143. The Oxa-di-π-methane Rearrangement of 1-Phenyl-3-acetylcyclopentene: Identification of the Reactive Triplet as the Localized Styrene π,π^*-State

Preliminary Communication

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Dedicated to Professor *V. Prelog* on his 70th anniversary

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Summary. 1-Phenyl-3-acetylcyclopentene¹) (**3**) undergoes triplet-sensitized oxa-di-π-methane rearrangement to a *ca.* 3:1 mixture of *endo-* and *exo*-1-phenyl-5-acetylbicyclo[2.1.0]pentane²) (**4**). The reactive triplet of **3** has been identified as the localized styrene π,π^*-state of $E_T = 59$ kcal/mol by comparison of its phosphorescence at 77 K in a rigid glass with that of 1-phenylcyclopentene, and by sensitization quantum yields at room temperature in liquid solution. These quantum yields are independent of sensitizer energy in the range of 61–74 kcal/mol and reach zero for product formation with a sensitizer of $E_T = 59$ kcal/mol. Although $S_1 \rightarrow T_1$ intersystem crossing is appreciable under phosphorescence conditions ($\Phi_p = 0.05$), direct irradiation of **3** at 20° does not lead to triplet rearrangement, and the typical singlet 1,3-acetyl shift to 3-acetyl-3-phenylcyclopentene³) (**8**) is observed only.

The electronic configuration of the reactive triplet-excited state in the oxa-di-π-methane (ODPM) rearrangement of β,γ-unsaturated ketones⁴) is currently still a matter of debate. *Schuster & Underwood* [4] proposed a rationalization based on spin density distribution of the $^3(n,\pi^*)$-state, whereas a CNDO/S calculation with configuration interaction by *Houk* [5] predicts π,π^* character of the ODPM reactive triplet. In the rearrangement of the cyclopentadiene-tropone [4 + 6] adduct it was argued that either the triplet n,π^* or charge-transfer state is responsible for reaction [6]. On the other hand, α,β-unsaturated δ-dioxo systems with a lowest-lying $^3(\pi,\pi^*)$-state [7] undergo also ODPM-type triplet rearrangements [8]. Furthermore, compounds in which the C=C double bond is part of a 1,1-diphenylethylene [9] or styrene system [10] are known to rearrange as well. *Dauben* [10a] made the particularly interesting although only qualitative observation that the ODPM rearrangement **1** → **2** proceeded with sensitizers possessing triplet energies as low as 56 kcal/mol, *i.e.*, energies which are definitely below the estimated range of the n,π^* triplet level [11a]⁵). Finally, *Engel* [11b] has shown that rearrangement may occur with low-

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¹) IUPAC-Nomenclature for **3**: (3-phenyl-cyclopent-2-enyl)-ethanone or methyl (3-phenyl-cyclopent-2-enyl) ketone.

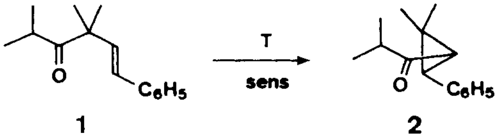
²) IUPAC-Nomenclature for **4**: *endo-* or *exo*-(4-phenyl-bicyclo[2.1.0]pent-5-yl)-ethanone.

³) IUPAC-Nomenclature for **8**: (1-phenyl-cyclopent-2-enyl)-ethanone.

⁴) For reviews of the field see [1]. References to more recent literature, and especially to results with acetylcyclopentenes, are given in [2]; *cf.* also [3].

