Pergamon

Tetrahedron Vol. 51, No. 32, pp. 8829-8834, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4020/95 $9.50+0.00

0040-4020(95)00464-5

Remarkable Substituent Effects on the Chemoselectivity of Rhodium(II) Carbenoids Derived from *N*-(2-Diazo-3-oxobutyryl)-*L*-phenylalanine Esters

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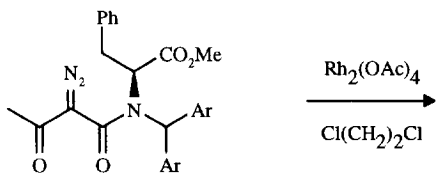
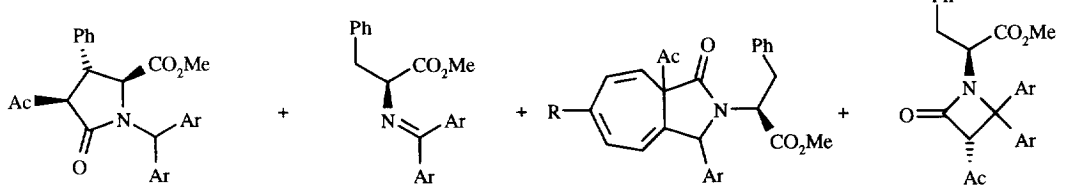
Abstract: Four different *N*-(alkyl/aryl)-*N*-(2-diazo-3-oxobutyryl)-*L*-phenylalanine methyl esters **1b-e** have been synthesized and subjected to rhodium(II) acetate catalyzed diazodecomposition. Thereby a strong dependence of the product distribution from the type of nitrogen bound substituent was observed. The bis(4-chlorophenyl)methyl derivative **1b** provided similar products in comparable yields as the benzhydryl derivative **1a**. The *N*-[bis(2-tolyl)methyl] diazoamide **1c** gave exclusively the cyclohepta[*c*]pyrrole **4c**, whereas the *N*-fluorenyl derivative **1d** yielded, upon treatment with $Rh_2(OAc)_4$, mainly the spirolactam **5d**. The *N*-(4-nitrophenyl) diazoamide **1e** gave, under the same conditions, the nitroindole **7**.

In an attempt to disclose a practical method for C-alkylating α-amino acids by intramolecular carbene C-H insertion it was found[2] that the rhodium(II) catalyzed decomposition of *N*-benzhydryl-*N*-(2-diazo-3-oxobutyryl)-*L*-phenylalanine esters (e.g., **1a**) yielded, albeit in low yield, the desired C-alkylation products (e.g., **2a**). In order to determine the dependence of the product distribution on the type of nitrogen bound substituent, the diazoamides **1b-e**[3] were synthesized and subjected to the action of rhodium(II) acetate. The following results were obtained:



1a (Ar = phenyl)
1b (Ar = 4-chlorophenyl)

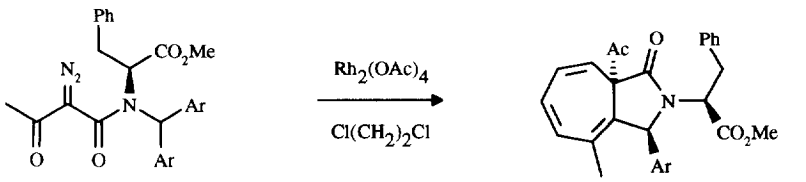


2a (12%)
2b (11%)

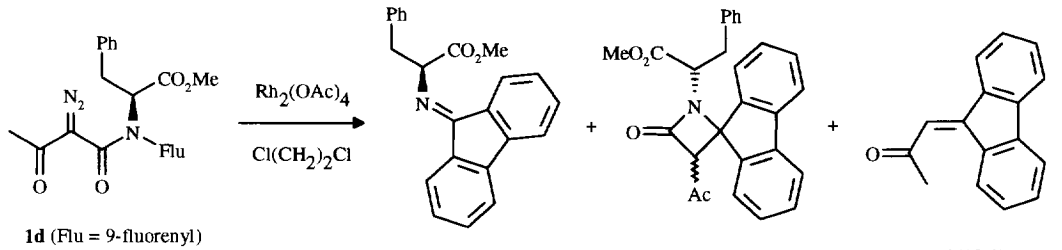
3a (22%)
3b (11%)

