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Photocyclization of a conjugated triaryl 'Y-enyne'[†]

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Abstract—Upon irradiation at 350 nm, in the presence/absence of oxygen, 'Y-enyne' **1** undergoes electrocyclic ring closure to photoproduct **4**. A mechanism involving an allene intermediate is proposed. In nonpolar solvents a [1,5] H shift affords the photoproduct, while in methanol protonation of the central allenic carbon occurs. Quantum yields of the photoreaction in the different solvents were measured. © 2001 Published by Elsevier Science Ltd

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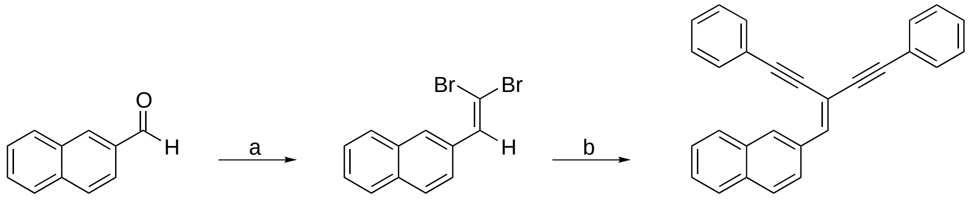
Interest in conjugated enynes has grown because of their wide range of applications in non-linear optics (NLO),[1,2] liquid crystals,[3] optical switches,[4] and medicine.[5] In order to investigate these properties, as well as to study the effect of stacking in the solid state on photodimerization and photocyclization, we have synthesized a series of conjugated triaryl enynes (so-called 'Y-enynes'). In this paper, we report the synthesis and photochemistry of 2-(ethynylphenyl)-1-(2-naphthyl)-4-phenyl-1-buten-3-yne **1**. Naphthaldehyde was converted via Corey–Fuchs reaction[6] to 1,1-dibromo-2-[2-naphthyl]-ethene **2**, which was coupled with phenylacetylene via Sonogashira coupling[7] affording 'Y-enyne', **1**[8] (Scheme 1).

Tinnemans and Laarhoven first reported on the photocyclization of enynes[9] proposing a radical mechanism[10] in nonpolar solvents (hexane and benzene) and an ionic mechanism in methanol. In a subsequent paper in the series,[11] Van Arendonk et al. proposed a 1,2,4-cyclohexatriene derivative formed from the singlet-excited *cis*-1,4-diaryl-butenyne as the primary reaction intermediate. This led to product via either a radical intermediate, an ionic intermediate or under an argon atmosphere directly by intramolecular hydrogen shift. We suggest photocyclization of **1** occurs entirely via an intermediate cumulene in methanol, hexane and benzene under both argon and air atmospheres (Scheme 2). Excited singlet state **1*** undergoes electrocyclic ring closure to form the allene **3**.[12] In CH_3OX, protonation/deuteration of the central allenic carbon (**3**) affords **4** or **5**. Previously, Rodríguez et al. reported deuterium incorporation in the allenic intermediate upon heating benzotriyne in CH_3OD.[13] The addition of trifluoroacetic acid increases the rate of photocyclization of **1** in CH_3OH due to the increase of H^+ concentration in the system and, as a result, protonation of the central allenic carbon occurs faster.

When a solution of **1** ($\lambda_{max} = 220$, 282, 292 and 354 nm; $10^{-4}\ \varepsilon = 2.8$, 2.7, 2.7 and 2.4 $M^{-1}\ cm^{-1}$, respectively) in MeOH (40 μM) was irradiated at 350 nm in the pres-



2 **1**

Scheme 1. Synthesis of 'Y-enyne' **1**: (a) CBr_4, CH_2Cl_2, PPh_3, argon, 4 h, 0°C; (b) $Pd(PPh_3)_2Cl_2$, CuI, THF, NEt_3, argon, 3.5 h, 70°C.

