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Journal of Organometallic Chemistry 691 (2006) 1075–1080
Journal of Organometallic Chemistry
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Note

Role of imino group in photochemical reactions of Fischer carbene complexes

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Received 29 September 2005; received in revised form 24 October 2005; accepted 9 November 2005
Available online 20 December 2005

Abstract

The photochemical cycloaddition of Fischer iminecarbene complexes bearing two kinds of substituent, imine and alkoxy or amino, has been explored with alkenes and alkynes. It was found that annulated product without CO insertion is formed.

Keywords: Fischer iminecarbene; Photochemistry; Alkene; Alkyne

1. Introduction

Group VI carbene complexes have a rich photochemistry [1]. Photoinduced cycloaddition reactions with unsaturated compounds have been used to generate a large number of products. For example, irradiation of chromium alkoxy- [2] or aminocarbenes [3] in the presence of a wide range of acyclic and cyclic imines allows the preparation of β-lactams. In a similar way, chromium alkoxycarbenes lead to the formation of β-lactones with aldehydes [4] or diazetidinones with azoarenes [5]. Regarding the carbon–carbon double bond, the photoreaction of alkoxy- [6] or aminocarbene [7] complexes with alkenes and dienes produces cyclobutanones (Scheme 1), while *Z*-dienyl-alkoxycarbene complexes are useful reagents for a photochemical variant of the Dötz benzannulation [8]. Interestingly, all of these photoinduced reactions undergo a CO insertion procedure, which is consistent with the prior formation of a short-lived metallacyclopropanone–metal–ketene complex [1].

In contrast to these results, we previously described the light-induced cyclopentannulation reactions of iminecarbene complexes in the presence of alkenes, alkynes (Scheme 2) and heteroatom-containing double bonds [9], where the CO moiety is not inserted into reaction products. This finding prompted us to explore the photochemical behaviour of carbene complexes bearing both kind of substituent (i.e., imine and alkoxy or amino). In this paper, we present our results from related investigations.

2. Results and discussion

Initially, we assessed the influence of the alkoxy group on the carbenic carbon. The pentacarbonyl[diphenylmethylene-amino]ethoxy-methylene]chromium(0) complex (**1**) was prepared according to the literature procedure [10]. We investigated the photoinduced reaction of **1** in the presence of unsaturated compounds (Scheme 3) [11]. The reaction with methyl vinyl ketone or ethyl acrylate led to the cyclopentannulated product **2** or **3**, respectively, without CO insertion. Irradiation of **1** in the presence of alkynes also gave the five-membered ring compounds **4** or **5**. These results indicate that imino group fixes the structure of the final product.

In order to further explore the photoreactivity of iminecarbenes bearing an alkoxy group, we carried out the synthesis of some of these complexes with a methoxy group on the iminic carbenic carbon (carbenes **6**–**9**, Scheme 4).

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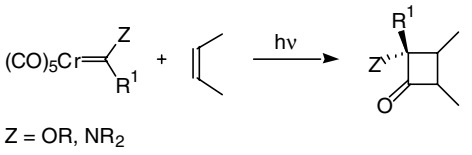
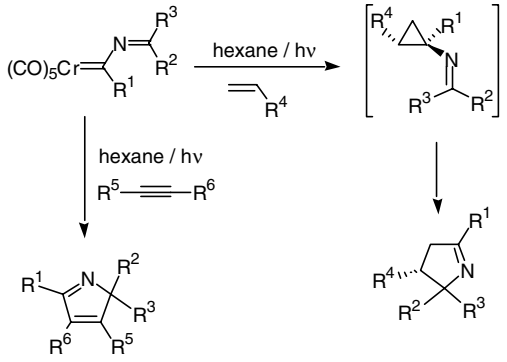
doi:10.1016/j.jorganchem.2005.11.025



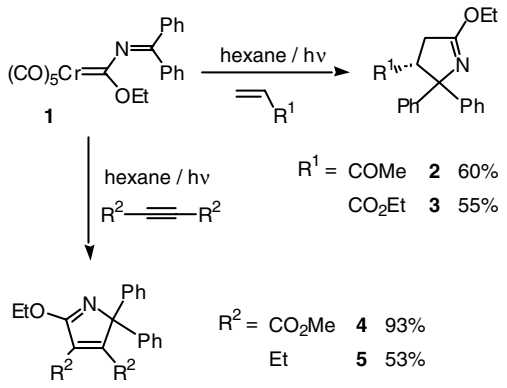
Scheme 1.



