

Wagner P J. Type II photoelimination and photocyclization of ketones.
Account. Chem. Res. 4:168-77, 1971.
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The title reactions occur by excited state intramolecular hydrogen abstraction. The resulting 1,4-biradical intermediates can be trapped. Rate constants respond to inductive effects of substituents in the same way as do those for alkoxy radical reactions. Only n,π^* excited states react, even when the lowest triplet is π,π^* . [The *SCI*® indicates that this paper has been cited in over 405 publications.]

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My work on the Norrish type II photo-reaction started largely as the result of a dare. While a postdoctoral fellow with George Hammond at Caltech in 1965, I noticed a disagreement in the literature over which excited state—triplet or singlet—was responsible for the photocleavage of aliphatic ketones to acetone. I wondered whether the reactivity of excited ketones might mimic that of alkoxy radicals such that the most reactive triplets might be undetectable. I presented these thoughts at the weekly informal organic chemistry seminar where faculty and students discussed unresolved topics of current interest, and the audience then did its best to shred the speaker's logic. I was greeted with healthy skepticism and a consensus that

no one would believe me unless some convincing experiments were performed. I quickly measured the quantum efficiency for reaction of both 2-pentanone and 2-hexanone as a function of added 1,3-pentadiene, which was reported to selectively quench triplets. To my delight, the results proved my original idea correct: 2-pentanone is quenched much more readily than is 2-hexanone. However, far more important was the totally unanticipated finding that each ketone reacts from both excited singlet and triplet! Our resulting publication¹ was widely appreciated not just because it settled a mechanistic puzzle but because it so vividly demonstrated the power of the quenching technique.

When I came to Michigan State, I undertook a systematic investigation of those aspects of the type II reaction that struck me as of most fundamental importance. By 1971 I could write a summary for *Accounts*. The gratifying frequency with which this paper has been cited must be due in large measure to the widespread occurrence and usefulness of the reaction itself. Recently, the reaction has been used to generate and study a wide variety of biradical² and enol³ intermediates, as well as to measure rate constants for radical⁴ and competing triplet⁵ reactions and to probe environmental effects on molecular geometry.⁶ In my heart, I hope that the paper is also recognized as being one of the first to make a fundamental photoreaction understandable to the average chemist, who 15 years ago tended to view photochemistry still as a form of alchemy.

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