J. Am. Chem. Soc. **1993,** *115,* 3105–3110

Photochemistry of α-(*o*-Tolyl)acetone and Some Derivatives: Triplet α-Cleavage and Singlet δ-Hydrogen Abstraction

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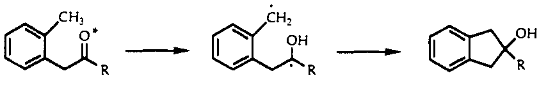
Received July 24, 1992

Abstract: Photolysis of α-(*o*-tolyl)acetone (TA) in 2-propanol was reported not to produce the indanol product expected from δ-hydrogen abstraction and cyclization of the resulting 1,5-biradical. A reinvestigation of this reaction reveals that the photolysis of solutions of TA does produce an indanol, albeit as a minor product. Similarly, photolysis of benzene solutions of *o*-tolylmethyl benzyl ketone (TBK) and *o*-tolylmethyl cyclohexyl ketone (TCK) results in the formation of indanols as minor products (ca. 5–10%). However, the photolysis of mesitylmethyl benzyl ketone (MBK) yields an indanol in significant yield (ca. 40%). In all cases, the diphenylethanes (DPEs) expected from free-radical recombination of benzylic radicals produced by α-cleavage are produced as dominant products. In order to determine the synthetic limitations of indanol formation from the photolysis of α-(*o*-tolyl)acetones, the mechanism of these photolyses was investigated. Sensitization with triplet acetone generated from the thermolysis of tetramethyl-1,2-dioxetane at 70 °C, quenching of the disappearance of ketone by isoprene, and isoprene quenching of the formation of indanol and fluorescence demonstrate that α-cleavage occurs dominantly from the triplet state and that δ-hydrogen abstraction occurs exclusively from the singlet state. Rates of quenching of acetone phosphorescence by dibenzyl ketone (DBK) and TBK in acetonitrile are found to be about 1 order of magnitude less than the rate of diffusion control. The yield of indanol can be enhanced by the introduction of methyl groups to the aryl ring, an increase in the reaction temperature, the addition of a triplet quencher to the reaction mixture, and, as previously reported, the use of microheterogeneous media. The quantum yield measurements for product formation show that the efficiency of α-cleavage drops by half from DBK to TBK and by a factor of 3 from TBK to MBK. We interpret this inefficiency to result from a radiationless deactivation of the singlet state which occurs when the *o*-tolyl group is attached to the α-position of a dialkyl ketone and this radiationless transition is induced by an incipient but incomplete δ-hydrogen abstraction, as previously proposed for γ-hydrogen abstraction.

Introduction

Photochemically induced 1,6-hydrogen abstraction (δ-hydrogen abstraction) of *o-tert*-butylbenzophenones and of α-(*o*-tolyl)acetophenones and the subsequent cyclization of the 1,5-biradical thus formed can be a key step in the syntheses of indanols and has provided a rich field for mechanistic and theoretical analysis of biradical intermediates.[1,2] Investigations of the photochemistry of *o-tert*-butylbenzophenones and of α-(*o*-tolyl)acetophenones[1–3] have provided definitive evidence that *triplet* 1,5-biradicals are key intermediates in indanol formation and that conformational factors are critical to the rate and efficiency of the formation and then cyclization of the 1,5-biradical.

In contrast to the wealth of information on the photochemically induced δ-hydrogen abstraction reaction of *o-tert*-butylbenzophenones and of α-(*o*-tolyl)acetophenones, reports on the analogous reactions of α-(*o*-tolyl)acetones (eq 1) are scarce. We are aware of only one report[4] dealing with the photochemistry of α-(*o*-tolyl)acetone in 2-propanol in which the authors were able to isolate products of α-cleavage (1,2-di(*o*-tolyl)ethane) and a pinacol, but the indanol product (In) expected from δ-hydrogen abstraction (eq 1) was not detected by gas chromatographic analysis. This putative result is both unfortunate and challenging. It is unfortunate because, although several excellent examples of the use of δ-hydrogen abstraction followed by cyclization in synthesis involving dialkyl ketones have been reported,[5–8] evidently the factors determining the scope of this reaction may be limited; it is challenging because an understanding of the mechanistic details of the reaction may provide insights which remove these synthetic limitations by appropriate manipulation of reaction conditions and ketone structure. Indeed, an unpublished result mentioned in a more recent report indicates that irradiation of α-(*o*-tolyl)acetone in surfactant solution leads to an indanol.[9] This unpublished result is consistent with our own recent report that an indanol is a minor product of the photochemistry of *o*-tolylmethyl benzyl ketone (TBK) and that the yield of the indanol is a function of the environment, increasing from ca. 6% in benzene to 20–25% in various microheterogeneous media.[10] The enhancement of indanol formation in solid-state photolysis when there is a competition between hydrogen abstraction and α-cleavage at the triplet state was also reported.[3b]



(1)

(R = Alkyl) B (1,5-Biradical) In (2-Indanol)

