Pergamon

Tetrahedron Letters 39 (1998) 2437–2440

TETRAHEDRON
LETTERS

A Novel Photochemical Rearrangement of 1,3-Diaryl-1,2-dihydropentalenes to the 1,5-Isomers and their Domino Diels-Alder Reactions

Vijay Nair*, G. Anilkumar, C. N. Jayan and Nigam P. Rath

Organic Chemistry Division, Regional Research Laboratory (CSIR), Trivandrum-695 019, INDIA.

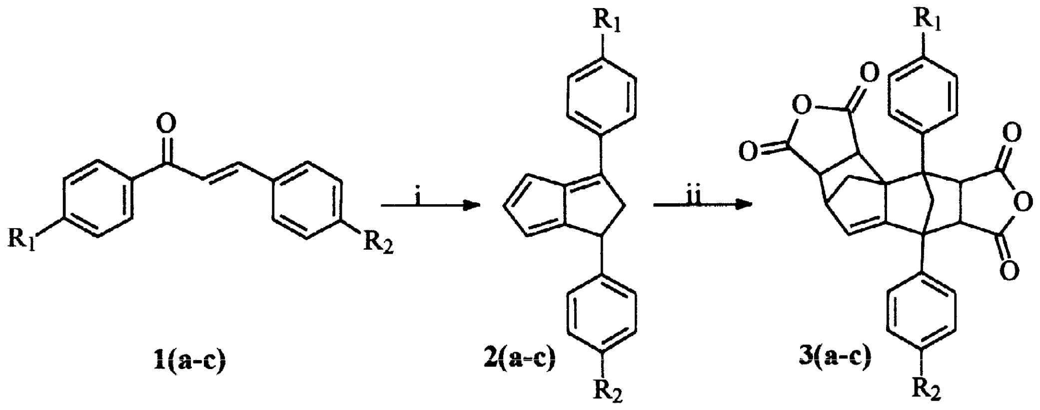
Received 16 December 1997; accepted 23 January 1998

***Abstract**: Novel photochemical rearrangement of 1,3-diaryl-1,2-dihydropentalenes to 1,5-isomers and the subsequent domino Diels-Alder reactions of the latter with maleic anhydride are described.* © 1998 Elsevier Science Ltd. All rights reserved.

The chemistry of dihydropentalenes has been of interest primarily due to their value as synthons for polyquinane frameworks that are present in a number of important sesquiterpenoid natural products.[1] The Diels-Alder cycloadditions of 1,2-dihydropentalenes with DMAD and other dienophiles leading to 1,7-cyclopentanonorbornadienes have been investigated.[2] Also known are their thermal and acid catalysed rearrangements to 1,5-dihydropentalenes.[3] Recently, we have investigated the cycloadditions of pentafulvenes with *o*-quinones[4] and subsequently unraveled the multiple cycloaddition profiles of 6-arenylfulvenes[5] that are isomers of dihydropentalenes. During these studies we encountered a novel photoinduced transformation of 1,3-diaryl-1,2-dihydropentalenes to the 1,5-isomers and the domino Diels-Alder reactions of the latter.[6] We have explored these reactions and the results are presented here.

The present investigations involved the novel 1,3-diaryl-1,2-dihydropentalenes **1(a-c)** and these were synthesized from the corresponding chalcones by reaction with cyclopentadiene in presence of pyrrolidine. The red crystalline products **2(a-c)** on treatment with maleic anhydride in benzene afforded the domino Diels-Alder diadducts **3(a-c)** of the 1,5-dihydropentalenes (Scheme 1). The products **3(a-c)** were purified by silica gel column chromatography which afforded colourless crystalline solids.[7] Conclusive evidence for the structure of the diadducts was obtained by single crystal X-ray analysis of **3a**.[8] It was evident from the structure of **3(a-c)** that 1,2-dihydropentalenes **1(a-c)** underwent an isomerisation to 1,5-dihydropentalenes prior to cycloaddition.

