The Formation of Aryltetralin Derivatives in the Photolysis of Two *trans*-Cinnamoyl Moieties at Both Ends of a Polyethylene Glycol Chain in the Presence of Lithium Perchlorate

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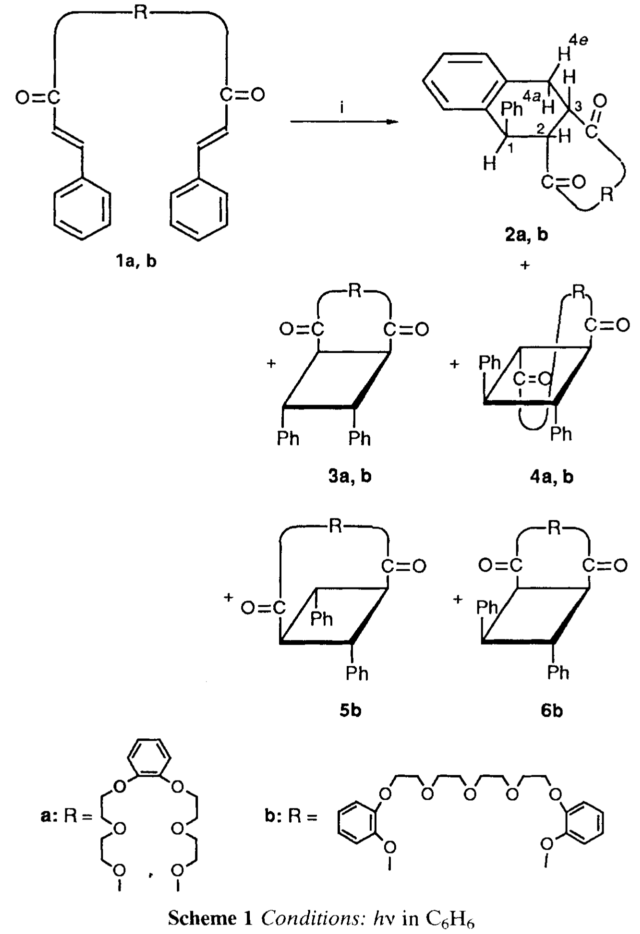
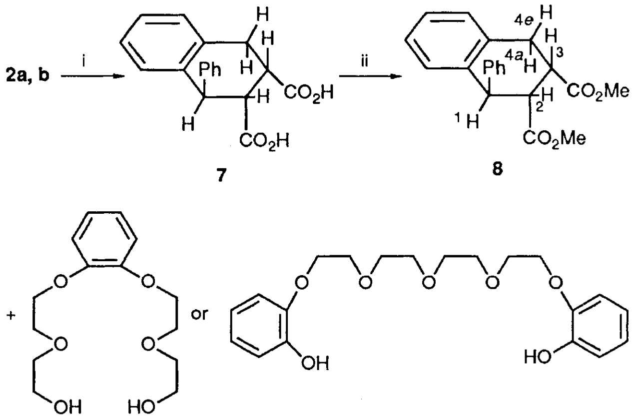
A straightforward photochemical route to aryltetralin derivatives **2a,b** from a podand system containing a pair of *trans*-cinnamoyl moieties is reported.

Although there are many reports of the regio- and stereoselective [2π + 2π] photocycloaddition of *trans*-cinnamoyl moieties both in plants and in the solid state,[1,2] formation of aryltetralin derivatives as [4π + 2π] photoadducts has not been reported in the photochemistry of *trans*-cinnamoyl moieties under any conditions. We have accidentally discovered a straightforward route to aryltetralin derivatives **2a,b** from podands containing a pair of *trans*-cinnamoyl moieties. We now report this unusual but important photochemistry and the structural analysis of **2a,b**.

We have prepared the podands **1a,b**, the topology of which can be controlled through circumferential organization by alkali metal cations.[3,4] The irradiation of a homogeneous MeCN solution of these podands in the presence of metal perchlorates gave mainly the δ-truxinate derivatives **4a,b**. However, after irradiation of a sonicated suspension of $LiClO_4$ in a benzene solution of the podand **1a** or **1b** in the presence of a sensitizer, we unexpectedly observed the formation of **3a,b** and the aryltetralin derivatives **2a,b** as photoproducts. The structures of the photoproducts are shown in Scheme 1 and their yields are summarized in Table 1. Products were isolated by preparative HPLC (COSMOSIL-5C 18, 4.5 × 150 mm, 80% aq. methanol, 254 nm UV detector), and their structures deduced on the basis of spectroscopic data (^{1}H NMR, IR, UV and mass). Compounds **2a** and **2b** were converted to compounds **7** and **8** as shown in Scheme 2.† The coupling constants between the protons on the saturated six-membered ring of **8** and those of an authentic sample reported by Durst are similar.‡[5] Sonication prior to irradiation was important for the formation of **2a,b** and the β-truxinate crown ethers **3a** and **3b** in benzene. It is not yet clear why sonication is necessary, but it will reduce the particle size of the salt. After sonication, about 50% of the podand was adsorbed on the salt in benzene, and this adsorption probably provides a suitable molecular topology for the formation of **2a**, **2b**, **3a** and **3b**. When $Me(CH_2)_{11}OSO_3Li$ was used as a soluble metal salt in benzene to avoid complications arising from the size of the salt, aryltetralin derivatives were not formed. Compounds **4a** and **4b** remained the sole products in a homogeneous acetonitrile solution of **1a** and **1b** in the presence of $LiClO_4$.



