MECHANISTIC INVERSION OF PHOTOINITIATED ELECTRON TRANSFER PROCESSES IN ARYL IMIDAZOLIDINONES

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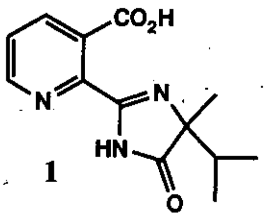
Abstract- Aryl imidazolidinones having *o*-carboxylic acid and ester containing aryl substituents were found to undergo different photochemical reactions. Although both reactions are suggested to proceed by electron transfer mechanisms, the donor and acceptor groups are interchanged.

Photochemically initiated single electron transfer reactions are well documented in the literature.[1] It is expected and found that small structural changes that affect the donor or acceptor ability of the donor acceptor pair can have dramatic effects on the nature of these reactions.[1,2] We wish to report an interesting case wherein a small change in structure (esterification) of two closely related compounds apparently can cause a switch of donor moiety to acceptor and vice verse.



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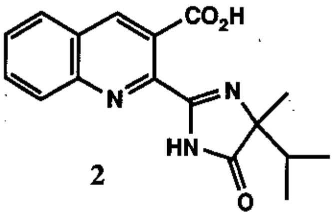

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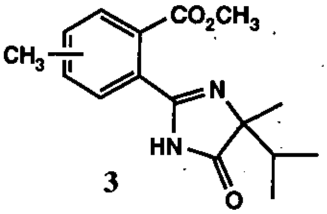

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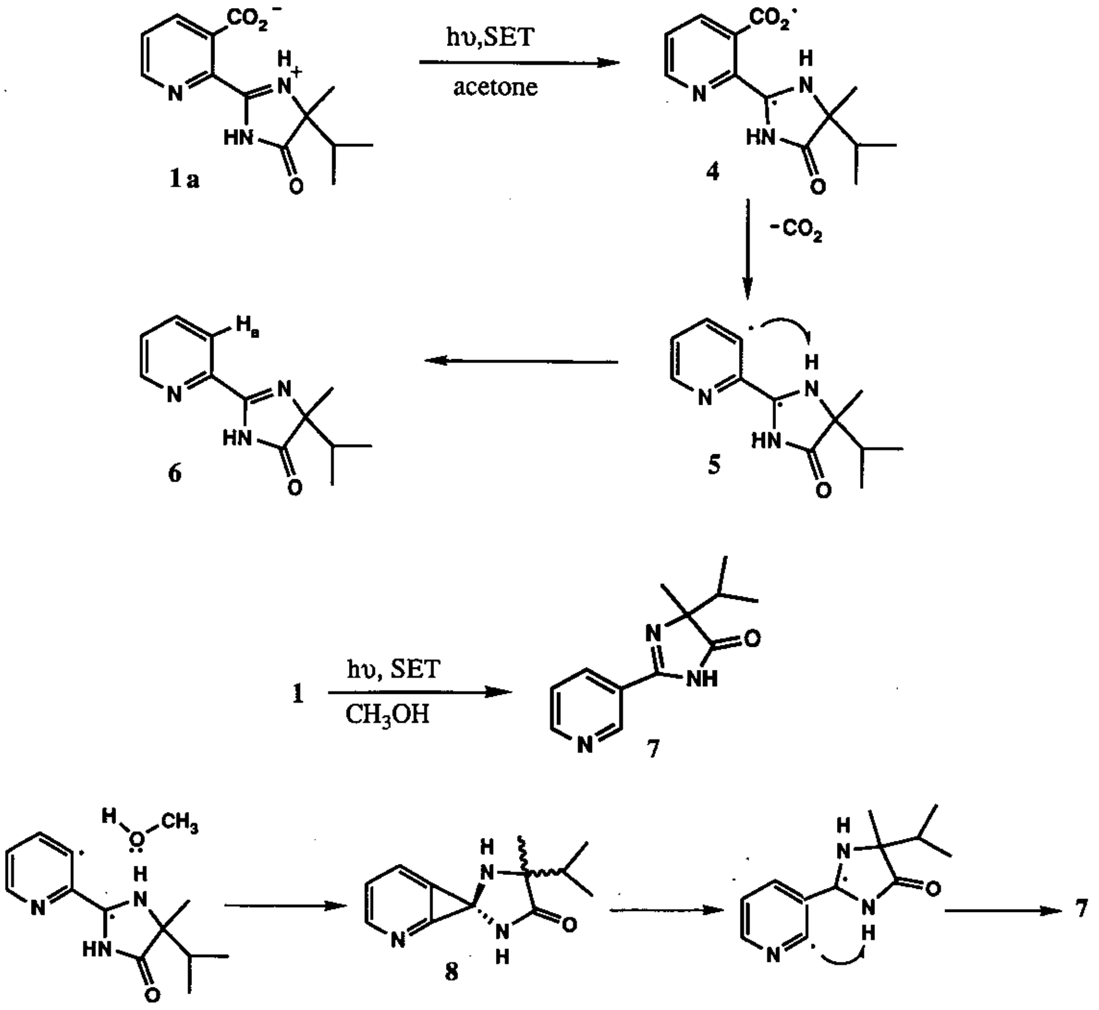
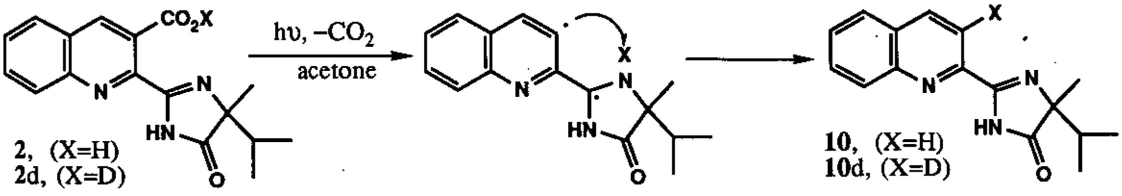
Although our original interest in the heterocycles (**1**, **2** and **3**) was due to their herbicidal properties,[3] interesting preliminary results on their photochemistry lead us to conduct mechanistic investigations. Irradiation of a solution of **1** in acetone resulted in the formation of **6** in 17% yield.[4] Simple electron transfer initiated decarboxylation is well documented in the literature[5] and this case is closely analogous to those observed with iminium salts.[6] The proposed mechanism shown in Scheme 1 leads to the obvious questions about the existence of biradical (**5**) and the source of the aromatic hydrogen in **6** (Ha), that is, does an intramolecular or intermolecular hydrogen atom transfer occur. The first question was answered fortuitously when **1** was irradiated in methanol yielding rearranged product (**7**) in 42% yield.[4] We propose that in methanol hydrogen bonding of the NH proton in **5**[7] prevents intramolecular H atom transfer thereby prolonging biradical lifetime and allowing ring closure to intermediate (**8**). Subsequent ring opening and H transfer leads to **7**.