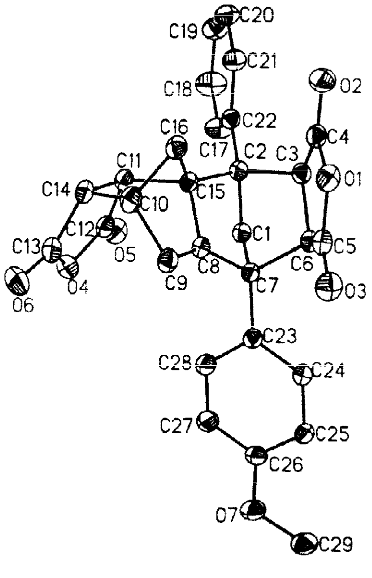
0040-4039/98/$19.00 © 1998 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(98)00219-6



Entry	Enone	Substituents	1,2-Dihydropentalene	Yield (%)*	Diadduct	Yield (%)*
1	**1a**	R_1= H, R_2= OMe	**2a**	42	**3a**	80
2	**1b**	R_1= OMe, R_2= OMe	**2b**	32	**3b**	62
3	**1c**	R_1= Me, R_2= OMe	**2c**	35	**3c**	85

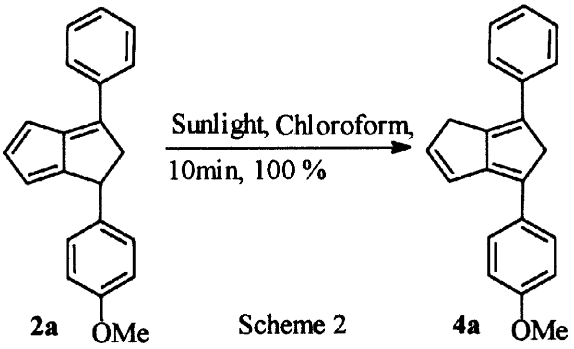
i, Cyclopentadiene (3 eqts), pyrrolidine (2 eqts), MeOH, RT, 24 h. ii, Maleic anhydride (2.5 eqts), benzene, RT, 24h
*Isolated yield

Scheme 1



X-ray structure of **3a**

Our initial suspicion that this interesting rearrangement may be photoinduced has its origin in the casual observation of a change in the NMR spectrum of a sample solution left exposed to laboratory light; during this process the red solution turned yellow. The photochemical nature of the isomerisation was further confirmed by the fact that no rearrangement occured in the dark. This change of 1,2-dihydropentalene **3a** to the 1,5-dihydropentalene **4a** (Scheme 2) can be viewed as a photoinduced 1,5-hydrogen shift.



Scheme 2

The structure of **4a** was assigned by spectroscopic methods.[7] Moreover, the reaction of **4a** with maleic anhydride in benzene afforded the same diadduct **3a** in 75% yield under identical conditions.

The transformation was monitored by carrying out the photolysis using 200 W Xenon mercury lamp and simultaneously recording the absorption spectra on a Shimadzu UV-2100 spectrophotometer. On photolysis of **2a** in $CHCl_3$ (10^{-4} Molar solution) by means of monochromatic light of wavelength 450 nm, the absorption intensity at 320 nm and 450 nm were found to decrease, while a new peak was formed at 386 nm corresponding to the formation of **4a**. The change of UV absorption spectra corresponding to the isomerization is illustrated in Figure 1. Similar photochemical isomerizations were observed in the case of **2b** and **2c** also, yielding the corresponding 1,5-dihydropentalenes. In all the cases, the photorearrangement was characterized by three isosbestic points.

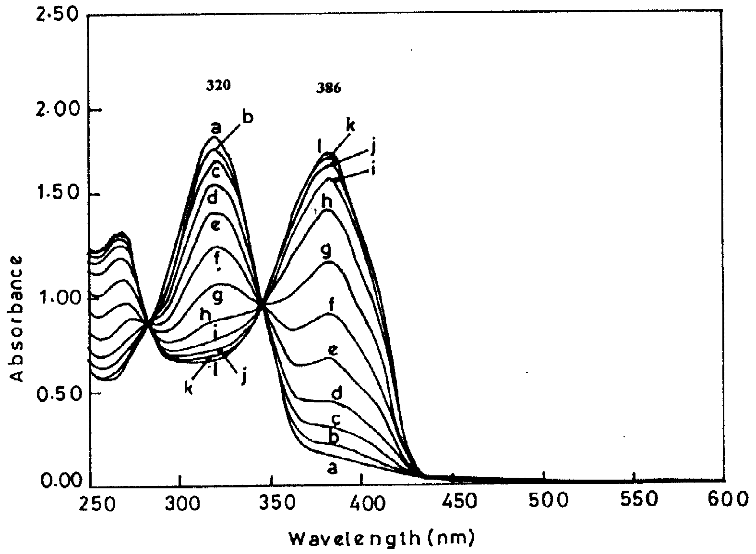


Figure 1. Photolysis of 1,2-dihydropentalene **2a** (curve *a*) to yield 1,5-dihydropentalene **4a** (curve *l*). The absorption curves *a* to *l* were measured at 30 sec intervals.

