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A Laser Flash Photolysis Study of the Mechanism of the Photocyclization of α-Chloro-o-methylacetophenones[1]

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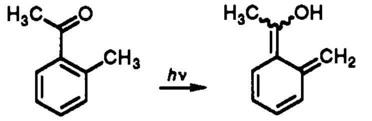
Abstract: Photolysis of α-chloro-2′,5′-dimethylacetophenone (I) leads to 6-methyl-1-indanone in high quantum yields. Laser flash photolysis experiments reveal the intermediacy of a triplet state with a lifetime of 270 ns in methanol; however, this triplet is not responsible for product formation. The products derive from a much shorter triplet ($\tau \leq 1$ ns), which is not detectable with nanosecond resolution. Only one photoenol is detectable; this is attributed to the *E* enol that has a lifetime of ca. 20 μs in methanol and 225 ns in benzene. It is believed that the *Z* enol (which has the prefered conformation for reketonization) is very short lived. Dye laser irradiation of the *E* photoenol leads to a *decrease* in the yield of product formation, which is attributed to $E \rightarrow Z$ photoinduced isomerization.

Introduction

Ketones bearing o-alkyl substituents are known to readily form the corresponding enols under photochemical excitation, as shown in reaction 1.



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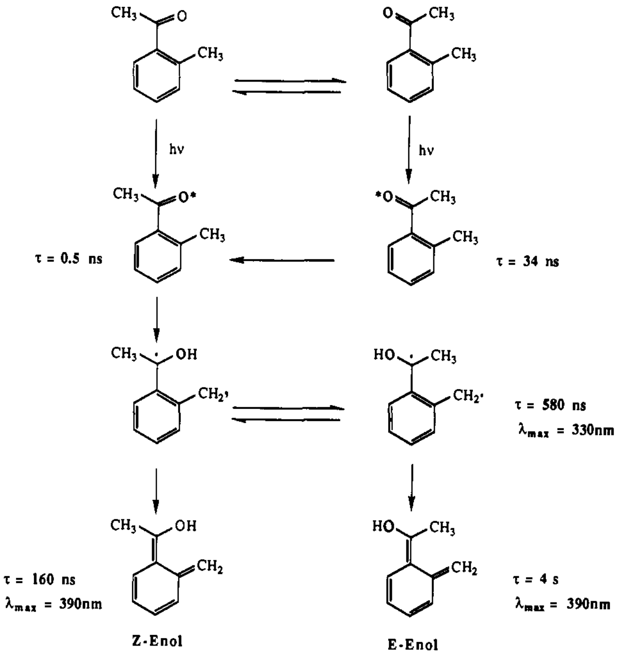
This reaction, involving an initially generated mixture of kinetically distinct triplet states, proceeds through a rotationally equilibrated biradical formed by intramolecular hydrogen abstraction. This biradical gives two different enols with very similar spectroscopic properties, but vastly different kinetic behavior. This is shown in Scheme I, using o-methylacetophenone as an example.[4–6]

The lifetimes given in Scheme I all correspond to acetonitrile–water, except for the *E* enol where the value corresponds to cyclohexane. The lifetime of the transoid triplet state is believed to be controlled by the bond rotation leading to its interconversion to the reactive cisoid form.[5,7] The 1,4-biradical is the same species as the triplet state of the photoenol, and there are examples where either the radical-like or excited-state characteristics are expressed, depending on the property monitored. Recent experiments with oxygen and β-carotene as energy acceptors illustrate well the excited-state characteristics of the biradical.[8,9]

In the absence of trapping agents (e.g. dienophiles), photoenols frequently decay by reverse hydrogen transfer to regenerate the parent ketone, although recent reports suggest that cyclobutenol formation may be more common than generally believed.[10]

There are a few examples in which these intermediates undergo intramolecular reaction to form new products. For example, 2-substituted o-ethylbenzophenones undergo efficient elimination of the 2-substituent upon UV irradiation, with concomitant formation of o-vinylbenzophenone,[11] and 2,4,6-triisopropylbenzophenone gives the corresponding cyclobutenol by an intramolecular [2 + 2] cycloaddition from the photogenerated enol with a quantum yield of 0.6.[12–14]

Scheme I



On the other hand enolizable α-chloro ketones can lead to substituted indanones in good yields together with some other products. Bergmark et al., in two leading papers on the subject,[15,16] have established the basic concepts involved in understanding the mechanism for this reaction and have shown that the *Z* enol is not involved in product formation. Bergmark suggested that either the *E* enol or the biradical could lead to chloride elimination, depending on which kind of product is formed (photocyclization, photosolvolysis, or photofragmentation).