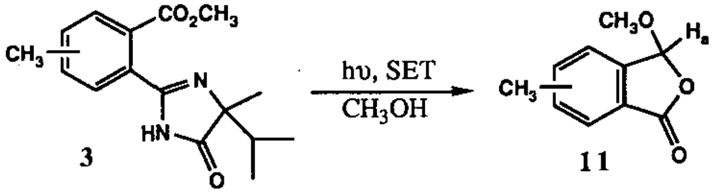
Scheme 1

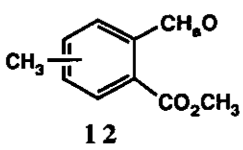


Confirming evidence for the intramolecular H transfer came from experiments with **2**. Exchange of **2** under neutral conditions resulted in the replacement of only the carboxylic proton by deuterium. Irradiation of **2**d in acetone resulted in the formation of a 1:1 mixture of **10** and **10**d as determined by ^{1}H nmr.[7] In a corollary experiment no deuterium was incorporated into **10** when **2** was irradiated in acetone-d$_6$, confirming that there was no exchange with the solvent. This result is entirely consistent with the intermediacy of **9**.



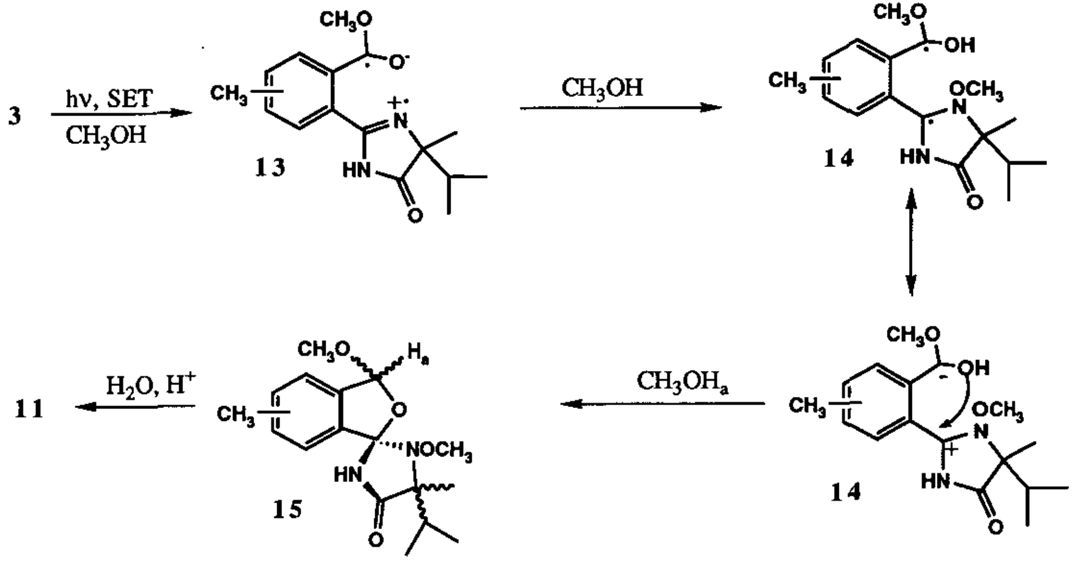
The nature of the photochemistry of **3** appears to be completely the reverse of that of **1** and **2** with the carboxylic ester now the acceptor group and the imine the donor. Irradiation of **3** in methanol gave **11** in 14% yield.[4]





