Photochemical and Photophysical Properties of 4-Acyl[2.2]paracyclophanes

Henning Hopf and Thomas Laue
Institute of Organic Chemistry of the University of Braunschweig, FRG

Maximilian Zander
Rüggerswerke AG, Castrop-Rauxel, FRG

Dedicated to Professor Kurt Schaffner on the occasion of his 60th birthday

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Photochemical and photophysical properties of 4-benzoyl[2.2]paracyclophane (3) and 4-acetyl[2.2]paracyclophane (5) have been studied. In contrast to benzophenone and acetophenone, respectively, the lowest triplet state of 3 and 5 is of the π, π*-type. 3 is photochemically reactive. Photoenolization (in solution at lower temperature) is the main reaction pathway while bond fission of an exocyclic C–C bond of the formed photoenol leading to an alkylated open-chain benzophenone derivative takes place to a minor degree. Photoenolization of 3 is the first example of this type of photochemical reaction observed with a cyclophane compound, and at the same time is a novel example of the violation of Bredt’s rule. Under certain experimental conditions 3 and 5 may be usable as chiral triplet sensitizers in photochemical reactions.

The photoenolization of ortho-alkylated benzophenones 1 leading to ortho-quinodimethane derivatives 2 was discovered in 1961 [1] and has since then been thoroughly studied by many authors [2, 3]. It was only recently, however, that a first example of this type of photochemical reaction was observed with a bridged ketone of the [2,2]paracyclophane series [4]. When solutions of 4-benzoyl[2.2]paracyclophane (3) were irradiated at lower temperature, formation of the photoenol 4 occurred. The structure of 4 was determined indirectly by H/D exchange and subsequent nmr study of the labelled photoproducts. Photoenolization of 3 is remarkable in that it leads to an anti-Bredt compound.

In this paper we wish to report on additional results regarding the photochemistry and photophysics of 3 and of the structurally related 4-acetyl[2.2]paracyclophane (5).

Results and Discussion

The onset of the uv/vis absorption spectrum of 3 in ethanol lies at 400 nm and the first absorption maximum is recorded at 290 nm. When the colourless solution is irradiated at 88 K with unfiltered light of a mercury lamp or with 320 nm radiation the solution turns yellow and a new band appears in the absorption spectrum at 430 nm. The uv/vis absorption spectrum (ethanol, 88 K) of the irradiated solution is given in Figure 1. In our previous paper [4] we have shown that the 430 nm band stems from the photoenol 4. On warming the yellow solution to room temperature the thermal back reaction 4 → 3 takes place, and the 430 nm band disappears. These processes are completely reversible and may be repeatedly performed with the same solution. No indication was obtained that enolization 3 → 4 can also occur as a thermal reaction. In the presence of a two-fold molar excess of...
sodium alcoholate the spectrum of 3 does not change in the dark and correspondingly no H/D exchange is observed, not even under conditions which are particularly suited for H/D exchange reactions (DMSO/CD$_3$OD/NaOCD$_3$, 60 °C) [3, 5].

Radiation experiments in various solvents at low temperature (88 K) and subsequent uv/vis spectroscopic examination indicate that the extent to which photoenolization $3 \rightarrow 4$ occurs depends strongly on the solvent used. 4 is rapidly formed in high concentrations in ethanol, ethanol/methanol mixtures and 2-methyl-tetrahydrofuran, respectively, while only a weak shoulder at $\sim 430$ nm appears in the spectrum of the irradiated solution when a methylcyclohexane/n-pentane mixture (4:1, vol/vol) is employed. No unambiguous indication of 4-formation was obtained in CCl$_4$ and CHCl$_3$. In our previous paper [4] the use of 3 as a chiral triplet sensitizer in photochemical reactions has been proposed. Clearly, this possible application of 3 is restricted to experimental conditions under which competing photochemical reactions of 3 are negligible.

Phosphorescence measurements show that the enol 4 is not unlimitedly stable under photochemical conditions. In Fig. 2 the decrease in intensity of the phosphorescence band at 503 nm of the starting ketone 3 during irradiation is shown as a function of irradiation time for a typical experiment (ethanol, 77 K, 2.5 · $10^{-4}$ M solution, radiation source: xenon lamp, radiation wavelength: 320 nm). After an irradiation time of about 30 min a new spectrum becomes recognizable, whose intensity increases steadily with time. In Fig. 3 curve a represents the phosphorescence spectrum of the starting ketone 3 (before irradiation) and curve b the phosphorescence spectrum of the solution after 2 h of irradiation. The new phosphorescence
with maxima at 404, 430 and 465 nm and a phosphorescence lifetime of 3.5 ms (phosphorescence lifetime of 3: 128 ms) stays unchanged when the solution is warmed up to room temperature, again cooled down to 77 K and excited to phosphoresce. It can be excluded that this effect stems from the photoenol 4 because no phosphorescence is observed when the solution is excited with 430 nm light, i.e. in the strong absorption band of 4 (vide supra). As has been confirmed by additional experiments, 4 is virtually non-phosphorescent. It is assumed, however, that the phosphorescence observed after relatively long irradiation time stems from a secondary reaction product which is formed photochemically and/or thermally from 4. Both the band positions and lifetime of the phosphorescence of this secondary reaction product closely resemble that of benzophenone and mono-methyl benzophenones. While benzophenone could be excluded by spectra comparison the reaction product most likely is an alkylated open-chain benzophenone derivative formed by bond fission of an exocyclic C–C bond of 4 followed by stabilization reactions like hydrogen migration. Even after extended irradiation (2 h, irradiation wavelength: 320 nm) the intensity of the phosphorescence of 3 did not change and no benzophenone-like phosphorescence was observed when methylcyclohexane/n-pentane mixture (77 K) was used as the solvent.

