

Photochemistry of 5-Phenyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one: Upper Singlet Excited State Involved in Intramolecular [2 + 2] Photocycloaddition and Long-lived Triplet Excited State in Photodimerisation

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Upon π, π^* excitation, 5-phenyltricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one predominantly undergoes intramolecular [2 + 2] photocycloaddition probably *via* the higher singlet excited state (S₂), while, upon n, π^* excitation, it undergoes predominantly photodimerisation *via* a relatively long-lived triplet excited state.

3-Phenylcyclopenten-2-one is known to undergo photochemical dimerisation presumably *via* the π, π^* triplet excited state to give a 'head-to-head', *cis-anti-cis* photodimer.¹ On the other hand, during the course of our study on acid-catalysed rearrangements of 4-substituted 1,3-bis(homo)cubanones **2a-c**, which were prepared by irradiation of corresponding 5-substituted tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-one **1a-c**, we noted that the phenyl derivative **1a** gave a considerable

amount of photodimer **3**[†] along with the cage product **2a**, while the other derivatives **1b** and **c** gave exclusively the cage compounds **2b** and **c**, respectively.² We now show that on π, π^* excitation **1a** (the absorption spectrum of which is shown in

[†] The structure of the compound **3** has been assigned by X-ray crystallography. Details will appear in the full paper.

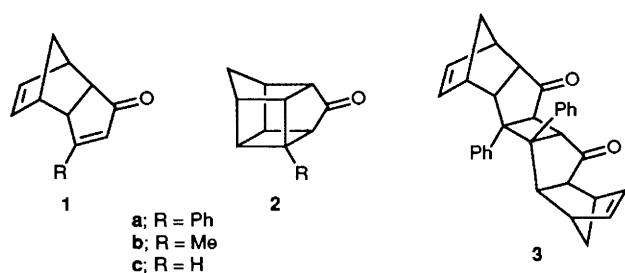


Table 1 Wavelength dependence of product distribution in the photolysis of **1a**^a

Wavelength of exciting light/nm	Conversion (%)	Yield (%)		
		2a	3	Φ_{2a}/Φ_3
366 ^b	18.2	2.3	15.9	0.29
313 ^c	16.7	5.3	11.4	0.93
254 ^d	12.9	6.8	6.1	2.2

^a Analyses were performed by HPLC. No products other than **2a** and **3** were detected. ^b The solutions of **1a** in benzene (3.0×10^{-3} mol dm⁻³) were irradiated with a 500 W high-pressure mercury lamp fitted with a Uranil filter. ^c The benzene solutions (3.0×10^{-3} mol dm⁻³) were irradiated with a 500 W high-pressure mercury lamp in Pyrex tubes with an NiSO₄ solution filter. ^d The cyclohexane solutions (3.0×10^{-3} mol dm⁻³) were irradiated with a 10 W low-pressure mercury lamp in quartz tubes.

Fig. 1) predominantly undergoes the intramolecular [2 + 2] cycloaddition *via* the S₂(π, π^*) state, whereas on n, π^* excitation it mainly undergoes photodimerisation to give **3** *via* a triplet excited state. Although some photorearrangements of cyclic enones from upper excited singlet states in solution are known,³ this is the first example of photocycloaddition of enones to double bond from S₂.

Under irradiation in benzene with 366 nm light, the formation of **3** was considerably sensitized by benzophenone ($E_T = 287$ kJ mol⁻¹),⁴ while the production of **2** was less affected by this sensitizer.‡ The results of Stern–Volmer analyses (Fig. 2) conducted under similar conditions using *trans*-stilbene ($E_T = 209$ kJ mol⁻¹)⁴ disclosed that the formation of **3** was completely quenched by the triplet quencher (Fig. 2, □), whereas a part (*ca.* 20%) of **2a** was not quenched even in the presence of quencher enough for **3** to be quenched, indicating that a singlet state (presumably, n, π^* in this case) is also involved in the formation of **2a** (Fig. 2, △).

It was found that the photoreaction of **1a** is wavelength dependent. Thus, as can be seen from Table 1, n, π^* excitation leads to **3** as the major product, while π, π^* excitation mainly leads to **2a**.§ Furthermore, the difference observed in the Stern–Volmer plots for the quenching of the production of these two compounds is more striking when **1a** was irradiated with 254 nm light in cyclohexane. In this case, the formation of

‡ A set of solutions of **1a** (3.01×10^{-3} mol dm⁻³) were irradiated with and without benzophenone (6.06×10^{-3} mol dm⁻³) for 50 min under Ar atmosphere. The yields of **2a** and **3** for the former case are 3.0 and 73%, respectively, while for the latter case 2.2 and 15%, respectively.

§ The photoreversion of **3** is found not to have a significant effect on the wavelength dependence of the photoreaction of **1a** by the following fact. Irradiation of a solution of **3** (cyclohexane, 1.5×10^{-3} mol dm⁻³) by 254 nm light performed together with the solution of **1a** (cyclohexane, 3.0×10^{-3} mol dm⁻³, see entry 3 in Table 1) in a 'merry-go-round' only gave **1a** in 7.3% yield and **2a** in 3.8% yield. This means that the contribution of the photoreversion of **3** to the yield of **2a** in the reaction of **1a** is less than 0.23%. The compound **2a** is photostable.