Since there is no information on the transients involved in this class of photoreactions, we have undertaken a detailed study of the dynamics and mechanism of chloride elimination from α-chloro-2′,5′-dimethylacetophenone (I). The results are compared

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(1) Issued as NRCC-32842.

(2) Universidade Federal Rural do Rio de Janeiro.

(3) National Research Council.

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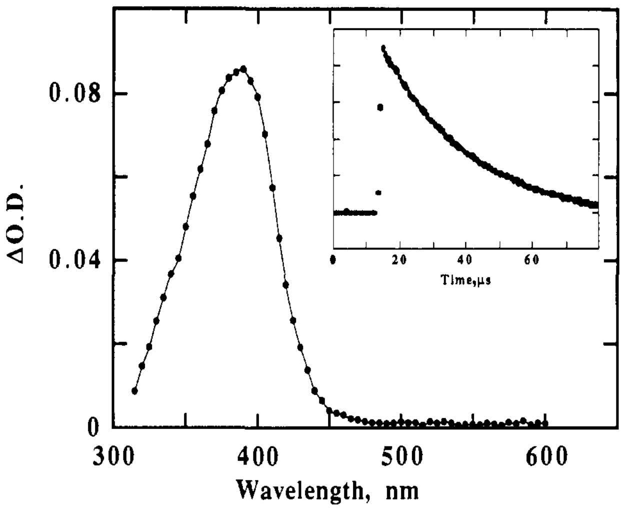
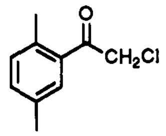


Figure 1. Transient absorption spectrum obtained on 308-nm excitation of 1 mM α-chloro-2′,5′-dimethylacetophenone in methanol. Insert: Decay trace at 380 nm due to the *E* enol generated as above.

with those for other photoenolizable ketones. Exploratory work has also been carried out on the related ketones II and III.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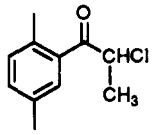
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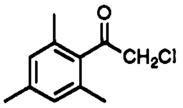

III

Experimental Part

Materials. Methanol and benzene were Aldrich Gold Label products and were used as received. 1,3-Cyclohexadiene (Aldrich) was vacuum distilled in a trap-to-trap apparatus prior to use.

Ketones I–III and VI were synthesized following the procedures described in the literature.[16] In all cases the crude material was vacuum distilled and then purified by preparative thin-layer chromatography (silica gel, using as eluent a 99:1 mixture of hexane and ethyl acetate). The physical and spectroscopic properties for these ketones agree with those in the literature.

2′,4′-Dimethylacetophenone (V) (Aldrich) was distilled prior to use.

General Techniques. UV–visible spectra were recorded on a HP-8541A diode array spectrometer. GC analyses were carried out on a Perkin-Elmer Model 8320 capillary gas chromatograph employing a 12-m J & W bonded phase vitreous silica BP1 column. GC–MS analyses were performed on a Hewlett-Packard Model 5995 system.

Melting points were determined on a Mel-Temp apparatus and were not corrected.

Laser Flash Photolysis. Due to efficient product formation, samples of ketones I–III were studied with use of flow cells in order to ensure that each laser pulse irradiated a fresh volume of solution. The flow cells were constructed of 7 × 7 mm^2 Suprasil. The samples were deaerated by bubbling with oxygen-free nitrogen in a container attached to the photolysis flow cell with Teflon lines.

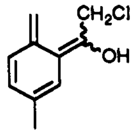
The samples were irradiated with the pulses from a TE-860-2 Lumonics excimer laser with a Xe–HCl gas mixture (308 nm, ~5 ns, ≤20 mJ/pulse). In the two-laser experiments a Candela dye laser was used as the excitation source, and the 420-nm pulses were obtained by employing Stilbene-420 dye. Further details on our laser equipment have been reported elsewhere.[17,18]

Results

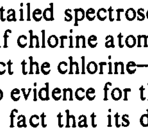
Laser excitation (308 nm) of ketone I in methanol leads to the formation of a short-lived transient with λ_{max} 340 nm and a long-lived species with λ_{max} 380 nm; the latter is illustrated in Figure 1.

