Tetrahedron Letters,Vol.27,No.28,pp 3293-3296,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

THE NOVEL PHOTOCHEMICAL 1,4-ADDITION OF AZADIENOL ESTERS TO CYCLO-OCTA-1,3-DIENE.

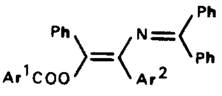
Diego Armesto[a*], William M. Horspool[b], Maria J. Ortiz[a], Rafael Perez-Ossorio[a], and Santiago Romano[a].

a: Departamento de Química Orgánica, Facultad de Ciencias Químicas,
Universidad Complutense, 28040-Madrid, Spain.
b: Department of Chemistry, The University, Dundee DD1 4HN, Scotland.

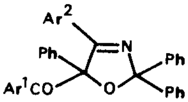
Summary: The unprecedented photocycloaddition of azadienol esters to cyclo-octa-1,3-diene (COD) yields cis- and trans-isomers of 4-aryl-2,2,5-triphenyl-5-(4'-aroyl-cis-cyclo-oct-2'-enyl)-2,5-dihydro-oxazole derivatives. The cycloaddition could arise by COD-trapping of an intermediate produced by intramolecular electron transfer in the azadienol ester.

We recently reported[1] the first example of a 1,2-benzoyl migration in an enol ester system following the irradiative conversion of the azadienol esters (1) into the 2,5-dihydro-oxazoles (2). This process falls into the general di-π-methane framework[2] and following the suggestion of Adam et al.[3] our process is defined as a 1,3-dioxa-di-π-methane rearrangement. These high yield reactions are brought about by direct irradiation and we were interested in establishing the excited state involved.

This problem was approached in the conventional way making use of quenching by added diene such as cyclo-octa-1,3-diene (COD)[4]. The results from this were surprising and are outlined below. The photo-behaviour of azadiene (1a) was dependant upon the concentration of COD. Thus at 0.6M COD the reaction was unaltered from the photoreaction in the absence of COD and yielded the oxazole (2a, 77%) and recovered starting material (1a, 16%). At 2.7M COD a trace of oxazole (2a) was detected but the main reaction path gave a 1:1 ratio of two new compounds in a total yield of 54%. Starting material (1a, 23%) was also recovered. At 3.6M COD no oxazole was detected and the same new compounds were obtained. The irradiation of azadienol ester (1a) was also carried out in hex-1-ene but this yielded only oxazole (2a) and starting material (1a). Similar behaviour to that of (1a) in COD was observed for the other azadienes (1b,c) at high concentrations of COD. The new, colourless, crystalline compounds from all the azadienol esters (1) can be separated readily by chromatography on silica gel. The normal spectroscopic data (^{1}H and ^{13}C n.m.r., i.r., and mass spectra) were recorded and from these it was clear that the pairs of compounds from each of the azadienes were isomeric 1:1 adducts of the azadienes and COD. The data for the adducts from azadienol ester (1b) are given in detail[5]. In these data the ^{13}C n.m.r. spectra of both adducts, Isomer A and Isomer B, show recognisable absorptions for a 2,5-dihidro-oxazole moiety[1] as well as an aryl keto group. The ^{1}H n.m.r. spectra had well resolved absorptions for two vinyl hydrogens as well as two deshielded methine protons. These data alone did not permit complete identification of the compounds and this was solved for Isomer A by an X-ray diffraction study which showed it to be the cis-1:1-adduct (3b)[6].



