Two-photon processes in the photo-Claisen and photo-Fries rearrangements. Direct observation of dienic ketenes generated by photolysis of transient cyclohexa-2,4-dienones

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Using the two-laser two-colour technique it has been possible to promote two photon chemistry in the cases of benzyl phenyl ether 1a and phenyl acetate 1b; this is based on the photolysis of the transient cyclohexa-2,4-dienone intermediates 2a,b of the photo-Claisen and photo-Fries rearrangement to the dienic ketenes 4a and 4b.

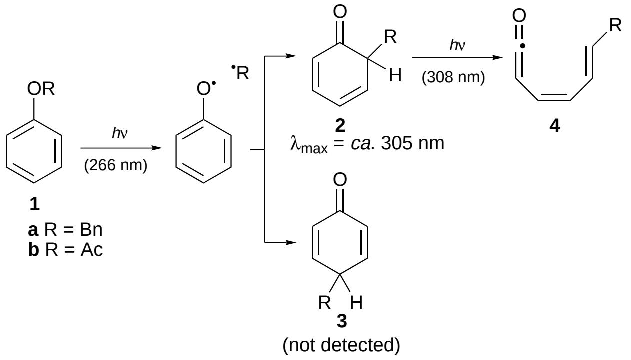
The classical Claisen and Fries rearrangements have been known for nearly 90 years.[1] Their photochemical equivalents were first reported in 1952 and 1960, respectively.[2] Since then, a considerable number of reports have appeared in connection with the synthetic as well as mechanistic aspects of both photorearrangements. Much of this work was done during the first two decades since their discovery and is summarized in several reviews.[3] A satisfactory understanding of the mechanism has been achieved by using laser flash photolysis,[4] CIDNP[4e,5] and transient Raman spectroscopy,[6] as well as studies on magnetic isotope effects and magnetic fields effects.[7]

The above contributions support the idea that photo-Claisen and photo-Fries rearrangements occur from an excited singlet state, *via* homolysis of the aryloxy–alkyl (or acyl) bond, to give radical pairs enclosed in a solvent cage. Radical recombination leads to the rearranged alkyl (or acyl) migration products, while out-of-cage hydrogen abstraction by the aryloxy radical leads to the formation of phenols. This picture has been confirmed by independent generation of the involved radicals *via* Norrish type I photoreaction of ketones in the presence of phenols, which leads to aryl ethers (or esters) plus *C*-alkyl (or *C*-acyl) phenols.[8]

Being the prototypes for geminate cage recombination/escape of relatively large radicals, both photorearrangements have attracted recent attention as model reactions to study the influence of constraining media such as cyclodextrins,[9] micelles,[10] zeolites,[11] supercritical carbon dioxide[12] and stretched low-density polyethylene films.[13]

There is some spectroscopic evidence for the involvement of non-enolized cyclohexadienones as intermediates.[4] If such transient species were actually intervening, it should be possible in principle to photolyse them at their absorption maxima using the recently developed two-laser two-colour technique.[14] If the typical photoproducts of cyclohexadienones were thus formed,[15] this could constitute an additional proof for their involvement in the photo-Claisen and photo-Fries rearrangements. Besides, this methodology could provide a direct entry to two-photon chemistry of aryl ethers and esters, which still remains to be explored.

Laser flash photolysis of deareated 5 mM solutions of benzyl phenyl ether **1a** in methylcyclohexane was carried out with a Nd-YAG laser (fourth harmonic, 266 nm, < 10 ns, ≤ 20 mJ pulse^{-1}) using a 90° excitation geometry and a quartz beam diffuser in front of the sample (Scheme 1). A transient signal appeared, which was assigned to the cyclohexa-2,4-dienone **2a** by comparison with the known properties of these species.[4] In a second experiment, two-laser two-colour laser flash photolysis was employed to examine the effect of laser excitation on the above mentioned reaction intermediate. The same 266 nm laser was used as synthesis laser to generate **2a**, while a 308 nm excimer laser (HCl/Xe/Ne, 6 ns, 70 mJ pulse^{-1}) was used to photolyse the intermediate. The wavelength of the latter was selected to match the optical absorption of cyclohexa-2,4-dienone (maximum at *ca.* 300 nm). The synthesis laser was incident from the front face, while for the photolysis laser a 90° geometry was adopted. The most remarkable result was a permanent and irreversible bleaching of the transient signal as monitored at 295 nm (Fig. 1, insert). In the absorption spectrum obtained after photolysis of **2a**, an enhancement was observed at 260–270 nm, accompanied by a decrease at 300–320 nm. The difference spectrum displayed a well-defined maximum at 270