We propose the mechanism in Scheme 2 for this process. After initial electron transfer to **13**, methanol addition and electron reorganization to **14** followed by intramolecular nucleophilic attack by the hydroxyl group and protonation leads to **15** which hydrolyzes to **11**. Alternative mechanisms proceed through the intermediacy of **12**.[9] The mechanism in Scheme 2 requires that the methoxy group in **11** come from **3** not solvent and that proton Ha in **15** come from solvent. The alternative mechanisms require that Ha in **12** appear as Ha in **11**. Two simple experiments verified that this was, in fact, the case. Irradiation of **3** in CD_3OH gave unlabeled **11** whereas irradiation in CH_3OD gave **11** with Ha completely replaced by deuterium suggesting that our proposed mechanism is correct.

Scheme 2



The unique examples presented here are interesting because they demonstrate how seemingly small structural changes can completely change, in this case reverse, the nature of the electron transfer process. More detailed mechanistic investigations are underway.

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2. Y. Kanaoka, C. Nagasawa, H. Nakai, Y. Sato, H. Ogiwara, and T.Mizoguchi, *Heterocycles*, **1975**, *3*, 553; P. H. Mazzocchi, P. Wilson, and S. Minamikawa, *J. Org. Chem*, **1985**,*106*, 2681.

3. For general reference, see (a) A.S.Crafts "The Chemistry and Mode of Action of Herbicides", Interscience Publisher, Third printing, 1967, New York. (b) "Degradation of Herbicides", ed. by P.C.Kearney and D. D. Kaufman, Marcel Dekker, Inc., 1969, New York. Compounds (**1, 2** and **3**) are members of a new class of herbicides which are sold under the trade names Arsenal, Scepter and Assert respectively. These materials presumably work by inhibition of the acetohydroxy acid synthase responsible for the production of valine, leucine and isoleucine in plants. They are characterized by very low application rates and toxicity.

4. The structures of all new compounds were characterized by, and are fully consistent with their ir, ^{1}H and ^{13}C nmr, and high resolution mass spectra.

5. a) J. R. Barnett, A. S. Hopkins, and A. Ledwith. *J. Chem. Soc., Perkin Trans. 2*, **1973**, 80 ; b) D. R. G. Brimage, R. S. Davidson, and P. R. Steiner, *J. Chem. Soc., Perkin Trans. 1*, **1973**, 826 ; c) R. Noyori, M. Kato, M. Kawanishi, and H. Nozaki, *Tetrahedron*, **1969**, *25*, 1125 ; d) I. Ahmad and G. Tollin, *Photochem. Photobiol.*,**1981**, 34 ; e) M. Novak, A. Miller, T. C. Bruice, and G. Tollin, *J. Am. Chem. Soc.*, **1980**, *102*, 1465 ; R. S. Davidson and P. R. Steiner, *J. Chem. Soc., Perkin Trans. 2,* **1972**, 135 and references therein; J. Libman, *J. Am. Chem. Soc.*, **1975**, *97*, 4139 .

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7. A similar effect has been noted in the type II process of alkyl phenyl ketones. It has been suggested that back hydrogen atom transfer in the intermediate biradical causes starting material racemization and a decrease in type II quantum yield. In alcohol solvents hydrogen bonding prevents back transfer and leads to more efficient biradical cleavage and type II products. P. Wan, S. Culshaw, and K. Yates, *J. Am. Chem. Soc.*, **1982**, *104*, 2509.

8. Although **9** has apparent symmetry will only be the case if rotation is fast with respect to H abstraction. The lack of an obvious kinetic isotope effect on product formation suggests that rotation and H abstraction occur at competitive rates.

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