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Di-π-methane photorearrangement of *trans*-1,3-diphenylpropene upon excitation to higher singlet states in polar solvents

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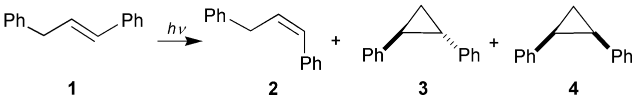
A dramatic enhancement of the di-π-methane rearrangement is observed upon excitation of *trans*-1,3-diphenylpropene (1) to its higher singlet states in acetonitrile, which leads to *trans*-1,2-diphenylcyclopropane (3) as a major photoproduct.

The photochemistry of *trans*-1,3-diphenylpropene (**1**) has attracted considerable attention in the past.[1–10] In addition to the *cis* isomer **2**, small amounts (*ca.* 5%) of *trans*- and *cis*-1,2-diphenylcyclopropane (**3** and **4**) were also detected after 17 h irradiation in benzene or cyclohexane with 254 nm UV-light (Scheme 1).[1] Under these conditions, the quantum yield of cyclopropane formation was found to be *ca.* 5×10^{-3}, and the reaction rate constant was *ca.* 8×10^{-5} s^{-1}.[10] This cyclization, which in the original paper[1] appeared 'to be without analogy', is considered 'one of the earliest examples of the di-π-methane rearrangement',[7] a reaction named according to Zimmerman and extensively investigated during the last decades.[11–13]

In spite of the considerable efforts devoted to the study of both the synthetic and mechanistic aspects of the di-π-methane rearrangement, there are two issues that have not been studied in a sufficiently systematic way and therefore require further investigation: the wavelength effects and the influence of polar solvents. We have undertaken a study of these two aspects in the case of *trans*-1,3-diphenylpropene (**1**) and found dramatic variations of the reaction efficiency. According to the obtained results, the di-π-methane rearrangement of **1** is markedly enhanced upon excitation to higher singlet states in polar solvents. This provides new mechanistic insights into the reaction and can be used as a tool to increase its preparative value.

Compound **1** was prepared following a known procedure.[14] Solutions of **1** (5 mM) in the indicated solvents were irradiated inside a Luzchem multilamp photoreactor, using the light from four 8W-lamps with emission maxima at 254 or 300 nm (Gaussian distribution), through quartz or Pyrex, respectively. The course of the reaction was followed by GC and ^{1}H-NMR; the degrees of conversion, the product distributions and the mass balances were determined using adequate standards. The results are shown in Fig. 1.

As expected,[1] very minor amounts of *trans*-1,2-diphenylcyclopropane (**3**) were formed in cyclohexane as solvent, whichever the irradiation wavelength employed. Prolonged irradiation at 254 nm resulted in partial isomerization of **3** to the *cis*-cyclopropane **4** (data not shown); in any case the combined yield of cyclopropanes never exceeded 10%. By contrast, upon irradiation of **1** in acetonitrile solution at 254 nm the di-π-methane rearrangement was dramatically enhanced, and **3** became the major product (after 100 min, the chemical yield was almost 50%). This effect was not observed when irradiation of **1** was performed at longer wavelengths. The same trend was found in solvents of intermediate polarity, where **3** was also obtained in significant yields (*e.g.* 30% in THF after 100 min irradiation at 254 nm).



Scheme 1

In order to obtain more reliable quantitative data, the di-π-methane rearrangement quantum yields were determined using the *trans*–*cis* isomerization of β-methylstyrene ($\phi = 0.2$)[15] as actinometer. Table 1 shows that, while in a hydrocarbon solvent $\phi_{\text{di-}\pi}$ was lower than 10^{-2} (in agreement with the literature data of 5.10^{-3}), in acetonitrile it was at least one order of magnitude higher.

As the di-π-methane rearrangement of **1** and related systems is thought to occur from excited singlet states, it appeared of interest to characterise such excited states by carrying out a steady-state and time-resolved fluorescence study in the two solvents. The obtained results are shown in Table 1.

The emission spectrum consisted of a band with maximum at 308 nm. It was found to be independent of the excitation wavelength. The main maximum of the excitation spectra was located at 254 nm; smaller bands appeared at 285 and 294 nm (see Fig. 2). Thus, **1** emits from its lowest lying singlet state, even upon excitation to the higher singlet states.

The fluorescence quantum yields and the singlet lifetimes were smaller in acetonitrile than in hexane (Table 1). No significant effect of the excitation wavelength on these parameters was observed.