Scheme 1 *Conditions*: *hν* in C_6H_6



Scheme 2 *Conditions:* i, HCl (1 mol dm^{-3}); ii, CH_2N_2

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† Tetralin **2a**: colourless oil; *m/z* (70 eV) 546 (M^+, 2%); ^{1}H NMR: δ 2.97 (septet, $J_{3,4a}$ 10.8, $J_{3,4e}$ 6.4, $J_{3,2}$ 3.4 Hz, 1H, 3-H), 3.17 (dd, $J_{4a,3}$ 10.7, $J_{4a,4e}$ 17.6 Hz, 1H, 4*a*-H), 3.50 (dd, $J_{2,3}$ 3.4, $J_{2,1}$ 3.0 Hz, 1H, 2-H), 3.64–3.74 (m, 6H), 3.77 (t, *J* 4.8 Hz, 2H), 3.87 (t, *J* 4.8 Hz, 2H), 4.09 (t, *J* 4.8 Hz, 2H), 4.14 (t, *J* 4.8 Hz, 2H), 4.22 (t, *J* 4.8 Hz, 2H), 4.82 (d, $J_{1,2}$ 3.0 Hz, 1H, 1-H), 6.91 (s, 4H), 6.96 (d, *J* 10.0 Hz, 1H), 7.00 (d, *J* 10.0 Hz, 2H), 7.07 (m, 1H), 7.15–7.21 (m, 3H) and 7.24–7.26 (m, 2H)

Tetralin **2b**: m.p. 146–147 °C; IR ν 1760 cm^{-1}; *m/z* (70 eV) 638 (M^+, 6.3%); ^{1}H NMR δ 3.33–3.58 (m, 12H), 3.62–3.64 (m, 2H), 3.73–3.86 (m, 3H), 3.96–4.02 (m, 1H), 4.06–4.12 (m, 2H), 5.10 (d, *J* 3.0 Hz, 1H), 6.80–7.00 (m, 6H), 7.05–7.20 (m, 6H), 7.20–7.28 (m, 2H) and 7.30–7.35 (m, 3H).

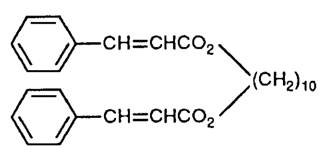
Spectral data (^{1}H NMR, IR, UV and mass) for **3a**, **3b**, **4a**, **4b**, **5b**, **6b**, **7** and **8** were available as supplementary material for the referees.

‡ Comparison of ^{1}H NMR data (δ values, *J* in Hz) for **8** (500 MHz) and (in parentheses) reported data (300 MHz) for an authentic sample:[5] 1-H 4.82 (4.83); 2-H 3.48 (3.48); 3-H 2.97 (2.97); 4-H 3.16 (3.16); 5-H 3.33 (3.34); Ar 6.95–7.27 (7.0–7.4); OMe 3.65 and 3.67 (3.65 and 3.67); $J_{1,2}$ 3.0 (3.0); $J_{2,3}$ 3.4 (3.6); $J_{3,4a}$ 10.8 (11.0); $J_{3,4e}$ 6.4 (6.2); $J_{4a,4e}$ 17.6 (17.5).

Table 1 Product distribution in the sensitized photoreaction of podands **1a,b**[a]

Podand	Sensitizer	Additive	Product, yield (%)				
			2	**3**	**4**	**5**	**6**
1a	Xanthone	—	—	—	37.3	—	—
1a	Xanthone	$LiClO_4$	10.3	48.0	10.3	—	—
1a	MK[b]	$LiClO_4$	—	56.7	6.8	—	—
1b	Xanthone	—	—	—	11.7	2.7	—
1b	Xanthone	$LiClO_4$	1.0	17.7	7.3	1.2	—
1b	MK	—	—	—	25.4	3.2	—
1b	MK	$LiClO_4$	5.0	29.7	16.1	0.5	9.9
1b	Fluorenone	$LiClO_4$	—	—	—	—	—

[a] At room temperature in benzene. [b] Michler's ketone.



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In order to evaluate the role of the oxygen atoms in the polyethylene glycol chain, we analysed the photoproducts of the xanthone sensitized photoreaction of the polymethylene bridged dicinnamate **9** in benzene in the presence of $LiClO_4$.[3] Only the δ-truxinate derivative was detected. Further, in the case of methyl *trans*-cinnamate, we could not detect any trace of the corresponding aryltetralin derivatives. The oxygen atoms in the polyethylene glycol chain are obviously important for the formation of **2a** and **2b**.

Wilson *et al.* pointed out the importance of finding a probable route to aryltetralin lignans from biogenetic precursors,[6] and Kikuchi *et al.* drew attention to the role that radical-cation chemistry might play in the formation of the neolignan magnoshinin from biogenetic precursors.[7] We tested the possibility of using 9,10-dicyanoanthracene or 1,4-dicyanobenzene as an electron acceptor. However, no trace of NMR signals attributable to **2**, **3** or **4** was observed. Since the efficiency of photosensitized [2π + 2π] cycloaddition is maximized for carbonyl sensitizers which have a triplet energy close to that of the substrate,[8] we surveyed two more sensitizers in the presence of $LiClO_4$ (Table 1). The fact that fluorenone did not act as a sensitizer shows that the triplet state excitation energy of **1b** is between 53.3 and 61 kcal mol^{-1} (1 cal = 4.184 J). In the case of **1b**, the total yield of products from the reaction sensitized by use of Michler's ketone is higher than that for the xanthone sensitized reaction.

The effect of other alkali metal perchlorates ($NaClO_4$ and $KClO_4$) was examined; aryltetralin derivatives were not detected by NMR spectroscopy and HPLC.[2a]

These findings thus suggest the possibility of a straightforward correlation between the biological generation of tetralin lignans and photosensitized Diels–Alder cyclization biogenetic precursors.

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