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McLAFFERTY REARRANGEMENT AND TYPE II PHOTOCLEAVAGE OF BENZOYLACETANILIDE

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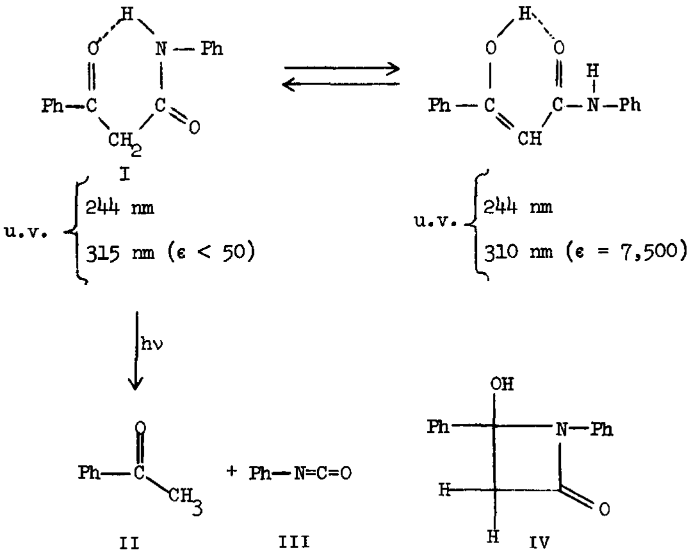
The analogy between the Norrish type II photoelimination and the electron impact McLafferty rearrangement of carbonyl compounds is well established and both reactions have been intensively studied (2,3). These reactions involve transfer of a γ-hydrogen atom to the carbonyl oxygen and cleavage to yield olefins and enols of smaller carbonyl compounds.

β-Ketoanilides are capable of undergoing a type II photoelimination, a photo Fries reaction, or both. If the photoreaction occurs from the excited singlet state of the anilide chromophore, a photo Fries rearrangement would result (4). Direct excitation or intramolecular energy transfer to the carbonyl chromophore should lead to a type II process. Reisch and Niemeyer (5) have recently published a brief account of the photolysis of β-ketoamides without discussing the mechanistic implications of their findings. We herein report our results on the mechanism of this photoreaction and the electron impact decomposition.

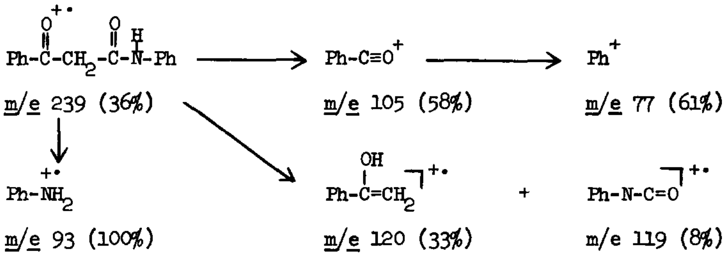
Irradiation of a 1% solution of benzoylacetanilide (I) in benzene, alcohols, or aqueous solution with 2537 or 3130Å light resulted in a quantitative conversion to the type II photoelimination products of acetophenone (II) and phenylisocyanate (III) or solvent addition products of phenylisocyanate. The quantum yield at 3130Å for the photoelimination reaction is 0.12 in benzene and 0.04 in methanol. Even though the 2537Å light directly excites the anilide chromophore, we could detect no traces of the photo Fries rearrangement products. Presumably, intramolecular energy transfer to the singlet manifold of the benzoyl chromophore or direct intersystem crossing to benzoyl triplet state occurs at a much faster rate than the singlet photo Fries rearrangement.

We could also detect no traces of 1,4-diphenyl-2-azetidinone (IV) which could have arisen from coupling of an incipient biradical -- generated by intramolecular hydrogen abstraction. This lack of cyclization could be due to the intrinsic steric strain involved in the formation of the azetidinone ring system (6).

Another important aspect of this investigation is that benzoylacetanilide in solution exists as an equilibrium mixture of the keto and enol isomers (7). In nonpolar solvents the enol content of benzoylacetanilide is much greater than the keto isomer, whereas in aqueous solution the keto content is greater than 99%. When a benzene solution of I is irradiated with 3130Å light, more than 99% of the light is absorbed by the enol isomer and less than 1% of the incident energy is directly absorbed by the keto isomer. However, in view of the electron-impact fragmentation of I and analogy with other type II photoeliminations, the photoelimination reaction of I would be expected to occur only from the keto isomer. Since the quantum yield of photoelimination in benzene is 0.12, excitation of the keto isomer must occur by intermolecular energy transfer from the enol isomer or isomerization of the excited singlet or triplet state of the keto isomer. Sensitization of an aqueous solution of I, in which the keto isomer accounts for more than 99% of I, with acetone (E_T = 80 kcal) and acetophenone (E_T = 74 kcal) suggests that energy transfer to the keto form of I is diffusion controlled and the photoelimination is quite efficient. The triplet energy of cinnamoylanilide is not known but triplet energies of cinnamoyl esters have been estimated to be greater than 90 kcal/mole (8), so it is quite conceivable that intramolecular energy transfer could be the prevailing mechanism.



The mass spectrum of benzoylacetanilide at 70 ev exhibits the expected peaks at m/e 105, 93, and 77. The rearrangement ion at m/e 93 (base peak) is common to acetanilides (9) and a recent paper suggests that this ion probably has the aniline structure (10). The ions at m/e 120 (C_8H_8O) and 119 (C_7H_5NO) (11) are the products of γ-hydrogen transfer (confirmed by deuterium labelling) from the amide nitrogen to the benzoyl moiety and subsequent (or concomitant) cleavage. This parallels the Norrish Type II photodecomposition of the compound and illustrates yet another example of the similiarities between mass spectrometry and photochemistry (12).



The structures of the ions at m/e 120 and 119 are represented as the acetophenone enol ion (13) and the molecular ion of phenyl isocyanate. The acetophenone enol ion is formed with loss of phenyl isocyanate as the neutral fragment and, conversely, formation of the phenyl isocyanate ion is probably accompanied by loss of the acetophenone enol as a neutral fragment. A metastable ion for the $M^+ \rightarrow 120$ process confirms the one-step nature of this fragmentation, but no metastable ion is observed for the $M^+ \rightarrow 119$ process. Stevenson's rule (15) would seem to account for the predominance of the m/e 120 ion over the m/e 119 ion, but the decline of the 120/119 ratio from 4.2 at 70 ev to 1.4 at 9 ev suggests that further examination of this rearrangement might yield interesting data concerning the competing rates of the fragmentation.

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