Thus, this recent evidence shows that photocyclization of α-(*o*-tolyl)acetones to indanols is not only possible but may be manipulated by varying the reaction conditions. In order to determine the potential use of α-(*o*-tolyl)acetones in the synthesis of indanols expected from δ-hydrogen atom abstraction and to elucidate the mechanistic aspects of the photochemistry of α-(*o*-tolyl)acetones (see Scheme I for structures of the substrate

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Scheme I. Photolysis of Several Ketones

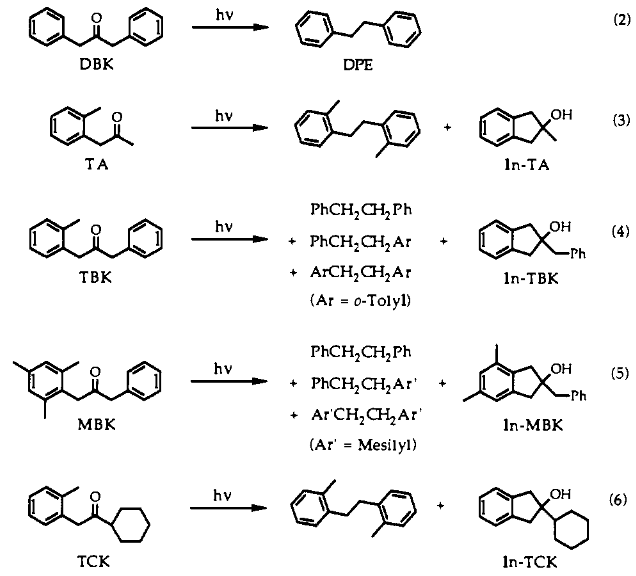

Table I. Chemical Yields of DPEs and Indanols from Various Photolysis Conditions in Organic Solvents[a]

ketone	conditions	DPEs (%)	indanol (%)
DBK	hν(313), *b*	98 ± 3	0
TBK	hν(313), *b*	81 ± 4	6 ± 1
TBK	hν(313), 72 °C	78 ± 3	10 ± 1
TBK	TMD, 72 °C	100 ± 5	0
MBK	hν(313), *b*	51 ± 3	39 ± 2
MBK	hν(313), 70 °C	48 ± 4	47 ± 3
MBK	TMD, 70 °C	94 ± 4	0
TCK	hν(313), *b*	24 ± 2[c]	4 ± 1
TA	hν(313) *b*	23 ± 2[c]	4 ± 1
TA	hν(313), *b*, 2-propanol	16 ± 2[c]	5 ± 1

[a] The solvent is benzene unless specified. [b] Room temperature. [c] Mass balance is less than 50%. Number is from 1,2-di(*o*-tolyl)ethane, see text.

investigated), we have examined the photochemistry of α-(*o*-tolyl)acetone (TA), *o*-tolylmethyl benzyl ketone (TBK), mesitylmethyl benzyl ketone (MBK), and *o*-tolylmethyl cyclohexyl ketone (TCK). In this investigation, we compare the photochemistry of these four ketones to that of dibenzyl ketone (DBK). In particular, we have determined (1) the products of the reaction and their variation with reaction conditions and the structure of the starting ketone, (2) the quantum yields of reactions, and (3) the reactive excited state responsible for the observed products from the reaction quenching with isoprene and the reaction sensitization (triplet acetone produced through thermolysis of a dioxetane).

Results

Product Structures and Chemical Yields. The structures of the products (diphenylethanes and 2-indanols) produced by the photolysis (313 nm) of DBK, TA, TBK, MBK, and TCK at room temperature in benzene are shown in eqs 2–6 of Scheme I. The yields of products are given in Table I. The photochemistry of DBK has been thoroughly investigated,[11] and we use it here as a control. As reported previously,[11] 1,2-diphenylethane (DPE) is the only photoproduct detectable by GC analysis and is formed in nearly quantitative yield. For the photolysis of TBK and MBK, DPEs (1:2:1 statistical mixture of the three possible benzyl radical coupling products) are produced in addition to a low yield of the indanol expected from cyclization of the 1,5-biradical produced from δ-hydrogen abstraction of a benzylic hydrogen. Although the yield of indanol is low for TBK (ca. 6%), it is substantial for MBK (39%). In contrast to the literature report,[4] a low yield of indanol (4–5%) is produced in the photolysis of TA in both benzene and 2-propanol, although a poor mass balance, as reported,[4] was found. A poor mass balance was also found for the case of TCK, as was a low yield (4%) of indanol.

Table II. Quantum Yields of the Formations of DPEs and Indanols in the Photolysis at 313 nm in Benzene

ketones	DPEs	indanol
DBK	0.84 ± 0.06	0
TBK	0.31 ± 0.02	0.023[a]
MBK	0.11 ± 0.01	0.083
TCK	0.029[b]	<0.005

[a] The quantum yield is experimentally indistinguishable in methanol or benzene as solvent. [b] Number is from 1,2-di(*o*-tolyl)ethane.

