Notiz / Note

Photoenolization of 4-Naphthoyl[2.2]paracyclophanes

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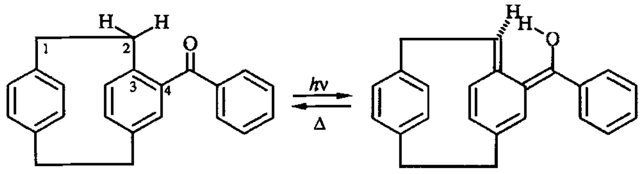
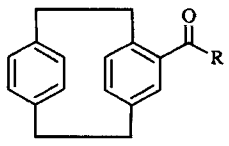
When ethanolic solutions of 4-(1-naphthoyl)[2.2]paracyclophane (3) and 4-(2-naphthoyl)[2.2]paracyclophane (4) are subjected to UV irradiation at low temperature, 1,5-hydrogen migration of the 2-H bridge proton to the carbonyl group takes place, leading to the enol of type **2**. In the context of mechanistic considerations the triplet spectroscopic properties of **3** and **4** are discussed.

We previously reported on the photochemistry of 4-benzoyl[2.2]paracyclophane (**1**) in hydroxylic solvents, e.g. ethanol, at low temperature[1,2]. Under these conditions photoenolization of **1** leading to the enol **2** is the main reaction pathway. A probable characteristic of enols of type **2**[3] is that they exhibit a broad absorption band near 400 nm (**2**: 430 nm, ethanol, 88 K). Due to the high rate at which reketonization of **2** takes place on warming, isolation of the enol in substance proved impossible. However, the structure of **2** was determined indirectly by photochemically induced H/D exchange and subsequent ^{1}H-NMR and mass spectroscopic study of the labelled products. To test whether photoenolization is a general reaction type for 4-aroyl[2.2]paracyclophanes we have now extended our studies to 4-(1-naphthoyl)[2.2]paracyclophane (**3**) and 4-(2-naphthoyl)[2.2]paralcyclophane (**4**).



1 **2**



3: R = 1-naphthyl

4: R = 2-naphthyl

Results and Discussion

On UV irradiation of ethanolic solutions of **3** and **4** at 103 K a color change to yellow is observed, and the characteristic (thermally reversible) enol band appears in the low-temperature absorption spectrum. The band of the **3** enol lies at shorter wavelengths (424 nm) than that of the **4** enol (440 nm). This is probably due to reduced conjugation between the naphthyl and the enol group as a result of stronger steric hindrance and hence a larger torsion angle of the naphthyl group in the **3** enol.

Photochemical H/D exchange experiments were performed with **3** and **4** in C_2H_5OD (in the presence of catalytic amounts of sodium ethanolate) at ca. 190 K. While photochemically induced H/D exchange occured with both compounds to a significant degree, no thermal H/D exchange (absence of light, reflux temperature, 2 h) was observed. After an irradiation period of 15 min (450-W mercury lamp), the recovered ketone **3** contained 46% of mono- and 13% of dideuterated material, the degree of deuteration being calculated from the reduced MS signal intensities. The corresponding values for **4** are: 21% of mono- and 6% of dideuteration. The sites of deuteration were determined by ^{1}H-NMR spectroscopy making use of the fact that the signal of the *syn*-2 proton of 4-acyl[2.2]paracyclophanes is shifted downfield while that of the *anti*-2 proton is shifted to higher field as compared with the signals of all other bridge protons[1]. For the ketone recovered from the photolyzed solution of **4** it was found that deuteration had occurred to the same extent in the *syn*- and *anti*-2 position while in ketone **3** a ratio of 2:1 of the *syn*- and *anti*-substituted products was obtained. It is very likely that the mechanism[1] proposed previously for the photochemically induced H/D exchange of **1** also applies to **3** and **4**.

All available mechanistic studies[3,4,5] of the photoenolization of *ortho*-alkylated acetophenones, benzophenones, and related derivatives refer to compounds where the lowest electronically excited states are of the n,π* type. In most cases photoenolization occurs exclusively from the ^{3}n,π* state, but in a few cases both the singlet and the triplet n,π* states are photochemically reactive giving different enol stereoisomers. Here the photochemical reaction competes with the very fast intersystem crossing between the n,π* states. In contrast, the lowest electronically excited state of the 4-acyl[2.2]paracyclophanes is of the π,π* type (^{3}π,π*). Photophysical data (triplet energy T_1, phosphorescence lifetime τ_p, and phosphorescence quantum yield Y_p) of **1**, **3**, and **4** are listed in Table 1 (ethanol, 77 K) together with the data of some reference compounds. The cyclophanes are nonfluorescent. The most likely explanation is that n,π* states (^{3}n,π* and/or ^{1}n,π*) lie between the lowest singlet

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Table 1. Photophysical data (triplet energy, T_1; phosphorescence lifetime, τ_p; phosphorescence quantum yield, Y_p) in ethanol at 77 K

Compound	T_1 (cm^{-1})	τ_p (sec)	Y_p
4-Methyl [2.2]paracyclophane	21050	2.4	0.17
1	19880	0.13	0.27
3	20080	0.63	0.62
1-Naphthyl phenyl ketone	20100[a]	0.74[a]	0.53
4	20660	1.24	0.41
2-Naphthyl phenyl ketone	20700[b]	1.25[b]	0.38

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and triplet excited π,π* state, thus facilitating effective intersystem crossing to the lowest triplet state[6].