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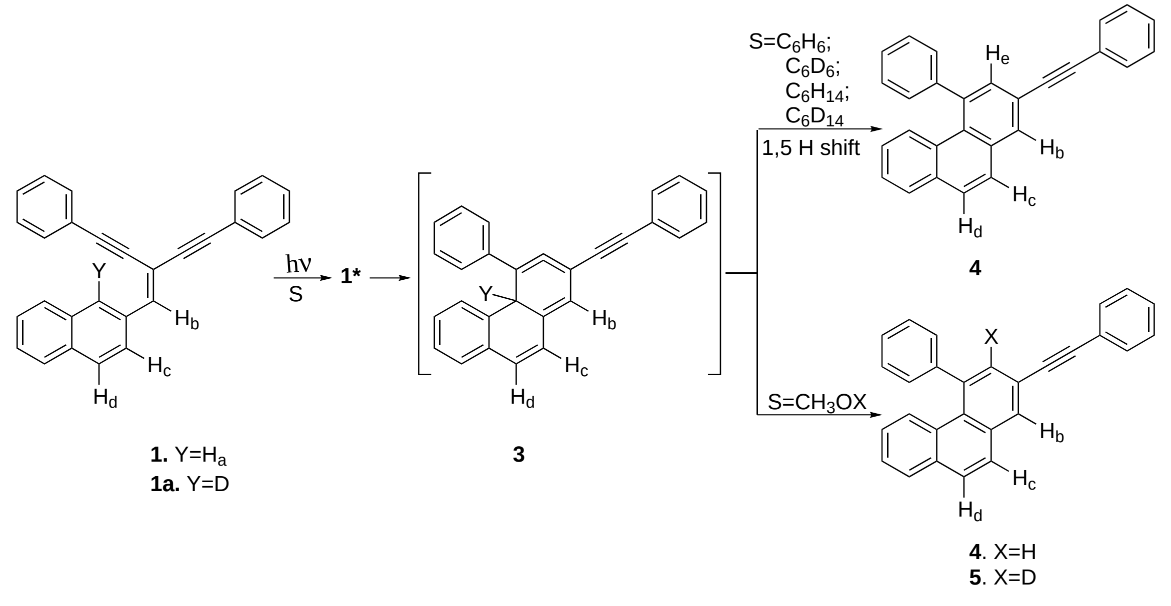

Scheme 2. Proposed mechanism for photocyclization of **1**.

ence of air, the UV spectrum showed two clear isobestic points indicating the conversion of **1** to a single new product (Fig. 1).

When followed by NMR, the reaction of **1** in C_6D_6 gives the spectra in Fig. 2. The starting material **1** shows two distinct peaks (Fig. 2a) with the most downfield peak, a broad singlet due to *meta* coupling with H_c, assigned to H_a. The latter is a doublet of doublets ($J_{meta} = 1.4$ Hz). Irradiation at 350 nm in benzene caused the two peaks of the starting material to disappear and, eventually, four new peaks to appear. H_b, H_c and H_e are assigned to photoproduct **4** (Fig. 2c).[14] H_b and H_e are *meta* coupled, while H_c is coupled to H_d and is therefore a doublet. Similar results were observed when **1** was irradiated in C_6H_6, C_6D_6, C_6H_{14}, C_6D_{14}, indicating that these solvents are not involved in the photoreaction. The proposed H-shift was confirmed by irradiating the deutero-labeled Y-enyne[15,16] **1a** in hexane. This leads exclusively to **5**.[17]

Irradiation of **1** in CH_3OD led to deuterium incorporation (GC/MS and ^1H NMR), but no deuteration was observed when irradiation was carried out in CD_3OH. The H_b peak in the photoproduct found upon irradiation in MeOH, a doublet *meta* coupled with H_e, became a singlet upon irradiation of **1** in CH_3OD. This was accompanied by the disappearance of the H_e peak (Fig. 2d). GC/MS (DIP) indicated a MW of 355 (MW of **1** is 354).

The quantum yields of the photoreaction in hexane, methanol and benzene were 9.8×10^{-3}, 1.04×10^{-3} and 9.0×10^{-4}, respectively. Since oxygen fails to quench the photoreaction, we suggest that the reaction occurs from the singlet state ($E_s = 88$ Kcal/mol).

In summary, 'Y-enyne' **1** photocyclizes through an allene intermediate under both argon and air atmospheres. It appears that the presence of an additional ethynylphenyl group in **1** has changed the mechanism of photocyclization from those previously reported. Studies of this change are ongoing.