Quantum Yields of Products. Valerophenone (0.25 M) photolyzed in *tert*-butyl alcohol was used as an actinometer for quantum yield measurements (disappearance of valerophenone was observed and a quantum yield of 1.0 was assumed).[12] Conversions of ketones were kept under 20%. The quantum yields for product formation from the photolyses of DBK, TBK, MBK, and TCK are given in Table II. The quantum yield for disappearance of DBK is in reasonable agreement with values in the literature.[11,13] It is important to note that we monitor the absorption of the photolyzed solutions of DBK as a function of partial conversion and see no reduction in the optical density of the sample at the excitation wavelength (313 nm), indicating the formation of a species which adds to the optical density of the sample. This phenomenon has been observed previously[11,13] and is suggestive of the production of a light-absorbing species possessing a large extinction coefficient relative to DBK. Thus, we consider the measured quantum yield of 0.84 as a lower limit to the accurate value; however, we believe that the relative values of the quantum yields are reliable for comparison. A clear trend is noted for the effect of methylation of the α-phenyl group; the quantum yield for formation of DPEs decreases (from 0.84 to 0.11) with increasing methyl substitution. The quantum yield for the formation of 1,2-di(*o*-tolyl)ethane, the major product detected in the photolysis of TCK, is about 0.03. The efficiency of formation of free-radical coupling products is only about 0.12 if one assumes statistical distribution of the coupling products.

Quenching Experiments. Although isoprene is a quencher of triplet ketones,[14] this diene also quenches singlet ketones, though with a much diminished rate constant.[15] Under favorable conditions, both singlet and triplet ketone quenching by isoprene can be investigated. Stern–Volmer quenching of fluorescence, the disappearance of the starting ketone, and the appearance of indanol for TBK were all measured with isoprene as quencher. Stern–Volmer quenching of the disappearance of DBK was measured as a control, and the results agree with the literature data.[11] Measured Stern–Volmer constants for the disappearance of TBK and fluorescence quenching by isoprene are 0.47 ± 0.03 M^{-1} and 0.035 ± 0.001 M^{-1}, respectively. Stern–Volmer quenching for the formation of indanol is identical, within the experimental error, to that for fluorescence quenching. For both TBK and MBK, the yields of indanols increase relative to the yield of DPEs as the quencher concentration is increased. For example, in the photolysis of TBK in the presence of 1.5 M isoprene, the yield of 2-benzyl-2-indanol (In-TBK, Scheme I) is increased from 6% to 9% at 20% chemical conversion, which represents a 50% increase in the yield of indanol. In the photolysis of MBK, the yield of In-MBK increases from 39% to 73% with

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Table III. Quenching Parameters for Triplet–Triplet Energy Transfer from Triplet Acetone in Acetonitrile

quenchers	$k_q\tau$ (M^{-1})	τ (μs)	k_q (M^{-1} s^{-1})
acetone[a]			1×10^6
DBK	1425	13.5	1.1×10^8
TBK	2217	13.5	1.6×10^8
biacetyl[b]			5.0×10^9

[a] Taken from ref 19. [b] Taken from ref 18.

1.5 M isoprene and to 87% with 3 M isoprene, representing better than a 100% increase in the yield of indanol.

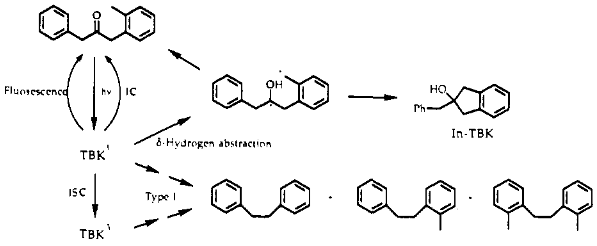
Thermal Sensitization Experiments with Tetramethyl-1,2-dioxetane. Thermolysis of TMD produces acetone triplets selectively (triplet to singlet acetone ca. 50:1[16,17]). The photochemistry of TBK and MBK was sensitized by triplet acetone formed by the thermolysis of tetramethyl-1,2-dioxetane (TMD).[16] Since the thermolysis of TMD occurs at a convenient rate at 70 °C, the photochemical reactions of TBK and MBK were repeated at this temperature in order to make a meaningful comparison between the photochemical results and the sensitized thermolysis. The results are summarized in Table I. The striking result is that the dioxetane sensitization produces only diphenylethane products for both TBK and MBK, i.e., *the indanol products are absent in the triplet acetone sensitization experiment.* The distribution of DPEs is in the same statistical ratio as the photolysis at the same temperature, and the indanol product is completely absent (<0.1%) by GC analysis. A control experiment demonstrates that In-TBK (Scheme I) from TBK is stable to the thermolysis conditions in the presence of dioxetane. Thus, the absence of the indanol cannot be ascribed to its formation and subsequent destruction by the thermolysis conditions.

