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# PHOTOELIMINATION OF STILBENE FROM β,γ-DIPHENYLBUTYROPHENONE

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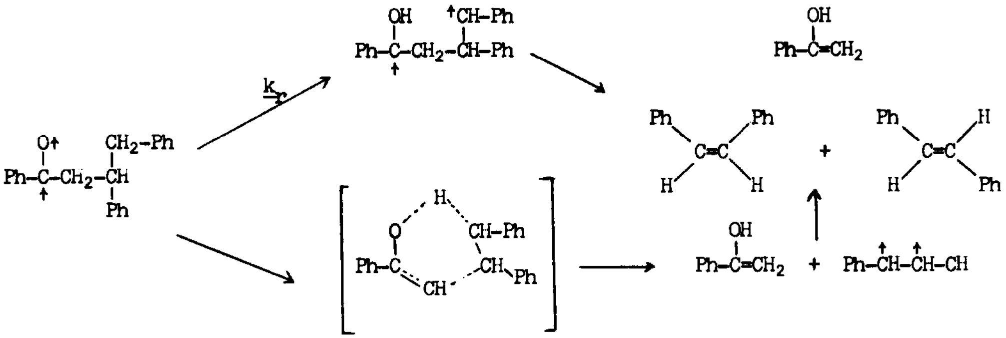
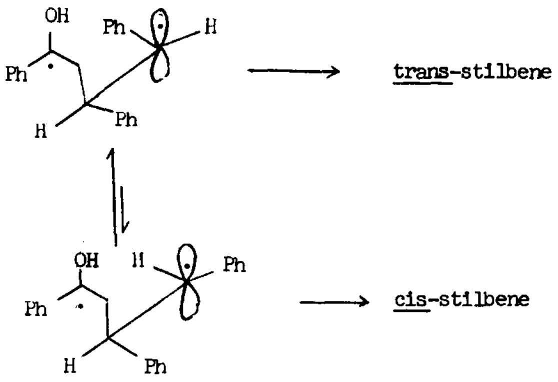
There is now considerable evidence that triplet state Norrish Type II photoelimination of ketones involves biradical intermediates (1-3). There is some evidence that the corresponding singlet state reaction of aliphatic ketones may proceed concertedly (4). One of the more intriguing current questions in photochemistry is under what conditions can a triplet state reaction proceed concertedly. The normal spin factors presumably would slow down a triplet —> singlet chemical reaction. However, if a triplet product could be formed, no adverse spin factors would affect the rate. The energetics of (ketone —> enol + olefin) demand that a concerted elimination of a simple, unconjugated olefin triplet be endothermic, since the triplet excitation energies of alkenes generally exceed those of ketones. Therefore γ-hydrogen atom abstraction is faster. Phenyl ketones eliminate a hydroxystyrene as enol, yet all the evidence implicates biradical formation as the only triplet state chemistry. The title compound I should provide a good test for possible concerted triplet state fragmentation. Stilbene, the expected olefin product, has a triplet excitation energy no greater than 50 kcal (5), while that of phenyl alkyl ketones exceeds 73 kcal (6); so the photocleavage could otherwise be 23 kcal endothermic and still produce triplet stilbene.

3660-Å Irradiation of I (7) in benzene solution does indeed produce acetophenone and stilbene in equal yields. At this wavelength the stilbene does not absorb. The <u>trans/cis</u> stilbene ratio is 65/1 at low conversions. This value decreases at very high conversions, presumably because of secondary sensitized isomerization of the stilbene. The reaction is quenched by dienes. A linear Stern-Volmer plot with 2,5-dimethyl-2,4-hexadiene has a slope of 2.4 $M^{-1}$. The Type II quantum yield is 0.11 in benzene, 0.19 with 2M <u>t</u>-butyl alcohol added. Actual total quantum yields for ketone reaction are probably about 10% greater because of the expected cyclobutanol formation (8).



If triplet stilbene were formed, the trans/cis ratio should equal the known decay ratio of 41/59 (5). If the reaction proceeds concertedly, all the triplet excitation must reside in the enol fragment. However, the triplet excitation energy of the styrene chromophore is significantly higher than that of stilbene (5). It would be very unusual if a concerted electronic rearrangement proceeded completely by the less exothermic of two otherwise similar paths, especially in the absence of any steric constraints. The reaction instead probably proceeds via a moderately long lived biradical which is affected normally by polar solvents (1). A further conclusion is that the biradical, which is formed as a triplet, must lose its spin identity before cleavage occurs. Since γ-hydrogen transfer must be 10-20 kcal exothermic, it seems that any triplet character would necessarily show up preferentially in the lower excitation energy cleavage product, i.e., stilbene rather than enol. Spin correlation in a 1,4-biradical may well be so weak that singlet-triplet distinctions are practially nonexistent. The actual product ratio probably reflects the most stable conformation of the biradical and approaches the actual thermodynamic difference.

The quenching results provide an estimated triplet lifetime $\tau$ of $0.5 \times 10^{-9}$ sec for I. We expected both $\Phi$ and $\tau$ to be very similar to those for γ-phenylbutyrophenone II (3). The chemical reaction for both ketones involves abstraction of a secondary benzylic hydrogen and both biradical intermediates have identical radical sites. The β-phenyl group should exert only a weak inductive effect on the chemical reactions. In fact, $\Phi$ is only 1/5 as large for I as II; $\tau$ for I is 1/5 $\tau$ for II. This phenomenon of low quantum yields and very short



triplet lifetimes is characteristic of β-phenylketones and will be reported separately. The combined data furnish a $\underline{k_r}$ value of $4 \times 10^8$ sec$^{-1}$ for triplet I, the same as that for II (3). The fact that the $\underline{k_r}$ values for the ketones which can eject conjugated olefins are so in line with those for ketones which eject simple alkenes is further evidence that only hydrogen abstraction occurs.

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