ELSEVIER

Journal of Organometallic Chemistry 643–644 (2002) 363–368

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

# A facile and diastereoselective access to substituted cyclopentanones from Fischer alkenyl carbene complexes and 1-amino-1-azadienes

José Barluenga *, Alfredo Ballesteros, Javier Santamaría, Miguel Tomás

*Instituto Universitario de Química Organometálica 'Enrique Moles' (Unidad Asociada al CSIC), Universidad de Oviedo, Julian Claveria 8, 33071 Oviedo, Spain*

Received 17 July 2001; accepted 20 September 2001

**Abstract**

Fischer alkenyl carbene complexes **1** undergo cyclopentannulation to alkenyl *N*,*N*-dimethylhydrazones (1-amino-1-azadienes) **2** to furnish substituted cyclopentenes **3** (45–55%) in a regio and diastereoselective way, along with minor amounts of pyrroles **4** (25–28%). Enantiopure carbene complexes derived from (−)-8-phenylmenthol **7a** and (−)-8-(2-naphthyl)menthol **7b** afforded, in addition to pyrrole **4a** (12–15%), *trans*,*trans*-cyclopentenes **8**/**9** (35–43%) and *cis*,*cis*-cyclopentenes **10**/**11** (23–25%) with fairly to excellent face selectivity (78% for **7a** and 92% for **7b**). © 2002 Published by Elsevier Science B.V.

*Keywords:* Fischer carbene complexes; Hydrazones; Metal migration; Cyclopentanones

## 1. Introduction

Since their discovery by Fischer and Maasböl [1] the heteroatom stabilized carbene complexes have demonstrated to be highly useful in synthesis of acyclic and cyclic molecules [2]. In particular, Group 6 alkenyl and alkynyl carbene complexes are being recognized as valuable C3 building blocks for carbo- and heterocyclization reactions, making a diversity of five- and seven-membered rings readily accessible [2,3]. Moreover, we noted that the cyclization reactions involving Fischer carbene complexes and substrates containing a nitrogen functionality are very efficient, particularly in terms of selectivity. For instance, the cyclopropanation of alkenylimines [4] and alkenyloxazolines [5] was found to occur with unexpectedly high diastereoselectivity.

We report here that readily available α,β-unsaturated hydrazones are very suitable reagents towards alkenyl carbene complexes of chromium giving rise to cyclopentanoids with high selectivity along with minor amounts of substituted pyrroles. The preliminary studies on the asymmetric cyclopentannulation are also displayed [6].

## 2. Results and discussion

Thus, chromium alkenyl carbene complexes **1** were treated with alkenyl hydrazones **2** (one equivalent) in refluxing THF overnight. Removal of the solvent left behind a mixture of *trans*,*trans*-cyclopentenes **3** and pyrroles **4** which were separated by column chromatography to afford pure **3** (45–55% yield) and **4** (25–28% yield) (Scheme 1).

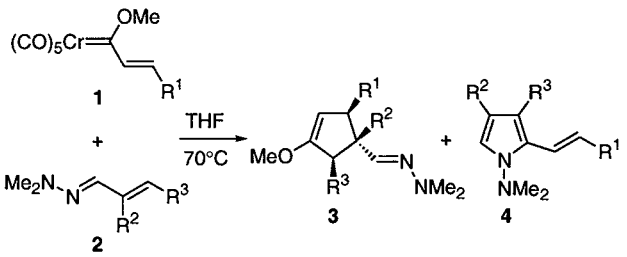
Aminopyrroles **4** arise from a [4 + 1] cyclization, a process which is rather uncommon for Fischer carbene complexes [4,7]. The formation of adducts **3** involves a [3 + 2] cyclization reaction wherein two or three stereogenic centers are created in a single operation. Interestingly, this process takes place with complete regio and diastereoselectivity.

In turn, the chemoselective and total hydrolysis of the cycloadduct **3a** was effected in nearly quantitative yield to produce the hydrazinoyl cylopentanone **5** and the formyl cyclopentanone **6**, respectively (Scheme 2).

* Corresponding author. Tel./fax: +34-98-5103450.

*E-mail address:* barluenga@sauron.quimica.uniovi.es (J. Barluenga).

