Mechanistic studies of the photogeneration and photochemistry of *ortho*-xylylenes

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Abstract : A variety of *ortho*-xylylenes have been generated photochemically using ketone precursors *via* either CO elimination from appropriately substituted 2-indanones or γ-hydrogen transfer in ortho substituted aromatic ketones. The solution lifetimes of these xylylenes range from nanoseconds to minutes and their decay involves a rich variety of intra- and intermolecular processes. Examples are presented where the effects of xylylene irradiation ranges from a dramatic acceleration of the reaction to examples where the effect of irradiation is to change the product ratios or to a decrease in yields through promotion of the back reaction.

INTRODUCTION

Laser photolysis techniques have proven useful in the study of a wide range of organic reaction intermediates. In this report we deal with one specific group of intermediates, *ortho*-xylylenes, and analyze the mechanisms of their photochemical generation from ketone precursors as well as compare the spontaneous and photochemical decay of selected *ortho*-xylylenes.

Alkyl substituted *ortho*-xylylenes can be produced from a variety of precursors (ref. 1, 2); *some of these routes are illustrated in Scheme I.*

Scheme I
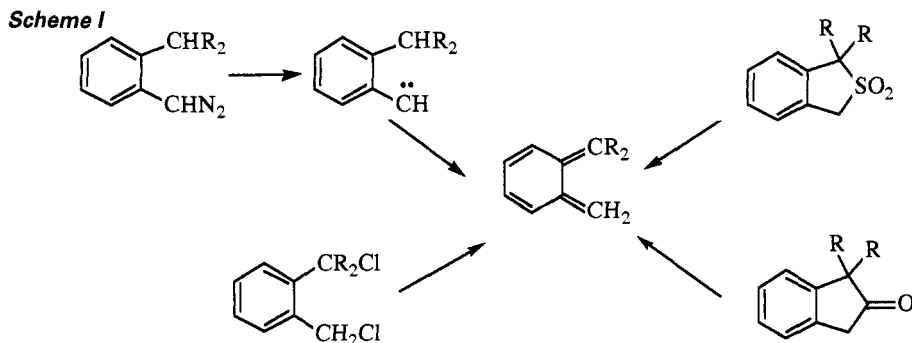
Hydroxy substituted *ortho*-xylylenes can be produced by photoinduced γ-hydrogen transfer in the corresponding ketone or aldehyde (ref. 3). The process is analogous to the well known Norrish Type II reaction and is called photoenolization. While the "photoenols" are normally produced in this way, their generation from the corresponding 2-indanone is also possible as illustrated in Scheme II.

The photoenols frequently undergo reketonization although a number of examples where they undergo cyclization are also well known (ref. 4-7).

Scheme II

"Photoenol"
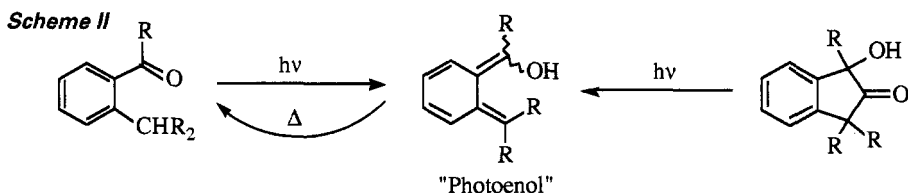
Some aspects of this report involve two-laser two-color irradiations. Over the last few years we have carried out a series of studies involving this technique, in which a transient generated by excitation by a first '*synthesis*' laser is then excited by a second '*photolysis*' laser. The technique is very powerful in mechanistic studies and is employed in some of the work reported here. The reader can find details on the technique in earlier reports from our laboratory (ref. 8-10).

