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A NOVEL PHOTOCHEMICAL 1,2-ACYL MIGRATION IN AN ENOL ESTER. THE SYNTHESIS OF 3-OXAZOLINE DERIVATIVES.

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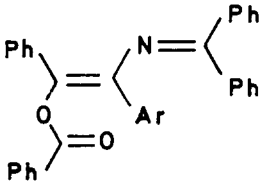
Summary: Irradiation of 3-Aryl-4-benzoyloxy-1,1,4-triphenyl-2-aza-buta-1,3-dienes gives 3-oxazoline derivatives in high yield by a novel 1,2-acyl migration, in clear contrast with the normal behaviour of other enol esters.

Photochemical acyl migrations occur in two main areas, the well known oxa-di-π-methane reaction[1] and the Photo-Fries[2a] and related enol ester processes[2b]. The β,γ-unsaturated ketones undergo either 1,3- or 1,2-acyl migration (oxa-di-π-methane rearrangement) dependent on whether a singlet or a triplet state is involved. On the other hand the Photo-Fries and enol ester rearrangements are typified by 1,3-acyl migrations and the Photo-Fries, at least, arises from the singlet excited state[3]. 1,5-Migrations[4] are uncommon in this latter reaction and as far as we are aware 1,2-acyl migrations are unknown.

We would like to report the results of the rearrangement of the yellow 2-aza-1,3-dienes (1)[5]. Thus the irradiation of (1a) in methylene chloride under nitrogen, using Pyrex-filtered light from a medium pressure mercury arc lamp, brings about rapid conversion, in high yied, to a single colourless product which is readily isolated by column chromatography on silica gel. The i.r. spectrum of this product showed that the vinyl ester carbonyl absorption (1730 cm^{-1})

had disappeared and had been replaced by a keto group at 1670 cm^{-1} . ^1H n.m.r. was particularly unhelpful in assignment of structure. However ^{13}C n.m.r. showed the presence of two low field carbons at 198 and 167 δ which could be attributed to the presence of a keto and an imine group respectively and two resonances at 99 and 112 δ for two saturated atoms to which electron withdrawing groups are attached. This n.m.r. evidence and the failure of attemps to hydrolize the photo-products suggested that a cyclic structure had been formed and that possible open-chain structures such (2) and (3) from 1,3- or 1,5-acyl migration, could be rejected from consideration.



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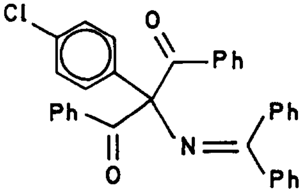
1a: Ar= p-Cl-C_6H_4
1b: Ar= p-CH_3-C_6H_4
1c: Ar= C_6H_5



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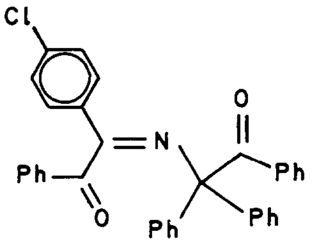

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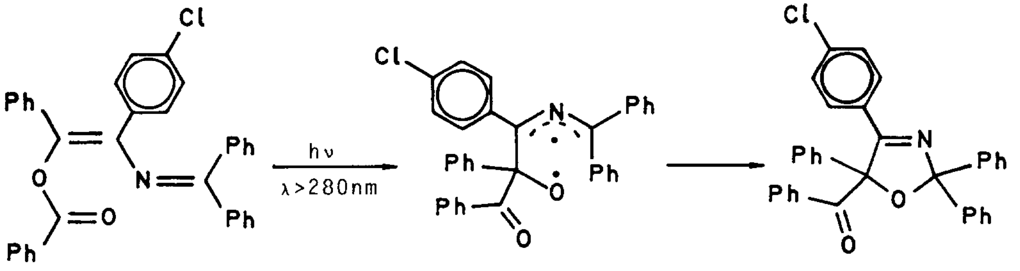
It thus seems likely, among the possible cyclic structures, that the photoproduct is the 3-oxazoline (4). A possible route to its formation is by a hitherto unknown 1,2-acyl migration with the enol ester yielding a biradical (5). Bonding then affords the isolated product (4).



1 **5** **4**

Such a structure is in agreement with the ^{13}C n.m.r. recorded for the compound and also with ^{13}C data reported for other oxazolines in the literature[6].

Final irrefutable proof of structure (4) was obtained by the determination of the crystal structure by X-ray analysis[7].

The reaction described above appears to be quite general. Each of the azadienes (1a-c) is readily converted by irradiation into the corresponding 3-oxazolines (4). The n.m.r. data and i.r. frequencies are recorded in the Table.

Table Yield (%) and physical constants of 3-oxazolines[5b]

Ar	^{13}C n.m.r. (δ)	i.r.(KBr) (cm^{-1})	m.p.	Yield[a] (%)
p-Cl-C_6H_4	99 (C_2), 112 (C_5) 125-144 (C-aromatic) 167 (C_4), 198 (C=O)	1670 (C=O) 1628 (C=N)	228	59
p-CH_3-C_6H_4	21 (CH_3), 100 (C_2) 112 (C_5) 126-145 (C-aromatic) 168 (C_4), 199 (C=O)	1670 (C=O) 1625 (C=N)	245	71
C_6H_5	99 (C_2), 112 (C_5) 125-143 (C-aromatic) 168 (C_4), 198 (C=O)	1670 (C=O) 1640 (C=O)	194	60

a) Isolated yields after column chromatography are shown.

It is clear that the rearrangement described above could be considered analogous to the di-π- and oxa-di-π-methane reactions. Examples in the literature[8,9], where the vinyl groups are separated by an oxygen appear not to rearrange by group migration across the oxygen atom but tend to find alternative reaction modes such as fragmentation, or phenyl migration. We believe that the reaction described by us is the first example of such a process resulting in a 1,2-migration across the oxygen atom.

Experiments are now in hand to determine the multiplicity of the reaction and to establish the position of the rearrangement in the di-π-methane framework. The scope of the reaction is also of considerable importance since this novel rearrangement provides the first route to the synthesis of 5-acyl substituted 3-oxazolines.

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