

Diastereomer-differentiating photoisomerization of 5-(cyclopent-2-en-1-yl)-2,5-dihydro-1*H*-pyrrol-2-ones

Matthias N. Wrobel and Paul Margaretha*

Institut für Organische Chemie, Universität Hamburg, D-20146 Hamburg, Germany

The diastereomeric *l*- and *u*-dihydropyrroles **1** and **2** photoisomerize to azatetracyclodecanones **3** and **4**, respectively.

According to the reactant-based Izumi–Tai classification,¹ reactions wherein a *l*(ike) and an *u*(n)like diastereomer exhibit differing behaviour are termed ‘diastereomer differentiating’. Here we report the first example of a photochemical reaction where two diastereomeric hexa-1,5-dienes undergo photoisomerization to a crossed and a straight cycloadduct,² respectively. The 1:1 diastereomeric mixture of *tert*-butyl 5-(cyclopent-2-en-1-yl)-2-oxo-2,5-dihydro-1*H*-pyrrole-1-carboxylates **1** and **2** was available in 36% yield by alkylation of *tert*-butyl 2-*tert*-butyldimethylsilyloxy-1*H*-pyrrole-1-carboxylate³ with 3-bromocyclopentene. Separation was achieved by chromatography (SiO₂, Et₂O–hexane 1:1) affording the *u*-diastereomer **1**, mp 86 °C, whose structure was confirmed by X-ray analysis, and the *l*-diastereomer **2**, mp 104 °C. Both (CD₃)₂CO-sensitized⁴ (300 nm) or direct (254 nm) irradiation of **1** afford the Boc-protected 5-azatetracyclo[4.4.0^{2.8}.0^{3.7}]dec-4-one **3** (mp 94 °C) in nearly quantitative yield. In contrast,

sensitized irradiation of **2** affords the Boc-protected 4-azatetracyclodecan-3-one **4** (oil) selectively (9:1) in 75% yield, but on direct irradiation a 1:1 mixture of **3** and **4** is formed. In both sets of experiments the conversion of **2** to product(s) proceeds slower than that of **1**.

The fact that in the sensitized runs both diastereomers undergo regioselective intramolecular [2 + 2]cycloaddition but on direct irradiation only **1**, and not **2**, exhibit this behaviour can be explained in terms of differential ratios of efficiencies of cycloadduct formation vs. cleavage to a radical pair for singlet and triplet excited states of **1** and **2**, respectively. The results indicate that only for singlet excited **2** does this racemization, which causes cleavage, become competitive, most probably reflecting the higher activation energy barrier in the formation of a bicyclo[2.2.0]hexane unit, as in **4**, compared to the less strained⁵ bicyclo[2.1.1]hexane moiety of **3**. This differential behaviour is expected to be typical for all compounds containing a 3-(cyclopent-2-en-1-yl)cyclopentene framework.

The new compounds **1–4** have been fully characterized and have spectroscopic properties compatible with the structures assigned.

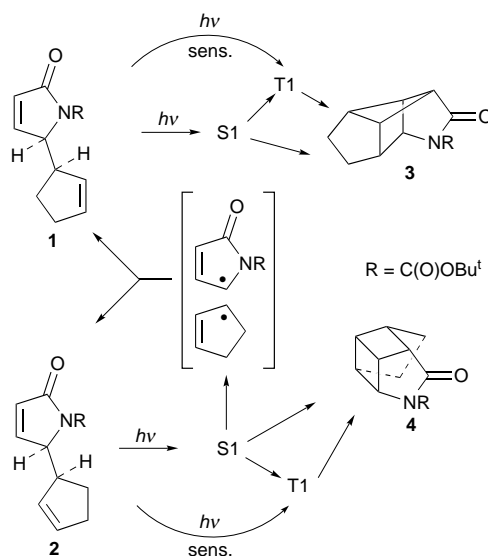
We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for support.

Notes and References

* E-mail: margpaul@chemie.uni.hamburg.de

- 1 Y. Izumi and A. Tai, *Stereo-Differentiating Reactions*, Academic Press, New York, 1977; G. Helmchen, *Nomenclature and Vocabulary of Organic Stereochemistry*, in *Houben–Weyl, Methods of Organic Chemistry*, Thieme, Stuttgart, 1995, vol. E 21a, p. 1.
- 2 A. R. Matlin, C. F. George, S. Wolff and W. C. Agosta, *J. Am. Chem. Soc.*, 1986, **108**, 3385; S. A. Fleming, C. L. Bradford and J. J. Gao, *Regioselective and Stereoselective [2 + 2] Photocycloadditions*, in *Organic Photochemistry*, ed. V. Ramamurthy and K. S. Schanze, Marcel Dekker, New York, 1997, p. 187.
- 3 F. Zanardi, L. Battistini, G. Rassu, M. Cornia and G. Casiraghi, *J. Chem. Soc., Perkin Trans. 1*, 1995, 2471.
- 4 In (hexaprotio)acetone H-abstraction products from the solvent are formed as by-products, cf. M. N. Wrobel and P. Margaretha, *J. Photochem. Photobiol., A*, 1997, **105**, 35.
- 5 A. Greenberg and J. Liebman, *Strained Organic Molecules*, Academic Press, New York, 1978, p. 72.

Received in Liverpool, UK, 19th November 1997; 7/08365C



Scheme 1