4a (R = H; 18%)
4b (R = Cl; 21%)

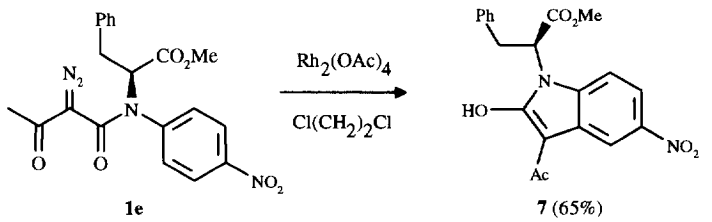
5a (16%)
5b (8%)



1c (Ar = 2-tolyl) **4c** (main isomer shown, 87:13; 61%)



1d (Flu = 9-fluorenyl) **3d** (15%) **5d** (66%, 1:1) **6** (10%)



1e **7** (65%)

The bis(4-chlorophenyl)methyl derivative **1b** gave, upon treatment with rhodium(II) acetate, the same type of products in comparable yields as the unsubstituted benzhydryl derivative **1a**. Under the same conditions the *N*-[bis(2-tolyl)methyl] diazoamide **1c** yielded the triene **4c**[4] [two diastereomers, 87:13 (^{1}H NMR)], resulting, as **4a,b**, from the cyclopropanation and rearrangement of one of the aryl groups. The exclusive isolation of **4c** from the rhodium(II) catalyzed decomposition of the diazoamide **1c** indicates that the formation of imines of the type of **3a,b** and azetidinones like **5a,b** can be prevented by sterically shielding the benzylic C-H bond of the nitrogen bound diarylmethyl group. However, the increased bulkyness of the bis(2-tolyl)methyl moiety did not lead to a higher degree of C-alkylation of the amino acid carbon framework, since cyclopropanation of one of the tolyl groups, followed by a norcaradiene-cycloheptatriene rearrangement, is in this case evidently the more favorable pathway. Unexpectedly, the rhodium(II) catalyzed decomposition

of the 9-fluorenyl derivative **1d** gave mainly the spirolactam **5d** together with minor amounts of the imine **3d** and the ketone **6**.[5] The spirolactam **5d** was isolated as a mixture of two diastereomers (50:50, ^{1}H NMR), which resisted all attempts to be separated by fractional crystallization. In addition to the diarylmethyl derivatives **1b-d**, the *N*-(4-nitrophenyl) diazoamide **1e** was synthesized and subjected to rhodium(II) acetate catalyzed decomposition. Surprisingly[6], the exclusive alkylation of the nitrophenyl group took place, yielding cleanly the nitroindole **7**.

These reactions suggest, that the regioselectivity of the rhodium carbenoid is mainly determined by steric or conformational effects and not by electronic effects.[7] Otherwise, if the electron density of the attacked fragment would have been decisive, higher yields of **2b** and smaller amounts of **4b** (in comparison to the yields of **2a** and **4a** respectively) should have resulted. The high yield of spirolactam **5d** may be due to the reduced steric encumbrance (if compared to **1b**) of the C-H bond into which the insertion takes place. The formation of the imines **3a,b,d** can be rationalized[2] by a hydride shift from the electron rich diarylmethyl group to the electrophilic rhodium carbenoid, followed by a fragmentation of the resulting *N*-acyliminium enolate into the observed imines and acetylketene. For the formation of the ketone **6** no convincing mechanism can presently be proposed. In order to exclude the fragmentation of the spirolactam **5d** either into the imine **3d** and acetylketene[8] or into the ketone **6** and an isocyanate[9] as a possible mechanism for the formation of **3d** and **6**, a mixture of **5d**, rhodium(II) acetate and 1,2-dichloroethane was refluxed for 10 hours. No reaction occurred and only unchanged **5d** could be recovered.

