# Novel Photoisomerization of 2,3-Bis-(*p*-methoxyphenyl)benzofuran into 2,6-Dimethoxy-9-(2-hydroxyphenyl)anthracene

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Photolysis of 2,3-bis-(*p*-methoxyphenyl)benzofuran in benzene under $N_2$ using either a mercury lamp or sunlight yields besides the expected phenanthrene derivative (**6**), the novel rearranged anthracene (**5**).

The photoclosure of *cis*-stilbenes in the presence of oxidising agents is a standard preparation of phenanthrenes.[1] Substantial experimental evidence exists indicating that ring closure in the excited singlet state, followed by oxidation of the resulting dihydro-compound, is the likely mechanism.[2] A notable single exception has been the reported formation of 2,6-bis(ethoxycarbonyl)anthracene (**1**) from 4,4′-bis(ethoxycarbonyl)stilbene (**2**), presumably in air with oxygen as the oxidant,[3] together with the expected 3,6-bis(ethoxycarbonyl)phenanthrene (**3**) in a 1:4 ratio.

We now report the photoconversion of 2,3-bis-(*p*-methoxyphenyl)benzofuran (**4**) into a 4:1 mixture of the anthracene (**5**) and the furanophenanthrene (**6**). Both 24 h exposure to sunlight and 4 h irradiation with a 450 W medium-pressure Hanovia mercury lamp of benzene solutions of (**4**) under $N_2$ yield the same ratio of (**5**):(**6**) and no other products (h.p.l.c.). In contrast, irradiation in the presence of either piperylene (1 M) or air completely suppresses anthracene formation. Notably in air an essentially quantitative conversion into the furanophenanthrene (**6**) (m.p. 140—141 °C) as sole product (h.p.l.c.) occurs. In the presence of piperylene only 20% conversion of (**4**) into (**6**) occurs, (**4**) being mostly unchanged.

The evidence suggests intersystem crossing to a reactive triplet state that undergoes a deep-seated rearrangement involving both opening of the furan ring and formal separation of C-2 and C-3. While the above-noted stilbene (**1**) had structural features that were compatible with closure *via* a simple *transoid* triplet intermediate, an analogous transient is not readily visualized from (**4**), although if the stilbene carbon–oxygen bond cleaves first, this might be possible. In addition, formation of (**5**) is an isomerization and not a net oxidation. In an attempt to shed light on the mechanism, we have irradiated 5-methyl-2,3-diphenylbenzofuran (**7**) both under $N_2$ and air, and in both instances obtain only conventional closure to phenanthrene. Clearly photophysical requirements for anthracene formation are strongly dependent on structure. Since the high electron-donating potential of the bis-(*p*-methoxyphenyl) substituted furan (**4**) suggests radical cation pathways, we have also studied photolysis of (**4**) and (**7**) under nitrogen with a range of π-acceptors.[4] Chloranil, 1,4-naphthoquinone, and 2,3,5,6-dichlorodicyanobenzoquinone all gave clean conversion into the phenanthrene for both examples. Moreover, the phenolic

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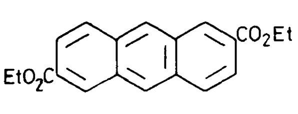
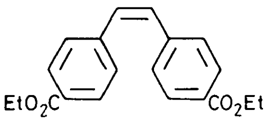


(1)



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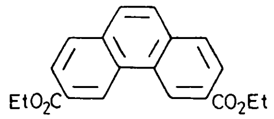

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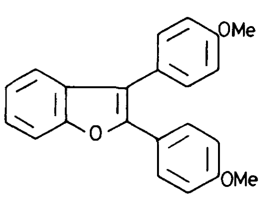

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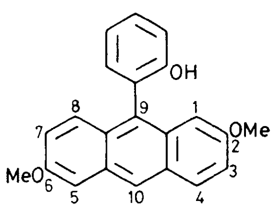
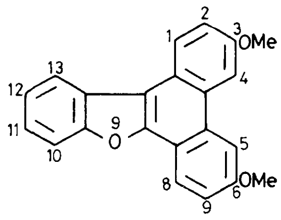


(5)



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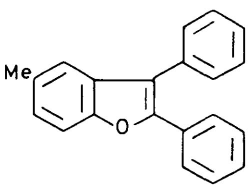

(7)

product (**5**) is stable towards both chloranil and dilute hydrochloric acid.

Experimentally the structure of the phenolic anthracene (**5**) (m.p. 156—157 °C) was based on its molecular ion at *m/z* 330 (chemical ionisation), a 3540 cm$^{-1}$ (OH) i.r. band, a u.v. spectrum characteristic of 9-phenylanthracene[5] and not a phenanthrene such as (**6**), and its $^{1}$H and $^{13}$C n.m.r. spectra. In the $^{1}$H n.m.r. (250 MHz) spectrum of (**5**) the characteristically deshielded singlet due to H-10 is at $\delta$ 8.25 with H-4 at $\delta$ 7.82 (d, $J_{3,4}$ 9.2 Hz), while H-8 appears at $\delta$ 7.49 (d, $J_{7,8}$ 9.6 Hz) and H-1 at $\delta$ 6.76 (d, $J_{1,3}$ 2.2 Hz) in exact agreement with similarly substituted anthracene spectra which have been assigned.[6] All remaining aryl protons are at $\delta$ 7.07—7.46, with the methoxy singlets at $\delta$ 3.90 and 3.66 and OH at $\delta$ 4.63. In contrast the phenanthrene (**6**) shows H-1 and H-8 as deshielded doublets ($J$ 8.8 Hz) at $\delta$ 8.54, 8.42, with the normally deshielded sterically crowded protons H-4,5 as doublets ($J$ 2.6 and 2.2 Hz) at $\delta$ 8.08 and 8.04, shielded by the adjacent methoxy protons. The relatively deshielded benzofuran protons H-13,11 appear as multiplets at $\delta$ 8.33—8.28 and 7.77—7.71, while H-2,7,10,12 are at $\delta$ 7.5—7.3 and the OMe protons at $\delta$ 4.058 and 4.062. In its $^{13}$C n.m.r. (**5**) shows 11 distinct aryl-CH lines in the range $\delta$ 132—102 p.p.m. whereas (**6**) shows 10 in the range $\delta$ 125—105 p.p.m. which are assignable,[6] consistent with their proposed structures.

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