GENERATION AND DECAY OF TETRAMETHYL-*ortho*-XYLYLENE

Our first example deals with the case of tetramethyl-*ortho*-xylylene *1* that can be readily produced by photodecomposition of 1,1,3,3-tetramethyl-2-indanone (*2*) (ref. 11).

$$\text{2} \xrightarrow{\; h\nu \;} \text{1} \tag{1}$$
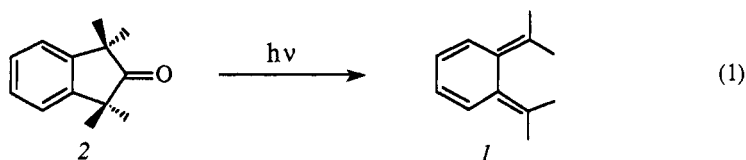
Excimer laser excitation (308 nm) of a solution of *2* in benzene leads to the long lived *1* which has an absorption band centered at 358 nm. The spectra in other solvents were essentially identical to that in benzene (ref. 12). *1* is too long lived for its decay to be studied by laser or conventional flash photolysis. In fact, in benzene we determined a lifetime of 9.1 minutes at room temperature. The xylylene is sufficiently long lived that it can be detected by infrared spectroscopy in solution at room temperature. This is illustrated in Figure 1 which shows the difference spectrum recorded two minutes after completion of irradiation of *2* by 1000 laser shots.
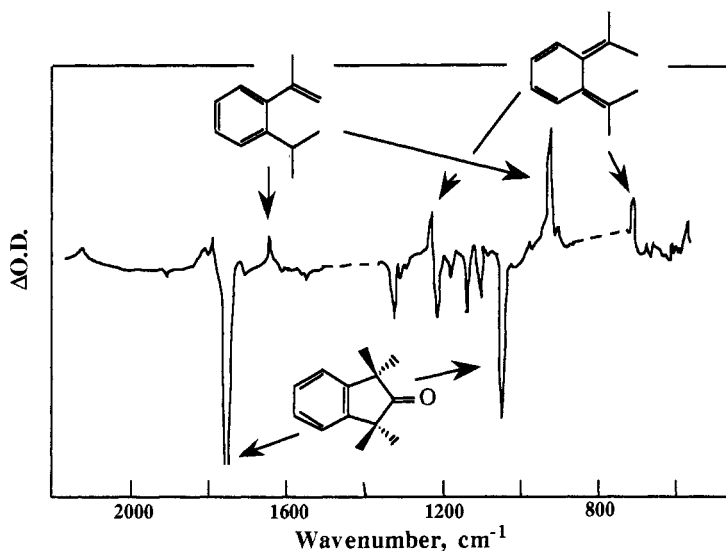

Figure 1: Difference infrared spectrum obtained upon laser irradiation of a solution of *2* in carbon tetrachloride. The dashed lines correspond to regions masked by solvent bands. (from ref. 12 © American Chemical Society; reproduced with permission).

The two negative bands correspond to the starting indanone which gives only depletion signals in the difference spectrum. The bands at 681 and 1212 cm^{-1} correspond to a transient species and are assigned to *1*, while the signals at 900 and 1657 cm^{-1} do not decay and are assigned to the final stable product of the reaction, *3*, produced *via* 1,5-hydrogen shift.

Transient phenomena on short time scales following laser excitation reveal that *1* is not formed "instantaneously", but rather, its formation shows a build-up which occurs with a lifetime of 580 ns in benzene at room temperature. The formation of *1* occurs concurrently with the decay of a transient that can be observed at shorter wavelengths and can be readily monitored at 320 nm (ref. 12). We assign this short lived absorption to the precursor of *1*. In principle, this precursor could be either an excited state of *2* or one of the intermediate biradicals, *4* or *5*.
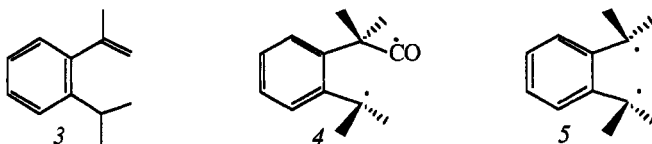
The possibility of an excited state of *2* can be readily ruled out. First, 580 ns is too long a lifetime for a carbonyl singlet state. Second, addition of up to 1M 1,3-cyclohexadiene (an excellent triplet quencher) has little or no effect on the yield of *ortho*-xylylene or the lifetime of the intermediate. This is conclusive evidence that the triplet state of *2* must live less than 1 ns. Biradicals *4* and *5* cannot be readily distinguished spectroscopically, since in both cases the spectrum will be dominated by the presence of the benzylic chromophore. An interesting approach first used by Das *et al.* (ref. 13) in the study of photoenols allows the distinction between these two species. While *4* is a "true" biradical, *5* is in fact the triplet state of *1*, *3 1**. Thus, we anticipate that *5* may be able to transfer its triplet

energy to a suitable acceptor, while *4* would not. β-Carotene is an ideal substrate for experiments of this type: its triplet energy (ref. 14) is only 19 kcal/mol and its intersystem crossing yield is very small. In experiments of this type we found that β-carotene quenches the short lived intermediate quite efficiently with a rate constant of 1.7×10^{10} M^{-1}s^{-1} in benzene (ref. 12). Further, triplet β-carotene is formed concurrently with the decay of the short lived absorption.