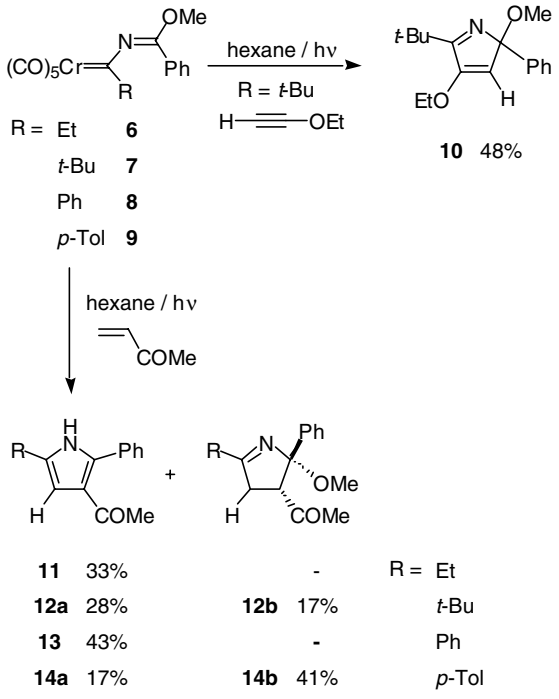
Scheme 2.

The synthesis of these targets was achieved by heating pentacarbonyl[methoxy(phenyl)carbene]chromium(0) in the presence of the appropriate nitrile. The reaction involves insertion of a carbon–nitrogen triple bond into the carbene–metal bond [12].

The corresponding cyclopentannulation reaction products were also obtained by irradiation of complexes **6**–**9** in the presence of unsaturated systems (Scheme 4) [13]. The photoreaction involving **7** and ethyl ethynyl ether gave 2*H*-pyrrole **10**, while the reaction with alkenes led to a mixture of 1-pyrrolines and the corresponding pyrrole – resulting from spontaneous loss of methanol due to aromatization. The pyrrolines were detected by ^{1}H NMR spectroscopy in all cases but they proved to be too unstable to be purified – with the exception of **12b** and **14b**. In these two cases, the pyrroline could be isolated and characterized. However, treatment of solutions of pyrrolines **12b** and **14b** with one equivalent of HBF_4 led to the quantitative formation of the corresponding pyrrole in a few hours.



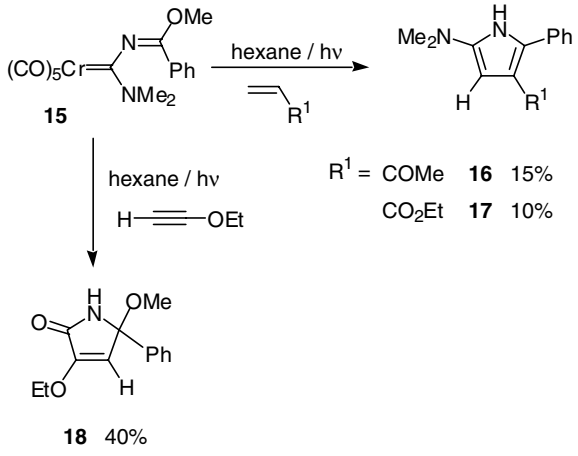
Scheme 3.



Scheme 4.

The configurational assignment of compounds **10**–**14** was made on the basis of difference NOESY experiments and comparison of their spectral data with those of similar compounds whose X-ray structures are available [9].

We subsequently modified the structure of the imine-carbene complex by including an amino instead of an alkoxy group on the carbenic carbon. In this respect, we prepared carbene **15** from dimethylcyanamide [14] and investigated its photochemical behaviour in the presence of some unsaturated compounds (Scheme 5). Irradiation of carbene **15** in the presence of methyl vinyl ketone or ethyl acrylate led to the formation of the corresponding pyrrole derivatives **16** or **17**, respectively. Aminopyrroles **16** and **17** were obtained with a large amount of polymeric material and it was observed that they decompose



Scheme 5.

during the work up procedure (column chromatography, hexane/ether), which explains the low yields. Moreover, irradiation of carbene **15** in the presence of ethyl ethynyl ether gave pyrrolone **18** in 40% yield, with the enamine moiety being hydrolyzed during the course of the reaction. This kind of compound has previously been synthesized [15], was found to show a range of biological activity [16] and has been used for the synthesis of different natural products [17].