Quenching Parameters in the Sensitization Experiments. In order to establish that the rate constants for energy transfer from triplet acetone, produced by thermolysis of TMD, are of a reasonable value to be consistent with the sensitization experiments, we measured the rate constants for energy transfer from acetone to DBK and to TBK in acetonitrile solvent (selected for comparison with the literature[18,19]). The phosphorescence of acetone produced by dioxetane thermolysis was monitored at room temperature, and Stern–Volmer quenching experiments with DBK and TBK as quenchers were performed. The results are summarized in Table III. The lifetime of acetone phosphorescence in acetonitrile at room temperature was measured by the laser flash photolysis technique, and the reported rate constants were computed on the basis of this lifetime (13.5 μs). The rate constants are about 1 order of magnitude less than the diffusion controlled rate constant[18] but 2 orders of magnitude greater than the rate constant for "self-transfer" between acetone triplets and the acetone ground state.[19]

Discussion

The concerns of this investigation are both synthetic and mechanistic. At the synthetic level, we address the relationship of the structure (compositional and conformational) of α-(o-tolyl)acetone and its derivatives to the yield of indanol products, as well as the possible means available to manipulate ketone structure or reaction conditions to enhance the yield of indanol. At the mechanistic level, we identify the excited state responsible for indanol formation, the characteristics of formation and reaction of the putative 1,5-biradical precursor to the indanol, and the role of conformational factors and environmental factors in determining the overall efficiency and chemical yield of indanol formation.

Scheme II. Mechanistic Description of the Photolysis of TBK



At the synthetic level, it is clear that DPEs produced from α-cleavage of the ketone and subsequent coupling of the free radicals are the dominant products for TA, TCK, and TBK. Indanol formation is minor (<10%). However, for MBK, the yield of indanol is substantial (ca. 40%). Good mass balances are achieved for TBK and MBK. For these ketones the primary geminate benzyl–acyl radical pairs undergo rapid formation of free radicals, and the acyl radical efficiently decarbonylates to produce a second benzyl radical. For TA and TCK, which produce acyl radicals that undergo relatively slow decarbonylation, other still unidentified products are produced.

Strategies to improve the chemical yields of indanol can be rationally designed if key mechanistic factors and competing reactions are elucidated. In order to examine these factors the accepted mechanism for the photochemistry of dialkyl ketones,[20] with TBK as a concrete exemplar, will be considered as a working paradigm (Scheme II).

The first question to be addressed is the identification of the states (S_1 or T_1) responsible for the primary photochemical processes of α-cleavage and δ-hydrogen abstraction. Are the photochemical processes selective or competitive for each excited state? The answer to this question is important because, if *both* α-cleavage, which leads to DPEs, and δ-hydrogen abstraction, which leads to indanols, proceed from the *same* excited state, then conformation, temperature, and environment are the main variables for manipulating the product ratio.

On the other hand, if *both* primary photochemical processes occur from *different* excited states, then the possibility of specific sensitization or quenching is also available to manipulate product selectivity. For example, if α-cleavage occurs from T_1 and δ-hydrogen abstraction occurs from S_1, then specific triplet quenching could lead to selective formation of the indanol.

Experimentally, the formation of indanol in the photolysis of TBK is weakly quenched by isoprene ($K_{SV} < 0.1$ M^{-1}), whereas the disappearance of the ketone is strongly quenched by isoprene (K_{SV} ca. 0.5 M^{-1}),[21] and sensitization by dioxetane does not lead to the formation of measurable amounts of indanol (Table I) but results in the formation of DPEs. Thus, *both the quenching results and the dioxetane sensitization results are consistent with the postulate that T_1 does not lead to significant amounts of indanol, i.e., δ-hydrogen abstraction occurs exclusively, within the experimental error, from S_1.* We note that the results concerning the possible participation of S_1 in the α-cleavage are not definitive in a quantitative sense but are consistent with the dominating source of DPEs being T_1, i.e., the disappearance of the starting material and the appearance of DPEs is strongly quenched by isoprene. Nevertheless, on the whole, our results are broadly consistent with δ-hydrogen abstraction from S_1 and α-cleavage from T_1. A quantitative investigation of the extent of singlet

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participation in α-cleavage of DBK is the subject of a separate publication.[21]

Is it reasonable, based on literature precedent, that such selectivity should occur? It has been established that the rate constant for α-cleavage of dialkyl ketones is often 2 orders of magnitude faster from T_1 than S_1.[22] Thus, there is ample precedent for high selectivity of α-cleavage in T_1 relative to S_1. However, in the case of δ-hydrogen abstraction, the situation is more complex and more intriguing. Dialkyl ketones are known to undergo γ-hydrogen abstraction in *both* T_1 and S_1.[23,24] Although studies of comparative processes are relatively few in number, in some cases the rate of γ-hydrogen abstraction from S_1 is much higher than from T_1. For *tert*-butyl alkyl ketones it was found that γ-hydrogen abstraction arises predominantly from a singlet excited state.[25] A more rapid rate for hydrogen abstraction from the singlet state may be rationalized on the basis of the higher energy of S_1 and appear to the common relationship between rate and exothermicity in radical reactions.[1] We conclude that the combination of an inherently slower rate of α-cleavage in S_1 and an inherently faster rate of δ-hydrogen abstraction in S_1 leads to the selectivity observed for TBK.