In order to determine the identity of the two species mentioned above, we determined their spectroscopic properties and studied their interaction with several substrates. The short-lived species mentioned above has a lifetime of 270 ns in methanol and is readily quenched by typical triplet quenchers, such as conjugated dienes and oxygen, and is therefore assigned to the triplet state of ketone I. The rate constants for quenching can be readily obtained by monitoring the dependence of the decay rate on the concentration of added quencher; for 1,3-cyclohexadiene the rate constant for triplet quenching is 1.4×10^{10} M^{-1} s^{-1} in methanol. The Stern–Volmer constant ($k_q\tau_T$) that can be calculated from this data is ca. 3800 M^{-1}. This value should be compared with $k_q\tau_T = 1.02$ M^{-1}, which was reported by Bergmark[16] and obtained from product quenching studies. Clearly, the triplet observed by laser flash photolysis cannot be the same one responsible for product formation.

Interestingly, neither oxygen nor dienes in concentrations up to 0.01 M had any effect on the lifetime or intensity of the long-lived signal (ca. 20 μs) at 380 nm. The transient spectrum recorded for this species is in agreement with those usually recorded for photoenols, and we therefore assign the long-lived species structure IV, corresponding to only one (vide infra) of the photoenols derived from I. The lack of quenching suggests that product and enol formation could have a common precursor.


IV

The excellent first-order decay followed by the 380-nm species makes it very unlikely that this would be the result of a mixture of two species (see insert in Figure 1). While the spectral characteristics of IV are very similar to those of other photoenols, such as those derived from V and VI, the dynamic behavior is quite different, since both V and VI lead to a bimodal decay that is best interpreted as resulting from two species with very similar spectra but very different lifetimes. For these ketones λ_{max} 380–385 nm and the lifetimes for the *Z* enol are 1.0 and 1.2 μs, respectively, with *E* enol lifetimes exceeding 10 μs for both.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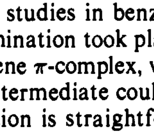
VI

The lifetime of IV is much shorter in benzene than in methanol; in the former, first-order analysis of the decay traces leads to $\tau = 225$ ns. In this case, the triplet state must be very short lived, since we could not detect any diene-quenchable species.

In order to test for possible homolytic C–Cl bond cleavage, we carried out detailed spectroscopic studies in benzene. We anticipated that if chlorine atom elimination took place, we would be able to detect the chlorine–benzene π-complex, which has λ_{max} 490 nm.[19] No evidence for this intermediate could be obtained in spite of the fact that its detection is straightforward in the photolysis of α-chloroacetophenone. We therefore conclude that chlorine atom elimination is not an important triplet decay pathway in the photochemistry of I. The same conclusion was obtained in the cases of II and III.

In benzene solvent we also observed an absorption at 325 nm with a lifetime ca. 500 ns that we could not assign. This species is not quenched by oxygen or 1,3-cyclohexadiene and thus cannot be assigned to a triplet state.

The enol IV is readily quenched by sodium hydroxide (up to 0.55 mM) in methanol with a rate constant of 1×10^8 M^{-1} s^{-1}. At higher concentrations of base there is a considerable curvature in the quenching plot, which leads to an increase in the observed quenching rate constant, i.e. $k_q = 1 \times 10^9$ M^{-1} s^{-1} (see Figure 2).

Two-Laser Two-Color Experiments. The enol IV is readily photobleached by excitation of this transient species with the pulses

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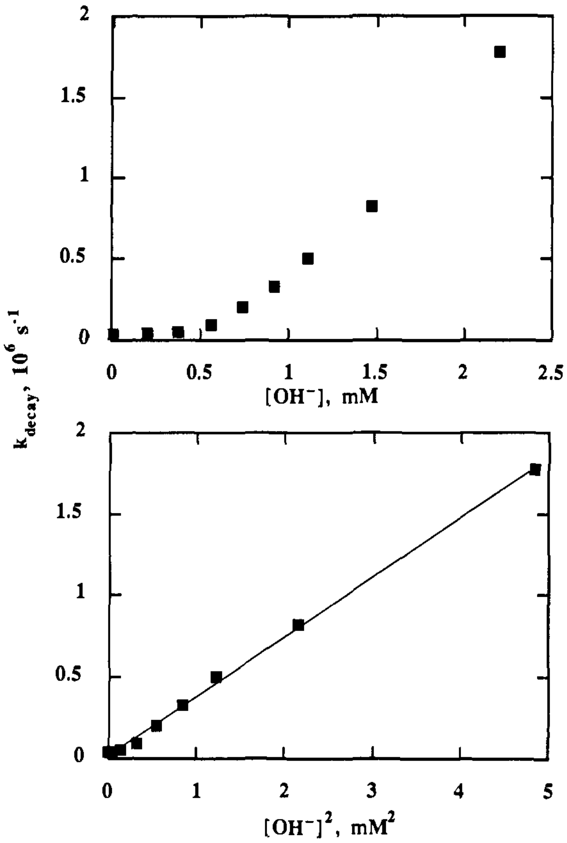


