

Dienamide Photochemistry

Christophe Bochu, Axel Couture,* Pierre Grandclaoudon, and Alain Lablache-Combier

Laboratoire de Chimie Organique Physique, U.A. 351, Université des Sciences et Techniques de Lille, 59655 Villeneuve d'Ascq Cedex, France

In contrast to monocyclic dienamides which undergo a photochemical Fries rearrangement, photolysis of the corresponding bicyclic compounds yields exclusively condensed six-membered rings possessing a spiro heterocyclic framework.

Owing to mesomerism which confers to the amide group a partial double bond character, aromatic enamides, compounds in which this chromophore connects two unsaturated systems, exhibit photochemical behaviour similar to that of conjugated hexatrienic models. Indeed, u.v. irradiation of aromatic enamides induces the cyclization of the 6 π -electron system, thus providing a general approach to the synthesis of a wide variety of six-membered lactams.¹ Paradoxically, few reports have dealt with the photochemical behaviour of dienamides, a class of compounds in which the amide group is connected to a dienic system. In this paper we report the photoreactivity and the potential of such models in organic synthesis. To avoid problems arising from the photoisomerization of these polyenic compounds, we have focused our investigation on the monocyclic and bicyclic compounds (**1a,b**) and (**3a–e**).

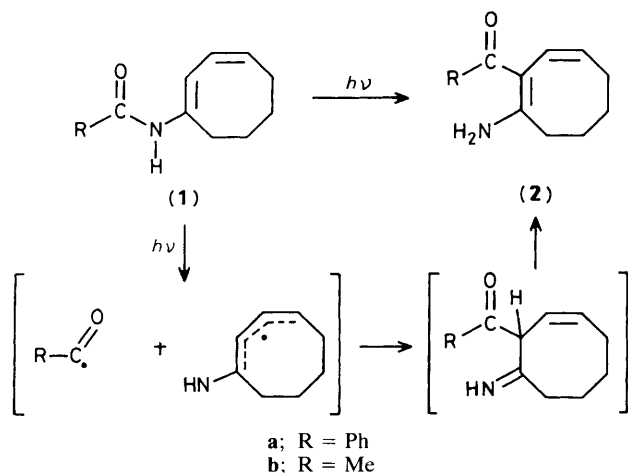
The secondary dienamides (**1a,b**) and (**3a–e**) are readily accessible by direct condensation of the appropriate carboxamide with cyclo-octen-3-one² and (cyclohex-1-enyl)-cyclohexan-2-one³ respectively. Reactions are carried out in a Dean–Stark apparatus. A mixture of the carboxamide (0.1 mol) and ketone (0.1 mol) in toluene is refluxed for 24 h in the presence of a catalytic amount of β -naphthalene sulphonic acid. The yields for the formation of (**1a**) and (**3a**) are estimated at 57 and 65%, respectively. Dienamides (**3a–e**) may also be obtained, although in lower yield (38%), by reacting directly the aromatic carboxamide with cyclohexanone. This reaction dramatically contrasts with aliphatic carboxamides, which under the same conditions, give rise exclusively to mono-enamides.⁴

Irradiation (Rayonet RPR 2537 and 3000 Å lamps, 2 h) of a carefully degassed 10^{-2} M hexane solution of the dienamides (**1a,b**) in a quartz reactor leads exclusively (yield 85%) to the dienaminoketones (**2a,b**) as shown in Scheme 1. No trace of a

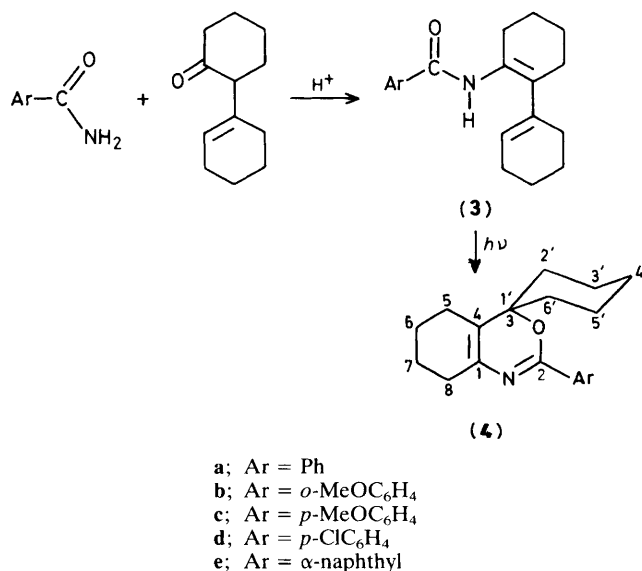
cyclized compound could be detected in the photoproduct of (**1a**), in contrast to the reported photocyclization of rather similar systems in which the double bond α to the nitrogen atom is further conjugated with a carbonyl group.⁵ Furthermore it should be noted that the photoproducts (**2a,b**) are formed in an exclusive 1,3-acyl migration (Scheme 1).

