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Facial Diastereoselectivity in the [2+2]-Photocycloaddition of Chiral Vinylglycine-Derived *N,N*-Diallyl Amines

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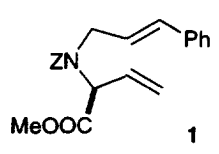
Abstract: The vinylglycine-derived *N*-cinnamyl-*N*-allyl carbamates **1**, **4** and **7** were prepared and their sensitized intramolecular [2+2]-photocycloaddition to the *exo*-products **2**, **5** and **6** was studied (53-77% yield). Perfect facial diastereoselection (d.r. = >95/5) was observed in the photocycloaddition of the rigid oxazolidinone **4** and of the conformationally fixed acyclic carbamate **7**.

Keywords: Amino acids and derivatives; Asymmetric induction; Cycloadditions; Photochemistry.

In view of the potential use of 2-substituted 3-azabicyclo[3.2.0]heptanes for the synthesis of chiral nitrogen heterocycles by subsequent ring opening reactions we were interested in their stereoselective preparation starting from α-substituted vinylglycine-derived *N,N*-diallyl amines by [2+2]-photocycloaddition reactions [1]. The substituent at the stereogenic center (e.g. COOMe, CMe_2OH) was expected to serve as the decisive device for the facial diastereoselection in these *N,N*-diallyl amines. The facial diastereoselectivity in the sensitized photocycloaddition [2] of the benzyloxycarbonyl(Z)-protected *N,N*-diallyl amine **1** which was prepared from methionine [3] was low (d.r. = 66/33) and the reaction yielded the *exo*-product **2** in 53% yield.



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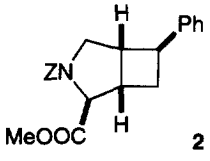

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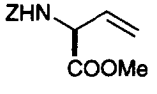

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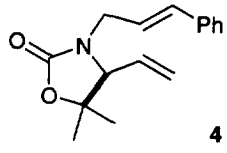

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The oxazolidinone **4**, however, which was prepared in two steps from the Z-protected vinylglycine methyl ester (**3**) by Grignard addition and base-induced cyclization/allylation [4] proved to be a superior substrate for the photocycloaddition. The reaction proceeded smoothly and yielded the tricyclic compound **5** as the only product [5] the relative configuration of which was elucidated by X-ray crystallography [6]. As anticipated the 3-azabicyclo[3.2.0]heptane possessed *exo*-configuration and the facial diastereoselectivity was induced by the bulky substituent at the stereogenic center of the 3-cinnamyl-4-vinyloxazolidinone **4**.

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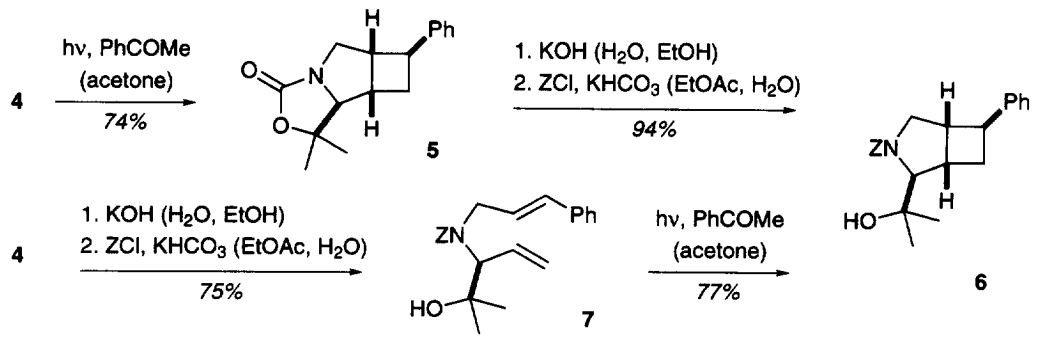

Upon treatment with base it became obvious that the tricyclic product **5** is highly strained. The otherwise more tedious hydrolysis proceeded readily within one hour and generated an amino alcohol which was subsequently Z-protected. Compound **6** so obtained was identical to the product received by treatment of ester **2** with an excess of MeMgI which proved the assignment of the relative configuration for **2**. The very same product **6** was also obtained from the acyclic *N,N*-diallyl carbamate **7** which is conformationally fixed due to 1,3-allylic strain and which yielded the *exo*-product **6** with perfect control of the facial diastereoselectivity.

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References and Notes

Author to whom inquiries about the crystal structure analysis should be addressed.

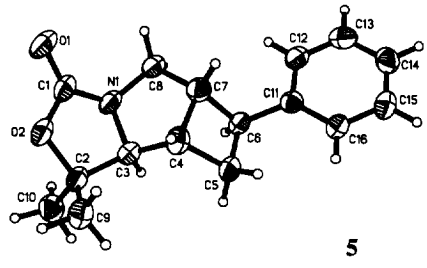
[1] Margaretha P in Houben-Weyl Methoden der Organischen Chemie 4th ed., Vol. E17e; (ed.: de Meijere A), Thieme, Stuttgart, 1997: 149-162 and refs. cited therein.

[2] Steiner G, Munschauer R, Klebe G, Siggel L. Heterocycles 1995, 40: 319-330.

[3] Afzali-Ardakani A, Rapoport H. J. Org. Chem. 1980, 45: 4817-4820.

[4] Huwe CM, Blechert S, Synthesis 1997, 61-67.

[5] A molecule of compound **5** in the crystal:
Further details of the crystal structure investigations related to this compound may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, on quoting the full literature citation.



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[6] Experimental: A quartz tube was charged with a solution of oxazolidinone **4** (1.05 mmol, 269 mg) and acetophenone (1.6 mmol, 173 mg) in 10 ml of acetone. The sample was irradiated at λ=300 nm for 24 h (Rayonet RPR 3000 Å). The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (2 × 15 cm; pentane/*t*-butyl methyl ether = 80/20). Product **5** was isolated in diastereomerically pure form as a white solid (191 mg, 74%). M.p.: 110 °C. ^{1}H NMR ($CDCl_3$): δ = 1.39 (s, 3 H), 1.60 (s, 3 H), 2.18 (ddd, *J* = 11.5 Hz, *J* = 8.7 Hz, *J* = 1.8 Hz, 1 H), 2.36 (ddd, *J* = 11.5 Hz, *J* = 8.9 Hz, *J* = 7.6 Hz, 1 H), 2.50 (virt qd, *J* ≅ 7.7 Hz, *J* = 1.8 Hz, 1 H), 3.10-3.29 (m, 2 H), 3.43 (virt q, *J* ≅ 8.0 Hz, 1 H), 3.86 (d, *J* = 7.1 Hz, 1 H), 3.98 (dd, *J* = 12.8 Hz, *J* = 8.8 Hz, 1 H), 7.13-7.41 (m, 5 H). ^{13}C NMR ($CDCl_3$): δ = 23.2, 29.3, 29.5, 35.5, 44.6, 48.6, 52.4, 75.5, 79.8, 126.1, 126.3, 128.4, 143.4, 159.8.