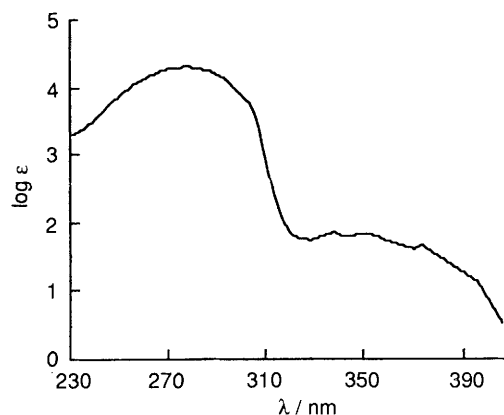


Fig. 1 The UV absorption spectrum of **1a** in cyclohexane

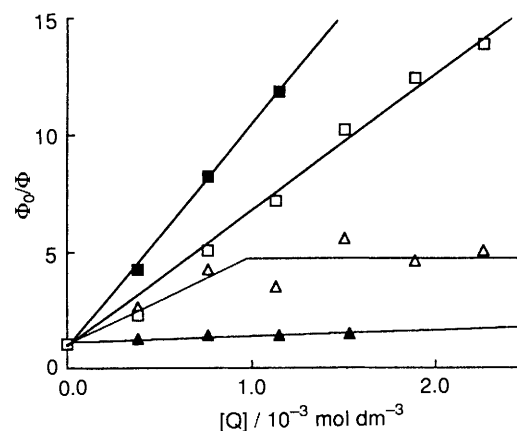


Fig. 2 Stern–Volmer plots for quenching by *trans*-stilbene of formation of products: △ and □, **2a** and **3** on irradiation with 366 nm light in benzene, respectively; ▲ and ■, **2a** and **3** on irradiation with 254 nm light in cyclohexane, respectively. (Initial concentration of **1a** is 3.0×10^{-3} mol dm⁻³ for both benzene and cyclohexane solutions.)

2a was almost unquenched by *trans*-stilbene (Fig. 2, ▲), while the formation of **3** was efficiently quenched (Fig. 2, ■). These studies leave no doubt that, unlike other ordinary enones such as cyclopenten-2-one, which has been established to undergo photocycloaddition to a double bond *via* the triplet state,⁵ the formation of **2a** occurs directly from the S₂(π, π^*) state in competition with the internal conversion to S₁(n, π^*) and following intersystem crossing. We consider that the non-quenchable excited state species is not the short-lived T₂ state, because it seems to be unlikely that only π, π^* excitation leads to this triplet excited state and n, π^* excitation does not.

As to the nature of the triplet state of **1a**, which mainly proceeds to the dimer **3**, the following information is available. Although measurement of phosphorescence spectra of **1a** failed, we succeeded in observing a S–T absorption spectrum with a highly concentrated iodoethane solution (Fig. 3). The shape of the bands look to be the mirror image of the reported phosphorescence bands of 3-phenylcyclopenten-2-ones^{1,6} and the wavelengths of 0–0 band in these spectra are very close to each other (465 nm for the S–T absorption spectrum of **1a**, *ca.* 475 nm for the emission spectrum of 3-phenylcyclopenten-2-one). Furthermore, using k_q values of $2\text{--}3 \times 10^9$ dm³ mol⁻¹ s⁻¹ reported for quenching of the 3-phenylcyclopenten-2-one triplet by several quenchers in cyclohexane at room temperature,⁷ we obtained from the Stern–Volmer slopes (Fig. 2, ■) a triplet lifetime of 3–5 μ s in cyclohexane, comparable to those reported for a transient species trapped by laser flash photolysis of 3-phenylcyclo-

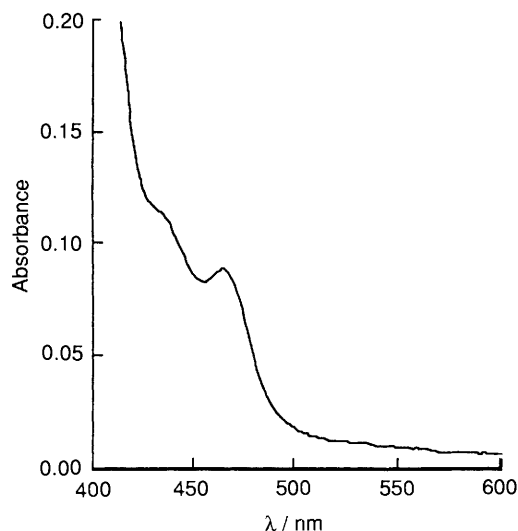


Fig. 3 S-T absorption spectrum of **1a**. Concentration: 0.27 mol dm^{-3} in $\text{C}_2\text{H}_5\text{I}$ (1 cm).

ten-2-one at room temperature (between 1 and 20 μs , in cyclohexane depending on conditions).⁷ The latter is thought to have π, π^* nature on the basis of its relatively long lifetime. From these observations, we consider that the reactive triplet state of **1a** has π, π^* character rather than n, π^* character and has a non-twisted (non-relaxed) geometry as the spectroscopic triplets observed for 3-phenylcyclopenten-2-one by laser photolysis⁷ and emission.^{1,6} The lifetime of the reactive triplet state of cyclopenten-2-one for dimerisation estimated by

quenching experiments is of the order of nanoseconds.⁸ Conjugation with the phenyl group and localization of excitation in the styrene unit should be responsible for the longer lifetime of triplet state of **1a**. Moreover, since styrenes such as 1-phenylcyclohexene are known to undergo photocycloaddition *via* singlet excited state,⁹ we consider that the styrene unit also plays an important role in the S_2 state of **1a**.

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