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The Photoaddition of Enaminoketonatoboron Difluorides with trans-Stilbene

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The photochemical reactions of enaminoketonatoboron difluorides **1** with *trans*-stilbene gives cyclobutanes **2** and azetidines **3** in a regio- and stereo-specific manner.

The photochemical cycloaddition of 1,3-diketones (from their enols) with olefins has been generally known as the de Mayo reaction.¹ These photoadducts are versatile intermediates that can be useful in natural products synthesis.^{2–6} However, the photoreaction of a corresponding carbonyl compound containing an α -enamine group has not been investigated; in such a case the expected photoadducts may serve as potential intermediates leading to nitrogen-atom containing compounds in a variety of ways.

Irradiation of the enaminoketones with trans-stilbene through a Pyrex filter in acetonitrile did not give any photoadducts. Recently, one of us demonstrated that the reactivity of 1,3-diketones toward olefins is enhanced by complex formation with boron trifluoride.7 Therefore, we prepared enaminoketonatoboron difluorides 1a-f from reaction with boron trifluoride8 and confirmed that the BF2 complexes 1a-f have lower reduction potentials than the parent enaminoketones in the same manner as the 1,3diketones. The photoreactions of the BF_2 complexes **1a-f** with trans-stilbene were examined and the results obtained are listed in Table 1. While N-methyl compounds 1a-c yielded cyclobutane 2a-c and azetidine derivatives 3a-c, N-phenyl compounds 1e, f afforded only 1,5-diketones 4e, f in analogy to the case of the 1,3-diketones.⁷ The formation of the azetidines is very interesting, since [2 + 2] photocycloadditions of olefins to carbon-nitrogen double bonds have been encountered less frequently in comparison to the formation of oxetanes.

 $P^{h} \xrightarrow{R^{2}}_{H} \xrightarrow{R^{3}}_{H} + P^{h} \xrightarrow{Ph}_{Ph}$ $1 \xrightarrow{h \vee 0 \circ C / MeCN, 24 h}_{H} \xrightarrow{Ph}_{H} \xrightarrow{Ph}_{H}$

Table 1 Photoreaction of 1 with trans-stilbenea

	Sub atitus and a			Products yield(%)			Recovered
Substrate	R ¹	R ²	R ³	2	3	4	yield(%) 1
1a 1b 1c 1d 1e	Me Ph Ph Me Ph	Me Me Ph Me Me	Me Me Me Ph Ph	12.0 39.0 74.0	13.5 31.5 8.2 	 52.0	54.7 — 93.3 46.3
lf	Ph	Ph	Ph		—	35.4	61.4

^{*a*} Solutions of 1 (0.5 mmol dm⁻³) and *trans*-stilbene (5.0 mmol dm⁻³) in acetonitrile (25 ml) were irradiated with a high-pressure mercury lamp through a Pyrex filter for 24 h.

The structures of the cyclobutanes 2 and the azetidines 3 were determined on the basis of spectral data. Typically, the mass spectrum of 2b showed that the molecular ion peak (M+ 403) indicated the addition of stilbene to 1b. Its ¹H NMR spectra showed the signals due to three methine groups (δ 4.07, 4.33 and 5.11) characteristic of cyclobutane formation. A ¹³C signal for the imine carbon atom was observed at δ 183.8. The structure was confirmed by alkaline hydrolysis to give 1,2,3-triphenylhexan-1,5-dione (46%) 4b, by a retroaldol ring cleavage, and 3,4,5-triphenylcyclohexen-2-one (42%) which was produced by a subsequent aldol cyclizationdehydration. The stereochemistry of 2b was mainly determined by the NOESY (nuclear Overhauser effect spectroscopy) experiments. A cross peak appeared between H2 and H3, but no NOE was observed between H3 and H4. That is, H2-H3 have a cis-orientation and H3-H4 a trans-orientation. The determination of the structure of the azetidine 3 was considered in more detail. On a COLOC (correlation by long-range coupling) spectrum of 3b, for example, a cross peak appeared between the N-methyl proton (δ 2.52) and the ¹³C at C4 of the ring (δ 66.5), but no cross peak between the N-methyl proton and the ¹³C of the olefin carbon atoms (δ 151.2) was observed. These observations indicated that 3b should have an azetidine structure, and not an oxetane. The



NOESY spectra of **3b** showed that H3–H4 is a *trans*-orientation and H4–N–Me is also a *trans*-orientation.

From similar photocycloadditions of N-phenyl compounds **1e**, **f**, the ring-cleaved products by hydrolysis during work-up, 1,5-diketones **4e**, **f**, were obtained instead of cyclobutane derivatives. The increased susceptibility of the N-phenyl derivatives of the initial photoproducts **2** to hydrolysis may be associated with reduced strength of the B–N coordinate bond.

Furthermore, the present photoaddition has some interesting features in the following respects. (i) The yields of the photoproducts are governed by the reduction potentials.[†] (ii) Under the present conditions, the photoreaction of **1b** with *cis*-stilbene gives the same cyclobutane **2b** and azetidine **3b** in lower yields than those of *trans*-stilbene. (iii) The R¹/C4–Ph of the cyclobutanes **2** and the R³/C4–Ph of the azetidines **3** have a sterically unfavoured *cis*-configuration. Finally, although **1** should have an equilibrium between **1A** and **1B**, only **1B** is the photoreactive species to give 2 and 3 (Scheme 2). The steric configurations and the reactivity indicate that this photoaddition may proceed *via* a common singlet exciplex intermediate formation. The exciplex geometry is a normal sandwich type,⁹ in which there should exist the optimum overlap of a phenyl group of *trans*-stilbene and \mathbb{R}^1 (Ph for 1b, c) of 1.

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[†] Reduction potential of each compound: **1a**; -2.42, **1b**; -2.00, **1c**; -1.81, **1d**; -2.16, **1e**; -1.82, **1f**; -1.52 V. (MeCN, Et₄NClO₄, glassy carbon cathode, ref. electrode Ag/AgCl, 25 °C).