Tetrahedron Letters No. 8, pp 565 - 568, 1973. Pergamon Press. Printed in Great Britain.

BIACETYL SENSITIZED DECOMPOSITION OF TETRAMETHYL-1,2-DIOXETANE. AN EXAMPLE OF AN ANTI-STOKES SENSITIZATION INVOLVING A "MASKED" EXCITED STATE.

Nicholas J. Turro and Peter Lechtken
Department of Chemistry
Columbia University
New York, New York 10027

(Received in USA 15 December 1972; received in UK for publication 11 January 1973)

Examples of biphotonic processes (i.e., reactions involving two electronically excited molecules) which can be usefully employed in organic photochemistry are very rare because their rates are generally proportional to the square of the concentration of electronically excited molecules (eq. 1). Such reactions therefore proceed at negligibly slow rates relative to unimolecular reactions of the excited state or bimolecular reactions involving an excited state and a ground state. We demonstrate here a system in which a molecule possessing very high energy content serves as a "masked" electronically excited state, the latter capable of being released from the "masked" molecule by either heat or photosensitization.

$$D^* + A^* \longrightarrow \text{Products} \qquad (1)$$

Demonstration of this effect was possible by using the Type II reaction of valerophenone[1] as a probe for electronically excited molecules. This reaction is known to proceed exclusively via the valerophenone triplet, which possesses an energy content of about 74 kcal/mole in excess of its ground state. Thus, it is impossible to efficiently sensitize the Type II reaction of valerophenone with biacetyl triplets, since the latter only have an energy content of about 56 kcal/mole greater than their ground states.[2] Indeed, exciting biacetyl (0.01 M) in benzene in the presence of valerophenone (0.3 M) with 436 nm light results in no significant production of acetophenone even after extensive periods of irradiation (eq. 2). However, similar excitation of biacetyl (0.01 M) in a benzene solution containing valerophenone (0.3 M) and tetramethyl-1,2-dioxetane (**1**, 0.22 M), at 6^{o}C, results in smooth formation of acetophenone (eq. 3). We interpret these results to mean that an excited state of biacetyl has sensitized formation of excited acetone which, in turn, transfers its excitation to valerophenone which rapidly cleaves in a Type II process (Figure 1).

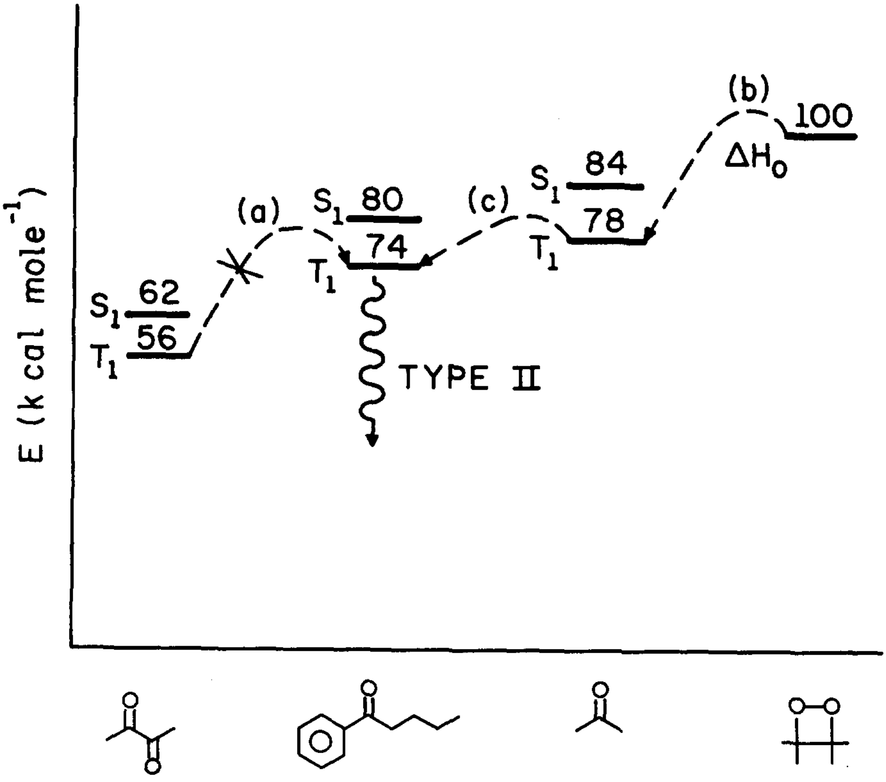
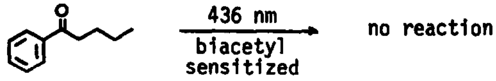
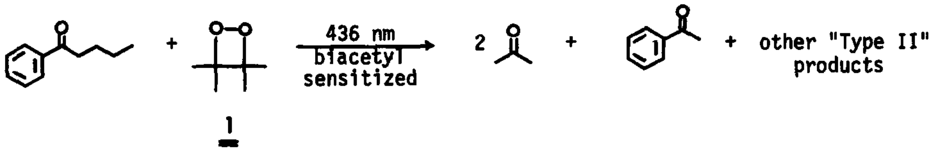