Figure 2. Quenching of *E* phototenol derived from α-chloro-2′,5′-dimethylacetophenone by sodium hydroxide in methanol (top) and quadratic plot of the same data (bottom).

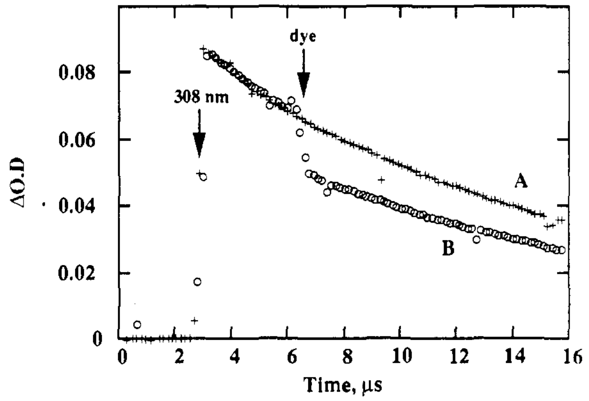
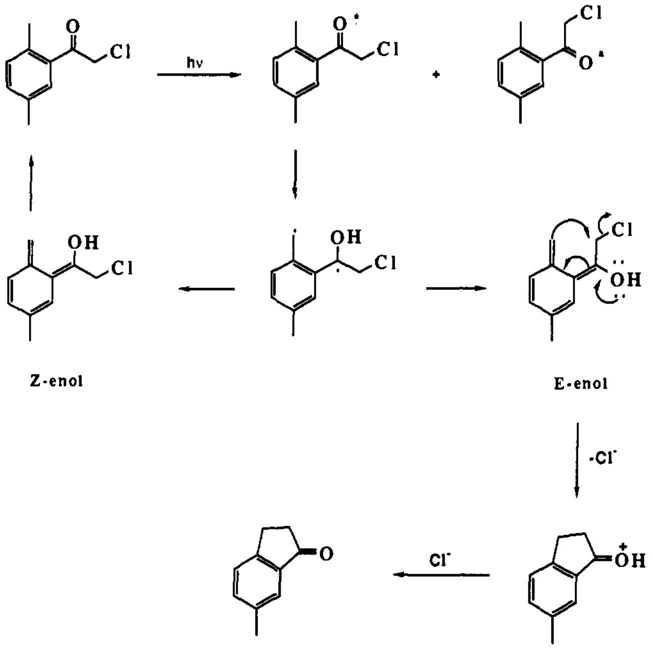


Figure 3. Decay of transients produced from α-chloro-2′,5′-dimethylacetophenone in methanol, monitored at 380 nm for 308-nm excitation (trace A) and 308-nm excitation followed by a 420-nm laser pulse (trace B).

from a dye laser tuned at 420 nm (Figure 3). Product studies in static samples under conditions of two-laser excitation and at conversions ≤5% reveal a *decrease* of about 25% in the indanone yield, which is not accompanied by the formation of any new products. These results are fully consistent (vide infra) with a mechanism involving two enols that do not interconvert thermally, only one of which is responsible for product formation. While there was some indication of enhanced reactant recovery under conditions of two-laser excitation, the low conversion in these experiments prevented a truly quantitative evaluation of changes in reactant consumption. Thus, dye laser excitation promotes the isomerization of the product-forming enol to the unreactive isomer.

Scheme II



Discussion

In laser flash photolysis work it is frequently a safe assumption that the reaction intermediates observed in photoreactions with high quantum yields are part of the product-forming reaction steps. This is clearly not the case in the systems studied herein, in spite of reported quantum yields in methanol of 0.42 and 0.76 for I and II, respectively. Thus, Bergmark[15,16] reports triplet lifetimes of <1 ns on the basis of product-quenching studies, while our own work reveals triplet states with lifetimes around 250 ns in methanol. The laser photolysis experiments show unequivocally that quenching of this "detectable" triplet does not lead to any reduction in the yield of photoenol.