Although singlet selectivity is qualitatively reasonable, is the rate constant for δ-hydrogen abstraction of the correct quantitative order to be competitive with other modes of deactivation of singlet states of dialkyl ketones? The singlet decay of DBK has been experimentally measured[26] to be ca. 5×10^8 s^{-1}, so the rate of singlet state δ-hydrogen abstraction must be of this magnitude or greater. Perhaps the closest literature analogue available is δ-hydrogen abstraction for α-(*o*-tolyl)acetophenone, for which the rate of the triplet hydrogen abstraction reaction is estimated[3] to be 1.6×10^8 s^{-1}. Since for triplet 2-pentanone k_γ is 0.16×10^8 s^{-1} and for singlet 2-pentanone k_γ is 1.8×10^8 s^{-1},[23d,24c] we can estimate a rate for singlet hydrogen abstraction given a rate for the triplet decay. By applying this factor to the rate constant for triplet δ-hydrogen abstraction for α-(*o*-tolyl)acetophenone, we estimate the rate constant of δ-hydrogen abstraction, k_δ, of a singlet aliphatic ketone, such as TBK, to be ca. 2×10^9 s^{-1}. This value is 4 times larger than the measured rate of deactivation of a DBK singlet (ca. 5×10^8 s^{-1})[26] and is, therefore, of the correct order to compete with intersystem crossing but not so fast as to completely dominate singlet deactivation, i.e., some intersystem crossing to produce a triplet that undergoes α-cleavage is expected.

We can also obtain an estimation of the rate constant for α-cleavage of the singlet state of DBK and TBK from literature data. The rate of the disappearance of triplet DBK has been estimated to be ca. 10^{10} s^{-1}.[11] Since the major pathway for this disappearance is α-cleavage, the rate of triplet α-cleavage is also ca. 10^{10} s^{-1}. From the ratio of the rates of α-cleavage of triplet (ca. 8×10^9 s^{-1}) and singlet (ca. 6×10^7 s^{-1}) di-*tert*-butyl ketone,[22] the rate of α-cleavage from singlet DBK is estimated to be ca. 10^8 s^{-1}. This value is of the order of or slightly smaller than the measured value (ca. 5×10^8 s^{-1})[26] for deactivation of singlet DBK and is consistent with the conclusion that α-cleavage cannot be a major mechanism for deactivation of singlet DBK. The additional *o*-methyl group in TBK is expected to increase the rate of α-cleavage by perhaps a factor of only about 1.5 (deduced from CIDNP experiments[21,27]), so the estimated rate of α-cleavage of TBK is still too slow to be a dominant path for deactivation of the singlet.

In summary, we estimate the rate of α-cleavage of singlet TBK to be ca. 10^8 s^{-1} and the rate of δ-hydrogen abstraction of TBK to be ca. 2×10^9 s^{-1}. Therefore, the conclusions that selective δ-hydrogen abstraction occurs in the singlet state and that selective α-cleavage occurs in the triplet state of TBK are without contradiction based on literature estimations. Furthermore, enhancing the reactivity toward δ-hydrogen abstraction by structural variations such as adding a second *o*-methyl group (MBK) could begin to make this singlet process a dominant mechanism. This expectation is confirmed by the observation of a low absolute quantum yield for the formation of DPEs for MBK (Table II).

We now take the issue of an excited-state precursor of the products as settled and consider briefly some further mechanistic and synthetic aspects of the results, particularly the effects of temperature, quenching, conformation, and environment on the chemical yield of indanol.

In Table I we note a temperature dependence on the relative yield of indanol, which is favored at the higher temperature. However, although increasing temperature provides a slight synthetic improvement for indanol formation, its mechanistic aspects are difficult to assess, since temperature can influence populations of conformers, efficiencies of biradical formation, and efficiencies of reactions of the biradical.[1]

In Table II, we note that the quantum yields for reaction of the three dibenzyl ketone derivatives are strongly dependent on ketone structure. In particular, quantum yields clearly decrease as the number of methyl groups associated with the ketone increases. Since the mass balances are excellent for each of these cases, there must be some increasing source of reaction inefficiency which develops with increasing methyl substitution at the ortho position. Since the main course of reaction for DBK is very efficient α-cleavage and product formation from T_1 and since the rate constant for α-cleavage is extremely high (ca. 10^{10} s^{-1}), we do not believe that the source of inefficiency which results from methyl substitution can originate in T_1. This means that the inefficiency must result from (1) a radiationless process from S_1, (2) enhanced photoreactivity to form a singlet 1,5-biradical with return of the singlet biradical to the starting ketone as the result of methyl substitution, or (3) reversible α-cleavage of a singlet radical pair. For the first possibility (1), of the two unimolecular radiationless processes available to S_1, internal conversion and intersystem crossing, we reject the latter as being the significant cause of the inefficiency, because increased formation of T_1, as discussed above, is not expected to decrease the quantum yield for product formation and would be expected to increase the relative yield of DPE, in contrast to the observations. This leaves internal conversion and reformation of starting material from the singlet radical pair (α-cleavage) or singlet biradical (δ-hydrogen abstraction) as the viable possibilities for the sources of inefficiency.

