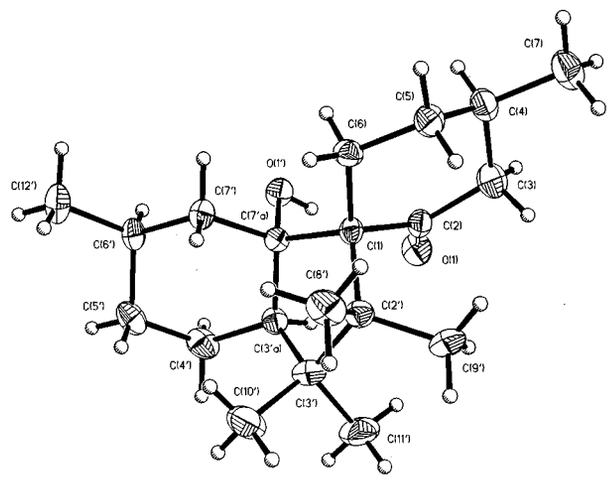


Fig. 8 ORTEP diagram of compound **14**.

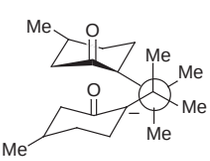


Fig. 9 Arrangement for pulegone-cyclodimer precursor.

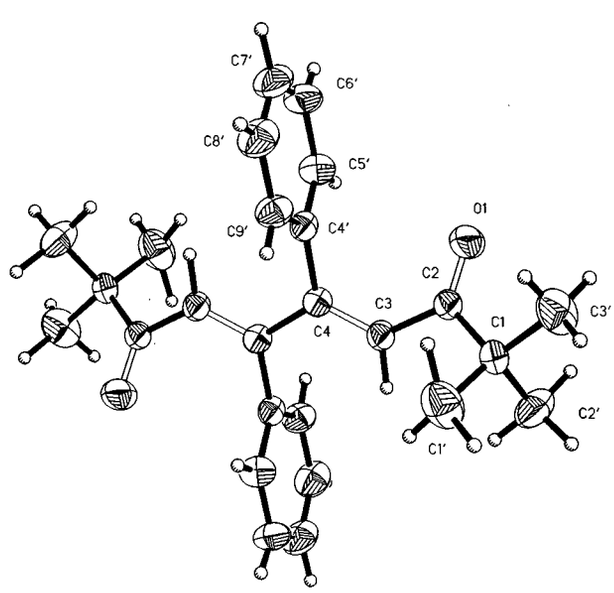
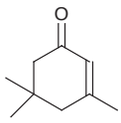
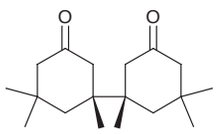
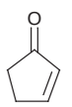
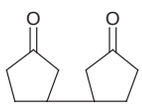
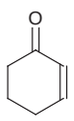
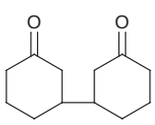
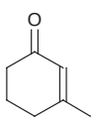
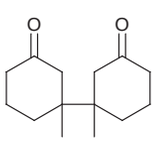
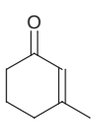
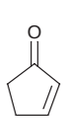
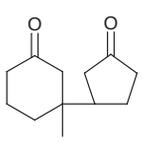
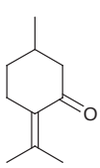
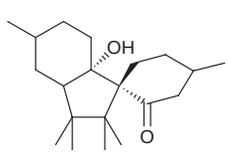


Fig. 10 ORTEP diagram for compound **15**.

represented in Fig. 8. A conformation of type **A** is possible (Fig. 9), minimizing the steric effects of all substituents as well as the relative spatial position of the carbonyl groups allowing the cyclodimerization.