EXPERIMENTAL

General procedures

The diazoamides **1b** and **1c** were prepared as **1a**[2], using bromobis(4-chlorophenyl)methane[10] and bromobis(2-tolyl)methane[11] as alkylating agents. The diazoamide **1d** was prepared by N-alkylation of *L*-phenylalanine methyl ester with 9-bromofluorene [diisopropylethylamine, MeCN, reflux, 4 h; (2*S*)-2-[(fluoren-9-yl)amino]-3-phenylpropionic acid methyl ester; slightly yellow crystals, mp 125-127 °C (toluene), $[\alpha]_D^{20}$ -48° (*c* 1.3, $CHCl_3$)], acetoacetylation[12] (84% for two steps) and diazo group transfer with 2-azido-1-ethylpyridinium tetrafluoroborate[13] (67%). The diazoamide **1e** was prepared by N-arylation of *L*-phenylalanine methyl ester with 4-fluoronitrobenzene [DMF, 110 °C, 10 h, 30%; (2*S*)-2-[(4-nitrophenyl)amino]-3-phenylpropionic acid methyl ester; yellow crystals, mp 94-96 °C (ethanol), $[\alpha]_D^{20}$ +153° (*c* 1.1, $CHCl_3$)], acetoacetylation[12] (71%) and diazo group transfer with tosyl azide (90%). Melting points: Gallenkamp MPD 350 melting point apparatus, uncorrected. - Optical rotations: Perkin Elmer 241 MC polarimeter. - NMR: Brucker AC-200P spectrometer; internal standard: TMS. - Flash chromatography: Silica gel 60 (0.040-0.063 mm, Merck), gradient elution with mixtures of heptane and methyl acetate. - TLC: Macherey-Nagel Polygram Sil G/UV_{254} silica gel plates. All solvents were dried and distilled before use. All reactions were carried out under argon, and commercially available reagents were used as purchased. All the intermediates were fully characterized and featured spectral as well as microanalytical data consistent with their structures. Only the diazoamides which could not be crystallized displayed in their elemental analyses deviations from the theoretical carbon content of approx. 1%.

*(2S)-2-{[Bis(4-chlorophenyl)methyl](2-diazo-3-oxobutyryl)amino}-3-phenylpropionic acid methyl ester (**1b**).* Yellow oil: $[\alpha]_D^{20}$ -44° (*c* 1.1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.16 (s, 3H), 3.19 (dd, *J* = 8.5,

14.1 Hz, 1H), 3.35 (dd, J = 5.9, 14.1 Hz, 1H), 3.72 (s, 3H), 4.09 (m_c, 1H), 5.72 (s, 1H), 6.82-7.38 (m, 13H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.61 (q), 35.20 (t), 52.08 (q), 62.06, 65.96 (2d), 75.01 (s), 126.67, 128.36, 128.51, 128.67, 128.71, 129.18, 130.83 (7d), 133.32, 134.11, 136.46, 137.18, 138.50, 161.64, 170.38, 188.15 (8s).

*(2S)-2-{[Bis(2-tolyl)methyl](2-diazo-3-oxobutyryl)amino}-3-phenylpropionic acid methyl ester (**1c**).* Yellow oil: $[\alpha]_D^{20}$ -5.4° (*c* 2.3, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.05 (s, br, 3H), 2.26 (s, br, 3H), 2.34 (s, 3H), 3.61 (s, 3H), 3.62-3.74 (m, 2H), 4.19 (dd, J = 3.6, 9.2 Hz, 1H), 6.42 (s, 1H), 6.75 (s, br, 2H), 6.91-7.35 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.93, 27.03 (2q), 36.55 (t), 51.80 (q), 61.76, 61.82 (2d), 72.16 (s), 126.07, 126.28, 126.64, 127.80, 127.95, 128.49, 129.01, 130.74, 130.99 (9d), 136.18, 136.54, 136.85, 137.36, 138.29, 162.56, 170.41, 190.16 (8s).