In an attempt to confirm the photochemical nature of these transformations, we carried out the same processes in the dark at room temperature for 3 h, but no reaction took place. However, when compound **8** was heated at 80 °C in the dark for 36 h in the presence of methyl vinyl ketone, the formation of pyrrole **13** (40% yield) was detected. When complex **15** was heated in the presence of the unsaturated systems shown in Scheme 5 only carbene decomposition products and polymeric material were found.

3. Conclusions

A thorough investigation into the photochemical behaviour of carbene complexes bearing two kinds of substituent (imine and alkoxy or amino) with unsaturated systems has been performed. It was found that the presence of the imino group determines whether the annulated product without CO insertion is formed. These results suggest that the imino group inhibits the formation of transient metalketene complexes and complete loss of one CO molecule should occur after irradiation.

4. Experimental

4.1. General comments

All solvents were purified and dried by standard procedures and freshly distilled under dry Ar prior to use. ^{1}H and ^{13}C spectra were recorded on a Bruker ARX-300 spectrometer in $CDCl_3$ with TMS as internal standard. Electrospray mass spectra were obtained on an HP 5989 B apparatus with an HP 59987 A interface in either negative-ion mode or positive-ion mode. GC/MS spectra were recorded on an HP G1800A apparatus. IR spectra were obtained on a Perkin–Elmer 1000 spectrophotometer in CH_2Cl_2. UV spectra were recorded on an HP 8451A spectrophotometer. Elemental analyses were performed using a Model 1110 CE instrument. Melting points were obtained on a Büchi SMP-20 apparatus and are uncorrected. Reagents were of commercial grades.

4.2. General procedure for the preparation of iminecarbene complexes *1*, *6*–*9*, and *15*

The formation of compounds **1** [10], **7**–**8** [12], and **15** [14] has been reported previously.

The iminecarbenes **6** and **9** were prepared as follows. The alkoxycarbene complex (3 mmol) was dissolved in 20 mL of deoxygenated toluene and the corresponding nitrile (15 mmol) was added. The mixture was stirred at 80 °C until the carbene had been consumed (1–2 days, TLC, hexane/ether 2:1). The solvent was removed under vacuum. Purification of the residue by column chromatography (silica gel, hexane or hexane/ether 9:1) and recrystallization (hexane/ether) gave carbenes **6** and **9** as yellow and orange solids, respectively.

4.3. Pentacarbonyl{[(methoxyphenylmethylene)amino]-ethylmethylene}chromium(0) (*6*)

Yellow solid. Yield: 0.23 g, 21%. ^{1}H NMR: δ 1.02 (t, $J = 7$ Hz, 3H, CH_2CH_3), 3.30 (q, $J = 4$ Hz, 2H, CH_2CH_3), 3.89 (s, 3H, OCH_3), 7.49–7.62 (m, 5H, H arom.). ^{13}C NMR: δ 11.3 (CH_2CH_3), 47.0 (CH_2CH_3), 55.6 (OCH_3), 126.0, 127.5, 129.2, 132.2, 139.0, 217.5 (CO-*cis*), 223.8 (CO-*trans*), 254.2 (C=Cr). ES-MS (–): *m*/*z* 366 (M−1), 338 (M−CO−1), 310 (M−2CO−1). IR (CH_2Cl_2): *v* 1303 (w), 1601 (w), 1809 (m), 1922 (s), 1968 (sh), 2049 (m) cm^{-1}. UV (hexane): λ 226 nm ($\varepsilon \approx 30910$), 249 nm ($\varepsilon \approx 36768$), 368 nm ($\varepsilon \approx 5607$). Mp: 48–50 °C. Anal. Calc. for $C_{16}H_{13}NO_6Cr$: C, 52.33; H, 3.57; N, 3.81. Found: C, 52.40; H, 3.61; N, 3.75%.