In order to obtain more information about the behaviour of SmI_2 with α,β-unsaturated ketones, we carried out the reaction with 4,4-dimethyl-1-phenylpent-1-yn-3-one. From the reaction only the s-*trans*-butadiene conformer **15** was isolated. Fig. 10 shows its X-ray structure. Its formation can arise through a possible anionic intermediate shown in Fig. 11. This conform-

Table 2 Reductive coupling of cyclic α,β-unsaturated ketones with SmI_2

Entry	Substrate	Products	Yield (%)
VII		 **9**	35.9[b] 70.2[b,c]
VIII		 **10**	82.3[a] 87.0[a,c]
IX		 **11**	70.2[a] 87.0[a,c]
X		 **12**	52.7[a] 83.3[a,c]
XI	 + 	 **13** +**10** + **12**	34.3[a] 74.1[a,c] (in 1 : 1 : 1 ratio)
XII		 **14**	26.0[b,c]

[a] Yield determined by GC and/or GC-MS. [b] Isolated product. [c] Reaction in presence of HMPA.

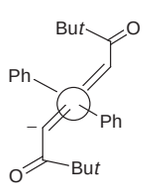


Fig. 11 Arrangement for 1,4-diene-derivative precursor.

ation should be favoured, thus allowing the formation of dimer **15**. Again in this case, the carbonyl groups are too far from each other to promote the coordination with Sm^{3+} species.

Reactions of coordinated α,β-unsaturated ketones

Table 3 shows that when enones are coordinated in η^2- or η^4-mode to $Fe(CO)_4$ or $Fe(CO)_3$ moieties, reaction with the SmI_2–THF system leads to the 1,4-reduced products, along with small quantities of the cyclodimers. When HMPA is used the only products obtained are the 1,4-reduced compounds. We did not study further this reaction with coordinated enones, but we assume that electronic and steric effects of the iron carbonyl species are involved in the process.

Conclusion

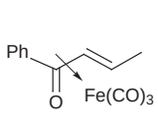
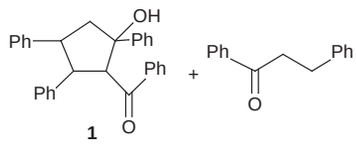
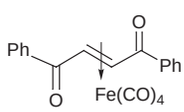
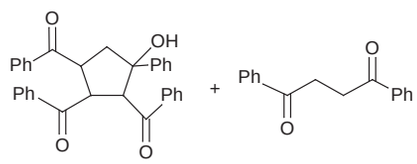
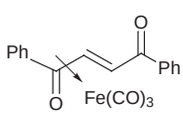
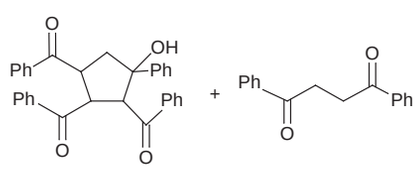
The behaviour of SmI_2–THF and SmI_2–HMPA–THF systems applied to the reaction with some aliphatic, aromatic and alicyclic α,β-enones has been studied. When the process is carried out in the absence of alcohol, we observed regio- and stereocontrol, to give the hydro- and cyclodimers (only two stereoisomers from sixteen possibilities in some cases). We suggested the possibility of the formation of non-staggered, low energy conformers, with the two carbonyl groups close enough to coordinate and stabilize the ionic samarium species. The latter should generate a template with adequate geometry to modulate the stereochemistry of the reaction products. THF used as solvent was found to be the proton donor in the process.

Experimental

General procedures

All unsaturated ketones were purchased from Aldrich and were used as received. Samarium(II) iodide 0.1 M solution in THF was purchased from Aldrich. Iron complexes were prepared from $Fe_2(CO)_9$ according to the literature procedures.[19] Solvents

Table 3 Reaction of coordinated α,β-unsaturated ketones with SmI_2

Entry	Substrate	Products	Yield (%)
XIII		 **1**	24 + 76 0 + 100[a]
XIV		 **2**	19 + 81 0 + 100[a]
XV		 **2**	18 + 82 0 + 100[a]

Yields were determined by ^{1}H NMR. [a] Reaction in presence of HMPA.

were dried following conventional methods and distilled prior to use. All reactions were performed under nitrogen or argon, using syringes and Schlenk-type techniques. Compounds **9**–**13**[18] and 4,4-dimethyl-1-phenylpent-1-yn-3-one[20] were prepared according to the published procedures.