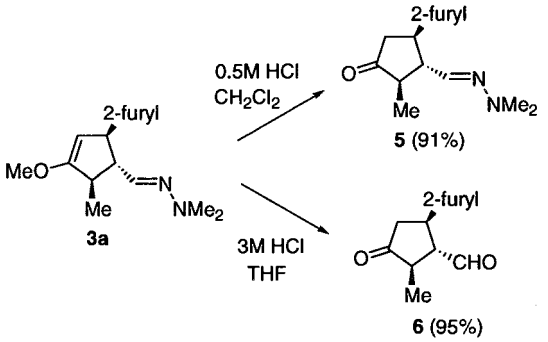
0022-328X/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0022-328X(01)01270-0



| Entry | $R^1$ | $R^2$ | $R^3$ | Yield[a] (%) 3 | 4 |
|---|---|---|---|---|---|
| a | 2-furyl | H | Me | 55 | 26 |
| b | Ph | H | Me | 45 | 28 |
| c | 2-furyl | Me | H | 52 | 25 |

[a] Yields after purification by column chromatography.

Scheme 1.

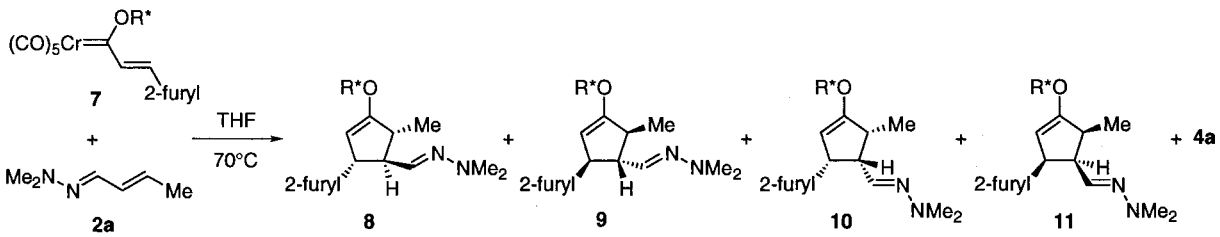


Scheme 2.

The initial studies on the enantioselective version of this reaction have been undertaken using enantiopure carbene complexes **7a** and **7b**, derived from (−)-8-phenylmenthol and (−)-8-(2-naphthyl)menthol, respectively (Scheme 3). Thus, the treatment of carbenes **7** with the hydrazone **2a** ($R^2 = H$; $R^3 = Me$) in refluxing THF yielded the pyrrole **4** (12–15%) and a diastereomeric mixture containing not only the expected *trans,trans*-cyclopentenes **8** and **9**, but also the *cis,cis*-cyclopentenes **10** and **11**. The pairs **8**/**9** and **10**/**11** could be separated by column chromatography and isolated in yields of 35–43% and 23–25%, respectively. The facial selectivity of the cyclization is measured by the ratio of **8**:**9** and **10**:**11**. Curiously, such selectivity appears to be nearly the same for both pairs. It is worth noticing, while starting with carbene **7a** a moderate asymmetric induction of 78% was found (89:11 for **8a**/**9a**; entry a), the selectivity raised to 92% (96:4 for **8b**/**9b**; entry b) when the carbene **7b** was employed.

The structural determination of compounds **3**–**11** is based on the NMR spectra and the relative stereochemistry of cycloadducts **3**, **5**, **6**, **8**/**9**, **10**/**11** was evidenced from NOE experiments. Unfortunately, we could not prove the absolute stereochemistry of cycloadducts **8**/**9** and **10**/**11**, but their complete structure is proposed on the basis of: (i) the mechanism shown below, and (ii) the steric effect exerted by the auxiliary group which shields preferently the *re*-face of the metal carbene functionality, probably because of a π-stacking interaction [8], as demonstrated previously for the Michael addition reaction [9].

The mechanistic proposal for the formation of the cyclopentene and pyrrole rings is outlined in Fig. 1 and features two basic steps: the nucleophilic addition to the metal–carbon double bond and the metal-induced cyclization [10]. First, pyrroles **4** would be formed by nucleophilic 1,2-addition of the nitrogen lone pair to the metal carbene function to form **I**, followed by cyclization to **II** [11] and elimination of the corresponding alcohol (via A). On the other hand, the mechanism accounting for the [3 + 2] carbocyclization reaction is not so apparent [12]. Our proposal is illustrated for the



**7a**: R* = (1*R*, 2*S*, 5*R*)-8-phenylmenthyl
**7b**: R* = (1*R*, 2*S*, 5*R*)-8-(2-naphthyl) menthyl

| Entry | 8/9 Yield[a] | 8/9 dr(%)[b] | 10/11 Yield[a] | 10/11 dr(%)[b] | 4a Yield[a] |
|---|---|---|---|---|---|
| a | 35 | 89:11 | 23 | 85:11 | 15 |
| b | 43 | 96:4 | 25 | 96:4 | 12 |

[a] Yields (%) after purification by column chromatography.
[b] Diastereomeric ratio measured by $^1$H-NMR (300 MHz)

Scheme 3.