4.4. Pentacarbonyl{[(methoxyphenylmethylene)amino]-para-tolylmethylene}chromium(0) (*9*)

Orange solid. Yield: 0.51 g, 40%. ^{1}H NMR: δ 2.40 (s, 3H, CH_3-C_6H_4), 4.00 (s, 3H, OCH_3), 7.25 (d, $J = 8$ Hz, 2H, H arom.), 7.47–7.62 (m, 7H, H arom.). ^{13}C NMR: δ 21.6 (CH_3-C_6H_4), 55.7 (OCH_3), 126.6, 127.4, 128.4, 129.2, 129.5, 132.2, 138.1, 142.1, 142.7, 217.8 (CO-*cis*), 224.1 (CO-*trans*), 259.8 (C=Cr). ES-MS (–): *m*/*z* 428 (M−1), 400 (M−CO−1), 372 (M−2CO−1). IR (CH_2Cl_2): *v* 1264 (s), 1599 (w), 1796 (w), 1927 (s), 1972 (sh), 2054 (m) cm^{-1}. UV (hexane): λ 208 nm ($\varepsilon \approx 192346$), 255 nm ($\varepsilon \approx 45408$), 430 nm ($\varepsilon \approx 5177$). Mp: 106–108 °C. Anal. Calc. for $C_{21}H_{15}NO_6Cr$: C, 58.75; H, 3.52; N, 3.26. Found: C, 56.67; H, 3.47; N, 3.11%.

4.5. General procedure for irradiation

The carbene complex (0.25 mmol) was dissolved in 50 mL of deoxygenated hexane. Ten equivalents of the unsaturated compound were added and the mixture was irradiated at room temperature under an Ar atmosphere through Pyrex glass with a 125 W (**2**–**5**) or 400 W (**10**–**14**, **16**–**18**) medium-pressure mercury lamp. Irradiation was continued until the iminecarbene had been consumed (1–2 h, TLC, hexane/ether 3:1). The solvent was removed using a rotary evaporator and the crude product was filtered through Celite to remove chromium residues. The products were separated by column chromatography (silica gel, hexane/ethyl acetate or hexane/ether).

4.6. 4-Acetyl-2-ethoxy-5,5-diphenyl-1-pyrroline (**2**)

Yellow oil. Yield: 46 mg, 60%. ^{1}H NMR: δ 1.30 (t, $J = 7.1$ Hz, 3H, CH_3), 1.48 (s, 3H, $COCH_3$), 2.60 (dd, $J = 16.7$ Hz, $J = 8.6$ Hz, 1H, H_{3a}), 2.91 (dd, $J = 16.7$ Hz, $J = 3.9$ Hz, 1H, H_{3b}), 4.07 (dd, $J = 8.6$ Hz, $J = 3.9$ Hz, 1H, H_4), 4.26–4.42 (m, 2H, OCH_2), 7.06–7.20 (m, 6H, arom), 7.28 (t, $J = 7.9$ Hz, 2H, arom), 7.55 (d, $J = 7.5$ Hz, 2H, arom). ^{13}C NMR: δ 14.6 (CH_3), 29.6 (CH_3), 35.0 (N=C–CH_2), 60.1 (*C*HCO), 64.8 (OCH_2), 81.2 (CPh_2), 127.0, 127.1, 127.3, 127.7, 128.1, 128.3, 144.1, 146.6, 170.9 (C=N), 208.2 (C=O). GC–MS: *m*/*z* 307 (M, 10), 278 (M−Et, 31), 264 (8), 208 (52), 182 (100), 165 (42), 126 (83), 98 (42), 77 (50), 43 (25). IR (CH_2Cl_2): *v* 1651 (s), 1708 (s) cm^{-1}. Anal. Calc. for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.05; H, 6.80; N, 4.44%.

4.7. 2-Ethoxy-4-ethoxycarbonyl-5,5-diphenyl-1-pyrroline (**3**)

Yellow oil. Yield: 47 mg, 55%. ^{1}H NMR: δ 0.90 (t, $J = 7.1$ Hz, 3H, CH_3), 1.39 (t, $J = 7.1$ Hz, 3H, CH_3), 2.73 (dd, $J = 16.8$ Hz, $J = 9.5$ Hz, 1H, H_{3a}), 3.23 (dd, $J = 16.8$ Hz, $J = 6.2$ Hz, 1H, H_{3b}), 3.54 (m, 1H, $COCH_2$), 3.69 (m, 1H, $COCH_2$), 4.06 (dd, $J = 9.5$ Hz, $J = 6.2$ Hz, 1H, H_4), 4.35–4.50 (m, 2H, OCH_2), 7.09–7.20 (m, 5H, arom), 7.27 (m, 1H, arom), 7.37 (m, 2H, arom), 7.79 (d, $J = 7.6$ Hz, 2H, arom).^{13}C NMR: δ 13.8 (CH_3), 14.7 (CH_3), 35.3 (N=C–*C*H_2), 53.7 (*C*HCO), 60.9 (OCH_2), 64.8 (OCH_2), 82.0 (CPh_2), 126.9, 127.5, 127.6, 127.8, 128.2, 128.4, 130.2, 132.5, 144.2, 144.2, 170.2 (C=N), 172.2 (CO_2). GC–MS: *m*/*z* 337 (M, 12), 308 (M−Et, 48), 260 (10), 208 (100), 206 (65), 165 (48), 104 (27), 77 (69), 51 (23), 29 (21). IR (CH_2Cl_2): *v* 1659 (s), 1731 (s) cm^{-1}. Anal. Calc. for $C_{21}H_{23}NO_3$: C, 74.75; H, 6.87; N, 4.15. Found: C, 74.63; H, 6.80; N, 4.29%.