On the basis of this evidence we conclude that the intermediate with a 580 ns lifetime is *5* and that *4* must be substantially shorter lived. In fact, since we do not see any delay in the formation of *5* we believe that all its precursors (*4* and the singlet and triplet states of *1*) must live less than 10 ns.

To our surprise, we find that quenching of *5* by molecular oxygen, while quite rapid, does not yield detectable amounts of singlet oxygen[b]. This contrasts with the case of typical photoenols (e.g. from *ortho*-methylacetophenone) which interact with both β-carotene (ref. 13) and oxygen (ref. 15) by energy transfer. It is possible that singlet oxygen scavenging by *1* is so fast that singlet oxygen never escapes the geminate solvent cage in the case of *1*.

A different route to biradical 4

While the experiments above do not yield much information about *4*, we undertook a series of experiments to examine in some detail its behavior. For this purpose we carried out some experiments with the diketone *6*. There are some very interesting aspects of the intermolecular photochemistry of *6* on which we have reported separately (ref. 16). In particular, *6* strongly resembles biacetyl in its spectroscopic properties, but its photoreduction is exceptionally rapid and typical rate constants for hydrogen abstraction are about three orders of magnitude larger than for biacetyl and quite comparable with those for benzophenone. In this report we are only concerned with the intramolecular photochemistry of *6* which as a result of the reactivity mentioned above can only be monitored conveniently in non-hydrogen donating solvents. Thus, irradiation of *6* in benzene at low conversions yields two products, *2* and *3*, with the former being the most abundant one, i.e.,

(2)
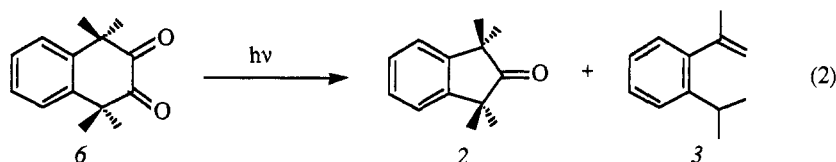
At high conversion the main product becomes *3* which can be readily explained since *2* eventually photolyses to *3* via the intermediacy of *1* (see reaction 1). The fact that *2*, rather than *3* is the main product from *6* indicates that most biradicals *4* cyclize to yield *2* rather than decarboxylate to yield *5*. The result is fully consistent with the fact that the quantum yield for product formation (*3*) from *2* is only ~0.17. Scheme III summarizes the relevant processes.

Scheme III
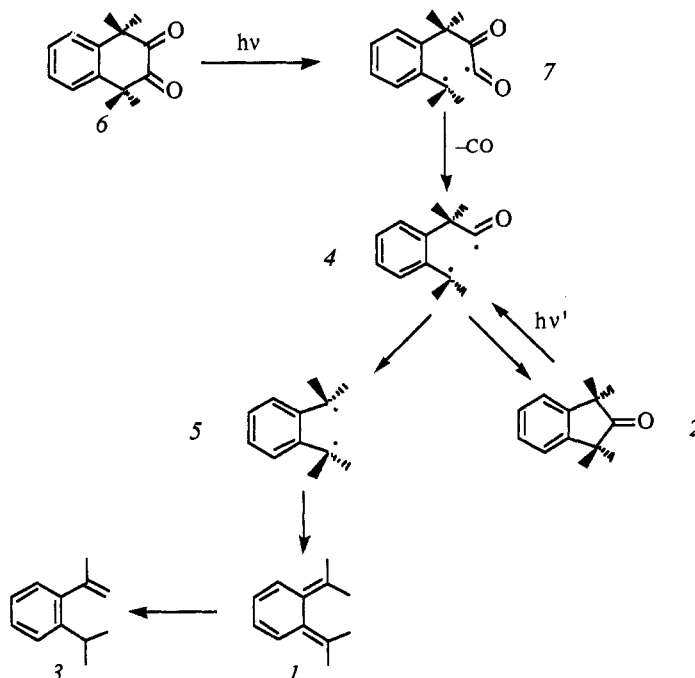
[b] As monitored by its near infrared luminescence at 1.27 μm.