Elemental analyses were performed by Galbraith Laboratories at Knoxville, USA. Infrared spectra were recorded on Perkin-Elmer 552 or Nicolet FTIR-Magna 700 spectrometers as $CHCl_3$ solutions. NMR spectra were recorded on Varian Gemini (^{1}H, 200 MHz, ^{13}C, 50 MHz) or Varian Unity Plus (^{1}H, 200 MHz, ^{13}C, 75 MHz) instruments. The chemical shifts are expressed in ppm, using TMS as internal standard, and *J* values are given in Hz. Peak assignments are based on DEPT and HETCOR experiments. GC-MS analyses were made on a JEOL JMS-AX 505HA mass spectrometer. The source conditions in EI measurements were: temperature 250 °C, electron energy 70 eV, accelerating voltage 3 kV and ionization current 100 μA. Accurate mass measurements for compound **3** were made at a resolution of 10000 using the data system.

Cyclization of α,β-unsaturated ketones

In a typical experiment, 5 cm^3 of a 0.1 M solution of samarium(II) iodide in THF was added to a solution of substrate (0.25 mmol) and of HMPA (0.2 cm^3, 1.14 mmol) in THF (5 cm^3). The mixture was stirred at room temperature for 5 minutes and water (10 cm^3) was added. The solution was extracted with diethyl ether (3 × 10 cm^3) and the combined organic extracts were dried over magnesium sulfate. After evaporation of the solvent, the oily residue was purified by column chromatography on silica (hexane–ethyl acetate mixtures).

NMR Data for compounds **1** and **2** are in accord with those previously published for the same products obtained by different methods.[10,21]

Compound 1. Obtained from chalcone (52 mg) as a white solid in 85% yield after recrystallization from dichloromethane–pentane; ν_{max}/cm^{-1} 1654(CO); δ_H ($CDCl_3$, 199.975 MHz) 7.65–7.00 (20 H, m, Ph), 5.24 (1 H, d, ^4J 1.2, OH), 4.54 (1 H, d, ^3J 12.0, 2-H), 4.11 (1 H, dd, ^3J 12.0, ^3J 10.1, 3-H), 3.79 (1 H, m, ^3J 10.1, ^3J 6.0, ^3J 10.9, 4-H), 3.00 (1 H, ddd, ^2J 14.5, ^3J 10.9, ^4J 1.2, 5-H$_b$), 2.59 (1 H, dd, ^2J 14.5, ^3J 6.0, 5-H$_a$); δ_C ($CDCl_3$, 50.289 MHz) 205.00 (C=O), 145.25, 143.96, 139.84, 137.56, 133.24, 128.50, 128.36, 128.07, 127.89, 127.60, 126.98, 126.89, 126.32, 124.85, 84.26 (C-1), 63.53 (C-2), 59.57 (C-3 or C-4), 51.35 (C-5 + C-3 or C-4).

Compound 2. Obtained from 1,2-dibenzoylethylene (59 mg) as white needles in 80% yield after recrystallization from dichloromethane–pentane; ν_{max}/cm^{-1} 1683(CO), 1655(CO), 1636(CO); δ_H ($CDCl_3$, 199.975 MHz) 7.80–7.00 (20 H, m, Ph), 5.05 (1 H, d, ^3J 10.3, 2-H), 4.90 (1 H, m, 4-H), 4.82 (1 H, dd, ^3J 10.3, 3-H), 4.68 (1 H, d, ^4J 1.6, OH), 2.60 (1 H, dd, ^2J 13.5, ^3J 8.2, 5-H$_a$), 2.47 (1 H, ddd, ^2J 13.5, ^3J 8.1, ^4J 1.6, 5-H$_b$); δ_C ($CDCl_3$, 50.289 MHz) 204.65 (C=O), 200.78 (C=O), 199.33 (C=O), 142.45, 137.03, 136.93, 133.64, 133.24, 132.66, 128.97, 128.40, 128.21, 127.77, 127.30, 124.90, 83.57 (C-1), 56.95 (C-2), 55.59 (C-3), 48.23 (C-5), 47.85 (C-4).