4.8. 2-Ethoxy-3,4-di(methoxycarbonyl)-5,5-diphenyl-2H-pyrrole (**4**)

Yellow solid. Yield: 88 mg, 93%. ^{1}H NMR: δ 1.40 (t, $J = 7.1$ Hz, 3H, CH_3), 3.69 (s, 3H, CO_2CH_3), 3.88 (s, 3H, CO_2CH_3), 4.45 (q, $J = 7.1$ Hz, 2H, OCH_2), 7.28 (bs, 10H, arom).^{13}C NMR: δ 14.4 (CH_3), 52.5 (CO_2CH_3), 53.6 (CO_2CH_3), 65.6 (OCH_2), 84.5 (CPh_2), 127.9, 128.0, 128.2, 128.3, 132.5, 139.5, 160.6 (C=O), 162.5 (C=O), 165.6 (C=N). GC–MS: *m*/*z* 379 (M, 73), 350 (M−Et, 37), 319 (100), 306 (19), 275 (8), 260 (12), 232 (56), 204 (29), 132 (56), 118 (81), 105 (25), 77 (52), 59 (42), 29 (23), 15 (12). IR (CH_2Cl_2): *v* 1588 (m), 1644 (m), 1731 (s) cm^{-1}. Mp: 95–97 °C. Anal. Calc. for $C_{21}H_{21}NO_5$: C, 69.64; H, 5.58; N, 3.69. Found: C, 69.51; H, 5.69; N, 3.60%.

4.9. 2-Ethoxy-3,4-diethyl-5,5-diphenyl-2H-pyrrole (**5**)

Colourless oil. Yield: 42 mg, 53%. ^{1}H NMR: δ 0.51 (t, $J = 7.6$ Hz, 3H, CH_3), 1.14 (t, $J = 7.5$ Hz, 3H, CH_3), 1.37 (t, $J = 7.1$ Hz, 3H, OCH_2CH_3), 2.31 (q, $J = 7.5$ Hz, 2H, C=C–CH_2), 2.40 (q, $J = 7.6$ Hz, 2H, C=C–CH_2), 4.37 (q, $J = 7.1$ Hz, 2H, OCH_2), 7.20 (m, 10H, arom).^{13}C NMR: δ 13.6 (CH_3), 13.7 (CH_3), 14.7 (CH_3), 17.7 (CH_2), 21.2 (CH_2), 63.7 (OCH_2), 83.9 (CPh_2), 126.9, 128.1, 128.2, 132.3, 142.5, 165.9.6, 172.4 (C=N). GC–MS: *m*/*z* 319 (M, 17), 290 (M−Et, 100), 262 (6), 180 (6), 165 (8), 129 (6), 105 (7), 77 (19), 29 (4). IR (CH_2Cl_2): *v* 1584 (m), 1658 (w) cm^{-1}. Anal. Calc. for $C_{22}H_{25}NO$: C, 82.72; H, 7.89; N, 4.38. Found: C, 82.61; H, 7.79; N, 4.27%.

4.10. 2-tert-Butyl-3-ethoxy-5-methoxy-5-phenyl-2H-pyrrole (**10**)