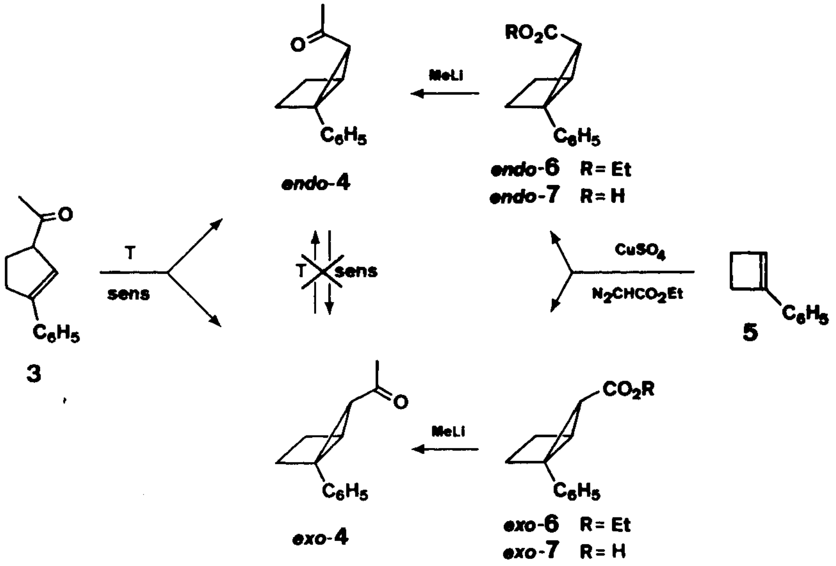
⁵) Compound **1** has been attributed a lowest triplet energy level of 68.8 kcal/mol by phosphorescence [12]. However, the phosphorescences in a rigid glass at 77 K of three other β,γ-unsaturated ketones, which were interpreted in terms of the lowest-lying $^3(\pi,\pi^*)$ states of these compounds [12], have recently been shown [11] to be impurity emission. Similar assignments to other β,γ-unsaturated ketones using the same technique may warrant reconsideration. We have observed phosphorescences reminiscent of those reported [12] from several C(1–3)-methylated 3-acetylcyclopentenes, and they have now also been traced to impurities [13].

energy sensitizers *via* exciplex formation, although with appreciable lower quantum yields than under exothermic energy transfer conditions.



In connection with our photochemical studies of acylcyclopentenes [2] [14] we have now prepared compound **3**[6]). We expected the lowest-lying triplet state of **3** to correspond closely to the relatively low-lying $^3(\pi,\pi^*)$-state of styrene with little perturbation by the carbonyl group. Moreover, twisting around the double bond is limited in the five-membered ring of **3** and its parent styrene, 1-phenylcyclopentene. Radiationless triplet deactivation should therefore be restrained in favor of emission at low temperature, and the lowest triplet energy of the two compounds should approximate the spectroscopic $S_0 \rightarrow T_1$ transition energy measured for styrene by absorption under high pressure of oxygen (61.7 kcal/mol) [15]. These expectations were met by experiment. Both ketone **3** and 1-phenylcyclopentene exhibited in ether/isopentane/ethanol 5:5:2 at 77K phosphorescences ($\Phi_p = 0.05 \pm 5\%$, $\tau_p = 120$ ms, and $\Phi_p = 0.003 \pm 50\%$, $\tau_p = 625$ ms, respectively) which are superimposable in spectral shape and energy (0–0 band at 483 nm = 59 kcal/mol). The excitation spectra were in good agreement with the corresponding absorption spectra.

Triplet sensitization of **3** gave a *ca.* 3:1 mixture of the *endo-* and *exo*-1-phenyl-5-acetylbicyclo[2.1.0]pentanes[2]) (**4**) which were not interconverted under the conditions



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[6]) Satisfactory analytical data have been obtained for all new compounds and will be reported in our full publication in this Journal. Key data are for **3**: IR. (CCl_4) 1718 cm^{-1}; UV. (isooctane) 254 (ε_{max} = 28000), 366 nm (13); NMR. (CCl_4) $\delta \sim 3.6/m$ (H–C(3)), $6.10/d \times t$ (J = 1 and 2 Hz, H–C(2)); for *endo*-**4**: IR. (CCl_4) 1710 cm^{-1}; for *exo*-**4**: IR. (CCl_4) 1705 cm^{-1}; for **8**: IR. (CCl_4) 1712 cm^{-1}; NMR. (C_6D_6) $\delta \sim 5.8/m$ (H–C(1) and H–C(2)).

of their formation. The constitution of the two products was established by synthesis from 1-phenylcyclobutene (**5**). $CuSO_4$-catalysed reaction of ethyl diazoacetate with **5** gave a 2:3 mixture of the *endo* and *exo* esters **6** which were hydrolysed separately with potassium hydroxide in aqueous methanol to the acids **7** and converted to the corresponding methyl ketones **4** with methyl lithium in *ca.* 18% overall yield for each stereoisomer. The full molecular structure was determined by an X-ray diffraction analysis of the acid *exo*-**7** (m.p. 131°) by *Bernardinelli et al.* [16].