Compound 3. Obtained from mesityl oxide (50 mg, 0.5 mmol) as a pale yellow oil in 82% yield; ν_{max}/cm^{-1} 1705(CO). δ_H ($CDCl_3$, 299.948 MHz) 5.21 (1 H, s, OH), 2.88 (1 H, s, 2-H), 2.23 (3 H, s, Me), 2.03 (1 H, d, ^2J 14.1, 5-H$_a$), 1.67 (1 H, d, ^2J 14.1, 5-H$_b$), 1.31 (3 H, s, Me), 1.06 (3 H, s, Me), 1.01 (3 H, s, Me), 0.95 (3 H, s, Me), 0.93 (3 H, s, Me); δ_C ($CDCl_3$, 75.429 MHz) 215.03 (C=O), 78.00 (C-1), 67.30 (C-2), 56.95 (C-5), 47.83 (C-3 or C-4), 43.11 (C-3 or C-4), 33.84 (Me), 32.04 (Me), 26.97 (Me), 24.32 (Me), 23.50 (Me), 21.47 (Me); HRMS, Calc. for $C_{12}H_{22}O_2$: 198.1620. Found: 198.1624.

Compound 4. Obtained from dibenzylideneacetone (59 mg) as white needles in 40% yield after recrystallization from dichloromethane–pentane (Found: C, 86.53; H, 6.39. Calc. for $C_{34}H_{30}O_2$: C, 86.77; H, 6.42%); ν_{max}/cm^{-1} 1668(CO), 1631 (C=C), 1600(C=C); δ_H ($CDCl_3$, 199.975 MHz) 7.40–7.10 (21 H, m, Ph + H$_{vinyl}$), 6.81 (1 H, d, ^3J 15.8, H$_{vinyl}$), 6.40 (1 H, d, ^3J 15.8, H$_{vinyl}$), 6.22 (1 H, d, ^3J 16.0, H$_{vinyl}$), 5.06 (1 H, s, OH), 3.86 (1 H, dd, ^3J 9.9, ^3J 11.9, 3-H), 3.65 (1 H, d, ^3J 11.9, 2-H), 3.58 (1 H, m, ^3J 9.9, ^3J 5.6, ^3J 11.0, 4-H), 2.66 (1 H, ddd, ^2J 14.4, ^3J 11.0, ^4J 1.4, 5-H$_b$) 2.29 (1 H, dd, ^2J 14.4, ^3J 5.6, 5-H$_a$); δ_C ($CDCl_3$, 50.289

Table 4 Crystal data and experimental crystallographic details for compounds **2**, **4**–**8**, **14**, **15**