Yellow oil. Yield: 33 mg, 48%. ^{1}H NMR: δ 1.36 [s, 9H, C–$(CH_3)_3$], 1.36 (m, 3H, OCH_2CH_3), 3.27 (s, 3H, OCH_3), 3.89 (m, 2H, OCH_2CH_3), 5.79 (s, 1H, CH), 7.23–7.34 (m, 3H, H arom.), 7.48–7.51 (m, 2H, H arom.). ^{13}C NMR: δ 14.6 (OCH_2CH_3), 27.6 [C–$(CH_3)_3$], 29.8 [*C*–$(CH_3)_3$], 51.5 (OCH_3), 66.6 (OCH_2CH_3), 115.7 (CH), 126.4, 127.9, 128.3, 129.0, 139.9 (*C*–OEt), 155.8 (C=N). ES-MS (+): *m*/*z* 274 (M+1). GC–MS: *m*/*z* 273 (M, 40), 244 (37), 216 (23), 188 (20), 161 (100), 126 (22), 115 (17), 105 (20), 102 (29), 77 (29), 69 (27), 28 (39). IR (CH_2Cl_2): *v* 1441 (m), 1461 (m), 1577 (m) cm^{-1}. Anal. Calc. for $C_{19}H_{19}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.58; H, 8.36; N, 4.98%.

4.11. 3-Acetyl-5-ethyl-2-phenyl-1-pyrrole (**11**)

Yellow solid. Yield: 18 mg, 33%. ^{1}H NMR: δ 1.29 (t, $J = 7$ Hz, 3H, CH_2CH_3), 2.29 (s, 3H, CO–CH_3), 2.64 (q, $J = 7$ Hz, 2H, CH_2CH_3), 6.39 (d, $J = 3$ Hz, 1H, CH), 7.33–7.44 (m, 3H, H arom.), 7.52–7.56 (m, 2H, H arom.), 8.48 (s, 1H, NH). ^{13}C NMR: δ 13.3 (CH_2CH_3), 20.6 (CO–CH_3), 29.1 (CH_2CH_3), 107.7, 122.0, 128.5, 128.5, 129.2, 132.8, 134.2, 135.4, 194.7 (*C*O–CH_3). ES-MS (+): *m*/*z* 214 (M+1). GC–MS: *m*/*z* 213 (M, 42), 199 (15), 198 (100), 91 (17), 77 (13), 43 (18). IR (CH_2Cl_2): *v* 1654 (s), 3424 (m) cm^{-1}. Mp: 50–52 °C. Anal. Calc. for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.75; H, 7.12; N, 6.50%.

4.12. 3-Acetyl-5-tert-butyl-2-phenyl-1-pyrrole (**12a**)

Yellow-brown solid. Yield: 25 mg, 41%. ^{1}H NMR: δ 1.34 [s, 9H, C–$(CH_3)_3$], 2.28 (s, 3H, CO–CH_3), 6.40 (d, $J = 6$ Hz, 1H, CH), 7.36–7.46 (m, 3H, H arom.), 7.55 (d, $J = 7$ Hz, 2H, H arom.). ^{13}C NMR: δ 29.1 (CO–*C*H_3), 30.3 [C–(*C*H_3)], 31.4 [*C*–(CH_3)], 105.9, 121.8, 128.5, 128.6, 129.3, 133.0, 135.3, 141.9, 194.9, (*C*O–CH_3). ES-MS (+): *m*/*z* 242 (M+1). GC–MS: *m*/*z* 242 (M+1, 12), 241 (70), 227 (16), 226 (97), 198 (44), 185 (15), 184 (100), 183 (34), 168 (20), 167 (13), 115 (15), 77 (16), 43 (64). IR (CH_2Cl_2): *v* 1664 (m), 3436 (m) cm^{-1}. Mp: 183–185 °C. Anal. Calc. for $C_{16}H_{19}NO$: C, 79.63; H, 7.94; N, 5.80. Found: C, 79.70; H, 8.00; N, 5.76%.

4.13. (4R,5S*)-4-Acetyl-2-tert-butyl-5-methoxy-5-phenyl-1-pyrroline (**12b**)*

Colourless oil. Yield: 11.6 mg, 17%. ^{1}H NMR: δ 1.31 [s, 9H, C–$(CH_3)_3$], 2.22 (s, 3H, CO–CH_3), 2.54 (dd, $J = 6$ Hz, 17 Hz, 1H, CH), 3.22–3.34 (m, 2H, CH_2), 3.27 (s, 3H, OCH_3), 7.31–7.40 (m, 5H, H arom.). ^{13}C NMR: δ 28.4 (CH_2), 31.3 (CO–CH_3), 35.7 [C–(CH_3)], 36.7 [C–(CH_3)], 52.2 (OCH_3), 108.0, 125.9, 127.9, 128.6, 143.2, 188.4 (C=N), 205.9 (CO–CH_3). ES-MS (+): *m/z* 274 (M+1). GC–MS: *m/z* 273 (M, 3), 230 (11), 147 (11), 138 (12), 136 (6), 123 (9), 115 (8), 106 (8), 105 (100), 77 (26), 43 (20). IR (CH_2Cl_2): ν 1134 (w), 1606 (w), 1654 (w) cm^{-1}. Anal. Calc. for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.60; H, 8.39; N, 5.04%.