*(2S)-2-{(9H-Fluoren-9-yl)(2-diazo-3-oxobutyryl)amino}-3-phenylpropionic acid methyl ester (**1d**).* Yellow oil: $[\alpha]_D^{20}$ -63° (*c* 1.3, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.41 (s, br, 3H), 2.70-2.90 (m, 1H), 2.95-3.09 (m, 1H), 3.45-3.71 (m, 4H), 5.91 (s, br, 1H), 6.46 (s, br, 2H), 6.85-7.90 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.66 (q), 37.30 (t), 51.54 (q), 59.96, 64.50 (2d), 73.27 (s), 119.65, 120.04, 125.89, 127.02, 127.64, 127.75, 128.92, 129.08 (8d), 138.31, 139.63, 140.26, 140.68, 161.04, 169.56, 188.06 (7s).

*(2S)-2-[(2-Diazo-3-oxobutyryl)(4-nitrophenyl)amino]-3-phenylpropionic acid methyl ester (**1e**).* Yellow oil: $[\alpha]_D^{20}$ +55° (*c* 4.1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.46 (s, 3H), 3.40-3.55 (m, 2H), 3.84 (s, 3H), 4.38 (dd, J = 6.9, 9.0 Hz, 1H), 6.71 (m_c, 2H), 7.11-7.40 (m, 5H), 8.07 (m_c, 2H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.95 (q), 34.18 (t), 52.47 (q), 66.90 (d), 75.16 (s), 124.88, 126.93, 127.13, 128.77, 128.93 (5d), 137.38, 145.92, 148.02, 160.61, 169.70, 189.97 (6s).

*Rhodium(II) acetate catalyzed decomposition of diazoamide **1b**; typical procedure*

A solution of the diazoamide **1b** (1.98 g, 3.77 mmol) in 1,2-dichloroethane (50 mL) was added within 9 h to a refluxing suspension of $Rh_2(OAc)_4$ (46 mg, 0.10 mmol) in 1,2-dichloroethane (40 mL). When the addition was completed, the reaction mixture was concentrated and the residue was subjected to flash chromatography (100 g silica gel, gradient elution with heptane/methyl acetate). The following products were isolated:

*(2S,3R,4R)-4-Acetyl-1-[bis(4-chlorophenyl)methyl]-5-oxo-3-phenylpyrrolidine-2-carboxylic acid methyl ester (**2b**).* 203 mg (11%) of an oil; mixture of a keto and an enol tautomer (keto/enol 66:34): $[\alpha]_D^{20}$ -16° (*c* 1.1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.67 (s, 0.34 x 3H), 2.43 (s, 0.66 x 3H), 3.41 (s, 0.34 x 3H), 3.45 (s, 0.66 x 3H), 3.66-3.78 (m, 1H), 3.97-4.20 (m, 2H), 6.14 (s, 0.66H), 6.30 (s, 0.34H), 6.82-7.50 (m, 13H), 11.81 (s, br, 0.34H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.53, 28.84 (2q), 42.85, 44.99 (2d), 52.11, 52.17 (2q), 58.70, 60.74, 62.42, 65.75, 66.58 (5d), 100.95 (s), 126.70, 126.82, 127.69, 127.80, 128.48, 128.53, 129.06, 129.42, 130.68, 131.26 (10d), 133.22, 133.57, 134.04, 135.75, 135.88, 136.45, 137.17, 140.65, 141.85, 166.51, 170.08, 170.95, 171.28, 173.22, 199.70 (15s). Anal. Calcd. for $C_{27}H_{23}Cl_2NO_4$ (496.4): C, 65.33; H, 4.67; N, 2.82. Found: C, 65.14; H, 4.77; N, 2.75.