Compound	**2**	**4**	**5**	**6**	**7**	**8**	**14**	**15**
Empirical formula	$C_{34}H_{26}O_4$	$C_{34}H_{30}O_2$	$C_{32}H_{30}O_4$	$C_{34}H_{36}N_2O_2$	$C_{32}H_{26}O_4$	$C_{45}H_{38}O_3$·0.9313 $CHCl_3$	$C_{20}H_{34}O_2$	$C_{26}H_{30}O_2$
M	474.53	470.58	478.6	504.65	474.50	738.00	306.48	374.50
Crystal system	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	$C2/c$	$C2/c$	$P\bar{1}$	$P2_12_12_1$	$P2_1/c$	$Pbca$	$P2_12_12_1$	$P2_1/c$
a/Å	27.393(3)	37.449(5)	5.874(2)	6.1993(3)	9.346(2)	12.108(2)	6.870(1)	10.638(1)
b/Å	10.617(1)	5.571(1)	11.693(2)	20.503(1)	13.857(3)	24.041(5)	8.199(1)	5.876(1)
c/Å	21.138(2)	25.759(4)	19.147(2)	21.694(1)	10.087(2)	26.255(5)	31.933(4)	18.755(2)
α/°	90.00	90.00	95.66(2)	90.00	90.00	90.00	90.00	90.00
β/°	128.00(1)	106.76(1)	94.26(2)	90.00	107.87(2)	90.00	90.00	98.91(1)
γ/°	90.00	90.00	97.08(2)	90.00	90.00	90.00	90.00	90.00
V/Å^3	4844.4(8)	5145.8(14)	1293.8(2)	2757.3(2)	1243.3(6)	7643(4)	1798.7(4)	1158.2(3)
Z	8	8	2	4	2	8	4	2
D_c/g cm^{-3}	1.301	1.215	1.228	1.216	1.268	1.283	1.132	1.074
μ/cm^{-1}	6.79	5.73	6.36	5.85	6.61	23.55	0.70	0.66
F(000)	2000	2000	508	1080	500	3088.69	680	404
Crystal size/mm	0.40 × 0.28 × 0.12	0.80 × 0.12 × 0.02	0.40 × 0.06 × 0.04	0.48 × 0.22 × 0.06	0.32 × 0.20 × 0.08	0.76 × 0.10 × 0.10	0.36 × 0.32 × 0.32	0.64 × 0.22 × 0.16
Colour	colourless	colourless	colourless	colourless	colourless	colourless	colourless	colourless
Shape	plate	needle	needle	plate	plate	prism	prism	prism
Radiation	CuKα	CuKα	CuKα	CuKα	CuKα	CuKα	MoKα	MoKα
θ range (°)	1.5/56.75	1.5/56.75	1.5/55.0	1.5/56.75	1.5/55.0	1.5/55.0	1.50/25.00	1.50/25.00
Index ranges	$h = 0 \longrightarrow 29$ $k = 0 \longrightarrow 11$ $l = -22 \longrightarrow 22$ plus Friedel pair	$h = 0 \longrightarrow 40$ $k = 0 \longrightarrow 6$ $l = -27 \longrightarrow 27$ plus Friedel pair	$h = 0 \longrightarrow 6$ $k = -12 \longrightarrow 12$ $l = -20 \longrightarrow 20$	$h = 0 \longrightarrow 6$ $k = 0 \longrightarrow 22$ $l = 0 \longrightarrow 23$ plus Friedel pair	$h = 0 \longrightarrow 9$ $k = 0 \longrightarrow 14$ $l = -10 \longrightarrow 9$	$h = 0 \longrightarrow 12$ $k = 0 \longrightarrow 24$ $l = 0 \longrightarrow 26$	$h = 0 \longrightarrow 8$ $k = 0 \longrightarrow 9$ $l = 0 \longrightarrow 37$	$h = 0 \longrightarrow 14$ $k = 0 \longrightarrow 8$ $l = -26 \longrightarrow 26$
Reflns. collected	6598	6935	3638	4300	1530	4370	1861	2149
Data/parameters	3231/404	3421/329	1832/339	3674/347	1063/164	2839/474	1860/203	1995/128
Final R	0.0406	0.0658	0.0618	0.0631	0.0565	0.0558	0.0572	0.0780
Final wR	0.0979	0.1434	0.0810[a]	0.1241	0.0593[a]	0.0746[a]	0.1091	0.1581
Goodness-of-fit	1.082	1.165	1.370	1.039	1.080	1.150	1.042	1.031
Largest diff. peak and hole/e Å^{-3}	0.135 and −0.154	0.335 and −0.163	0.170 and −0.190	0.118 and −0.129	0.130 and −0.140	0.310 and −0.290	0.164 and −0.174	0.217 and −0.167

R indices; $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ (based on F), $wR = [\Sigma(w|F_o^2 - F_c^2|)^2/\Sigma(wF_o^2)^2]^{\frac{1}{2}}$, (based on F^2). [a] $wR = [\Sigma(w|F_o - F_c|)^2/\Sigma(wF_o)^2]^{\frac{1}{2}}$.

MHz) 203.10 (C=O), 144.08, 143.99 (C_{vinyl}), 140.07, 136.70, 134.04, 133.71 (C_{vinyl}), 130.80 (C_{vinyl}), 128.80 (C_{vinyl}), 128.70, 128.52, 128.37, 127.83, 127.49, 127.08, 126.66, 126.58, 126.31, 82.91 (C-1), 65.21 (C-2), 59.10 (C-3 or C-4), 51.63 (C-3 or C-4), 48.36 (C-5).