Acknowledgements

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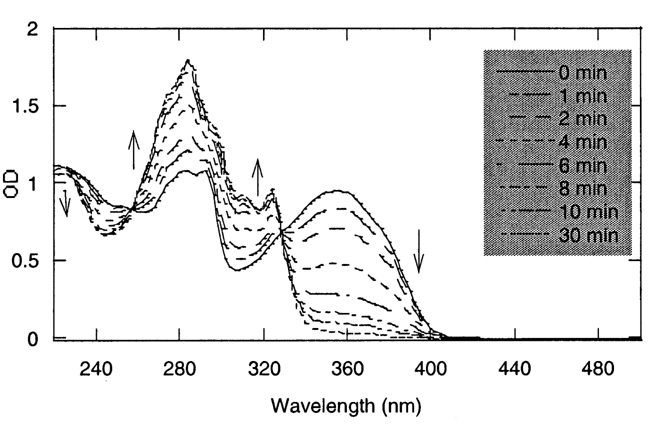

Figure 1. Steady state UV–vis absorption spectra of **1** in MeOH (40 μM) when irradiated at 350 nm in the presence of air.

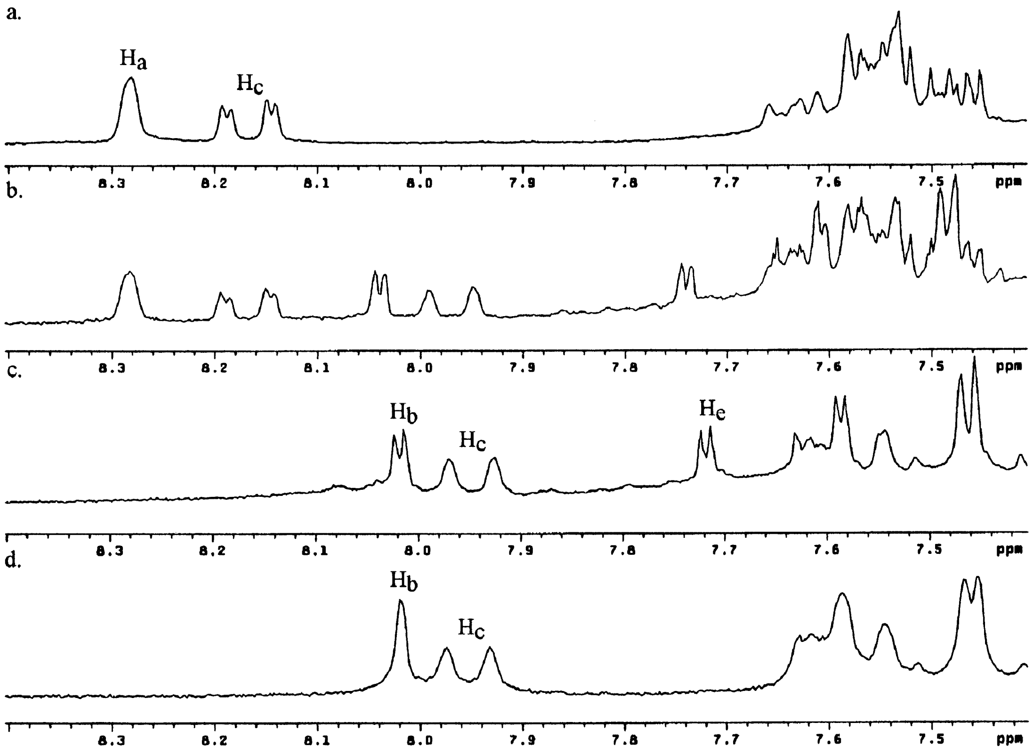

Figure 2. ^{1}H NMR spectrum of **1** in C_6D_6 upon 350 nm irradiations. Irradiation time is (a) 0 h; (b) 13 h; (c) 32 h (photoproduct **4**). (d) ^{1}H NMR spectrum of **5** dissolved in C_6D_6.