(1)

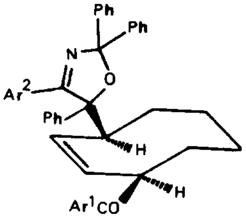


(2)

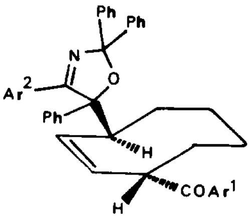
1a=2a=3a=4a : Ar^1=Ph, Ar^2=p-MeC$_6$H$_4$

1b=2b=3b=4b : Ar^1=p-ClC$_6$H$_4$, Ar^2=Ph

1c=2c=3c=4c : Ar^1=Ar^2=Ph



(3)



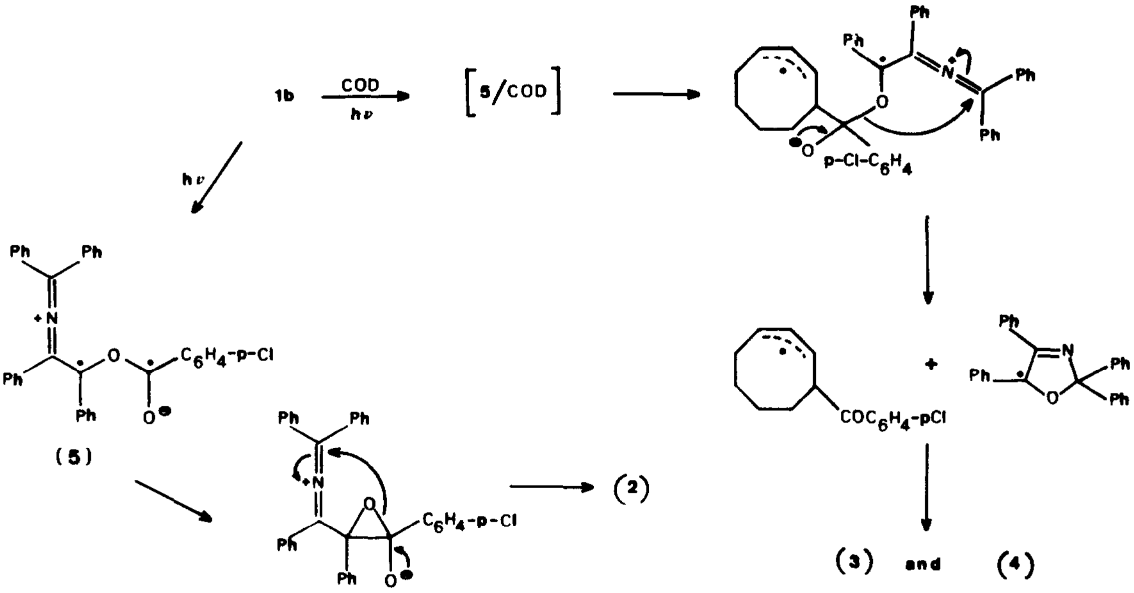
(4)

On the basis of the interconvertibility[7] of Isomer A and Isomer B together with the ^{1}H and ^{13}C n.m.r. spectra the structure of Isomer B is proposed as the trans-1:1-adduct (4b). The adducts (3b) and (4b) can interconvert by epimerization of C-1 in (3) and (4). The X-ray structure of (3b) indicates that the carbonyl group on C-1 should shield the proton on the adjacent vinyl carbon (C-2) while in the trans-isomer (4b) this shielding is absent. This change manifests itself in the Δ_δ values of the two vinyl proton resonances in the two isomers. Thus the cis-isomer (3b) has Δ_δ value of 0.6 ppm while the trans-isomer (4b) has a Δ_δ value of 0.2 ppm. This evidence can be used to identify the isomeric adducts[8] (3 and 4) where there are similar differences in the line positions of the vinyl hydrogens.

Two possible mechanisms were considered for the formation of the adducts (3) and (4).

1. A Norrish Type I fission of the ester carbonyl group followed by radical combination with the COD or
2. The interception by the COD of a radical-cation/radical-anion intermediate formed on photoexcitation of the azadienol esters.

The Norrish Type I path can be discounted on the grounds that the irradiation of the azadiene (1a) in hex-1-ene fails to yield 1:1 adducts of the azadiene and the alkene. We propose that irradiation of the azadienol esters in high concentrations of COD results in the formation of a complex[9] between COD and the intermediate (5) produced by an electron transfer[10] from the imine nitrogen to the ester carbonyl function following photo-excitation. The intermediate (5) normally rearranges[1] to 2,5-dihidro-oxazole (2) in the absence of COD but in this case (5) is trapped by the diene. While a concerted process is conceivable the formation of both isomers (3) and (4) at the same time precludes this mechanism. Thus the addition could follow the path illustrated below.