On the other hand, u.v. irradiation (quartz reactor, Rayonet RPR 2537 Å lamp, 2 h) of an oxygen-purged hexane solution (10^{-2} M) of the bicyclic dienamides (**3a–e**) leads exclusively and efficiently (yields in the range 78–82%) to the condensed six-membered heterocycles with a spiro carbon centre (**4a–e**) (Scheme 2). The structure of (**4**) was determined by ¹H n.m.r. spectroscopy which principally indicates the disappearance of both NH and olefinic protons of (**3a–e**) at δ ca. 7.5 and 5.62 [values given for (**3a**)]. The spirostructure of (**4a–e**) was mainly confirmed by 400 MHz ¹³C n.m.r. spectroscopy (C₆D₆) which exhibits resonance for (**4a**) at δ 154.3 (C-2), 136.0 (Ph), 134.3 (C-1), 130.7 (Ph), 128.3 (Ph), 128.0 (Ph), 120.2 (C-4), 78.6 (C-1'), 32.9 (C-2'–C-6'), 30.1 (C-8), 25.6 (C-4'), 23.6 (C-5), 23.1 (C-6, C-7), 21.2 (C-3'–C-5'). By comparison of DEPT spectra with different pulse angles θ compound (**4a**) was found to contain nine methylene, five methine (exclusively aromatic), and five quaternary carbon atoms. The quaternary character of the carbon nucleus C-1', α to the oxygen atom, unambiguously establishes the spiro structure of (**4a**).

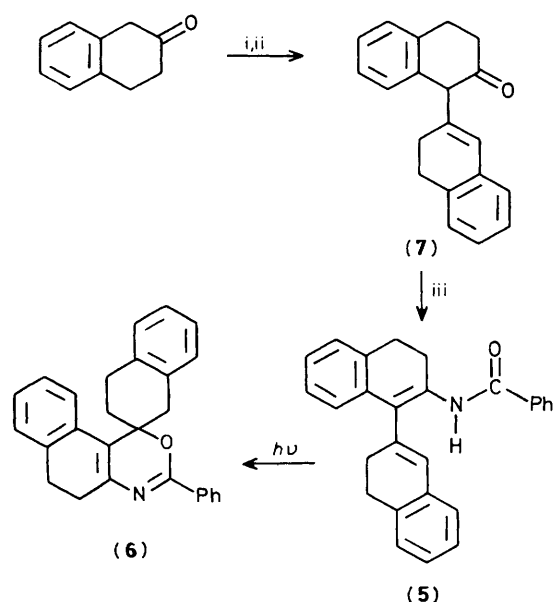
This type of photoaddition can be extended to the synthesis of polycyclic nitrogen compounds such as (**6**) (quaternary carbon C-1' at δ 88.5 in the 400 MHz n.m.r. spectrum) by u.v. irradiation of the appropriate dienamide (**5**), as illustrated by



Scheme 1



Scheme 2



Scheme 3. Reagents: i, TiCl_4 , CHCl_3 , -10°C ; ii, H_2O ; iii, benzamide, H^+ , toluene.

Scheme 3. The β,γ -unsaturated ketone (7) was originally synthesized by treatment of β -tetralone with titanium tetrachloride, as recently described by Eisenbraun *et al.* for the corresponding α -derivative.⁶

The inability of 1,3-acyl migration in (3) is probably the cause of the difference in photoreactivity of (1) and (3). A

similar phenomenon has been noted for mono- and di- β -substituted enamides.^{7,8} To our knowledge these photo-reactions illustrate a very rare example of an intramolecular addition of an amido group to an unsaturated system,⁹ via its tautomeric form and lead to the creation of a spiro centre in one step.¹⁰

Received, 21st October 1985; Com. 1501

References

- 1 I. Ninomiya and T. Naito, *Heterocycles*, 1981, **2**, 1433; *Alkaloids* (NY), 1983, **22**, 189.
- 2 N. Heap and G. H. Whitham, *J. Chem. Soc. (B)*, 1966, 164.
- 3 E. Wenkert, S. K. Bhattacharya, and E. M. Wilson, *J. Chem. Soc.*, 1964, 5617.
- 4 U. Zagavi and D. Ben Ishai, *J. Org. Chem.*, 1961, **26**, 1097; O. Meth-Cohn and K. T. Westwood, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1173.
- 5 I. Ninomiya and T. Naito, Abstracts of Papers, 22nd Kinki Regional Meeting, Pharmaceutical Society of Japan, Osaka, 1972, p. 23; I. Ninomiya, T. Kiguchi, and T. Naito, *J. Chem. Soc., Perkin Trans. 1*, 1973, 2257.
- 6 A. G. Holba, V. Premasager, B. C. Barot, and E. J. Eisenbraun, *Tetrahedron Lett.*, 1985, **26**, 571.
- 7 A. Couture, R. Dubiez, and A. Lablache-Combiere, *Tetrahedron*, 1984, **40**, 1835.
- 8 J. C. Gramain, Y. Troin, and D. Vallée, *J. Chem. Soc., Chem. Commun.*, 1981, 832.
- 9 O. L. Chapman and W. R. Adams, *J. Am. Chem. Soc.*, 1968, **90**, 2333.
- 10 For a review of heterocyclic spiro compounds, see A. Krapcho, *Synthesis*, 1978, 77.