Tetrahedron Letters,Vol.24,No.10,pp 1089-1092,1983 0040-4039/83/101089-04$03.00/0
Printed in Great Britain

THE PHOTOCHEMICAL REARRANGEMENT OF 3-AZA-1,2,2,4,4-PENTAPHENYLBUT-3-EN-1-ONE. A NOVEL REACTION IN A β,γ-UNSATURATED ENONE.

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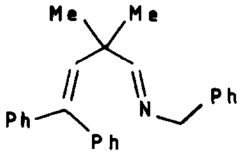
Summary: Irradiation of 3-aza-1,2,2,4,4-pentaphenylbut-3-en-1-one in t-butanol gives two photoproducts in good yield. The formation of these products is interpreted in terms of 1,3- or 1,5-benzoyl migration. This is the first report of an acyl migration from a saturated carbon into a substituent phenyl group.

Recently we have been interested in the modification of reactivity brought about in a molecule by the inclusion of an imine functional group in place of a carbon-carbon double bond. In this general study we have demonstrated the novel di-π-methane reactivity of the imine (1)[1] and also the surprising 1,2-acyl migration in the enol esters (2)[2]. In this present publication we



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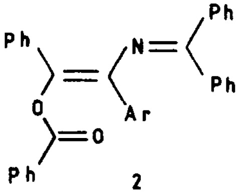

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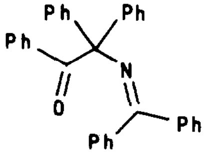

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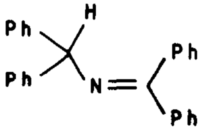

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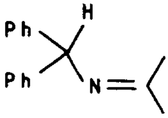

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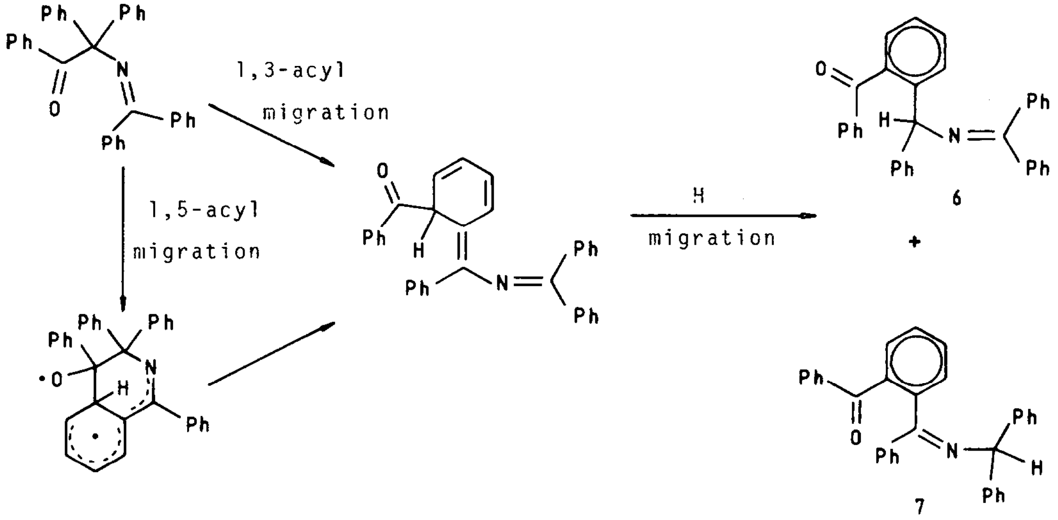
report our observation on the photochemical behaviour of the azaenone (3) which is readily prepared by benzoylation of the imine (4) (using HNa/HMPT as the base)[3].

Irradiation (Pyrex filtered) of (3) in t-butanol[4] leads to the formation of two products (ratio 1.3/1 from n.m.r. absortions) which could be separated and isolated by column chromatography on silica gel as crystalline solids. This separation also leads to some hydrolysis of the photoproducts on the column which results in the formation of 1,2-dibenzoylbenzene.



SCHEME

The mass spectra of the two photoproducts showed them to be isomers and also to be isomeric with the starting material. The ^{1}H n.m.r. spectra, in addition to aryl resonances, also showed resonances at 5.4 δ and 5.5 δ which were interpreted as evidence for the presence of the benzhydrylimine group (5) in both products. One reasonable rationalization for the formation of such a moiety from photoisomerization of (3) could be by a 1,3- or 1,5-acyl migration[5] giving (6) and (7) as the two photoproducts (Scheme). It is obvious that the hydrolysis of (6) or (7) would give 1,2-dibenzoylbenzene.

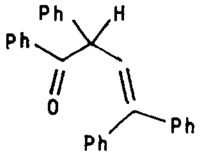
The structure (7) of the minor isomer was finally confirmed by determination of the crystal structure by X-ray analysis[6]. The physical data for the reactant and the two photoproducts are tabled.

Table Physical constants of starting material and photoproducts[a]

Compounds	^{1}H n.m.r. (δ)	i.r.(KBr) (cm^{-1})	m.p.
3	6.1-7.8 (m, aromatic)	1685 (CO), 1615 (CN)	159
6	5.4 (1H, s, CH) 6.9-7.7 (24H, m, aromatic)	1655 (CO), 1615 (CN)	100
7	5.5 (1H, s, CH) 6.9-7.7 (24H, m, aromatic)	1660 (CO), 1618 (CN)	114

a) All the compounds give satisfactory C, H, N microanalysis.

The 1,3 or 1,5-acyl migration into a phenyl substituent suggested by us to account for the formation of the products appears to have no literature precedence. In the related all carbon system (8) only a low yield of the 1,2-acyl migrated product (9) is formed[7]. Even in the case of the crowded ketone (10) phenyl migration occurs yielding the enol ether (11)[8] as well as many products of fragmentation.



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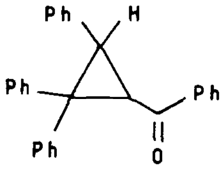

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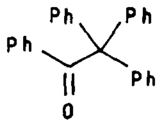

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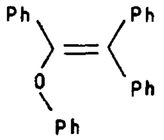

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The failure of both of the above to yield a 1,3-(or 1,5-)benzoyl-migration products highlights the novelty of our observation in a molecule where the carbonyl group is bonded to a carbon atom. It is, of course, well known that 1,3-acyl migration into a benzene ring is common in the Photo-Fries system[9] where the carbonyl group is part of an ester, thioester or amide. It is tempting, therefore, to implicate some involvement of the nitrogen in the outcome of the reaction described by us.

Current work is aimed at identifying the excited state involved in the reaction. It is also intended to synthesize compounds to allow the identification of which path is involved in product formation and whether a 1,3-degenerate migration along the aliphatic skeleton also is operative.

+ We thank the British Council for financial aid.

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4.- In a typical reaction 300 mg of (3) in 400 ml of t-butanol, is irradiated under nitrogen using a Pyrex filter and a 400W medium pressure mercury arc lamp and yields the two photoproducts in a total yield of c.a. 50%.

5.- In addition to these two possible reaction modes there is also the likelihood of a 1,3-degenerate acyl migration along the aliphatic skeleton which can not be detected in this system.

6.- We express our thanks to Drs.C. Ruiz-Valero, A. Monge and E. Gutierrez-Puebla for the determination of the X-ray structure of (6). For details see Acta Cryst., Submitted for publication.

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(Received in UK 9 December 1982)