Scheme 1

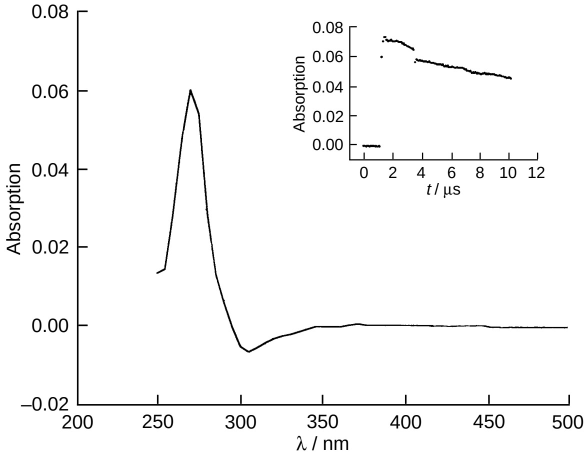


Fig. 1 Absorption spectrum of the dienic ketene **4a** obtained from the difference between the spectra of the reaction of **1a** after and before the 308 nm laser pulse. The insert shows the bleaching of the transient signal monitored at 295 nm.

nm and a less marked emission at 305 nm (Fig. 1). Taking into account the possibility of electrocyclic ring opening in the case of **2a**, a plausible structure of the intermediate absorbing at 270 nm would be that of a dienic ketene such as **4a**. This assignment was confirmed by comparison with the spectra of similar ketenes generated by photolysis of stable 6,6-disubstituted cyclohexa-2,4-dienones.[16]

The same experiments were carried out with phenyl acetate **1b**. Flash photolysis with the 266 nm laser gave rise to a transient signal whose structure was assigned to be **2b**. When this intermediate was photolysed at 308 nm in the two-laser two-colour experiment, a sharp enhancement of the signal monitored at 330 nm was observed (Fig. 2, insert). This was somewhat surprising as, in the case of the benzyl ether **1a**, the result was bleaching of the signal. The spectrum of the new intermediate was obtained in the usual way, by examining the difference between the spectra after and before the 308 nm laser pulse. This spectrum showed a maximum at longer wavelength (330 nm) than **4a** (Fig. 2). In principle, photochemical opening of 6-acetylcyclohexa-2,4-dienone **2b** to the corresponding dienic ketene **4b** was expected to occur, by analogy with the behaviour of the 6-benzyl derivative **2a** upon photolysis at 308 nm. Transient **4b** presents an extended conjugation, owing to attachment of the acetyl group at the end of the polyunsaturated system. This would explain the position of its absorption maximum and is in agreement with the proposed structure.

In summary, using the two-laser two-colour technique it has been possible to promote two photon chemistry in the case of benzyl phenyl ether **1a** and phenyl acetate **1b**. This is based on the photolysis of the proposed cyclohexa-2,4-dienone intermediates **2a**,**b** of the photo-Claisen and photo-Fries rearrangements and involves direct detection of the electrocyclic ring opening products, the dienic ketenes **4a** and **4b**.

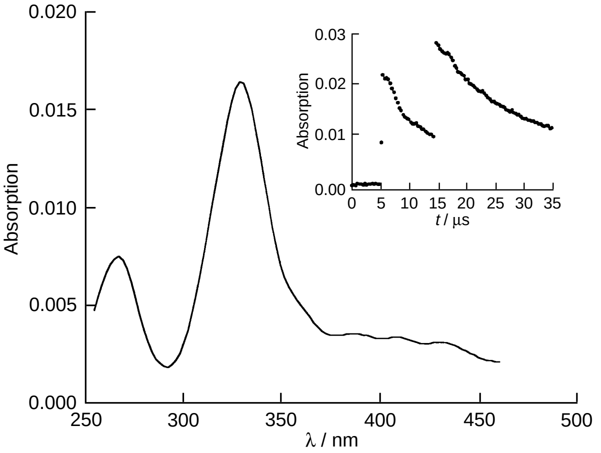


Fig. 2 Absorption spectrum of the dienic ketene **4b** obtained from the difference between the spectra of the reaction of **1b** after and before the 308 nm laser pulse. The insert shows the jump of the transient signal monitored at 330 nm.

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Footnotes and References

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