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

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

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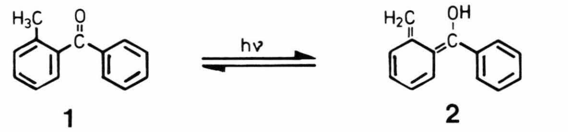
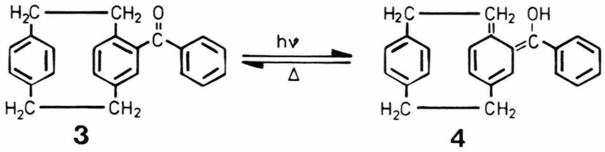
Photochemical and photophysical properties of 4-benzoyl[2.2]paracyclophane (**3**) and 4-acetyl[2.2]paracyclophane (**5**) have been studied. In contrast to benzophenone and acetophenone, respectively, the lowest triplet state of **3** and **5** is of the π, π*-type. **3** is photochemically reactive. 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.

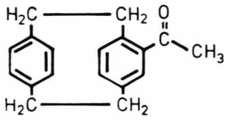
In this paper we wish to report on additional results regarding the photochemistry and photophysics of **3** and of the structurally related 4-acetyl[2.2]paracyclophane (**5**).



1 **2**



3 **4**



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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

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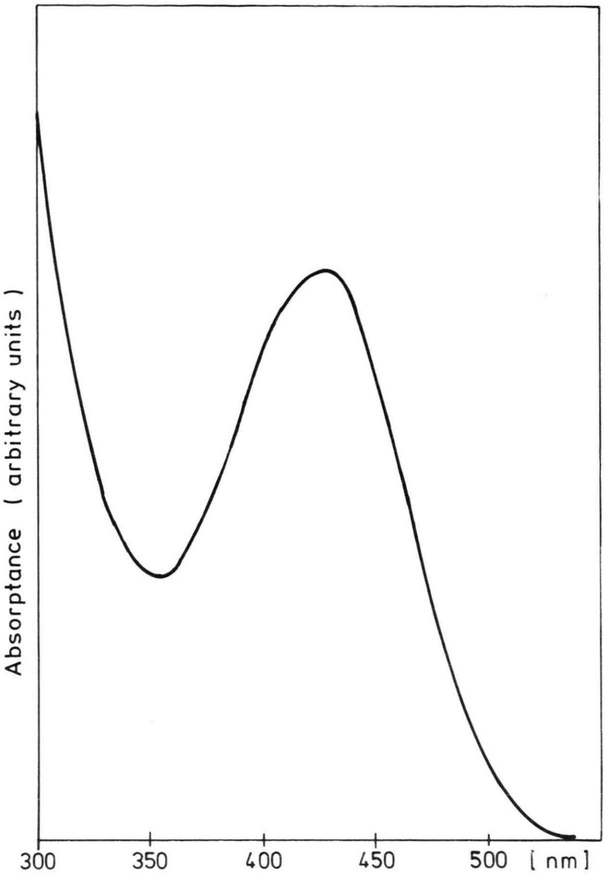

Fig. 1. UV/vis absorption spectrum (ethanol, 88 K) of photoenol **4**.

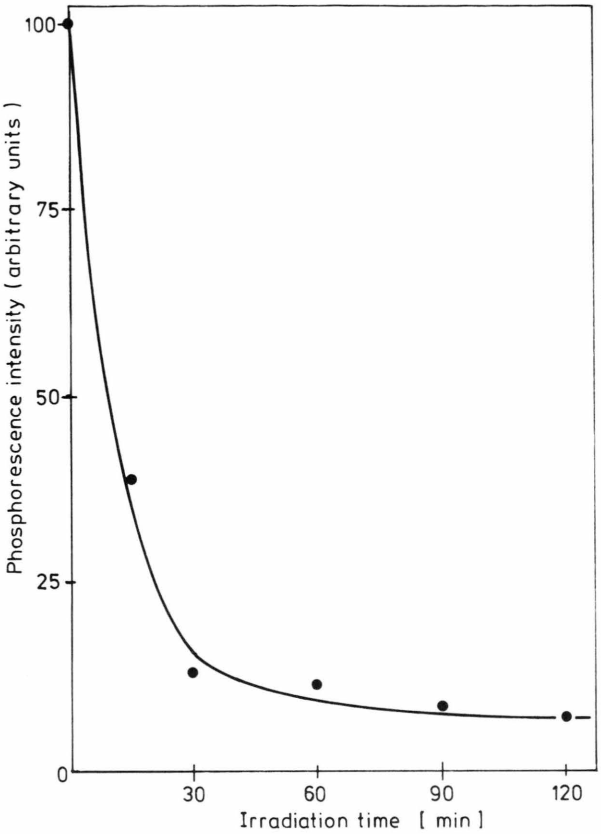

Fig. 2. Phosphorescence intensity (at 503 nm, excitation wavelength: 320 nm, ethanol, 77 K) of ketone **3** as a function of irradiation time. (Concentration of ketone before irradiation: $2.5 \cdot 10^{-4}$ M; radiation source: xenon lamp Canrad Hanovia 901 C 001 (150 W), 320 nm).