*4.14. 3-Acetyl-5,5-diphenyl-1-pyrrole (**13**)*

Pale yellow solid. Yield: 28 mg, 43%. ^{1}H NMR: δ 2.33 (s, 3H, CO–CH_3), 6.95 (d, $J = 3$ Hz, 1H, CH), 7.25–7.31 (m, 1H, H arom.), 7.38–7.47 (m, 5H, H arom.), 7.51–7.61 (m, 4H, H arom.), 8.77 (s, 1H, NH). ^{13}C NMR: δ 28.9 (CO–CH_3), 108.5 (CH), 123.3, 124.0, 127.2, 128.4, 128.8, 129.0, 129.1, 131.3, 131.7, 132.2, 137.0, 194.5 (CO–CH_3). ES-MS (+): *m/z* 262 (M+1). GC–MS: *m/z* 262 (M+1, 12), 261 (60), 247 (20), 246 (100), 217 (19), 115 (15), 109 (190), 77 (11). IR (CH_2Cl_2): ν 1671 (m), 3427 (w) cm^{-1}. Mp: 180–182 °C. Anal. Calc. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.68; H, 5.74; N, 5.30%.

*4.15. 3-Acetyl-5-para-tolyl-2-phenyl-1-pyrrole (**14a**)*

Pale-yellow solid. Yield: 12 mg, 17%. ^{1}H NMR: δ 2.36 (s, 3H, CH_3–C_6H_4), 2.38 (s, 3H, CO–CH_3), 6.93 (d, $J = 3$ Hz, 1H, CH), 7.21–7.26 (m, 2H, H arom.), 7.41–7.48 (m, 5H, H arom.), 7.59–7.63 (m, 2H, H arom.), 8.57 (s, 1H, NH). ^{13}C NMR: δ 21.3 (CH_3–C_6H_4), 29.21 (CO–CH_3), 108.1, 123.4, 124.1, 128.6, 128.7, 128.9, 129.3, 129.9, 132.1, 132.5, 136.9, 137.3, 194.7 (CO–CH_3). ES-MS (+): *m/z* 276 (M+1). GC–MS: *m/z* 275 (M, 74), 261 (20), 260 (100), 130 (12), 115 (11). IR (CH_2Cl_2): ν 1178 (w), 1661 (s), 3436 (m) cm^{-1}. Mp: 175–177 °C. Anal. Calc. for $C_{19}H_{17}NO$: C, 82.88; H, 6.22; N, 5.09. Found: C, 82.80; H, 6.28; N, 4.98%.

4.16. (4R,5S*)-4-Acetyl-5-phenyl-5-methoxy-2-para-tolyl-1-pyrroline (**14b**)*

Yellow oil. Yield: 32 mg, 41%. ^{1}H NMR: δ 2.27 (s, 3H, CO–CH_3), 2.44 (s, 3H, CH_3–C_6H_4), 2.95 (dd, $J = 8$ Hz, 17 Hz, 1H), 3.36 (s, 3H, OCH_3), 3.47–3.52 (m, 1H), 3.68 (dd, $J = 5$ Hz, 17 Hz, 1H), 7.26–7.46 (m, 7H, H arom.), 7.92 (d, 7H, H arom.). ^{13}C NMR: δ 21.7 (CH_3–C_6H_4), 31.2 (CO–CH_3), 37.0 (CH_2), 52.4 (OCH_3), 61.9 (CH), 108.5–143.2 (9C), 175.2 (CO–CH_3), 205.5 (C=N). ES-MS (+): *m/z* 308 (M+1). GC–MS: *m/z* 307 (M, 4), 292 (12), 264 (15), 233 (18), 275 (12), 172 (25), 129 (12), 115 (20), 105 (100), 77 (44), 43 (20). IR (CH_2Cl_2): ν 1618 (m), 1175 (m), 1708 (s) cm^{-1}. Anal. Calc. for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 78.02; H, 6.80; N, 4.50%.

