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LETTERS

Diastereoselective Photocycloaddition of an Axial Chiral Enamide

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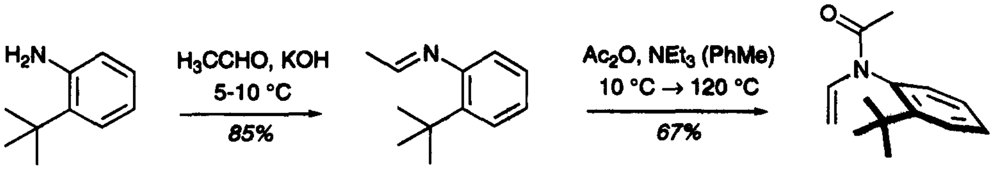
Abstract: The axial chiral enamide **3** was prepared from 2-*t*-butylaniline in two steps (58% overall yield). Its photocycloaddition to benzaldehyde yielded the oxetane **4a** as the major product (62% *de*), the structure of which was elucidated by single X-ray crystallography.

Keywords: Asymmetric induction; Cycloadditions; Photochemistry; Atropisomerism.

For a long time the phenomenon of axial chirality was essentially studied on allenes, alkylidenecycloalkanes, spiranes and atropisomeric biaryls [1]. Recently, non-biaryl-atropisomers have attracted considerably scientific interest [2]. In particular, 2-*t*-butylanilides [3-6] and *N,N*-dialkylsubstituted arenecarboxamides [7] have been investigated and it was shown that diastereoselective, so-called atroposelective [3] reactions are possible due to the presence of the chiral axis. Mostly, thermal atroposelective reactions have so far been performed. Photochemical reactions of this type have received little attention [2]. We now report on the Paternò-Büchi reaction of the atropisomeric enamide **3** with benzaldehyde.



1 **2** **3**

The racemic enamide **3** was prepared from 2-*t*-butylaniline (**1**) in two steps, i.e. by formation of imine **2** and subsequent *N*-acylation in the presence of NEt_3. The photocycloaddition to benzaldehyde was conducted in acetonitrile as the solvent [8,9] and yielded a mixture of four diastereoisomers which were not fully separable. The two *cis*-isomers **4a** and **4b** could be isolated in pure form and the relative configuration within the oxetane ring (C-2/C-3) was proven by ^{1}H-NOE experiments. As expected from previous results [8] the simple diastereoselectivity of the reaction was good and only minor amounts of the two *trans*-oxetanes were detected.

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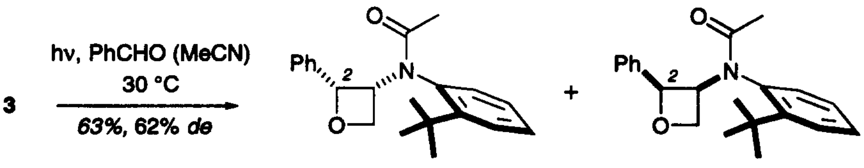

4a **4b**

The relative configuration of the major product **4a** was established by X-ray crystallography [10]. The diastereomeric excess (**4a** – **4b**/**4a** + **4b**) was obtained from ^{1}H-NMR spectra of the crude reaction mixture and amounted to 62% *de*. The products **4a** and **4b** were configurationally stable at room temperature. There was no significant interconversion of the two diastereoisomers. Current work in our group is dedicated to the preparation of enantiomerically pure compounds related to **3** and to their configurational stability.

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References and Notes

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

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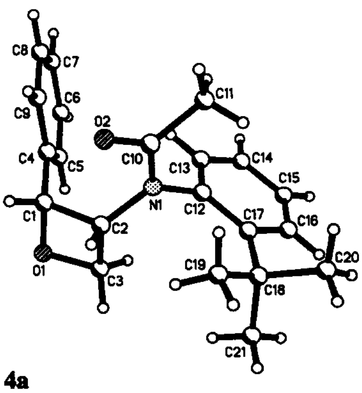
[9] Experimental: The photocycloaddition reaction was carried out on a 1.5 mmol scale as previously described [8]. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel (pentane/*t*-butyl methyl ether = 80/20). The diastereomeric oxetanes were not fully separable. A total yield of 308 mg (63%) was obtained. A fraction containing compound **4a** in pure form could be collected and it yielded 171 mg (35%) of oxetane **4a** as a white solid.
^{1}H NMR ($CDCl_3$): $\delta = 1.24$ (s, 9 H), 1.56 (s, 3 H), 4.13 (dd, $J = 8.7$ Hz, $J = 6.5$ Hz, 1 H), 4.63 (dd, $J = 8.6$ Hz, $J = 6.5$ Hz, 1 H), 5.34-5.39 (m, 1 H), 5.75 (virt q, $J \cong 8.0$ Hz, 1 H), 6.10 (d, $J = 7.5$ Hz, 1 H), 6.81-6.90 (m, 1 H), 7.16-7.25 (m, 1 H), 7.31-7.51 (m, 6 H).
^{13}C NMR ($CDCl_3$): $\delta = 23.2$, 32.1, 35.7, 55.3, 71.4, 87.6, 126.3, 126.7, 127.7, 128.1, 128.6, 129.5, 132.8, 136.3, 138.2, 147.1, 171.0.

[10] A molecule of compound **4a** 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.



4a