We suggest that the detectable triplet is the anti isomer which is very slow in its interconversion to the enol-forming syn conformer. On the other hand, the syn isomer reacts rapidly leading to two photoenols, only one of which is detectable. Thus, while laser studies lead to the detection of the anti triplet, this species is not a major player in product (or enol) formation. The involvement of two distinct triplets in the photoenolization of *o*-methylacetophenone and related derivatives is in fact well established.[5]

Clearly bond rotation in the triplet state of I must take at least 250 ns, compared with ca. 34 ns in the case of *o*-methylacetophenone.[20] The steric bulk due to the chlorine atom obviously slows down bond rotation, but in addition it probably favors the *syn* conformer in terms of its relative abundance. The fate of the anti triplet is not obvious from our data. We assume that it decays by a competition of anti–syn interconversion (a common process in photoenolizable ketones),[4-6] radiationless decay, and probably some minor degree of C–Cl bond cleavage. The relative partition between these paths cannot be obtained from our data.

The predominant enol-forming triplet is not detectable with nanosecond techniques. Our failure to detect the syn triplet, or to reduce the yield of photoenol by addition of typical triplet quenchers, is fully consistent with Bergmark's estimate of lifetimes of ≤1 ns. Further, we suggest that the syn conformer probably accounts for >80% of the initially formed triplets, so that the fate of the minor anti triplet has little or no effect on the product yields, and that quantum yields as high as 0.76 (for II in methanol) can be achieved.

Decay of the syn triplet presumably leads to a 1,4-biradical, which is the same species as the triplet state of the photoenols. We have failed to detect this biradical and/or any delayed formation of the photoenol IV. This requires biradical VII to have a very short lifetime, ≤20 ns.

This is a remarkably short lifetime for a photoenol biradical in a polar solvent.[6,9,20] For example, for *o*-methylacetophenone

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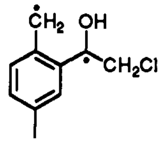
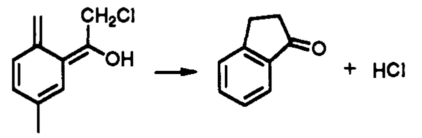


VII

(see Scheme I), the lifetime is 580 ns in acetonitrile/water. Unfortunately, there are no other examples in the literature involving halogen effects on excited photoenol lifetimes, and while it is not unusual for halogen atoms to assist intersystem crossing, the magnitude of the effect is rather surprising for chlorine.

Similar kinetic arguments can be applied to the *Z* photoenol, i.e. its lifetime must be ≤20 ns, again rather short for a species of this type in a polar, hydrogen-bonding solvent. The effect is perhaps easier to understand here, since chlorine substitution will make the OH group more acidic, thus favoring rapid reketonization. Thus, we expect the *Z* photoenol to contribute to the inefficiency of the photoreaction through its rapid reketonization.

The analysis above leaves the *E* photoenol, derived from the "undetected" syn triplet state, as the species responsible for indanone formation. This is illustrated in Scheme II. In methanol solvent, the indanone-forming step, reaction 2 has a rate constant of ca. 5×10^4 s^{-1}.



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VI

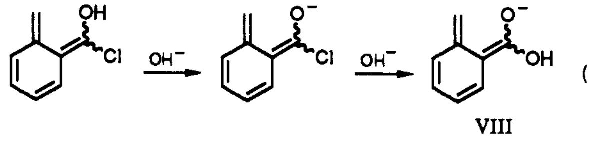
Interestingly, reaction 2 could find technical applications as a "photoacid" precursor.

Further support for the proposed mechanism can be derived from the two-laser two-color experiments described in the Results section. Thus, photoexcitation of IV leads to a *decrease* in the indanone yield. We would expect that the principal reaction induced by dye laser excitation would be *E*→*Z* photoconversion, therefore transforming reactive *E* photoenols into the unreactive *Z* isomer. This photoreaction is likely to take place from the excited singlet surface, since polyenes frequently show low intersystem crossing yields. Interestingly, one could suggest that products arise from the *Z* enol, with the *E* enol being too short for detection with our instrumentation; however, if this was the case, two-color irradiation should lead to an increase in product yield. Clearly this would be contrary to the experimental observations.