*(2S)-2-{[Bis(4-chlorophenyl)methylene]amino}-3-phenylpropionic acid methyl ester (**3b**).* 170 mg (11%) of an oil: $[\alpha]_D^{20}$ -197° (*c* 1.2, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.17 (dd, J = 9.3, 13.2 Hz, 1H), 3.27 (dd, J = 4.2, 13.2 Hz, 1H), 3.75 (s, 3H), 4.17 (dd, J = 4.2, 9.3 Hz, 1H), 6.40 (m_c, 2H), 6.96-7.52 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 39.51 (t), 52.18 (q), 67.28, 126.36, 128.16, 128.24, 128.44, 128.98, 129.68, 129.77 (8d), 133.68, 134.60, 136.66, 137.28, 137.66, 168.44, 171.69 (7s). Anal. Calcd. for $C_{23}H_{19}Cl_2NO_2$ (412.3): C, 67.00; H, 4.65; N, 3.40. Found: C, 66.00; H, 4.76; N, 3.67.

*(2S)-2-[3a-Acetyl-6-chloro-1-(4-chlorophenyl)-3-oxo-3,3a-dihydro-1H-cyclohepta[c]pyrrol-2-yl]-3-phenylpropionic acid methyl ester (**4b**).* 387 mg (21%) of an oil: $[\alpha]_D^{20}$ +30° (*c* 3.5, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.24 (s, 3H), 3.18-3.30 (m, 2H), 3.62-3.75 (m, 4H), 4.39 (s, br, 1H), 5.68 (dd, J = 2.3, 7.0 Hz, 1H), 5.94 (d, J = 10.2 Hz, 1H), 6.38 (dd, J = 1.4, 10.2 Hz, 1H), 6.49 (d, br, J = 7.0 Hz, 1H), 6.83-7.45

(m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 26.98 (q), 34.61 (t), 52.21 (q), 57.46 (d), 65.81 (s), 66.85, 121.28, 124.45, 127.00, 128.55, 128.69, 128.73, 128.94, 129.40, 130.37 (10d), 133.31, 134.58, 135.94, 136.94, 138.23, 168.49, 169.42, 200.31 (8s). Anal. Calcd. for $C_{27}H_{23}Cl_2NO_4$ (496.4): C, 65.33; H, 4.67; N, 2.82. Found: C, 65.63; H, 4.78; N, 2.80.

*(2S)-2-[(3R)-3-Acetyl-4-oxo-2,2-bis(4-chlorophenyl)azetidin-1-yl]-3-phenylpropionic acid methyl ester (**5b**).* 158 mg (8%) of colourless crystals, mp 155-157 °C (heptane/methyl acetate): $[\alpha]_D^{20}$ -197° (*c* 1.2, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.80 (s, 3H), 3.18-3.30 (m, 1H), 3.32 (s, 3H), 3.40-4.12 (m, 2H), 4.84 (s, 1H), 6.15-6.22 (m, 2H), 6.80-7.60 (m, 11H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 30.42 (q), 36.61 (t), 52.26 (q), 61.19, 69.18 (2d), 69.42 (s), 127.76, 128.35, 128.45, 128.55, 128.73, 128.88, 129.02, 129.81 (8d), 134.10, 134.95, 136.25, 136.73, 137.12, 165.05, 169.87, 200.43 (8s). Anal. Calcd. for $C_{27}H_{23}Cl_2NO_4$ (496.4): C, 65.33; H, 4.67; N, 2.82. Found: C, 65.40; H, 4.75; N, 2.78.