Two-laser two-color photochemistry of 2

In a series of two laser experiments (ref. 12) we observed that laser irradiation of *1* (337 nm, derived from the photolysis of *2*) leads to readily detectable and irreversible bleaching which is indicative of the formation of a final, stable product of reaction. However, gas chromatographic analysis reveals neither the formation of new products, nor any decrease in the yield of *3*, in spite of the fact that in the two laser experiments as much as 20% of the xylylene decayed photochemically, rather than thermally. From this we conclude that both thermal *and* photochemical decay of *1* involve a 1,5-hydrogen shift to yield *3*. Since the photochemical process occurs within the duration of the laser pulse (~8 ns) this process must be at least ten orders of magnitude faster than the equivalent thermal reaction. At first sight the observation may appear unusual, since 1,5 shifts are normally ground state allowed and excited state forbidden. However, in this case it has been suggested that steric congestion in *1* (ref. 7) forces the hydrogen transfer to be antarafacial and that therefore in this particular case the process is excited state allowed and ground state forbidden. Our results appear to confirm this explanation.

Interestingly, photolysis of *1* does not yield any evidence for the formation of triplet biradical *5*, suggesting that the photochemistry of *1* proceeds through the singlet manifold.

Photochemistry of 2-indanone

A few experiments with 2-indanone revealed that the unsubstituted xylylene *8* (λ_{max} 380 nm) decays by clean second order kinetics, Figure 2. The result is not unexpected, since the products from *8* are typically those from 2+4 and 4+4 dimerization (reaction 3) with the former being the major one (ref. 17)

$$(3)$$

8   *9*   *10*
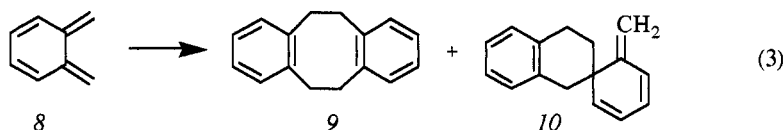
No evidence for the biradical (i.e. the triplet state of *8*) was obtained, presumably due to either a short lifetime or extensive spectral overlap with the other reaction intermediates in the system.
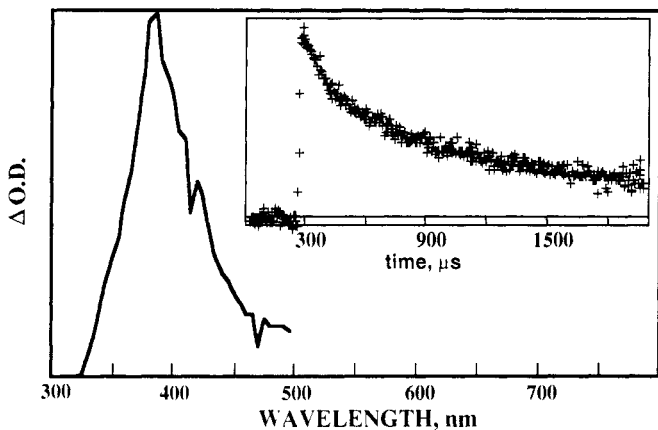

Figure 2: Spectrum of *8* from the photolysis (308 nm) of 2-indanone and decay trace (insert) monitored at 380 nm.
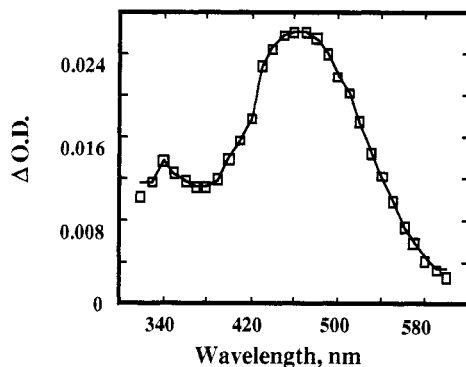

Figure 3: Transient spectrum of *12* obtained by 308 nm laser irradiation of *11* in benzene.(From ref. 18, © Pergamon Press, reproduced with permission.