The results described by us are novel and report for the first time the addition of azadienol esters (an enol ester) to a diene. Currently we are examining the reactivity of the azadienol esters with other dienes and also with electron rich alkenes in order to verify the mechanism and to establish the scope of this new addition reaction.

We gratefully acknowledge financial assistance from the British Council and the Comisión Asesora de Investigación Científica y Técnica.

REFERENCES AND NOTES

1. D. Armesto, M.J. Ortiz, R. Perez-Ossorio, and W.M. Horspool, *Tetrahedron Lett.*, 1983, 24, 1197; idem, *J. Chem. Soc. Perkin Trans., I*, 1986, in press.
2. S.S. Hixson, P.S. Mariano, and H.E. Zimmerman, *Chem. Rev.*, 1973, 73, 531.
3. W. Adam, A. Berkessel, K. Hildebrand, E. Peters, K. Peters, and H.G. von Schnering, *J. Org. Chem.*, 1985, 50, 4899.
4. N.J. Turro, *Modern Molecular Photochemistry*, Benjamin Cummings Publishing Co. Inc., Menlo Park, California, 1978.
5. Spectroscopic data Isomer A (3b): m.p. 220-222°C; ν max(KBr) 1680(C=O), 1630 (C=N); ^{1}H n.m.r.(CDCl$_3$) δ 1.2-2.0 (8H, m, CH$_2$), 2.1-2.3 (1H, q, CH), 3.1-3.3 (1H, quint., CH), 5.0-5.1 (1H, dd, CH), 5.7-5.8 (1H, dd, vinyl), 6.9-7.9 (24H, m, aryl); ^{13}C n.m.r.(CDCl$_3$) δ 25.3-29.4 (CH$_2$), 43.1 (CH), 47.8 (CH), 98.9 (oxazole), 110.5 (oxazole), 132.0-145.9 (aryl and vinyl), 169.5 (C=N), 199.6 (C=O). Spectroscopic data Isomer B (4b): m.p. 112-114°C; ν max(KBr) 1690 (C=O), 1630 (C=N); ^{1}H n.m.r.(CDCl$_3$) δ 1.1-2.2 (8H, m, CH$_2$), 3.9 (1H, dd, CH), 5.7 (1H, dd, vinyl), 5.9 (1H, dd, vinyl), 6.7-7.8 (24H, m, aryl); ^{13}C n.m.r.(CDCl$_3$) δ 27.4-37.3 (CH$_2$), 46.0 (CH), 48.9 (CH), 97.6 (oxazole), 110.0 (oxazole), 125.1-147.0 (aryl and vinyl), 170.4 (C=N), 198.4 (C=O).
6. J.M. Mohedano, F. Florencio, and S. Garcia-Blanco, *Z. Kristallogr.*, 1986, 172, 239.
7. The isomers (3) and (4) are interconvertible on prolonged standing in solution.
8. The cis-isomer (3a) has a Δ_δ value of 0.5 ppm while the trans-isomer (4a) has a Δ_δ value of 0.1 ppm. Similarly the Δ_δ value for (3c) is 0.6 and the Δ_δ value for (4c) is 0.4 ppm.
9. Normally one sees electron transfer processes involving electron rich alkenes (a) or dienes (b). (a) S.L. Mattes and S. Farid, *Org. Photochem.*, 1983, 6, 233; (b) F.D. Lewis, R.J. De Voe, and D.B. Mac Blane, *J. Org. Chem.*, 1982, 47, 1392.
10. P.S. Mariano and J.L. Stavinoha, *Synthetic Organic Photochemistry*, Ed. W.M. Horspool, Plenum Press, New York and London, 1984.

(Received in UK 28 April 1986)