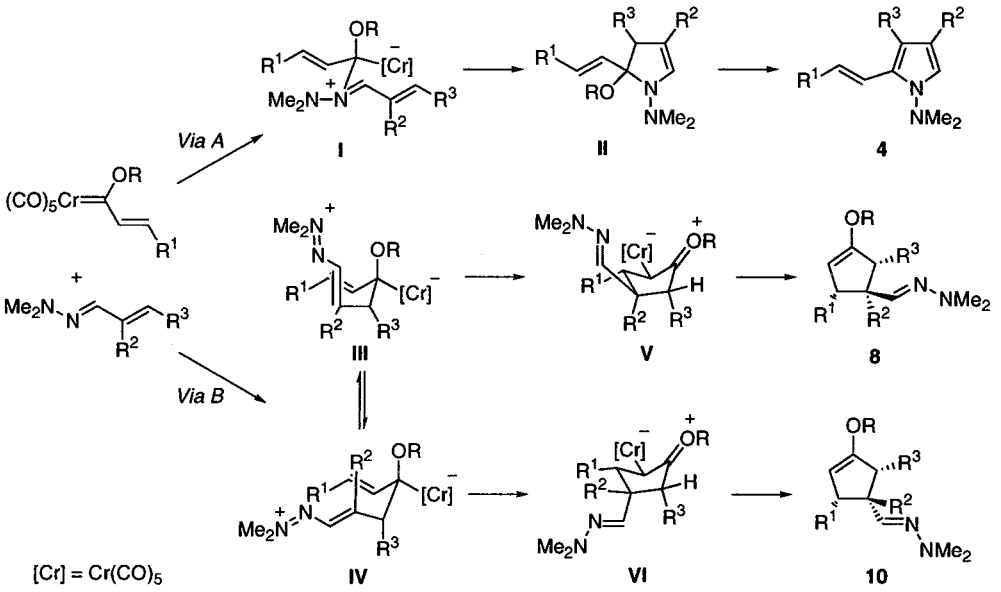



Fig. 1. Mechanistic proposal for the cyclization of carbene complexes **1**,**7** and hydrazones **2**.

formation of the major stereoisomers **8** and **10** (via B). In this case, the process must be initiated by nucleophilic 1,2-attack of the $C_\beta$ carbon of the hydrazone [13] to the less hindered face of the metal carbene to generate species **III** and **IV** (via B). Then, they would undergo a [1,2]-$Cr(CO)_5$ shift-promoted ring closure to give **V** and **VI**, which would give rise to the observed cycloadducts **8** and **10** via hydrogen transfer to chromium and reductive metal elimination.

## 3. Conclusions

In conclusion, we report here a new and very simple protocol for preparing functionalized cyclopentanones with up to three chiral centers in a regio and diastereoselective way via the [3 + 2] cycloaddition reaction of alkenyl Fischer carbene complexes and alkenyl hydrazones. Minor amounts of vinylpyrroles, which arise from an uncommon [4 + 1] cyclization and that eventually might be elaborated into heteropolycyclic compounds, are also produced. On the other hand, the preliminary results on the enantioselective carbocyclization using enantiopure carbene complexes are certainly promising.

## 4. Experimental

### 4.1. Synthesis of methoxycyclopentenes *3* and pyrroles *4*

To a solution of the alkenyl carbene complex **1** (1mmol) in THF (50 ml) was added the hydrazone **2** (1 mmol). The mixture was refluxed for 10 h and the solvent was removed under vacuum. Purification of the residue by column chromatograpy (silica gel, 5:1 hexane–ethyl acetate) allowed isolating cyclopentenes **3** and pyrroles **4**.