First, let us consider the possibility that reversible formation of a singlet radical pair may be the source of the reaction inefficiency. The quantum yield of DPE formation drops by a factor of 3 from DBK to TBK. Even if we assume that α-cleavage occurs exclusively from the singlet state and that the cage effect of singlet radical pair is 50%, this result would mean that the rate of singlet α-cleavage by methylation should be increased by a factor of 6. This possibility is unlikely since a methyl group is expected to increase the rate of α-cleavage by less than 2, as deduced from the relative intensities of geminate recombination products in CIDNP experiments.[21,27] The absence of any significant reversible formation of a singlet radical pair is also

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supported by the observation that less than 1% photostereoisomerization occurs in the photolysis of 2,4-diphenylpentan-3-one.[28] A significant cage effect from the singlet would be expected to produce a much greater extent of photostereoisomerization.

If internal conversion is the source of the inefficiency, then the addition of methyl groups must introduce a mechanism for going from S_1 to S_0. It is conceivable and there is precedence[1-3,29] for charge-transfer interactions being "turned on" by the substitution of a methyl group in an aromatic ring. However, in order to decrease the product formation quantum yield over that of DBK by a factor of 3 (the case for TBK), the new mechanism must have increased the rate of internal conversion by over 1 order of magnitude. Substitution effects on ISC from triplet ring-substituted β-phenylpropiophenones by laser flash photolysis and quenching with 1-methylnaphthalene have been studied.[29] *o*-Methylation of β-phenylpropiophenone increases the triplet lifetime by only 23%. While we cannot reject the charge-transfer possibility completely, it seems unlikely that methyl substitution could cause a large enough rate enhancement to result in competitive deactivation of the singlet.

The act of hydrogen abstraction may produce a surface crossing along the singlet reaction surface that serves as a special, "chemically assisted" internal conversion.[23,24,30,31] This type of inefficiency is well documented and accepted in the case of singlet 1,4-biradicals from the experimental results of Wagner and Yang on the Norrish type II reaction[23,24b] and from the theoretical models of Salem and Michl.[30] Based on these pioneering efforts, we interpret the increased inefficiency observed from the introduction of an *o*-methyl group to DBK as resulting from a δ-hydrogen-excited carbonyl interaction which either enhances internal conversion or leads to formation of a singlet 1,5-biradical which efficiently disproportionates to the starting ketone. Since the analogous *triplet* 1,5-biradical produced from α-(*o*-tolyl)-acetophenone cyclizes *efficiently* to an indanol, it is difficult to understand why the *singlet* 1,5-biradical produced from TBK would not cyclize efficiently. This result argues against a singlet 1,5-biradical which efficiently disproportionates to the starting ketone as a source of inefficiency. In addition, we find that the quantum yield for indanol formation is the same in benzene and in methanol (Table II), a result consistent with efficient cyclization of any intermediate biradical.

The conformational factors involved in the δ-hydrogen abstraction of α-(*o*-tolyl)acetones are expected to be similar to those for α-(*o*-tolyl)acetophenones since the yields of indanols are quite similar for TA, TBK, and TCK, suggesting little impact of the R group (eq 1) on conformational properties. Since the situation for α-(*o*-tolyl)acetophenone has been extensively discussed,[2,3b] we shall only briefly summarize the conclusions for this ketone and assume that they pertain to the systems investigated here.

In the case of α-mesitylacetophenone, both the additional inductive effect of the methyl groups and a more favorable conformational factor increase the efficiency of triplet hydrogen abstraction relative to α-(*o*-tolyl)acetophenone.[3] However, α-mesitylacetophenone shows less efficient cyclization of the *triplet* 1,5-biradical produced by photolysis than that found for α-(*o*-tolyl)acetophenone due to a charge-transfer quenching process which competes with the δ-hydrogen abstraction. (Recall that the triplet hydrogen abstracts much slower than the singlet and, therefore, is likely to be in competition with other modes of triplet deactivation.[3]) Significantly, the quantum yield of indanol from MBK relative to that for TBK *increased* by a factor of 3.5, which indicates the absence of any significant charge-transfer quenching process from *singlet* 1,5-biradical, as concluded above.

The fact that δ-hydrogen abstraction occurs from the singlet state of α-(*o*-tolyl)acetones and that conformational factors can enhance the chemical yield of indanol product allows us to postulate that a combination of environmental effects to enhance the population of conformations which are favorable for δ-hydrogen abstraction and of quenching the triplet which provided an irreversible route for α-cleavage products is an excellent strategy for enhancing the yield of indanols. Indeed, the photolysis of TBK in micellar solution results in a significantly higher chemical yield of indanol, possibly through the influence of solubilization in micelles on the conformation of TBK and through the enhanced cage effect of the primary pair due to the containment of the pair in a micellar supercage.[9,10] For example, in the case of TBK the yield of indanol is increased by ca. 300% in going from homogeneous solution (6–9%) to micellar solution (22%).[10]

The use of the mechanistic conclusion that indanol formation occurs exclusively from the singlet state suggests that the use of a specific triplet quencher should enhance the indanol yield. Indeed, in the case of MBK the yield of indanol is increased by >100% in going from a system without isoprene quencher (39%) to one with 3.0 M isoprene (87%).