Figure 1. Energy diagram sketching the proposed mechanism of reaction 3. Direct excitation of T_1 of valerophenone by biacetyl triplets (path a) is energetically unfavorable and not observed. T_1 of biacetyl, however, is able to generate acetone triplets from the dioxetane (path b). Acetone triplets, in turn, sensitize formation of valerophenone triplets, which then undergo Type II reaction (path c).



(2)



(3)

The efficiency of sensitization of valerophenone triplets was calculated to be 30% based on the known quantum yield of the Type II process. The phosphorescence, but not the fluorescence, of biacetyl is strongly quenched by **1** under our reaction conditions, so that we conclude that biacetyl triplets are involved in the sensitization step. Further evidence hereto is provided by our analysis of the self-quenching of dioxetane **1** (a quantum chain reaction) which involves acetone triplets.[3] Since the sensitization commences with a lower energy triplet (biacetyl) and terminates with a higher energy triplet (valerophenone), the net reaction (eq. 3) corresponds to an anti-Stokes sensitization[4] of the Type II reaction. This experimental observation demonstrates a new principle which has been heretofore unrecognized in any reported work, namely the efficient use of a molecule of high energy content as an excited state equivalent in a sensitization relay which eventuates in an electronically excited state whose energy is well to the "blue" of an initially absorbed photon. In effect, we are dealing with a "two quantum" process in which one of the quanta is masked in the chemical energy of the dioxetane. Since acetone is an effective sensitizer in many photochemical and photobiological systems,[5] it should be of special interest to organic chemists and to biochemists to generate excited acetone molecules employing long wavelength excitation and very mild conditions.

The most obvious mechanism for the sensitization involves production of acetone triplets after formation of a collision complex of **1** and triplet biacetyl. However, this mechanism may have difficulty in explaining the relatively high efficiency of formation of "free" acetone triplets, which then excite valerophenone, because acetone triplets in a cage with biacetyl should be efficiently quenched. Possibly a dioxetane triplet is generated which may leave the cage if its lifetime is $\geqslant 10^{-10}$ sec (eq. 4).

(4)

Acknowledgements: The authors gratefully acknowledge the support of the Air Force Office of Scientific Research (Grant AFOSR-70-1848) and the National Science Foundation (Grant NSF-GP-26602X).

References

1. P.J. Wagner, Accounts Chem. Res., 4, 168 (1971).
2. A.A. Lamola and N.J. Turro, "Energy Transfer and Organic Photochemistry," Interscience, New York, 1969.
3. P. Lechtken, A. Yekta and N.J. Turro, to be published.
4. C.A. Parker and C.G. Hatchard, Proc. Chem. Soc., 1962, 386 (1962).
5. A.A. Lamola, Mol. Photochem., 4, 107 (1972).
6. NATO Postdoctoral Fellow, 1971-1972.