### 4.2. *trans,trans-3-(2-Furyl)-1-methoxy-5-methylcyclopentene-4-carbaldehyde dimethylhydrazone (**3a**)*

Yield: 55%; oil. $^1$H-NMR ($CDCl_3$): $\delta = 1.15$ (d, 3H, $J = 6.9$ Hz), 2.6–2.9 (m, 2H), 2.8 (s, 6H), 3.7 (s, 3H), 3.85 (d, 1H, $J = 7.3$ Hz), 4.5 (s, 1H), 6.1 (m, 1H), 6.3 (m, 1H), 6.7 (d, 1H, $J = 6.5$ Hz), 7.4 (m, 1H). $^{13}$C-NMR ($CDCl_3$): $\delta = 163.1$ (s), 158.4 (s), 141.0 (d), 139.0 (d), 110.0 (d), 104.1 (d), 93.2 (d), 56.7 (q), 54.8 (d), 44.4 (d), 43.2 (q), 42.8 (d), 17.1 (q). HRMS: Calc. for $C_{14}H_{20}N_2O_2$ 248.1525. Found 248.1524. Anal. Found: C, 67.90; H, 8.17; N, 11.20. Calc. for $C_{14}H_{20}N_2O_2$ (248.32): C, 67.72; H, 8.12; N, 11.28%.

### 4.3. *trans,trans-1-Methoxy-5-methyl-3-phenylcyclopentene-4-carbaldehyde dimethyhydrazone (**3b**)*

Yield: 45%; oil. $^1$H-NMR ($CDCl_3$): $\delta = 1.15$ (d, 3H, $J = 6.9$ Hz), 2.45 (q, 1H, $J = 6.5$ Hz), 2.7 (s, 6H), 2.8 (m, 1H), 3.7 (s, 3H), 3.8 (d, 1H, $J = 7.7$ Hz), 4.5 (s, 1H), 6.7 (d, 1H, $J = 6.5$ Hz), 7.1–7.4 (m, 5H). $^{13}$C-NMR ($CDCl_3$): $\delta = 162.9$ (s), 145.6 (s), 139.4 (d), 128.2 (d), 127.4 (d), 126.1 (d), 95.8 (d), 58.9 (d), 56.7 (q), 51.1 (d), 43.3 (q), 43.1 (q), 17.1 (c). HRMS: Calc. for $C_{16}H_{22}N_2O$ 258.17321. Found 258.17334. Anal. Found: C, 74.52; H, 8.62; N, 10.80. Calc. for $C_{16}H_{22}N_2O$ (258.36): C, 74.38; H, 8.58; N, 10.84%.

*4.4. trans-3-(2-Furyl)-1-methoxy-4-methylcyclopentene-4-carbaldehyde dimethylhydrazone (**3c**)*

Yield: 52%; oil. $^1$H-NMR ($CDCl_3$): $\delta = 0.9$ (s, 3H), 2.3 (d, 1H, $J = 13.0$ Hz), 2.7 (s, 6H), 2.8 (d, 1H, $J = 13.0$ Hz), 3.7 (s, 3H), 4.0 (brs, 1H), 4.5 (brs, 1H), 6.1 (m, 1H), 6.3 (m, 1H), 6.8 (s, 1H), 7.3 (m, 1H). $^{13}$C-NMR ($CDCl_3$): $\delta = 160.4$ (s), 156.9 (s), 144.4 (d), 141.1 (d), 109.8 (d), 106.2 (d), 92.9 (d), 56.6 (q), 49.5 (d), 47.3 (s), 43.2 (q), 43.0 (t), 22.4 (q). HRMS: Calc. for $C_{14}H_{20}N_2O_2$ 248.1526. Found 248.1527. Anal. Found: C, 67.75; H, 8.18; N, 11.31. Calc. for $C_{14}H_{20}N_2O_2$ (248.32): C, 67.72; H, 8.12; N, 11.28%.

*4.5. 2-[(E)-2-(2-Furyl)ethenyl]-3-methyl-1-dimethylaminopyrrole (**4a**)*

Yield: 26%; oil. H-NMR ($CDCl_3$): $\delta = 2.25$ (s, 3H), 2.8 (s, 6H), 6.0 (m, 1H), 6.25 (m, 1H), 6.4 (m, 1H), 6.8 (d, 1H, $J = 16.5$ Hz), 6.95 (m, 1H), 7.2.(d, 1H, $J = 16.5$ Hz), 7.4 (m, 1H). $^{13}$C-NMR ($CDCl_3$): $\delta = 154.6$ (s), 141.0 (d), 125.7 (s), 116.2 (d), 115.7 (s), 113.1 (d), 113.0 (d), 111.5 (d), 109.4 (d), 106.4 (d), 47.5 (q), 13.5 (q). HRMS: Calc. for $C_{13}H_{16}N_2O$ 216.1263. Found 216.1270. Anal. Found: C, 72.33; H, 7.56; N, 12.90. Calc. for $C_{13}H_{16}N_2O$ (216.28): C, 72.19; H, 7.46; N, 12.95%.