As a final issue we consider the quenching of triplet acetone by DBK and TBK. In Table III we note that triplet quenching rate constants by DBK and TBK are about 1 order of magnitude slower than diffusion control[18] and 2 orders faster than the self-quenching by acetone.[19] The triplet energy of DBK can be bracketed by acetone[11a,20] (78 kcal/mol) and xanthone (74 kcal/mol).[32] Engel has suggested the triplet energy to be about 1 kcal/mol less than that of acetone on the basis of quenching and sensitization experiments.[11] If the difference in triplet energies is this small, then one would predict a rapid and efficient back energy transfer, and the overall rate of quenching of triplet acetone by DBK and TBK would appear less efficient in a similar manner to "self-transfer" between acetone triplets and the acetone ground state.[20] If the acceptor, though, undergoes a rapid reaction from its triplet state, we will see little contribution from this back energy transfer.[33] From the efficient triplet energy transfer from acetone to DBK as observed in the quenching of chemically excited acetone phosphorescence by aryl alkyl ketone,[33a] we may deduce that α-cleavage from the triplet state of DBK is very rapid. We also note that the rate constant for quenching of acetone triplet by TBK is slightly higher than that for quenching of acetone triplet by DBK. Although the effect is small, it is consistent with a slightly lower triplet energy or a more efficient α-cleavage for the methyl-substituted ketone.

Conclusion

Photolysis of TA, TBK, and TCK results in the formation of indanols, although generally in low yield. However, a 39% yield of indanol was observed in the photolysis of MBK. Sensitization and quenching experiments demonstrate convincingly that the mechanism of indanol formation involves a δ-hydrogen abstraction in the singlet state of the ketone, and when intersystem crossing occurs, the triplet undergoes exclusive and irreversible α-cleavage to form DPEs. The yield of indanol formation can be increased substantially by methylation of the aryl ring and, to a modest extent, by increasing the reaction temperature. The quenching results of acetone phosphorescence by DBK and TBK show that the quenching rate is high compared to their triplet energies and that the quenching rate of TBK is a little higher than that of DBK. Quantum yields of DPE formation significantly drop from DBK to MBK, while that of indanol formation increases significantly, but the overall efficiency of product formation is

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low. This inefficiency is attributed to the enhancement of internal conversion by interactions of one of the benzylic hydrogens of the *o*-tolyl group and the carbonyl oxygen of the n,π* excited state. From the synthetic standpoint, the yield of indanol is increased significantly by photolysis in microheterogeneous media such as micelles and by selective quenching of the triplet state.

Experimental Section

Instruments. Gas chromatographic analyses were carried out on a Hewlett-Packard 5890 gas chromatograph with either a 25-m Carbowax or a SE-30 capillary column. UV and IR spectra were recorded on a Perkin-Elmer Lambda Array 3840 spectrometer and Perkin-Elmer 1800 FT infrared spectrophotometer, respectively. Fluorescence spectra were recorded on a Perkin-Elmer LS-5 spectrofluorometer. NMR spectra were recorded on a Bruker WM-250 MHz NMR spectrometer.

Materials. DBK (Aldrich) was purified by recrystallization from ethanol. TBK, MBK, TCK, and TA were prepared and purified following the inverse Grignard reaction and Grignard reaction described for *p*-methylbenzyl benzyl ketone.[34] All ketones used were over 99% pure by GC analysis. TBK: ^{1}H NMR ($CDCl_3$) δ 7.33–7.13 (9 H, m, aromatic H), 3.73 (2 H, s, $-CH_2-$), 3.70 (2 H, s, $-CH_2-$), 2.12 (3 H, s, $-CH_3$); IR (CCl_4) 3030, 1721, 1496, 1454, 1326 cm^{-1}; MS (EI$^+$) 224, 133, 119, 105 (100), 91, 77. MBK: ^{1}H NMR ($CDCl_3$) δ 7.32–7.15 (5 H, aromatic H), 6.84 (2 H, s, aromatic H), 3.75 (2 H, s, $-CH_2-$), 3.70 (2 H, s, $-CH_2-$), 2.25 (3 H, s, $-CH_3$), 2.07 (6 H, s, $-CH_3$); IR (CCl_4) 3031, 2920, 1721, 1641, 1552, 1454 cm^{-1}; MS (EI$^+$) 252, 160, 133 (100), 105, 91. TCK: bp 106–107 °C at 0.75 mmHg; ^{1}H NMR ($CDCl_3$) δ 7.18–7.07 (4 H, m, aromatic H), 3.75 (2 H, s, $-CH_2-$), 2.46 (1 H, m, -CH-), 2.21 (3 H, s, $-CH_3$), 1.24–1.87 (10 H, cyclohexyl); IR (CCl_4) 2931, 1706, 1494, 1320, 1144 cm^{-1}; MS (EI$^+$) 216, 111, 105, 83 (100), 77. TA: ^{1}H NMR (C_6D_6) δ 7.10–6.85 (4 H, m, aromatic H), 3.23 (2 H, s, $-CH_2-$), 2.03 (3 H, s, $-CH_3$), 1.64 (3 H, s, $-CH_3$); MS (EI$^+$) 148, 105(100), 91, 77. TMD was prepared according to Kopecky's methods[35] and purified by recrystallization from pentane at low temperature. Isoprene was obtained from Aldrich and distilled before use.