Compound 5. Obtained from 4-methoxychalcone (60 mg) as colourless needles in 55% yield after recrystallization from dichloromethane–pentane (Found: C, 79.90; H, 6.23. Calc. for $C_{34}H_{30}O_4$: C, 80.31; H, 6.32%); ν_{max}/cm^{-1} 1652(CO); δ_H ($CDCl_3$, 299.950 MHz) 7.60–7.00 (14 H, m, Ph), 6.78 (2 H, d, Ph), 6.62 (2 H, d, Ph), 5.15 (1 H, s, OH), 4.47 (1 H, d, ^3J 12.0, 2-H), 4.01 (1 H, dd, ^3J 10.5, ^3J 11.0, 3-H), 3.74 (3 H, s, OMe), 3.65 (masked m, 4-H), 3.64 (3 H, s, OMe), 2.95 (1 H, dd, ^2J 14.4, ^3J 11.4, 5-H_b), 2.51 (1 H, dd, ^2J 14.4, ^3J 6.3, 5-H_a); δ_C ($CDCl_3$, 75.430 MHz) 205.06 (C=O), 158.40, 158.14, 145.53, 137.74, 136.10, 133.14, 132.00, 128.81, 128.55, 128.28, 128.13, 126.92, 124.86, 113.93, 113.79, 84.02 (C-1), 63.79 (C-2), 58.89 (C-3), 55.17 (OMe), 55.09 (s, OMe), 51.49 (C-5), 50.79 (C-4).

Compound 6. Obtained from 4-(dimethylamino)chalcone (63 mg) as yellow needles in 68% yield after recrystallization from dichloromethane–pentane (Found: C, 80.62; H, 7.28; N, 5.43. Calc. for $C_{34}H_{36}N_2O_2$: C, 80.92; H, 7.19; N, 5.55%); ν_{max}/cm^{-1} 1653(CO); δ_H ($CDCl_3$, 299.950 MHz) 7.54–7.51 (2 H, m, Ph), 7.35–7.04 (14 H, m, Ph), 6.61 (2 H, d, Ph), 6.46 (2 H, d, Ph), 5.12 (1 H, s, OH), 4.36 (1 H, d, ^3J 11.6, 2-H), 4.07 (1 H, dd, ^3J 11.6, ^3J 11.6, 3-H), 3.58 (1 H, m, ^3J 11.6, ^3J 8.2, ^3J 9.6, 4-H), 2.85 (masked dd, 5-H_b), 2.84 (6 H, s, Me), 2.76 (6 H, s, Me), 2.37 (1 H, dd, ^2J 13.9, ^3J 8.2, 5-H_a); δ_C ($CDCl_3$, 75.430 MHz) 200.43 (C=O), 148.51, 147.10, 137.64, 131.59, 128.35, 127.63, 127.32, 127.15, 125.66, 124.34, 112.15, 111.95, 81.70 (C-1), 65.59 (C-2), 54.55 (C-3), 52.86 (C-5), 49.56 (C-4), 39.87 (Me), 39.78 (Me), 39.67 (Me), 39.50 (Me).

For the experiment with deuterated THF, 0.5 cm^3 of SmI_2 solution were evaporated to dryness, and 0.5 cm^3 of dry THF-d_8 were added. This solution was added to a solution of 4-(dimethylamino)chalcone (6 mg) and 0.02 cm^3 of HMPA in 0.5 cm^3 of THF-d_8. After stirring for 5 minutes at room temperature, the solvent was evaporated under vacuum and the yellow residue analysed by mass spectroscopy.