*Rhodium(II) acetate catalyzed decomposition of 1.86 g of diazoamide **1c***

*(2S)-2-[(1S,3aR)-3a-Acetyl-8-methyl-3-oxo-1-(2-tolyl)-3,3a-dihydro-1H-cyclohepta[c]pyrrol-2-yl]-3-phenylpropionic acid methyl ester (**4c**).* 1.07 g (61%) of colourless crystals, mp 171-172 °C (heptane/methyl acetate); mixture of two diastereomers (87:13): $[\alpha]_D^{20}$ +127° (*c* 1.3, $CHCl_3$); mayor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.33 (d, *J* = 1.2 Hz, 3H), 1.92 (s, 3H), 2.20 (s, 3H), 3.22-3.31 (m, 2H), 3.57 (dd, *J* = 5.5, 9.2 Hz, 1H), 3.59 (s, 3H), 5.04 (s, br, 1H), 6.03 (d, br, *J* = 9.0 Hz, 1H), 6.27-6.45 (m, 3H), 6.89-7.41 (m, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 18.04, 18.32, 27.89 (3q), 34.45 (t), 51.70 (q), 57.56, 62.12 (2d), 65.82 (s), 124.49, 125.90, 126.63, 126.80, 127.41, 127.64, 128.44 (7d), 128.72 (s), 129.24, 129.53, 130.06 (3d), 132.64, 134.43 (2s), 135.85 (d), 136.08, 137.41, 168.67, 170.30, 202.52 (5s); characteristic signals of minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (d, *J* = 1.2 Hz, 3H), 2.05 (s, 3H), 2.24 (s, 3H), 3.14-3.31 (m, 2H), 3.65 (s, 3H), 3.79 (dd, *J* = 4.6, 10.1 Hz, 1H), 4.56 (s, br, 1H), 5.87 (d, br, *J* = 9.0 Hz, 1H), 6.12 (d, *J* = 10.0 Hz, 1H), 6.20 (dd, *J* = 5.5, 10.0 Hz), 6.59 (d, br, *J* = 8.3 Hz, 1H); signals at 6.9-7.5 ppm overlap with signals of main isomer; ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.08, 20.51, 27.72 (3q), 34.66 (t), 51.70 (s), 56.53 (d), 66.39 (s), 69.32 (d), 125.40, 125.96, 126.94, 127.05 (4d), 128.94, 130.99 (2s), 131.97, 132.98 (2d), 133.41 (s), 135.72 (d), 137.15, 137.99, 168.94, 170.03, 202.12 (5s). Anal. Calcd. for $C_{29}H_{29}NO_4$ (455.6): C, 76.46; H, 6.42; N, 3.08. Found: C, 76.55; H, 6.49; N, 3.10.

*Rhodium(II) acetate catalyzed decomposition of 2.53 g of diazoamide **1d***

*(2S)-2-[(Fluoren-9-ylidene)amino]-3-phenylpropionic acid methyl ester (**3d**).* 0.29 g (15%) of an oil: $[\alpha]_D^{20}$ -195° (*c* 1.0, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.35 (dd, *J* = 7.3, 13.5 Hz, 1H), 3.52 (dd, *J* = 6.3, 13.5 Hz, 1H), 3.69 (s, 3H), 5.42 (dd, *J* = 6.3, 7.3 Hz, 1H), 7.12-7.43 (m, 9H), 7.49-7.92 (m, 4H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 40.88 (t), 52.11 (q), 66.15, 119.16, 120.33, 123.16, 126.59, 126.93, 127.94, 128.28, 128.32, 129.42, 131.19 (11d), 131.47 (s), 131.54 (d), 137.60, 138.35, 140.93, 143.97, 164.71, 171.92 (6s). Anal. Calcd. for $C_{23}H_{19}NO_2$ (341.4): C, 80.92; H, 5.61; N, 4.10. Found: C, 80.65; H, 5.64; N, 4.51.