*4.17. 3-Acetyl-2-phenyl-5-(N,N-dimethylamino)-1-pyrrole (**16**)*

Yellow oil. Yield: 8.5 mg, 15%. ^{1}H NMR: δ 2.24 (s, 3H, CO–CH_3), 2.78 [s, 6H, N$(CH_3)_2$], 5.77 (d, 1H, $J = 3$ Hz, CH), 7.38–7.42 (m, 3H, H arom.), 7.50–7.54 (m, 2H, H arom.), 7.96 (s, 1H, NH). ^{13}C NMR: δ 29.1 (CO–CH_3), 42.4 [N–$(CH_3)_2$], 91.5 (CH), 121.6, 143.9 (7C), 194.76 (CO–CH_3). ES-MS (+): *m/z* 229 (M+1). GC–MS: *m/z* 228 (M, 100), 213 (52), 211 (180), 207 (12), 185 (14), 171 (19), 170 (21), 144 (15), 143 (13), 142 (14), 115 (22), 114 (12), 85 (25), 77 (20), 66 (16), 43 (40), 42 (21), 39 (11). IR (CH_2Cl_2): ν 1661 (m), 3426 (m) cm^{-1}. Anal. Calc. for $C_{14}H_{16}N_2O$: C, 73.66; H, 7.06; N, 12.27. Found: C, 73.53; H, 7.14; N, 12.09%.

*4.18. 3-Ethoxycarbonyl-2-phenyl-5-(N,N-dimethylamino)-1-pyrrole (**17**)*

Yellow-brown oil. Yield: 6.5 mg, 10%. ^{1}H NMR: δ 2.78 [s, 6H, N$(CH_3)_2$], 1.26 (t, $J = 7$ Hz, 3H, CO_2–CH_2CH_3), 4.21 (q, $J = 7$ Hz, 2H, CO_2–CH_2CH_3), 5.83 (d, 1H, $J = 3$ Hz, CH), 7.28–7.41 (m, 3H, H arom.), 7.55–7.59 (m, 2H, H arom.), 7.92 (s, 1H, NH). ^{13}C NMR: δ 14.5 (CO_2–CH_2CH_3), 42.6 [N$(CH_3)_2$], 59.7 (CO_2–CH_2CH_3), 92.4 (CH), 111.4, 127.8, 128.2, 128.9, 131.6, 132.5, 143.8, 165.2 (CO_2–CH_2CH_3). ES-EM (+): *m/z* 259 (M+1). GC–MS: *m/z* 258 (M, 50), 230 (15), 130 (27), 32 (29), 28 (100). IR (CH_2Cl_2): ν 1122 (w), 1723 (s), 3437 (w) cm^{-1}. Anal. Calc. for $C_{15}H_{18}N_2O_2$ C, 69.74; H, 7.02; N, 10.84. Found: C, 69.63; H, 6.91; N, 10.76%.

*4.19. 3-Ethoxy-5-methoxy-5-phenyl-1,5-dihydropyrrole-2-one (**18**)*

Yellow oil. Yield: 23 mg, 40%. ^{1}H NMR ($CDCl_3$): δ 1.43 (t, 3H, $J = 7$ Hz, OCH_2CH_3), 3.35 (s, 3H, OCH_3), 3.96 (qd, 2H, $J = 7$, 2 Hz, OCH_2CH_3), 5.49 (d, 1H, $J = 2$ Hz, CH), 6.25 (s, 1H, NH), 7.33–7.39 (m, 3H, H arom.), 7.50–7.53 (m, 2H, H arom.). ^{13}C NMR ($CDCl_3$): δ 14.3 (OCH_2CH_3), 50.5 (OCH_3), 66.7 (OCH_2CH_3), 90.0 (COMePh), 111.9, 125.5, 128.8, 158.8, 139.8, 150.1 (C=N), 167.3 (C=O). ES-EM (+Na): *m/z* 256 (M+23). IR (CH_2Cl_2): ν 1260 (vs), 1423 (s), 1710 (w), 3420 (w) cm^{-1}. Anal. Calc. for $C_{12}H_{15}NO_3$: C, 66.94; H, 6.48; N, 6.00. Found: C, 66.87; H, 6.36; N, 5.92%.

5. Supplementary material

Crystallographic data for the **6** and **9** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 218076 and 218077, respectively. Copies of the data can be obtained,

free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

This work was supported by the Spanish MCyT/FEDER (BQU2001-1625) and Comunidad Autónoma de La Rioja (ACPI 2003/08). M.C. and S.L.-S. thank the Spanish MEC for their fellowship. D.S. is financed by the Ramón y Cajal program from the MEC.

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