The sensitizers used and the quantum yields for consumption of starting material (Φ_{-3}) and product formation (Φ_4) are listed in the Table (runs 2–7). The *endo/exo* product ratio in runs 2–5 was determined by NMR. after each irradiation experiment, *i.e.*, at highest conversion, and it was constant in all cases. The quantum yields remained quite similar with the first four sensitizers and then became zero for product formation with donor energies of *ca.* 59 kcal/mol and lower (runs 6 and 7). This sharp drop in Φ_4 occurs at a point where triplet energies of donor (β-acetonaphthone) and acceptor (**3**) are about equal[7]) and an efficient exothermic transfer is not possible any more. *We conclude from these data that the lowest-lying styrene-type π,π^*-triplet of* **3** *is the excited state responsible for the ODPM rearrangement to* endo- *and* exo-**4**.

Table. *The Rearrangement of* **3** *on Direct Irradiation and Triplet Sensitization: Quantum Yields of Consumption* (Φ_{-3}) *and Product Formation* (Φ_4 *and* Φ_8) [a])

Run	Concentration of Ketone **3**	Sensitizer (E_T, kcal/mol)	Excitation (nm)	Conversion (%)	Quantum Yields Φ_{-3}	Φ_4	Φ_8
1	0.10 M	–	313	12–43	0.26	–	0.085
2	0.10 M	Acetophenone, neat (73.6)	313	9–45	0.085	0.020	–
3	0.10 M	0.10 M Benzophenone (68.5)	366	29–52	0.098	0.035	–
4	0.11 M	0.01 M Thioxanthone (65.5)	366	7–30	0.084	0.035	–
5	0.12 M	0.01 M *Michler*'s Ketone (61.0)	366	17–46	0.083	0.047	–
6	0.12 M	0.43 M β-Acetonaphthone (59.3)	366	2–13	0.03	–	–
7	0.10 M	0.22 M α-Acetonaphthone (56.4)	366	4–11	0.016	–	–

[a]) The quantum yields were determined in benzene solution (except for run 2) at 20° using an electronically integrating actinometer [17]. The product compositions were analysed by gas chromatography with dodecane or tridecane as an internal reference on a $^1/_4'' \times 10'$ steel column packed with 15% SE-30 on Chromosorb W-HP at 175°. Under these conditions thermal rearrangement of **4** to starting ketone (*cf.* [2]) is negligible. The Φ values given are averaged from multiple measurements at each of several conversions within the range indicated. Estimated experimental error, runs 1–5: ±10%; runs 6 and 7: ±30%.

Regardless of the failure of the α- and β-acetonaphthones to sensitize the ODPM rearangement to **4**, these compounds persist to destroy **3** although less efficiently than do the sensitizers of higher triplet energy. This behavior is reminiscent of similar observations by *Engel* [11] with several other β,γ-unsaturated ketones (*cf.* also [19]).

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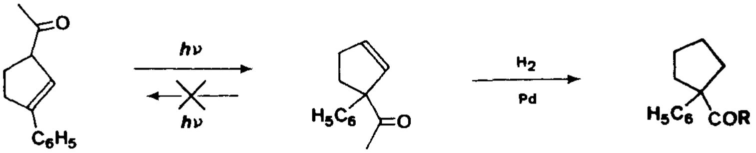
[7]) Note that the triplet energy data given here have all been measured in rigid glasses at low temperature. In fluid solution at room temperature these values tend to be lower by a few kcal's (*cf.* [18]). It is possible, therefore, that **3** is marginally higher in triplet energy than β-acetonaphthone under the conditions of sensitized irradiation.

The *direct photolysis of* **3** at room temperature resulted in a 1,3-acetyl shift to **8** (Table: run 1) characteristic of singlet-excited β,γ-unsaturated ketones1). On separate irradiation product **8** remained unchanged. Its structure was established by catalytic hydrogenation to compound **9** which was also prepared by hydrolysis of 1-phenylcyclopentane-1-carbonitrile [20] followed by treatment of the acid **10** with methyl lithium.



3 **8** **9** R = CH_3 **10** R = OH

The special interest in the result of the direct irradiation of **3** lies, ***inter alia,*** in the absence of the triplet products **4** despite the observation of $S_1 \rightarrow T_1$ intersystem crossing under phosphorescence conditions. We presently consider the possibility that radiationless deactivation modes of the excited singlet state (including photochemical processes) may become more important at room temperature of the conformationally flexible ketone **3**, to the extent of suppressing the intersystem crossing to triplet. Studies to clarify this possibility are under way.

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