An early communication by Bergmark[15] indicated that α-bromo-*o*-methylacetophenone does not undergo a reaction similar to the chloro compound, but rather it gives *o*-methylacetophenone in high yield. This can be readily interpreted by comparison with our study of the photochemistry of α-bromoacetophenone.[19] We found that photolysis of this compound leads to bromine atom loss through an unquenchable excited state (probably triplet). Clearly in α-bromo-*o*-methylacetophenone hydrogen abstraction leading to photoenolization does not compete with its exceptionally facile bromine loss. In contrast, in the case of α-chloroacetophenone, halogen loss is considerably slower and proceeds through a quenchable (and detectable) triplet state.

When the reaction is carried out in benzene, the quantum yield is much smaller than in methanol,[16] and the detectable enol is shorter lived. Clearly, indanone formation does not compete well with the rapid decay of the enol in nonpolar solvents. While this qualitative analysis of the data is straightforward, a more detailed analysis of the results shows some inconsistencies. Thus, in benzene the rate constant for reaction 2 must be close to 10^6 s^{-1}. That is, in fact, faster than in methanol. This suggests that a simple interpretation in terms of a stepwise, initial loss of chloride cannot be correct, or at least that an alternate mechanism must be feasible in nonpolar media. Our data do not allow us to decide whether a concerted mechanism is possible, except to point out that such an alternative would be favored when the O–H bond is not engaged in hydrogen-bonding interactions.

The effect of base, illustrated in Figure 2, is unusual and perhaps related to the mechanistic questions raised above. Low, submillimolar concentrations of base lead to modest photoenol quenching with rates comparable to those observed in other systems (e.g. *o*-benzylbenzophenone).[21] Addition of higher concentrations of base, in the 1–3 mM range for sodium hydroxide, leads to a much more rapid effect, which now leads to a rate constant of 1×10^9 M^{-1} s^{-1}. The intercept of this segment of the quenching plot is negative, thus suggesting that this is not a reaction of the enol itself, but rather of a species formed in the low-concentration regime. The obvious candidate is of course the enolate. Alternatively, these data can be explained assuming a quadratic dependence of quenching rate constants on base concentration (Figure 2, $r^2 = 0.998$). This implies that the sole reaction involved in this process is the S_N2 type reaction from the enolate (reaction 3). However, product studies suggest that quenching of the enol by base does not prevent it from yielding indanone. Thus, while an S_N2 reaction at the chlorine atom may be partially responsible for the high concentration quenching, indanone formation must remain a major pathway (reaction 4).



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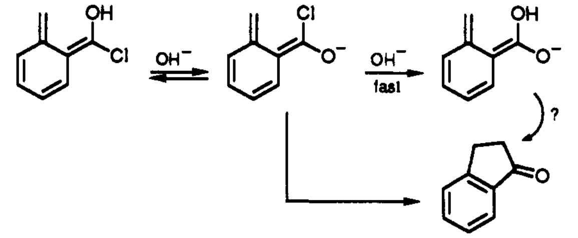
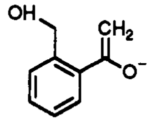
VIII



(4)

While we have interpreted our results on the basis of the intermediacy of VIII, it is clear that our proposal is speculative. Alternatively one could propose the involvement of IX (via allylic attack) to yield the same products.[22]



IX

In conclusion, photolysis of I and its analogues (II and III) leads to the efficient formation of substituted indanones, as observed before by Bergmark;[16] the triplet state detected by laser flash photolysis (τ ~250 ns) is not responsible for product formation. These indanones result from the shorter lived (<1 ns) syn triplet. Of the two possible photoenols, only the *E* isomer leads to product formation. The *Z* enol has not been detected and is believed to undergo rapid reketonization. The observation by Bergmark[16] of lower yields in benzene, as compared with methanol, is consistent with the dramatic shortening of the *E* enol lifetime in the former. Two-laser two-color experiments involving photoexcitation of the enol lead to a decrease in the yield of cyclization, which is interpreted in terms of *E*→*Z* photoisomerization.

Acknowledgment. Thanks are due to Mr. S. E. Sugamori and G. Charette for technical assistance.

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[21] *o*-Benzylbenzophenone in 1,1,1-trifluoroethanol can be quenched by bases with quenching rate constants ranging from 3.0×10^6 to 4.3×10^8 M^{-1} s^{-1}: Wintgens, V.; Netto-Ferreira, J. C.; Scaiano, J. C. Unpublished work.

[22] We are grateful to one of the referees for suggestions on this matter.