Compound 14. Obtained from (*R*)-(+)-pulegone (38 mg) as white crystals in 26% yield after the slow evaporation of a toluene solution (Found: C, 76.65; H, 10.93. Calc. for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18%, despite repeated recrystallizations, we were not able to obtain better elemental analysis); ν_{max}/cm^{-1} 1670 (CO). Due to the high number of signals in the same area, assignment and analysis of ^{1}H NMR spectra proved to be very difficult. δ_C ($CDCl_3$, 75.430 MHz) 220.77 (C=O), 81.37 (C-1), 64.46 (C-2), 51.77 (CH_2), 51.04 (C-5), 44.85 (C-3 or C-4), 43.10 (C-3 or C-4), 38.51 (CH_2), 30.24 (CH_2), 29.96 (CH), 28.87 (CH_3), 28.45 (CH_2), 27.56 (CH_3), 26.49 (CH_2), 25.69 (CH), 25.47 (CH_3), 23.70 (CH_3), 22.12 (CH_3), 21.53 (CH_3), 20.96 (CH_2).

Following the procedure described above, compound **15** was obtained from 4,4-dimethyl-1-phenylpent-1-yn-3-one (47 mg) in 24% yield as a white solid. Crystals suitable for X-ray analysis were obtained from the slow evaporation of a toluene solution; ν_{max}/cm^{-1} 1682(CO), 1582(C=C); δ_H ($CDCl_3$, 299.950 MHz) 7.32–7.15 (10 H, m, Ph), 6.24 (2 H, s, HC=), 0.94 (18 H, s, Me_3C); δ_C ($CDCl_3$, 75.430 MHz) 206.33 (C=O), 153.33 (Ph*C*=), 137.48, 137.64, 129.75, 128.85, 128.08, 127.91, 120.02 (HC=), 44.10 (*C*Me_3), 26.17 (Me_3C).

Reactions of iron complexes with samarium iodide

General procedure. To a solution of iron derivative (0.2 mmol) and HMPA (0.2 cm^3, 1.14 mmol) in THF (5 cm^3) was added 4 cm^3 of a 0.1 M solution of SmI_2 in THF. The mixture was stirred for 5 minutes at room temperature, and water (10 cm^3) was added. The solution was extracted with diethyl ether (3 × 10 cm^3) and the combined organic extracts were dried over magnesium sulfate. After evaporation of the solvent, the oily residue was purified by chromatography on silica (hexane–ethyl acetate). The nature and yields of the products obtained were evaluated by comparison of the ^{1}H NMR spectra of the mixture with the ^{1}H NMR spectra of the pure compounds (see Table 3).

X-Ray crystal structure determinations of compounds 2, 4, 5, 6, 7, 8, 14 and 15

Molecular structures of compounds **2**, **4**, **5**, **6**, **7**, **8**, **14** and **15** were analysed by X-ray diffraction methods following very similar procedures. Crystal data for the eight samples and details of the experimental results are shown in Table 4.

For each sample, crystals were mounted, in air, on glass fibres. Accurate cell parameters were determined by refinement from the setting of 25 reflections and diffraction intensities measured at 293 K using an ω–θ scan method on a Siemens P4/PC diffractometer equipped with graphite-monochromated radiation. The intensities of 3 standard reflections, recorded every 100 collected reflections, showed no changes. All data sets were corrected for Lorentz-polarization effects and a face-indexed numerical absorption correction was applied to the data set of compound **8** with 0.5512 and 0.8265 values for minimum and maximum transmission factor, respectively.

The structure of each compound was determined by direct methods (SIR92)[22] and refined by full-matrix least-squares methods using SHELXL90[23] (compounds **5**, **7** and **8**) or SHELXL93[24] (compounds **2**, **4**, **6**, **14** and **15**). Hydrogens, except in compound **2**, were set to ride on the parent C atoms. The non-hydrogen atoms were refined with anisotropic thermal parameters. The absolute configurations for compounds **6** and **14** were not determined.

Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 1*, available *via* the RSC Web pages (http://www.rsc.org/authors). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/260. The data deposited comprise ORTEP diagrams and crystallographic data for compounds **2**, **4**, **5** and crystallographic data for compounds **6**, **7**, **8**, **14**, **15**.