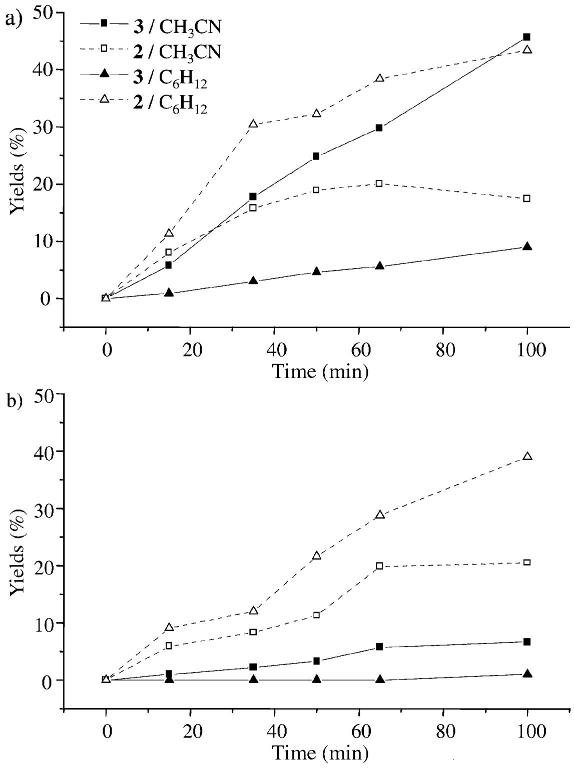


Fig. 1 Preparative yields of formation of **2** and **3**, upon irradiation of **1** in acetonitrile and cyclohexane for different times, a) at 254 nm and b) at 300 nm.

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Table 1 Photophysical and photochemical data of **1** at room temperature[a]

Solvent	ϕ_F	$10^{-7}k_F/s^{-1}$	τ_F/ns	$\phi_{di-\pi}$	$10^{-6}\,k_{di-\pi}/s^{-1}$	ϕ_{cis}
Hexane	0.27 (0.36)	5.5	6.1 (6.1)	< 0.01	< 1	0.12 (0.12)
Acetonitrile	0.13 (0.15)	10	2.5 (2.6)	0.11 (0.04)	44	0.10 (0.11)

[a] In general, the data have been obtained upon excitation at 254 nm. The fluorescence quantum yield and lifetimes using 285 nm as the excitation wavelength are given in brackets.

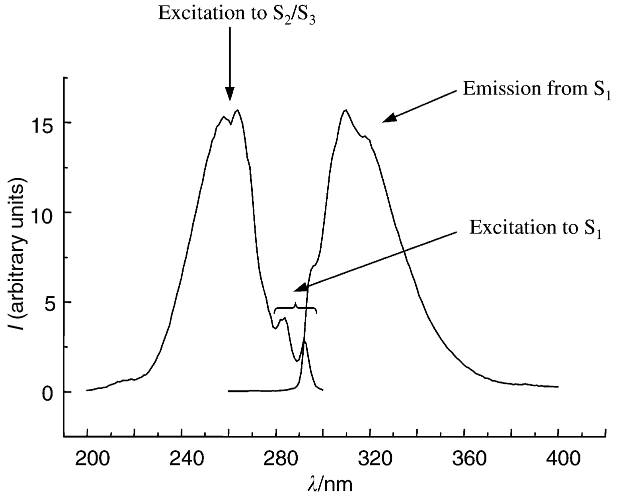

Fig. 2 Excitation and fluorescence emission spectra of **1** in hexane at room temperature.

All the accumulated experimental data on the photochemistry of **1** indicate that, although the nature of the emitting singlet state depends neither on the polarity of the solvent nor on the excitation wavelength, the di-π-methane rearrangement to **3** is strongly influenced by these factors. The sharp enhancement of this reaction upon excitation to higher singlet states in polar solvents is an unexpected behaviour, which is difficult to explain based on the currently accepted models.[11–13] In principle, **1** might photoionize from a higher singlet state in polar solvents, giving rise to the radical cation; this could be the actual rearranging species. An alternative possibility would be to start from the treatment of styrene photoreactivity based on conical intersections.[16] The order of vertically excited singlet states of styrene is believed to be $S_1 < S_2 + S_3$, where S_2 and S_3 (which possesses ionic character) overlap strongly. A conical intersection between S_3/S_2 and S_1 could provide a route to the di-π-methane product **3**. This would explain the need for excitation at shorter wavelength (to populate S_3) and the marked effect of solvents able to modify the energy surfaces of polar excited states.

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