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_3OD/$NaOCD_3$, 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 $\mathbf{3} \rightarrow \mathbf{4}$ 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 ≈ 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, $2.5 \cdot 10^{-4}$ 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

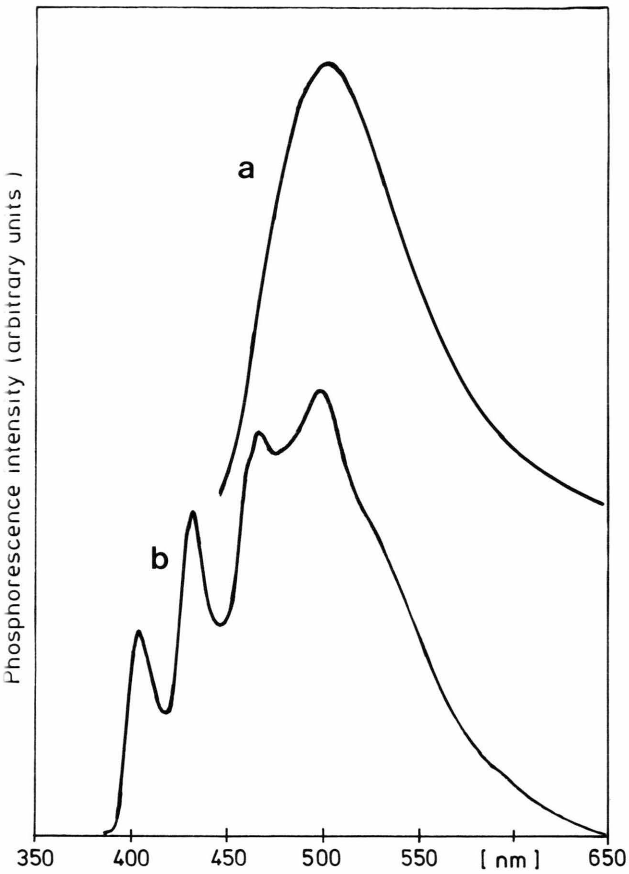

Fig. 3. Phosphorescence spectra (ethanol, 77 K) of ketone **3** (before irradiation) (curve a) and of the irradiated solid solution (curve b) (radiation source: xenon lamp Canrad Hanovia 901 C 001 (150 W), irradiation wavelength: 320 nm; irradiation time: 2 h). Spectra are normalized to equal height at 503 nm.

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 nonphosphorescent. 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 monomethyl 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.

Table 1. Photophysical data (triplet energy, T_1; phosphorescence lifetime, τ_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).

Compound	T_1 [cm^{-1}]	τ_p [ms]	Y_p	k_{PT} [sec^{-1}]	k_{GT} [sec^{-1}]
4-benzoyl[2.2]paracyclophane (**3**)	19880	128	0.27	2.1	5.7
benzophenone	24040	6[a]	0.75[b]	125	42
4-acetyl[2.2]paracyclophane (**5**)	19080	85	0.013	0.15	12
acetophenone	25640	8[a]	0.63[a]	79	46

[a] D. S. McClure, J. Chem. Phys. **17,** 905 (1949).

[b] E. Gilmore, G. Gibson, and D. S. McClure, J. Chem. Phys. **20,** 829 (1952).

It is well established that photoenolization of ortho-alkylated benzophenones and acetophenones proceed from the ^{3}n, π^* 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 π, π^* triplet. It can be assumed that the ^{3}n, π^* state is virtually localized at the C=O group (and thus has a similar energy as the ^{3}n, π^* state of benzophenone) while all π, π^* 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). For the reasons discussed for **3** in our previour paper

[4] it has to be assumed that the lowest (phosphorescent) triplet state of **5** is of the π, π* type. No unambiguous experimental indication (uv/vis absorption spectra, ethanol, 88 K) has been obtained that **5** photoenolizes 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 attachement, 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 perfomed in quartz cells at low temperature.

Acknowledgement

Thanks are due to Mr. Klaus Bullik for his observant experimental assistance.

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