In Figure 1 the phosphorescence spectra of **3** and 1-naphthyl phenyl ketone as well as **4** and 2-naphthyl phenyl ketone are depicted. The pairwise close similarity of the phosphorescence spectra, lifetime and quantum yields (Table 1) clearly indicates that phosphorescence of the cyclophanes occurs from the same chromophor as in the corresponding naphthyl phenyl ketones. Moreover, it is well established that the naphthyl phenyl ketones behave as bichromophoric systems and that their phosphorescence stems from the lowest triplet state of the naphthyl units which becomes populated by intramolecular triplet-triplet energy transfer originating in the ^{3}n,π* state of the C=O group[7].

Obviously, the same has to be assumed for **3** and **4**. From the potential energy surface of the naphthyl units in **3** and **4** photoenolization is not possible. Hence, the photochemical reaction of **3** and **4** occurs from a higher lying electronically excited state. However, the nature of this state is not yet known. Due to nonradiative deactivation processes the lifetime of this state is expected to be very short. Thus, photoenolization, competing with the nonradiative quenching of the photochemically reactive state, must occur with a comparatively high rate constant.

Experimental

^{1}H NMR: Bruker AC 400, TMS as internal standard. – MS: Finnigan MAT 8400 (70 eV). – IR (KBr): Perkin-Elmer 1420. – Low-temperature UV absorption spectra: Perkin Elmer 556 with low-temperature attachment. – Phosphorescence spectra and lifetimes: Aminco-Keirs spectrophosphorimeter equipped with a Tektronix 5403 oscillograph. – Phosphorescence quantum yields: Perkin-Elmer MPF 44 E for the measurement of quantum-corrected spectra; determination of quantum yields as described in ref.[8] (phosphorescence standard: chrysene, phosphorescence quantum yield 0.07[9]).

Ketones **3**[10] and **4**[10] were synthesized according to known procedures.

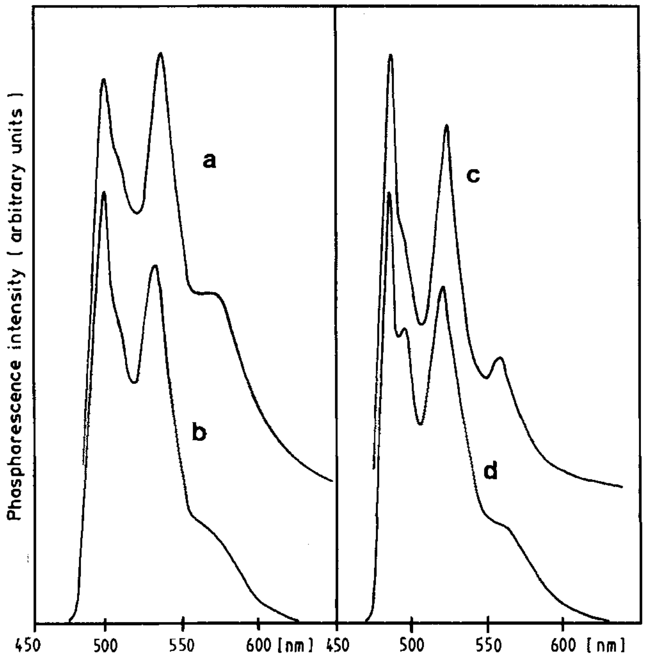

Figure 1. Phosphorescence spectra (ethanol, 77 K) of **3** (curve a), **4** (curve c), 1-naphthyl phenyl ketone (curve b), and 2-naphthyl phenyl ketone (curve d)

Photoenolization Experiments with Ketones **3** *and* **4**: In a quartz ampoule 25 mg of the ketone was dissolved in 10 ml of [D$_1$]ethanol, and a catalytic amount of sodium was added to the solution. It was degassed by three pump-and-freeze cycles and then irradiated for 15 min at −70 to −90°C. After warming of the photolyzed solution to room temp., the ketone was recovered and purified by TLC [silicagel 60 (70–130 mesh)/CH$_2$Cl$_2$]. Yield of recovered ketone: 85–90%.

Thermal H/D exchange experiments using solutions as described above were performed in the absence of light at reflux temp., reaction time: 2 h.

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