Photolysis and Analysis of Products. The concentrations of ketones in benzene were usually 0.10 M for quantum yield measurements and 0.025 M for quenching experiments with isoprene. The deoxygenated samples were irradiated through 0.002 M K_2CrO_4 in 1% aqueous K_2CO_3 with a 450-W Hanovia medium-pressure mercury lamp at room temperature (22–24 °C) or high temperature (70–72 °C). Samples were analyzed by GC. Hexadecane was used as an internal standard, and the integrated areas for the peaks were corrected by the appropriate response factors in the cases of DBK and TBK.

Spectroscopic data of photolysis products of TBK were reported elsewhere.[10]

2-Benzyldimethylindan-2-ol (In-MBK, Scheme I): ^{1}H NMR ($CDCl_3$) δ 7.29–7.19 (5 H, m, aromatic H), 6.80 (1 H, s, aromatic H), 6.76 (1 H, s, aromatic H), 3.12–2.68 (4 H, $-CH_2-$), 2.99 (2 H, s, $-CH_2$-Ph), 2.23 (3 H, s, $-CH_3$), 2.14 (3 H, s, $-CH_3$), 1.71 (1 H, br s, -OH); MS (EI$^+$) 252, 161 (100), 133, 105, 91. High-resolution mass spectra data: molecular formula, $C_{18}H_{20}O$, MW (calcd) 252.157, M$^+$ 252.151.

2-Cylochexyl-2-indanol (In-TCK): ^{1}H NMR ($CDCl_3$) δ 7.20 (4 H, m, aromatic H), 3.07 (2 H, d, $-CH_2-$), 2.88 (2 H, d, $-CH_2-$), 1.82–1.26 (12 H, cyclohexyl and -OH); MS (EI$^+$) 216, 133, 111, 105, 83 (100).

2-Methyl-2-indanol (In-TA): ^{1}H NMR (C_6D_6) δ 7.30–7.05 (4 H, m, aromatic H), 3.00 (4 H, dd, $-CH_2-$), 1.50 (3 H, s, $-CH_3$); MS (EI$^+$) 148, 133, 106, 105 (100), 91, 77. High-resolution mass spectra data: molecular formula, $C_{10}H_{12}O$, MW (calcd) 148.0942 M$^+$ 148.0883.

o-**Tolylcyclohexylmethane**: MS (EI$^+$) 188, 115, 106 (100), 91, 83.

Quantum yields were measured by comparison of actinometers. Valerophenone (0.25 M) in *tert*-butyl alcohol was used as actinometer.[12] The quantum yield for the disappearance of valerophenone was taken as 1.0. Conversions of ketones were kept under 20%. For quenching experiments, aerated solutions were used after confirming that the oxygen does not affect the quantum yield of the photolysis of DBK. For fluorescence quenching, the sample was irradiated at 320 nm, and the intensity of emission (410 nm) was corrected by the UV absorption at the excitation wavelength.

Sensitization of TBK and DBK with TMD. All glassware was washed with 1% aqueous ethylenediaminetetraacetic acid disodium salt (EDTA) and distilled water. A solution of TBK (0.10 M), TMD (0.19 M), and hexadecane in benzene was deoxygenated by six cycles of freeze–pump–thaw (0.003 mmHg) and heated at 72 °C for 5 h. The reaction mixture was analyzed by GC. 9.5% of TBK was consumed. DPEs were obtained quantitatively in 1:2:1 ratio.

Quenching Experiments of Acetone Phosphorescence by DBK and TBK. All glassware was washed with 1% aqueous EDTA and distilled water. A solution containing TMD (1.00×10^{-4} M) and DBK ($0-10 \times 10^{-4}$ M) was deoxygenated with argon bubbling at approximately −32 to −28 °C for 10 min. The emission intensity at 430 nm from triplet acetone at room temperature was measured with photomultiplier detector from Products for Research, Inc. and Ortec electronics. Concentrations of TBK used were from 0 to 12×10^{-4} M. The lifetime of triplet acetone in acetonitrile at room temperature after degassing was measured by a laser flash photolysis instrument. The triplet acetone was generated by photolysis at 308 nm with a Lamba Physik excimer laser (8 ns fwhm), and transient emission was monitored at 430 nm with a Pacific Precision Instruments Model 204 photomultiplier tube and processed by a Biomation Model 4500 digital oscilloscope.[36] The average of two from separate degassing cycles was 13.5 μs.

Acknowledgment. The authors thank the National Science Foundation and the Air Force Office of Scientific Research for their generous support of this research. We also thank Dr. E. Step for preliminary quenching studies and Dr. N. D. Ghatlia for helpful discussions and technical assistance.

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