Photoisomerization of imidazo[1,2-*a*]pyridines

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UV-illumination of (*Z*)-ketones 1 in toluene has been observed affording their mixtures with minor (*E*)-ketones 2 and major imines 3.

Photochemical transformations of various ketones cover an important area of organic photochemistry. We wish to report here a new type of photoizomerization of heterocyclic dienones involving furan ring formation.

Toluene solutions of (*Z*)-1,3-diphenyl-3-(2-phenylimidazo[1,2-*a*]pyridin-3-yl)prop-2-en-1-ones **1** readily accessible from substituted quaternary pyridinium salts,[1] have been irradiated with a medium pressure UV lamp under nitrogen at 22 °C for 8 h. In addition to small quantities of starting (*Z*)-ketones **1**, two isomeric products were formed, namely, minor (*E*)-1,3-diphenyl-3-(2-phenylimidazo[1,2-*a*]pyridin-3-yl)prop-2-en-1-ones **2** and major [(3,5-diphenylfuran-2-yl)phenylmethylene]pyridin-2-ylamines **3** (Table 1).[†]

(*E*)-Ketones **2** exhibit similar spectral patterns[‡] to the corresponding (*Z*)-isomers[2–4] including IR C=O stretching modes (ν 1652–1659 cm^{-1}) and the carbonyl ^{13}C NMR chemical shifts (δ 192.78–192.90). In addition, the three-side-chain olefinic ^{1}H NMR signals are more easily detected as separate singlets (δ 6.90–6.97). On the other hand, the spectral properties of imines **3** differ significantly from those of **1** and **2**. For example, the ^{13}C NMR spectra of imines **3** exhibit C=N signals which are somewhat down-field shifted (δ 161.61–163.99) and the furan ring proton singlets are easily recognized in the ^{1}H NMR spectra (δ 6.60–6.72). In all cases the signals are accompanied by satelites indicating *syn* and *anti* stereoisomerism of **3**. In addition, the absence of stretching C=O modes in the IR spectra and the occurence of an important ion **4** in the FAB mass spectrum of the photoisomer of **1** (R^1 = R^2 = R^3 = R^4 = H) are also in agreement with the structure **3**.[§]

The photoisomerizations (*Z*)-**1**→(*E*)-**2** can be considered as behaviour typical of α,β-unsaturated ketones,[5] but the formation of imines **3** has, to our knowledge, no direct analogy in organic photochemistry. Because of the lack of observable heavy atom effects in the photoisomerization of iodine derivative **1** (R^1 = R^3 = R^4 = H, R^2 = I, Table 1), all **1**→**3** transformations investigated might proceed *via* intermediate **5**-like triplet biradicals which then undergo scission of the C–N bond in a Grob fragmentation-type process. Quantum chemical calculations by the PM3 method[7,8] show that the lowest energy *n*-π* triplet lies only 0.067 eV above the corresponding π-π* triplet state of **1** (R^1 = R^2 = R^3 = R^4 = H) and the mechanistic assumptions seem to be justified.

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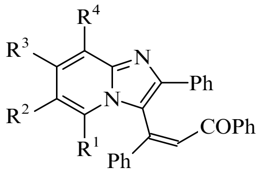
Table 1 Products after UV-illumination of (*Z*)-ketones **1**.

R^1	R^2	R^3	R^4	(*E*)-Ketone **2** (%)	Imine **3** (%)[a]
H	H	H	H	12	65
Me	H	H	H	< 1	71
H	Me	H	H	13	63
H	H	Me	H	< 1	75
H	H	H	Me	< 1	67
Ph	H	H	H	< 1	85
H	I	H	H	10	60

[a] Mixtures of *syn* and *anti* stereoisomers.



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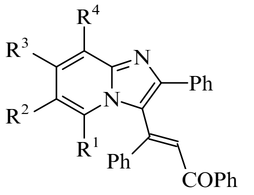

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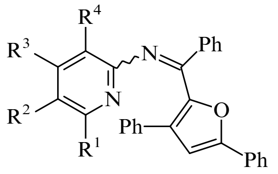

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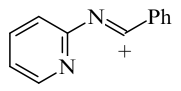

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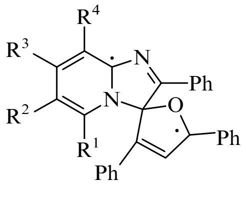

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[†] Mixtures of photoisomers were separated from impurities by chromatography on a silica gel column. In some cases (R^1 = R^3 = R^4 = H, R^2 = H, Me, I) individual substances were isolated. All samples gave satisfactory elemental analyses.

[‡] All NMR spectra (solutions in CDCl$_3$) were recorded on a GEMINI spectrometer at 300 MHz for protons and at 75 MHz for ^{13}carbon atoms. IR spectra (solutions in CHCl$_3$ and KBr-technique) were measured on a Nicolet 740 FTIR spectrometer.

[§] An iodo derivative monocrystal was found to consist of *syn*-molecules **3** (R^1 = R^3 = R^4 = H, R^2 = I) based on X-ray diffraction.[6] The mass spectrum of **3** (R^1 = R^2 = R^3 = R^4 = H) was recorded on a double-focusing Finnigan MAT 90 instrument of BE geometry. The standard saddle field FAB gun was operated at 2 mA current and 6 kV energy, using Xe as a bombarding gas (1×10^{-5} mBar). 3-Nitrobenzyl alcohol was used as a matrix. For high-resolution measurements a rotatable FAB target was used with sample deposited on one side and Ultramark 1600F as a standard on the other side. Measured/calculated: *m*/*z* 181.0759/181.0766 for **4** (relative intesity 50%). Independent syntheses of some of the compounds **3** are in progress.

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