

Short Communication

The formation of two photoenols via a common pathway in the photochemistry of 2-methylbenzophenone

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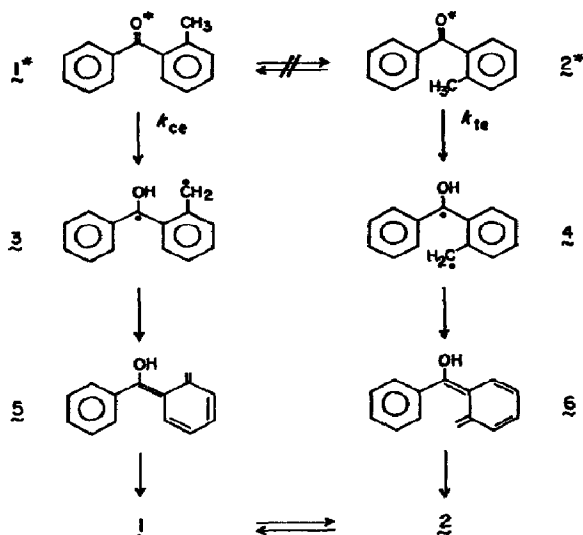
(Received May 2, 1979)

1. Introduction

Recent reports by Uji-Ie *et al.* [1, 2] on the photochemistry of 2-methylbenzophenone in solution have indicated that the *cis*- and *trans*-dienols are produced via two independent pathways from the *syn* and *anti* conformers of the ketone triplet, according to the mechanism in Scheme 1. The transient species $\underline{3}$ and $\underline{4}$ can be described either as the triplet states of the dienols or as 1,4-biradicals; we prefer the latter description [3], although it is clear that both nomenclatures are acceptable and describe the same species. Uji-Ie *et al.* [1, 2] have suggested that $\underline{3}$ and $\underline{4}$ do not interconvert. The question of the number of triplet dienols has been raised by Findlay and Tchir [4]. Other studies in related systems have led to the characterization of only one biradical, suggesting that the two conformations interconvert rapidly [3, 5, 6].

The unusual feature of Uji-Ie's mechanism is that hydrogen abstraction leading to $\underline{4}$ must occur by an all *trans* reaction path. The authors [1, 2] did not speculate how the carbonyl triplet abstracts a hydrogen atom from a *trans* methyl group; further, the reaction was reported to have a rate constant of about $1.4 \times 10^8 \text{ s}^{-1}$ [2].

Not only is such a mechanism most unusual, but it also implies that (1) the mechanism proposed by Wagner and coworkers [7, 8] involving the interconversion of the *anti*-triplet state to the reactive *syn*-triplet state, (2) our evidence for the presence of only one biradical in related systems [3, 5, 9], (3) the idea that the reaction is a radical-like process [10], and (4) the common assumption that both enols arise from a single biradical are totally meaningless. Quite clearly, if this were the case the mechanism of photoenolization would have to be re-evaluated; these ideas prompted us to carry out a series of experiments to test the validity of Uji-Ie's mechanism. This communication reports the results of these experiments, and confirms the validity of the mechanism proposed by Wagner and coworkers [7, 8] and supported by earlier experiments from Wirz's group [6] and from this laboratory [3, 5, 9].



Scheme 1.

2. Results and discussion

The conclusion [1, 2] that $\underline{5}$ and $\underline{6}$ in Scheme 1 arise from $\underline{1}^*$ and $\underline{2}^*$ via two independent reaction paths was based on a study of the quenching of the yields of both enols by naphthalene in aerated solutions [2]. The corresponding Stern-Volmer plots led to two different slopes suggesting the involvement of two different triplet precursors. The choice of quencher and experimental conditions was most unfortunate: triplet naphthalene has strong triplet-triplet absorptions in the region of interest [11]. Further, in non-degassed ethanol solutions its lifetime is not negligible, *i.e.* triplet naphthalene has a lifetime of $0.3 \mu\text{s}$ compared with about $3.5 \mu\text{s}$ for the *cis*-enol $\underline{5}$. Under these conditions singlet oxygen will be generated quite efficiently as a result of the quenching of naphthalene triplets; this in itself will be expected to be a complicating factor, since highly conjugated molecules (as in the case of $\underline{5}$ and $\underline{6}$) are known to interact with $^1\text{O}_2$ with rate constants in the neighborhood of $10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [12]. The presence of oxygen was probably regarded as important in order to decrease the lifetime of triplet naphthalene. Finally, triplet naphthalene could conceivably sensitize the interconversion of $\underline{5}$ and $\underline{6}$.