PHOTOCHEMISTRY OF 1,1,3-TRIPHENYL-2-INDANONE

Our next example deals with the case of 1,1,3-triphenyl-2-indanone (*11*) which upon photolysis yields xylylene *12* (λ_{max} 460 nm).

Laser excitation (308 nm) of *11* yields *12* (Figure 3) within the time resolution (<10 ns) of the experiment, suggesting that the excited states and biradicals involved in this reaction must be very short lived. Soon after the irradiation is started (with either a lamp or a laser), the accumulation of 9,10-diphenylanthracene (*13*) becomes evident from both the absorption and emission spectra of the solution. Gas chromatographic analysis reveals the formation of two major products, *13* and *14* along with trace amounts of oxygenated products. We presume that *13* results from oxidation of the corresponding dihydroanthracene, *15*.
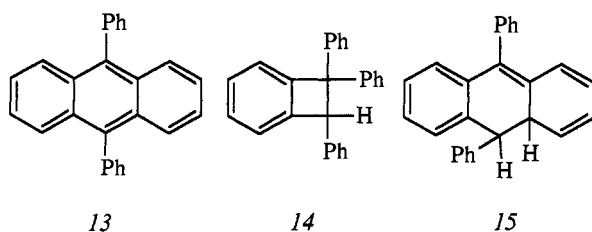

11   *12*

13   14   15
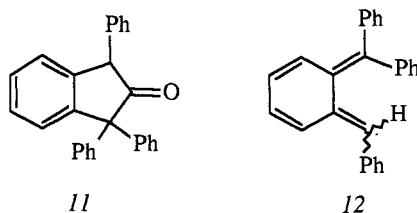
TABLE 1: Dependence of the product ratio in the photolysis of 1,1,3-triphenyl-2-indanone on the type of light source.

Light source	Wavelength	ratio 13/14
Lamp	~310 nm	0.94
Laser	308 nm	2.54
Two-laser	308 + 480 nm[a]	3.93

[a] The two laser pulses were separated by 2 μs.

Interestingly, the ratio of the yields for *13* to *14* is strongly dependent upon the type of irradiation (laser *vs.* lamp). This is illustrated in Table 1.

Transient experiments under the conditions of the last entry in Table 1 show that dye laser (480 nm) irradiation of the xylylene leads to essentially quantitative irreversible photobleaching (ref. 18). Naturally, under lamp irradiation one must be performing almost exclusively one-photon reactions, while single-pulse laser excitation probably involves a mixture of one- and two-photon processes. Clearly, two photon processes favor cyclization to anthracene-type products. This example contrasts with the case of *1* where both one- and two-photon processes led to the same product. A related example has been reported by Wilson et al. (ref. 5).

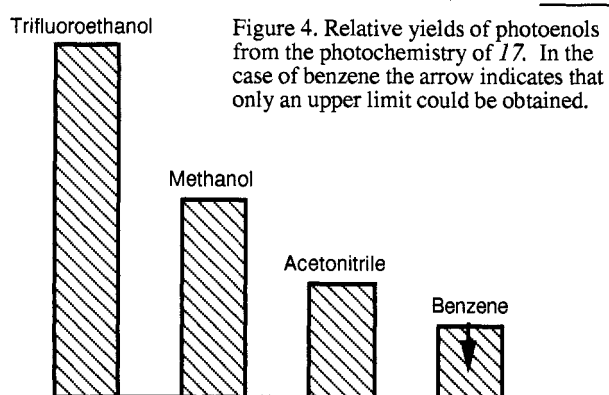## A COMPARISON OF ALTERNATE SOURCES OF PHOTOENOLS

This example and the one to follow are related to hydroxy substituted *ortho*-xylylenes (*photoenols*). Some of the possible routes for their formation have already been outlined in Scheme II, but a comparison of different sources (i.e. intramolecular H-transfer *vs.* CO elimination) has not been reported.

ortho-Benzylbenzophenone (*16*) and 1,3-diphenyl-1-hydroxy-2-indanone (*17*) photodecompose to yield the same photoenol, *18*.