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8. Pure product **1** (yellow solid) was isolated in 36% yield: mp 83–87°C; $R_f = 0.63$ (ethyl acetate:hexane, 1:9). ^{1}H NMR (200 MHz, acetone-d_6): δ 7.43–7.53 (m, 7H), 7.55–7.62 (m, 4H), 7.66–7.71 (m, 2H), 7.92–8.02 (m, 4H), 8.25–8.30 (dd, 1H, $J_1 = 8.4$, $J_2 = 1.4$ Hz), 8.54 (s, 1H); ^{13}C NMR (200 MHz, acetone-d_6): δ 123.79 (C), 127.23 (CH), 127.98 (CH), 128.47 (CH), 128.98 (CH), 129.40 (CH), 129.84 (CH), 129.96 (CH), 130.15 (CH), 130.55 (CH), 132.77 (CH), 134.62 (C), 135.09 (C), 144.58 (CH). HR-MS: calcd for m/z 354.140851, found m/z 354.140130.
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12. Wittig and Fritze originally demonstrated the existence of a six-membered cyclic allene, 1,2-cyclohexadiene.[12a] Other six-membered allenes have been reported and trapped by [2+2] cycloadditions and with Diels–Alder reaction.[12b,12c] The energetic plausibility of cycloadditions proceeding through these intermediates was also supported by ab initio calculations.[12d] Hopf et al. reported that the thermal isomerization of 1,3-hexadiene-5-yne derivatives proceeds via an allene intermediate. However, the main product was the dimer, and only traces of the cyclized isomer product were collected upon heating the dimer.[12e] Irradiation of the acyclic conjugated 'Y-enyne'-like structure led to an analogue of the Bergman rearrangement.[12f] (a) Wittig, G.; Fritze, P. *Angew. Chem., Int. Ed.* **1966**, *5*, 846–848; (b) Christl, M.; Braun, M.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 473–476; (c) Miller, B.; Shi, X. *J. Am. Chem. Soc.* **1987**, *109*, 578–579; (d) Burrell, R. C.; Daoust, K. J.; Bradely, A. Z.; DiRico, K. J.; Johnson, R. P. *J. Am. Chem. Soc.* **1996**, *118*, 4218–4219; (e) Hopf, H.; Berger, H.; Zimmermann, G.; Nüchter, U.; Jones, P. G.; Dix, I. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1187–1190; (f) Zheng, M.; DiRico, K. J.; Kirchhoff, M. M.; Phillips, K. M.; Cuff, L. M.; Johnson, R. P. *J. Am. Chem. Soc.* **1993**, *115*, 12167–12168.
13. Cyclization to phenanthrene rather than anthracene is confirmed by the disapperance of H_a peak (Fig. 2c).
14. The photoproduct **4**, 4-phenyl-2-phenylethynylphenanthrene (yellow solid) was isolated by preparative TLC in 90%: mp 134–137°C; $R_f = 0.72$ (ethyl acetate:hexane, 1:9). ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.08–7.16 (m, 2H), 7.35–7.40 (m, 3H), 7.46–7.47 (d, 5H, $J = 2.6$ Hz), 7.55–7.56 (d, 1H, $J = 2.2$ Hz), 7.58–7.60 (m, 1H), 7.61–7.62 (d, 1H, $J = 1.8$ Hz), 7.67–7.72 (d, 1H, $J = 8.8$ Hz), 7.76 (s,

2H), 7.81–7.85 (d, 1H, $J=8.8$ Hz), 8.07–8.08 (d, 1H, $J=1.8$ Hz); ^{13}C NMR (200 MHz, acetone-d_6): δ 123.2 (C), 125.77 (C), 127.95 (CH), 129.37 (CH), 129.74 (CH), 130.3 (CH), 130.61 (CH), 131.25 (CH), 131.41 (CH), 131.52 (CH), 131.96 (CH), 132.67 (C), 134.1 (CH), 134.32 (CH), 135.54 (CH), 136.58 (C), 136.63 (C), 143.77 (C), 147.19 (C). HR-MS: calcd for m/z 354.140851, found m/z 354.141069.

15. 2-(Ethynylphenyl)-1-(1-deutero-2-naphthyl)-4-phenyl-1-buten-3-yne **1a** was synthesized according to Scheme 1 using 1-deutero-2-naphthaldehyde, which was synthesized according to literature methods.[15a] (a) Wilcox, C. F.; Lahti, P. M.; Rocca, J. R.; Halpern, M. B.; Meinwald, J. *Tetrahedron Lett*. **1978**, 1893–1896.
16. Deuterium was incorporated in >90% in **1a** based on the ^{1}H NMR spectra. MS ($M^+=355$).
17. Deuterium was incorporated in >90% in **5** based on the ^{1}H NMR spectra. MS ($M^+=355$).