A far simpler approach can be followed. Dienes are excellent triplet quenchers [13], their triplet energy is even lower than that of naphthalene [14], they are transparent to the common (337.1 or 347.1 nm) laser sources, their triplet state is short lived and they have no transient absorptions in the region of interest; further, the presence of oxygen is not necessary. We used 2,5-dimethyl-2,4-hexadiene in ethanol and acetonitrile and *trans*-1,3-pentadiene in ethanol, and examined the yields of both enols according to the transient assignments of Uji-Ie *et al.* [1, 2] and the assignments of Haag *et al.* [6] corresponding to transients B and D (*cis* and *trans*) in Porter's nomenclature [15]. We found (Fig. 1) only one type of behavior,

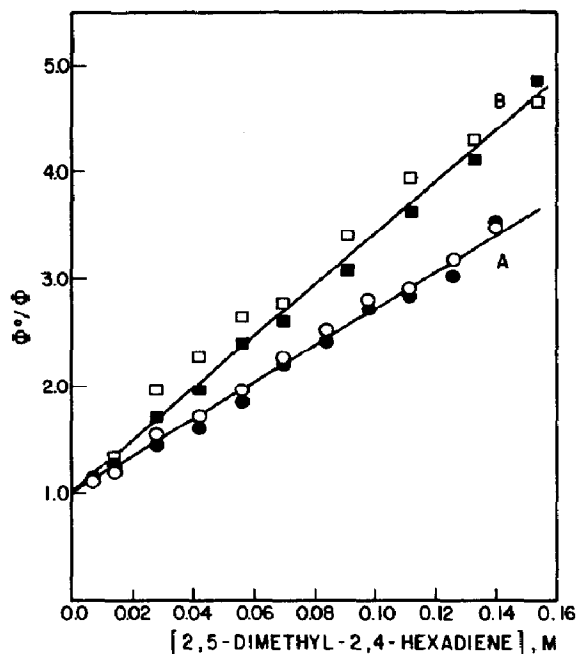
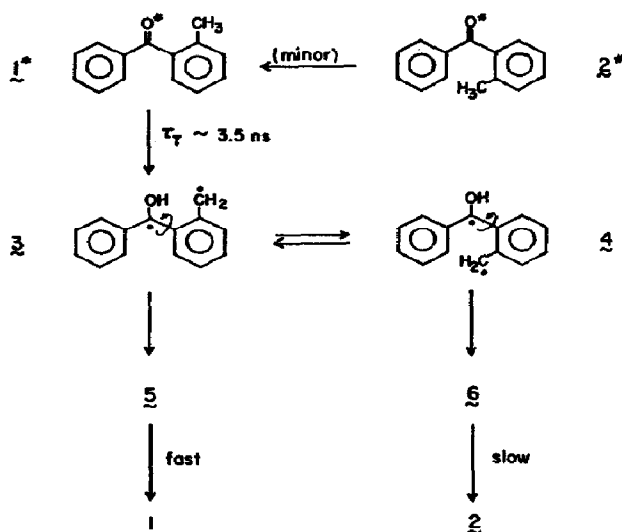


Fig. 1. Stern-Volmer plots for the yields of the *cis*-dienol (●, ■) and the *trans*-dienol (○, □) of 2-methylbenzophenone in degassed ethanol (A) and in acetonitrile (B). The triplet quencher is 2,5-dimethyl-2,4-hexadiene.

corresponding to a Stern-Volmer slope for 2,5-dimethyl-2,4-hexadiene of 17 M^{-1} in ethanol and 24 M^{-1} in acetonitrile. In ethanol, *trans*-1,3-pentadiene yields the same slope as 2,5-dimethyl-2,4-hexadiene and corresponds to a triplet lifetime of approximately 3.5 ns. The plots do not show any significant curvature, which is a common characteristic in systems involving two triplets [3, 5, 7]. The result can imply either that the two triplets have similar lifetimes or that one of them is responsible for most of the reaction; the latter is likely to be the correct explanation since 2-methylbenzophenone is known to be over 70% in the *syn* conformation [16]. The absence of substantial differences in the quenching plots for the enols means that there is a common stage in the reaction pathway for both species, and all earlier evidence [3, 5 - 9] suggests that the biradical is that species. Hydrogen abstraction is only expected to take place from the *syn* conformation. Scheme 2 shows the proposed mechanism.