*(2S)-2-{Spiro[(3-acetyl-4-oxoazetidin-1-yl)-2,9'-fluorene]}-3-phenylpropionic acid methyl ester (**5d**).* 1.57 g (66%) of colourless crystals, mp 124-126 °C (heptane/methyl acetate); mixture of two diastereomers (50:50): $[\alpha]_D^{20}$ -34° (*c* 1.3, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.61 (s, 1.5H), 1.75 (s, 1.5H), 2.95-3.72 (m, 6H), 4.37 (s, 0.5H), 4.52 (s, 0.5H), 5.83 (d, *J* = 7.6 Hz, 0.5H), 6.18 (d, *J* = 7.6 Hz, 0.5H), 6.79-7.69 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 29.28 (q), 35.28, 35.46 (2t), 51.67 (q), 58.50, 58.69 (2d), 68.28, 68.33 (2s), 69.67, 70.05, 119.46, 119.55, 119.82, 119.86, 122.55, 123.78, 124.39, 125.33, 126.47, 126.85, 127.21, 127.33, 127.67, 128.13, 128.17, 128.83, 129.06, 129.28, 129.52, 129.58 (22d), 136.29, 136.37, 137.61, 138.30, 139.82, 139.85, 140.17, 140.23, 140.92, 141.46, 162.84, 162.95, 169.08, 169.35, 198.49, 198.56 (16s). Anal. Calcd. for $C_{27}H_{23}NO_4$ (425.5): C, 76.22; H, 5.45; N, 3.29. Found: C, 76.31; H, 5.55; N, 3.37.

*1-(Fluoren-9-ylidene)propan-2-one (**6**).* 0.12 g (10%) of bright yellow crystals, mp 98-99 °C (heptane/methyl acetate; ref.[5]: mp 96-98 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.50 (s, 3H), 7.06 (s, 1H), 7.21-7.45 (m, 4H), 7.58-7.71 (m, 3H), 8.77 (d, br, *J* = 7.6 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 32.25 (q), 119.52, 119.83, 120.79, 121.06, 127.34, 128.18, 128.44, 130.61, 131.17 (9d), 135.29, 138.93, 141.28, 142.38,

145.86, 198.46 (6s). Anal. Calcd. for $C_{16}H_{12}O$ (220.3): C, 87.25; H, 5.49. Found: C, 87.23; H, 5.48.

Rhodium(II) acetate catalyzed decomposition of 1.75 g of diazoamide ***1e***

(2S)-2-(3-Acetyl-2-hydroxy-5-nitroindol-1-yl)-3-phenylpropionic acid methyl ester (7). 1.05 g (65%) of colourless crystals, mp 205-207 °C (heptane/ethyl acetate): $[\alpha]_D^{20}$ -278° (*c* 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 2.53 (s, 3H), 3.41 (dd, *J* = 10.7, 14.2 Hz, 1H), 3.63 (dd, *J* = 5.1, 14.2 Hz, 1H), 3.78 (s, 3H), 5.34 (dd, *J* = 5.1, 10.7 Hz, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 6.99-7.19 (m, 5H), 8.08 (dd, *J* = 8.8, 2.2 Hz, 1H), 8.20 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.67 (q), 34.78 (t), 52.94 (q), 55.25 (d), 100.09 (s), 108.98, 115.06, 121.39 (3d), 122.72 (s), 127.11, 128.58, 128.76 (3d), 139.93, 141.54, 143.14, 169.11, 171.10, 176.48 (6s). Anal. Calcd. for $C_{20}H_{18}N_2O_6$ (382.4): C, 62.82; H, 4.75; N, 7.33. Found: C, 62.88; H, 4.76; N, 7.30.

ACKNOWLEDGEMENTS

Financial support by the *Fonds der Chemischen Industrie* (Liebig-Stipendium) as well as generous donations of chemicals by the *Degussa AG* are gratefully appreciated. I also thank *Prof. Dr. P. G. Jones* for the X-ray structural analysis of compound **4c**.

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(*Received in Germany* 2 *March* 1995; *revised* 1 *June* 1995; *accepted* 9 *June* 1995)