The authors thank Mr. N. Manoj, Photochemistry Research Unit, RRL, Trivandrum for his valuable suggestions and help. GA and CNJ thank CSIR, New Delhi for research fellowships.

References and notes :-

1. a) Linder, H. J. *Pentalene und Dihydropentalene, In Methoden der Organischen Chemie* (Houben-Weyl), 4th Ed., *Vol. V/ 2c*, 103, George Thieme Verlag, Stuttgart, **1985**. b) Paquette, L. A.; Doherty, A. M.; *Polyquinane Chemistry*, Springer Verlag, Berlin-Heidelberg, **1987**.
2. Griesbeck, A. G.; Deufel, T.; Peters, K.; Peters, E-M.; von Selmering, H. G.; *Angew. Chem. Int. Ed. Engl.*, **1993**, *32*, 97.
3. Griesbeck, A. G. *Chem. Ber.*, **1991**, *124*, 403.
4. a) Nair, V.; Kumar, S.; Williard, P. G. *Tetrahedron Lett.*, **1995**, *35*, 1605 b) Nair, V.; Kumar, S. *Tetrahedron*, **1996**, *52*, 4029. c) Nair, V.; Kumar, S.; Anilkumar, G.; Nair, J. S. *Tetrahedron*, **1995**, 51, 9155. d) Review: Nair V.; Kumar, S. *Synlett*, **1996**, 1143.
5. a) Nair, V.; Nair, A. G.; Radhakrishnan, K. V.; Nandakumar, M. V.; Rath, N. P. *Synlett*, **1997**, 767. b) Nair, V.; Anilkumar, G.; Radhakrishnan, K. V.; Sheela, K. C.; Rath, N. P. *Tetrahedron*, **1997**, 0000.
6. An isolated example of a 1,5-dihydropentalene undergoing domino Diels-Alder addition has been reported. Adam, W.; Deufel, T.; Finzel, R.; Griesbeck, A. G.; Hirt, J. *J. Org. Chem.*, **1992**, *57*, 14, 3991.
7. Spectral data for illustrative examples **3a**: (MP. 212-215 °C). IR (KBr): 2944, 1864, 1786, 1616, 1582, 1520, 1448, 1314, 1228, 1085, 926, 888, 820, 770, 700 cm^{-1}. ^{1}H NMR in CDCl$_3$: δ 7.72 (d, J=7.6 Hz, 2H), 7.47 (m, 5H), 6.95 (d, J=8.6 Hz, 2H), 5.96 (d, J=2.4 Hz, 1H), 4.28 (d, J=10.8 Hz, 1H), 3.77 (m, 7H), 3.21 (d, J=6 Hz, 1H), 2.59 (d, J=11.6 Hz, 1H), 2.29 (d, J=9.2 Hz, 1H), 1.72 (d, J=9.6 Hz, 1H). ^{13}C NMR in CDCl$_3$: δ 172.86, 171.96, 171.46, 170.05, 158.60, 158.03, 138.04, 129.00, 128.70, 127.99, 127.33, 123.87, 114.05, 70.49, 56.86, 56.23, 55.10, 54.38, 54.10, 48.15, 47.61. Analysis: Found: C-72.28%, H-4.49 % (calculated: C-72.34%, H-4.39%) **4a**: (MP. 123-126 °C). IR, KBr: 2935, 1602, 1499, 1282, 1248, 1177, 1034, 822,755 cm^{-1}. ^{1}H NMR: δ 7.35 (m, 7H), 6.91 (m, 3H), 6.63 (m, 1H), 4.10 (s, 2H), 3.84 (s, 3H), 3.42 (brs, 2H). ^{13}C NMR: δ 158.02, 150.53, 147.90, 141.86, 136.81, 130.52, 130.21, 128.70, 127.78, 127.43, 126.99, 125.75, 125.57, 114.28, 55.42, 47.56, 33.49.
8. Crystal data for **3a** : $C_{29}H_{22}O_7$, Fw-482.47, 0.33x0.40x0.20 mm, Monoclinic, Space group C2/c, Unit cell dimensions a=24.0335(11) Å, α= 90°; b= 10.9341(5) Å, β= 96.306(5)°; c= 16.8561(9) Å, γ= 90°. R indices (all data) R1=0.0494, WR2= 0.1262. Volume, Z= 4402.7(4) Å^3, 8. Dcalc= 1.456 Mg/m^3. F(000)= 2016. Absorption Coefficient= 0.863 mm^{-1}; Reflections collected = 4022. (Sheldrick, G. M., Siemens, Analytical X-ray Division, Madison, WI, 1995).