*4.6. 3-Methyl-1-dimethylamino-2-[(E)-2-phenylethenyl]pyrrole (**4b**)*

Yield: 28%; oil. $^1$H-NMR ($CDCl_3$): $\delta = 2.3$ (s, 3H), 2.85 (s, 6H), 6.1 (s, 1H), 6.9 (m, 2H), 7.1–7.5 (m, 6H). $^{13}$C-NMR ($CDCl_3$): $\delta = 138.9$ (s), 128.5 (d), 126.4 (d), 126.2 (s), 125.7 (d), 125.3 (d), 117.9 (d), 115.3 (s), 112.6 (d), 109.5 (d), 47.6 (q), 13.8 (q). HRMS: Calc. for $C_{15}H_{18}N_2$ 226.1470. Found 226.1467. Anal. Found: C, 79.69; H, 8.12; N, 12.35. Calc. for $C_{16}H_{18}N_2$ (226.32): C, 79.61; H, 8.02; N, 12.38%.

*4.7. 2-[(E)-2-(2-Furyl)ethenyl]-4-methyl-1-dimethylaminopyrrole (**4c**)*

Yield: 25%; oil. $^1$H-NMR ($CDCl_3$): $\delta = 2.1$ (s, 3H), 2.8 (s, 6H), 6.1 (m, 1H), 6.3 (m, 1H), 6.4 (m, 1H), 6.75 (d, 1H, $J = 16.5$ Hz), 6.8 (s, 1H), 7.2 (d, 1H, $J = 16.5$ Hz), 7.4 (m, 1H). HRMS: Calc. for $C_{13}H_{16}N_2O$ 216.14700. Found 226.12654. Anal. Found: C, 72.26; H, 7.50; N, 12.99. Calc. for $C_{13}H_{16}N_2O$ (216.28): C, 72.19; H, 7.46; N, 12.95%.

*4.8. Hydrolysis of **3a**. Synthesis of trans,trans-4-(2-furyl)-2-methylcyclopentanone-3-carbaldehyde dimethylhydrazone (**5**)*

A solution of the cyclopentene **3a** (125 mg, 0.5 mmol) and 0.5 M HCl (30 ml) in $CH_2Cl_2$ (30 ml) was stirred for 2 h at room temperature (r.t.). The mixture was then extracted with $CH_2Cl_2$ ($3 \times 20$ ml), washed with water and dried over anhydrous $Na_2SO_4$. Removal of the solvents under reduced pressure and purification by column chromatography (silica gel, 5:1 hexane–ethyl acetate) afforded the cyclopentanone **5** (yield: 91%; oil).

$^1$H-NMR ($CDCl_3$): $\delta = 1.15$ (d, 3H, $J = 6.9$ Hz), 2.4 (m. 2H), 2.8 (m, 2H), 2.85 (s, 6H), 3.3 (m, 1H), 6.1 (m, 1H), 6.3 (m, 1H), 6.6 (d, 1H, $J = 5.6$ Hz), 7.4 (m, 1H). $^{13}$C-NMR ($CDCl_3$): $\delta = 217.1$ (s), 154.7 (s), 141.4 (d), 135.5 (d), 110.0 (d), 105.5 (d), 52.3 (d), 49.1 (d), 43.0 (q), 42.7 (t), 38.8 (d), 12.3 (q). HRMS: Calc. for $C_{13}H_{18}N_2O_2$ 234.1368. Found 234.1369. Anal. Found: C, 66.75; H, 7.79; N, 12.03. Calc. for $C_{13}H_{18}N_2O_2$ (234.30): C, 66.64; H, 7.74; N, 11.96%.

*4.9. Hydrolysis of **3a**. Synthesis of trans,trans-4-(2-furyl)-2-methylcyclopentanone-3-carbaldehyde (**6**)*

A solution of the cyclopentene **3a** (125 mg, 0.5 mmol) and 3 M HCl (30 ml) in THF (30 ml) was stirred for 7 h at r.t. The mixture was then extracted with $Et_2O$ ($3 \times 20$ ml), washed with water and dried over anhydrous $Na_2SO_4$. Removal of the solvents under reduced pressure and purification by column chromatography (silica gel, 3:1 hexane–ethyl acetate) afforded the cyclopentanone **6** (yield: 95%; oil).