The problem of explaining the difference in the Stern-Volmer slopes observed by Uji-*le et al.* [1, 2] still remains. We repeated the experiments and observed the same type of behavior, although the slopes we obtained were slightly different from those previously reported [1, 2]. If the effect of oxygen is to reduce the triplet lifetime it is better to saturate with oxygen than with air, since under these conditions the lifetime of triplet naphthalene is only 60 ns (in ethanol). The two curves are shown in Fig. 2. If 2,3-dimethyl-2-butene (TME) is added to the sample the two Stern-Volmer



Scheme 2.

plots become identical (see Fig. 2). TME is a well-known scavenger for singlet oxygen [12, 17], and singlet oxygen is expected to react with **5** and **6** quite efficiently [12]. We propose that the two enols give different Stern-Volmer slopes when naphthalene (or 1-methylnaphthalene) is used as a quencher in oxygen-containing solutions because (1) the *trans*-enol is long lived enough to undergo substantial depletion because of singlet oxygen attack, and (2) in air-saturated solutions the lifetime of triplet naphthalene (about $0.3 \mu\text{s}$) is long enough to yield absorptions that can be erroneously attributed (or added on) to the *cis*-enol.

Three solutions of 2-methylbenzophenone containing (1) oxygen, (2) oxygen and 0.1 M 1-methylnaphthalene and (3) oxygen, 0.1 M 1-methylnaphthalene and 0.25 M TME were examined. The relative yields of *trans*-dienol were 1.0:0.09: 0.40 for (1):(2):(3). The increase between the second and third figures is attributed to singlet oxygen scavenging by TME; the effect would be even larger if TME did not quench some triplets (see below).

The slope for the system containing TME (Fig. 2) is less than that in Fig. 1 because TME also quenches triplet 2-methylbenzophenone (therefore reducing the triplet lifetime), as suggested by an independent experiment in which the enol yields were monitored as a function of the TME concentration. The corresponding Stern-Volmer slope was 2 M^{-1} , which indicates that quenching by TME is around one order of magnitude slower than quenching by dienes, as expected [13].

In conclusion, the mechanism proposed by Uji-Ie *et al.* [1, 2] and shown in Scheme 1 is incorrect. The results obtained in oxygen-containing systems and using naphthalene as a quencher involve side reactions that vitiate the kinetic analysis. The mechanism we propose is shown in Scheme 2 and agrees well with earlier reports [3 - 10, 15].

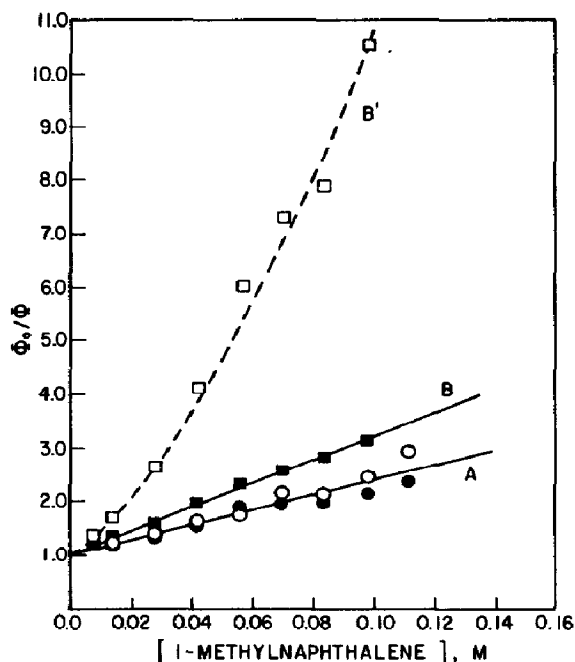


Fig. 2. Stern-Volmer plots for the yields of the *cis*-dienol (●, ■) and the *trans*-dienol (○, □) of 2-methylbenzophenone in oxygen-saturated ethanol in the presence (A) and absence (B,B') of 2,3-dimethyl-2-butene. The triplet quencher is 1-methylnaphthalene.

3. Experimental section

All the materials were commercially available. The transient absorptions were monitored with a laser photolysis system which used a Molecron UV-400 nitrogen laser for excitation. Further details on the equipment have been given elsewhere [3, 9, 18].

The concentration of 2-methylbenzophenone used was 0.025 M. The transient absorptions were monitored at a wavelength of 406 nm and the experimental ratio of *cis*-dienol to *trans*-dienol was about 3.

Acknowledgment

This work was supported by the Office of Basic Energy Sciences of the Department of Energy. This is document No. NDRL-2002 from the Notre Dame Radiation Laboratory.

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