It is well established that photoenolization of ortho-alkylated benzophenones and acetophenones proceed from the $3\pi, \pi^*$ state [2, 3, 6], which is the lowest (observable) excited electronic state in these systems. However, as shown in our previous paper [4] the lowest excited state of 3 is a $\pi, \pi^*$ triplet. It can be assumed that the $3\pi, \pi^*$ state is virtually localized at the C=O group (and thus has a similar energy as the $3\pi, \pi^*$ state of benzophenone) while all $\pi, \pi^*$ states of the (internal) benzene ring of the benzophenone moiety in 3 are shifted to lower energies as a result of ring bending and transannular interaction [7]. Additional work is necessary to clarify which of the excitation states of 3 is the reactive one in photoenolization.

Photophysical data (triplet energy, phosphorescence lifetime, phosphorescence quantum yield, rate constants of phosphorescence and $T_1 \rightarrow S_0$ intersystem crossing) of 4-benzoyl[2.2]paracyclophane (3), 4-acetyl[2.2]paracyclophane (5) and, for comparison, of benzophenone and acetophenone are listed in Table 1. Both 3 and 5 do not show fluorescence (ethanol, 77 K).

Table 1. Photophysical data (triplet energy, $T_1$; phosphorescence lifetime, $\tau_p$; phosphorescence quantum yield, $Y_p$; rate constants of phosphorescence, $k_{PT}$ and $T_1 \rightarrow S_0$ intersystem crossing, $k_{GT}$) Data refer to ethanol or EPA solutions, respectively, at 77 K.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_1$ [cm$^{-1}$]</th>
<th>$\tau_p$ [ms]</th>
<th>$Y_p$</th>
<th>$k_{PT}$ [sec$^{-1}$]</th>
<th>$k_{GT}$ [sec$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-benzoyl[2.2]paracyclophane (3)</td>
<td>19 880</td>
<td>128</td>
<td>0.27</td>
<td>2.1</td>
<td>5.7</td>
</tr>
<tr>
<td>benzophenone</td>
<td>24 090</td>
<td>6</td>
<td>0.75b</td>
<td>125</td>
<td>42</td>
</tr>
<tr>
<td>4-acetyl[2.2]paracyclophane (5)</td>
<td>19 080</td>
<td>85</td>
<td>0.013</td>
<td>0.15</td>
<td>12</td>
</tr>
<tr>
<td>acetophenone</td>
<td>25 640</td>
<td>8</td>
<td>0.63a</td>
<td>79</td>
<td>46</td>
</tr>
</tbody>
</table>

[4] it has to be assumed that the lowest (phosphorescent) triplet state of 5 is of the \( \pi, \pi^* \) type. No unambiguous experimental indication (uv/vis absorption spectra, ethanol, 88 K) has been obtained that 5 photo-enolizes on irradiation.

**Experimental**

**Substances:** 4-benzoyl[2.2]paracyclophane (3) and 4-acetyl[2.2]paracyclophane (5) have been synthesized according to [8] and [11], respectively. Phosphorescence spectra (ethanol, 77 K) did not change with excitation wavelength, and phosphorescence decays were monoexponential.

Ethanol was of Merck UVASOL quality.

**Measurements:** Low-temperature uv/vis absorption spectra were measured using a Perkin-Elmer 556 UV/VIS spectrometer with low-temperature attachment, uncorrected phosphorescence spectra as well as phosphorescence lifetimes with an Aminco-Keirs spectrophosphorimeter equipped with a Tektronix 5403 oscillograph, while quantum-corrected phosphorescence spectra were obtained with a Perkin-Elmer MPF 44 E luminescence spectrometer. Phosphorescence quantum yields and rate constants were obtained as described in [9] (phosphorescence standard: chrysene, phosphorescence quantum yield 0.07 [10]).

Photochemical experiments were performed in quartz cells at low temperature.

**Acknowledgement**

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