$^1$H-NMR ($CDCl_3$): $\delta = 1.15$ (d, 3H, $J = 6.9$ Hz), 2.5 (m, 2H), 2.9 (m, 2H), 3.6 (m, 1H), 6.1 (m, 1H), 6.3 (m, 1H), 7.4 (m, 1H), 9.9 (d, 1H, $J = 2.6$ Hz). $^{13}$C-NMR ($CDCl_3$): $\delta = 214.4$ (s), 200.5 (d), 153.3 (s), 142.1 (d), 110.3 (d), 106.0 (d), 60.6 (d), 45.6 (d), 41.9 (t), 34.7 (d), 13.0 (q). HRMS: Calc. for $C_{11}H_{12}O_3$ 192.0786. Found 192.0785. Anal. Found: C, 68.86; H, 6.34. Calc. for $C_{11}H_{12}O_3$ (192.21): C, 68.74; H, 6.29%.

*4.10. Synthesis of optically active cyclopentenes **8**–**11***

To a solution of the chiral, non-racemic carbene complex **7** (1 mmol) in THF (50 ml) was added the hydrazone **2a** (112 mg, 1 mmol) and the resulting mixture refluxed for 10 h. Then, removal of the solvent and purification of the resulting residue by column chromatograpy (silica gel, 5:1 hexane–ethyl acetate) afforded three fractions containing the *trans,trans*-cyclopentenes **8**/**9**, the *cis,cis*-cyclopentenes **10**/**11**, and the pyrrole **4a**.

*4.11. (3S,4R,5R)-3-(2-Furyl)-5-methyl-1-[(1R,2S,5R)-8-phenylmenthyloxy]cyclopentene-4-carbaldehyde dimethylhydrazone (**8a**)*

This compound was obtained as a mixture of diastereoisomers (**8a**/**9a**, 89:11); yield: 35%; oil. $^1$H-NMR ($CDCl_3$): $\delta = 0.8$–$1.5$ (m, 7H), 0.9 (d, 3H, $J = 6.4$ Hz), 1.1 (d, 3H, $J = 6.4$ Hz), 1.3 (s, 3H), 1.5 (s, 3H), 1.9

(m, 1H), 2.3 (brd, 1H, $J = 12.5$ Hz), 2.65 (m, 1H), 2.8 (s, 6H), 3.9 (m, 2H), 4.5 (brs, 1H), 6.1 (m, 1H), 6.3 (m, 1H), 6.75 (d, 1H, $J = 6.0$ Hz), 7.1–7.5 (m, 6H). $^{13}$C-NMR ($CDCl_3$): $\delta = 159.0$ (s), 158.8 (s), 150.1 (s), 140.9 (d), 139.2 (d), 127.8 (d), 126.0 (d), 125.1 (d), 109.9 (d), 103.9 (d), 93.6 (d), 79.1 (d), 54.5 (d), 51.3 (d), 44.6 (d), 43.6 (d), 43.2 (q), 40.5 (s), 39.6 (t), 34.7 (t), 31.3 (d), 30.6 (q), 27.3 (t), 24.3 (q), 21.8 (q), 17.3 (q). HRMS: Calc. for $C_{29}H_{40}N_2O_2$ 448.3090. Found 448.3122. Anal. Found: C, 77.74; H, 9.06; N: 6.20. Calc. for $C_{29}H_{40}N_2O_2$ (448.65): C, 77.64; H, 8.99; N: 6.24%.

### *4.12. (3S,4S,5R)-3-(2-Furyl)-5-methyl-1-[(1R,2S,5R)-8-phenylmenthyloxy]cyclopentene-4-carbaldehyde dimethylhydrazone (**10a**)*