Scheme IV

16   18   17
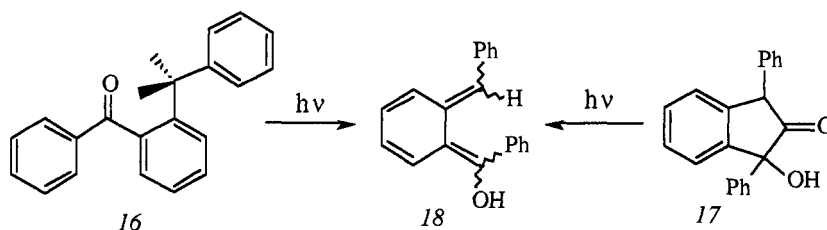
The enol *18* is readily detected (λ_{max} 445 nm) (ref. 19) and decays biexponentially with lifetimes of 0.18 μs and >50 μs in benzene. Another short lived transient (τ ~ 100 ns) can also be detected at ~ 330 nm and may be due to the biradical, although this has not been fully established at the present time.

Figure 4. Relative yields of photoenols from the photochemistry of *17*. In the case of benzene the arrow indicates that only an upper limit could be obtained.

The yield of enols from the photolysis of *16* is rather insensitive to the solvent used. By contrast, when the photoenol is produced from *17* (see Scheme IV) its yield is strongly solvent dependent. Figure 4 illustrates this remarkable effect.

We were very surprised by this dependence. Clearly the biradical intermediate, *19*, should be the same whether its is formed from *16* or *17* given that there is literature evidence (ref. 20) indicating that photoenol biradicals live long enough to undergo rotational equilibration.
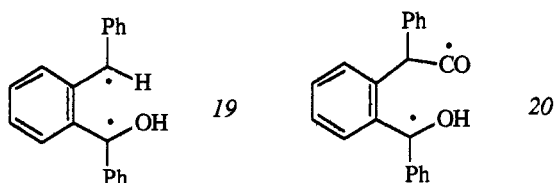
We would like to suggest three possible explanations for the solvent dependence observed for *17*. First, one of the possible reaction paths for biradical *19* is hydrogen transfer to generate *16* without the intermediacy of the photoenols. Second, the initially formed biradical, *20*, could reclose to *17* more favorably in non-polar than in polar solvents. Third, the α-hydroxy group may provide an intramolecular mechanism for triplet deactivation which is reminiscent of that which is common in *ortho*-hydroxybenzophenones and related compounds, i.e.


(4)
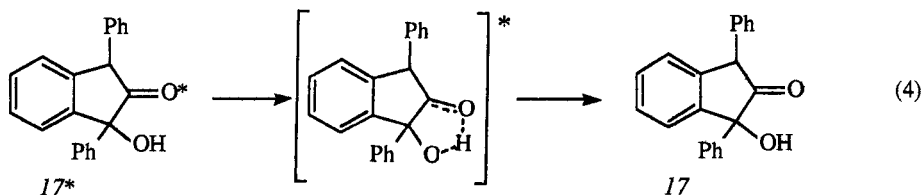
The first mechanism, involving hydrogen transfer in *19* can be readily ruled out, since the formation of *16* is very inefficient in benzene. We cannot distinguish conclusively between the other two alternatives, although we favor that of reaction 4 since our studies with several other 2-indanones (*vide supra*) do not appear to show much solvent dependence. Reaction 4 would be most effective in non-polar solvents such as benzene. On the other hand in hydroxylic solvents *intermolecular* hydrogen bonding will be expected to predominate and the mechanism of reaction 4 would be rendered ineffective. Under these conditions decarbonylation of *20* followed by photoenol generation should be the dominant process.

PHOTOCHEMISTRY OF α-CHLORO SUBSTITUTED ENOLIZABLE KETONES

Our next example deals with the case of α-chloro substituted photoenolizable ketones. We have examined ketones *21-23* and our discussion concentrates on *21*.
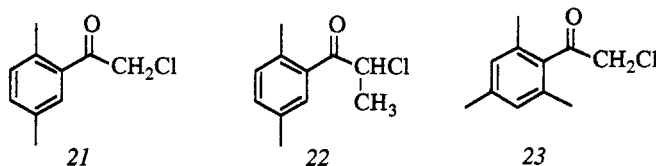

Ketone *21* and related compounds have been examined by Bergmark *et al.* (ref. 21, 22). Photolysis of *21* is known to result in the formation of methyl substituted 1-indanone, *24*.