Acknowledgements

We thank DGAPA-UNAM (IN216197) for financial support, G. Espinoza-Perez for some of the X-ray analyses, J. Perez-Flores for mass-spectra measurements and A. Janes for helpful discussions.

References

1 P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.*, 1980, **102**, 2693.
2 For reviews see (*a*) G. A. Molander, *Chem. Rev.*, 1992, **92**, 29; (*b*) G. A. Molander and C. R. Harris, *Chem Rev.*, 1996, **96**, 307.
3 A. Cabrera, N. Rosas, C. Alvarez, P. Sharma, A. Toscano, M. Salmón and J. L. Arias, *Polyhedron*, 1996, **15**, 2971.
4 J. Inanaga, S. Sakai, Y. Handa, M. Yamaguchi and Y. Yokoyama, *Chem. Lett.*, 1991, 2117.
5 J. Inanaga, Y. Handa, T. Tabuchi, K. Otsubo, M. Yamaguchi and T. Hamamoto, *Tetrahedron Lett.*, 1991, **32**, 6557.
6 A. Cabrera and H. Alper, *Tetrahedron Lett.*, 1992, **33**, 5007.
7 S. Fukuzawa, A. Nakanishi, T. Fujinami and S. Sakai, *J. Chem. Soc.*, *Perkin Trans. 1*, 1988, 1669.
8 Y. Fujita, S. Fukuzumi and J. Otera, *Tetrahedron Lett.*, 1997, **38**, 2121.
9 K. Otsubo, J. Inanaga and M. Yamaguchi, *Tetrahedron Lett.*, 1986, **27**, 5763.

10 K. Tataki, F. Beppu, S. Tanaka, Y. Tsubaki, T. Jintoku and Y. Fujiwara, *J. Chem. Soc.*, *Chem. Commun.*, 1990, 516.
11 J. Bao, M. Bei, J. Lu, J. Zhang and Q. Song, *Chin. Chem. Lett.*, 1993, **4**, 593 (*Chem. Abstr.*, 1994, **120**, 8221q).
12 E. J. Enholm and K. S. Kinter, *J. Org. Chem.*, 1995, **60**, 4850.
13 F. Fournier, J. Berthelot and J. J. Basselier, *Tetrahedron*, 1985, **41**, 5667.
14 The crystal structure of **1** was previously reported by M. Gaweda B. Kawalek, L. Lebioda, J. Misek and M. Cieckanowicz-Rutkowska, *Pol. J. Chem.*, 1978, **52**, 1747.
15 (*a*) H. B. Kagan, J. L. Namy and P. Girard, *Tetrahedron*, 1981, **37** (**Suppl.1**), 175; (*b*) H. B. Kagan, *New J. Chem.*, 1990, **14**, 453.
16 A. Cabrera, M. Salmón, N. Rosas, J. Perez Flores, L. Velasco, G. Espinoza-Perez and J. L. Arias, *Polyhedron*, 1998, **17**, 193.
17 Even though the by-products **7** and **8** were found in very low quantities, their existence supports the stereochemical preference of the reactions for the *trans*-R^2[C(3)]-R^2[C(4)] substituted cyclopentanes, thus making the process regiospecific. We considered it important to include them in Scheme 2.
18 A. Cabrera, N. Rosas, P. Sharma, R. Le Lagadec, L. Velasco, M. Salmón and J. L. Arias, *Synth. Commun.*, 1998, **28**, 1103.
19 J. A. S. Howell, B. F. G. Johnson, P. L. Josty and J. Lewis, *J. Organomet. Chem.*, 1972, **39**, 329.
20 H. Arzoumanian, M. Jean, D. Nuel, J. L. García and N. Rosas, *Organometallics*, 1997, **16**, 2726.
21 F. Barba and J. L. De La Fuente, *J. Org. Chem.*, 1993, **58**, 7685.
22 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
23 G. M. Sheldrick, SHELXTL/PC User's Manual, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1990.
24 G. M. Sheldrick, SHELXL-93, Program for Refinement of Crystal structures; University of Göttingen, Germany, 1993.

Paper 8/04269A