This compound was obtained as a mixture of diastereoisomers (**10a**/**11a**, 89:11); yield: 23%; oil. $^1$H-NMR ($CDCl_3$): $\delta = 0.8$–$1.0$ (m, 2H), 0.85 (d, 3H, $J =$ 6.4 Hz), 1.0 (d, 3H, $J = 7.3$ Hz), 1.2–1.6 (m, 5H), 1.4 (s, 3H), 1.5 (s, 3H), 1.9 (m, 1H), 2.25 (m, 1H), 2.6 (s, 6H), 2.8 (m, 1H), 3.9 (dt, 1H, $J = 10.3$ and 3.9 Hz), 4.1 (brd, 1H, $J = 8.2$ Hz), 4.5 (brs, 1H), 6.1 (m, 1H), 6.25 (d, 1H, $J = 8.6$ Hz), 6.3 (m, 1H), 7.1–7.4 (m, 6H). $^{13}$C-NMR ($CDCl_3$): $\delta = 161.4$ (s), 157.5 (s), 150.1 (s), 141.1 (d), 139.4 (d), 127.8 (d), 126.1 (d), 125.2 (d), 110.0 (d), 106.2 (d), 92.9 (d), 79.5 (d), 51.3 (d), 46.9 (d), 43.9 (d), 43.1 (q), 42.2 (d), 40.6 (t), 39.8 (s), 34.7 (t), 31.4 (d), 30.6 (q), 27.4 (t), 24.5 (q), 21.8 (q), 15.0 (q). HRMS: Calc. for $C_{29}H_{40}N_2O_2$ 448.3090. Found 448.3101. Anal. Found: C, 77.72; H, 9.04; N, 6.19. Calc. for $C_{29}H_{40}N_2O_2$ (448.65): C, 77.64; H, 8.99; N, 6.24%.

### *4.13. (3S,4R,5R)-3-(2-Furyl)-5-methyl-1-[(1R,2S,5R)-8-(2-naphthyl)menthyloxy]cyclopentene-4-carbaldehyde dimethylhydrazone (**8b**)*

This compound was obtained as a mixture of diastereoisomers (**8b**/**9b**, 96:4); yield: 43%; oil. $^1$H-NMR ($CDCl_3$): $\delta = 0.8$–$1.7$ (m, 7H), 0.9 (d, 3H, $J = 6.5$ Hz), 1.1 (d, 3H, $J = 6.9$ Hz), 1.4 (s, 3H), 1.5 (s, 3H), 2.85 (m, 1H), 2.3 (m, 1H), 2.7 (m, 1H), 2.8 (s, 6H), 3.9 (m, 2H), 4.5 (brs, 1H), 6.0 (m, 1H), 6.3 (m, 1H), 6.7 (d, 1H, $J = 6.5$ Hz), 7.3–7.8 (m, 8H). $^{13}$C-NMR ($CDCl_3$): $\delta =$ 159.0 (s), 158.8 (s), 147.6 (s), 141.1 (d), 139.2 (d), 133.2 (s), 131.4 (s), 127.9 (d), 127.3 (d), 127.2 (d), 125.9 (d), 125.6 (d), 125.1 (d), 123.0 (d), 110.0 (d), 104.0 (d), 93.7 (d), 79.0 (d), 54.5 (d), 51.0 (d), 44.6 (t), 43.6 (d), 43.2 (q), 40.8 (s), 34.7 (t), 31.4 (d), 30.5 (d), 29.6 (q), 28.3 (t), 24.5 (q), 21.9 (q), 17.3 (q). HRMS: Calc. for $C_{33}H_{42}N_2O_2$ 498.3246. Found 498.3211. Anal. Found: C, 79.40; H, 8.40; N: 5.73. Calc. for $C_{33}H_{42}N_2O_2$ (498.71): C, 79.48; H, 8.49; N, 5.62%.

### *4.14. (3S,4S,5R)-3-(2-Furyl)-5-methyl-1-[(1R,2S,5R)-8-(2-naphthyl)menthyloxy]cyclopentene-4-carbaldehyde dimethylhydrazone (**10b**)*

This compound was obtained as a mixture of diastereoisomers (**10b**/**11b**, 96:4); yield: 25%; oil. $^1$H-NMR ($CDCl_3$): $\delta = 0.8$–$1.8$ (m, 7H), 0.8 (d, 3H, $J = 6.0$ Hz), 1.1 (d, 3H, $J = 7.7$ Hz) 2.0 (m, 1H), 2.3 (brd, 1H, $J = 9.4$ Hz), 2.6 (s, 6H), 2.8 (m, 1H), 4.0 (dt, 1H, $J = 10.3$ and 3.9 Hz), 4.1 (m, 1H), 4.55 (brs, 1H), 6.0 (m,1H), 6.25 (d, 1H, $J = 8.6$ Hz), 6.3 (m,1H), 7.3–7.9 (m, 8H). $^{13}$C-NMR ($CDCl_3$): $\delta = 161.5$ (s), 157.4 (s), 147.7 (s), 141.1 (d), 139.3 (d), 133.1 (s), 131.4 (s), 127.9 (d), 127.3 (d), 127.2 (d), 125.7 (d), 125.3 (d), 125.1 (d), 123.7 (d), 110.0 (d), 106.3 (d), 93.0 (d), 79.5 (d), 51.0 (d), 46.8 (d), 43.9 (d), 43.2 (q), 42.2 (d), 40.8 (s), 39.9 (t), 34.7 (t), 31.3 (d), 30.8 (q), 27.6 (t), 24.1 (q), 21.8 (q), 15.0 (q). HRMS: Calc. for $C_{33}H_{42}N_2O_2$ 498.3246. Found 498.3101. Anal. Found: C, 79.55; H, 8.52; N, 5.59. Calc. for $C_{33}H_{42}N_2O_2$ (498.71): C, 79.48; H, 8.49; N, 5.62%.