(5)
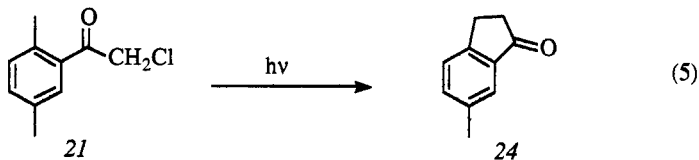
Laser excitation (308 nm) of *21* in methanol leads to the formation of a short lived intermediate (λ_{max} 340 nm, $\tau \sim 270$ ns) and a long lived species (λ_{max} 380 nm, $\tau \sim 20$ μs). The short lived intermediate is readily characterized as $\underline{a}$ triplet state of *21* on the basis of quenching studies with typical triplet quenchers, such as conjugated dienes. Interestingly, triplet quenching by dienes leads to a calculated[c] Stern-Volmer slope ($k_q\tau_T$) of 3800 M^{-1}; this contrasts with the value of 1.02 M^{-1} reported by Bergmark(ref. 22) and based on product quenching studies. Clearly, the difference is beyond the accumulated errors of both techniques. One must therefore conclude that the triplet detected in the flash experiments and that responsible for product formation are

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[c] Based on the product of the two parameters determined independently by laser flash photolysis.

not the same. The observation is consistent with the fact that neither oxygen, nor dienes had any significant effect on the lifetime or intensity of the 380 nm signal, which we assign to the corresponding photoenol, *25*.
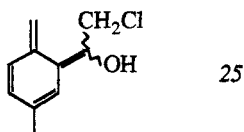
Since the 380 nm signal shows a clean first order decay with a rate constant of 5×10^4 s^{-1}, we suggest that only the E isomer of the enol is observed and that it is this species that is responsible for product formation, as illustrated in reaction 6.

$$+ \quad HCl \qquad (6)$$
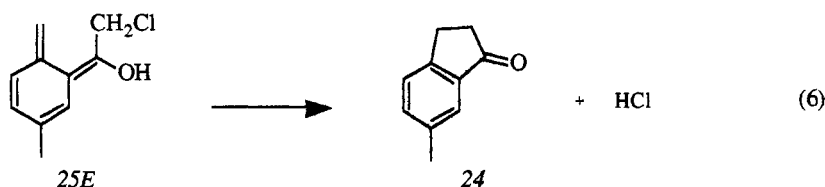
We assume that the Z enol is very short lived and that its decay from the system underlies the decay of other intermediates. In order to test for this we irradiated *25E* in a two laser experiment similar to those mentioned earlier. We observed enol photobleaching and that the yield of *24* decreased without formation of any new products. The observation can be readily explained in terms of the phototransformation of *25E* into *25Z*; i.e. the long lived but reactive intermediate converts to the short lived species which undergoes reketonization.

Finally, it is not uncommon for photoenolizable ketones to show two distinct triplet states.(ref. 20, 23) These are usually attributed to slow interconverting rotamers. The lifetime of 270 ns mentioned above is remarkably long and we can only speculate that in this case bond rotation is slowed down by the presence of the chlorine atom. Thus, *21* has two kinetically distinct triplet states. The longer lived one plays no, or only a minor role in product formation, while the *syn* triplet decays in less than 1 ns to form the enols, with the E isomer being responsible for product formation.

CONCLUSION

ortho-Xylylenes can be readily generated and studied under conditions of laser excitation. The biradical generated by CO elimination from 2-indanones or in the photoenolization reaction are the same species as the triplet state of the corresponding xylylene and participate readily in energy transfer reactions. Two laser techniques where the xylylene is photoexcited by a second laser pulse are very useful as mechanistic probes and can induce a rich variety of behaviors depending on the substrate. For example, in the case of *1*, laser excitation leads to the same reaction as spontaneous decay (i.e. conversion to *3*), but the photochemical process is at least 10^{10} times faster. In the case of *12* the ratio of the decay products *13* and *14* is very different under lamp and laser excitation. In the case of *25* laser excitation of the photoenol leads to a decrease in quantum yield for product (*24*) formation which is attributed to photoconversion of the E enol into the Z enol.

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