## Acknowledgements

Financial support from DGICYT (Ministerio de Educación y Cultura) is gratefully acknowledged. J.S. thanks FICYT (Consejería de Educación y Cultura, Asturias) for a fellowship.

## References

[1] E.O. Fischer, A. Maasböl, Angew. Chem. Int. Ed. Engl. 3 (1964) 580.
[2] (a) W.D. Wulff, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, Oxford, 1995, p. 469;
(b) J. Barluenga, J. Flórez, F.J. Fañanás, J. Organomet. Chem 624 (2001) 5;
(c) J.W. Herndon, Tetrahedron 56 (2000) 1257;
(d) D.F. Harvey, D.M. Sigano, Chem. Rev. 96 (1996) 271;
(e) A. de Meijere, H. Schirmer, M. Duetsch, Angew. Chem. Int. Ed. Engl. 39 (2000) 3964;
(f) R. Aumann, Eur. J. Org. Chem. (2000) 17.
[3] For a recent paper from this laboratory, see: J. Barluenga, J. Alonso, F. Rodríguez, F.J. Fañanás, Angew. Chem. Int. Ed. Engl. 39 (2000) 2460.
[4] J. Barluenga, M. Tomás, J.A. López-Pelegrín, E. Rubio, J. Chem. Soc. Chem. Commun. (1995) 665.
[5] J. Barluenga, A.L. Suárez-Sobrino, M. Tomás, S. García-Granda, R. Santiago-García, J. Am. Chem. Soc. 123 (2001) 10494.
[6] For the racemic cyclopentannulation using alkenyloxazolines and Fischer carbene complexes, see: J. Barluenga, M. Tomás, A.L. Suárez-Sobrino, Synthesis (2000) 935.
[7] (a) T.N. Danks, D. Velo-Rego, Tetrahedron Lett. 35 (1994) 9443;
(b) J. Pfeiffer, M. Nieger, K.H. Dötz, Eur. J. Org. Chem. (1998) 1011;

(c) M.A. Sierra, B. Soderberg, P.A. Lander, L.S. Hegedus, Organometallics 12 (1993) 3769;
(d) E.O. Fischer, K. Weiss, K. Burger, Chem. Ber. 106 (1973) 1581.

[8] G.B. Jones, B.J. Chapman, Synthesis (1995) 475.

[9] J. Barluenga, J.M. Montserrat, J. Flórez, S. García-Granda, E. Martín, Angew. Chem. Int. Ed. Engl. 33 (1994) 1392.

[10] This reaction pathway is of great generality for Fischer carbene complexes towards nucleophilic alkenes and dienes. See: (a) J. Barluenga, M. Tomás, A. Ballesteros, J. Santamaría, R.J. Carbajo, F. López-Ortiz, S. García-Granda, P. Pertierra, Chem. Eur. J. 2 (1996) 88;
(b) J. Barluenga, M. Tomás, A. Ballesteros, J. Santamaría, C. Brillet, S. García-Granda, A. Piñera-Nicolás, J.T. Vázquez, J. Am. Chem. Soc. 121 (1999) 4516.

[11] For this type of cyclization, see: J. Barluenga, A. Ballesteros, J. Santamaría, R. Bernardo de la Rúa, E. Rubio, M. Tomás, J. Am. Chem. Soc. 122 (2000) 12874.

[12] The formation of both types of cyclopentenes, particularly the observed relative stereochemistry of **10**–**11**, cannot be apparently understood on the basis of other accepted reaction pathways for cyclization of Fischer-type carbene complexes, e.g. cycloprapanation-rearrangement, Diels–Alder cycloaddition wherein the metal alkenylcarbene acts as the 4π-electron partner, etc.

[13] The behaviour of *N*,*N*-dialkylhydrazones as nucleophilic reagents (aza-enamines) towards strong electrophiles has been reviewed. See: R. Fernández, J.M. Lassaleta, Synlett (2000) 1228.