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THE PHOTOREARRANGEMENT OF *o*-VINYL DIARYL ETHERS INTO *o*-HYDROXY STILBENES
EVIDENCE AGAINST DIPOLAR INTERMEDIATES

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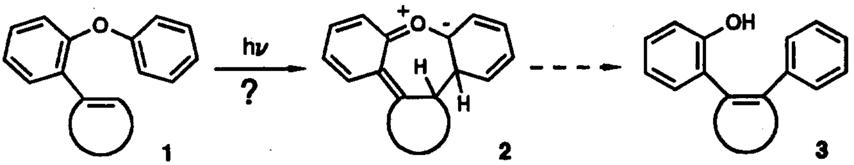
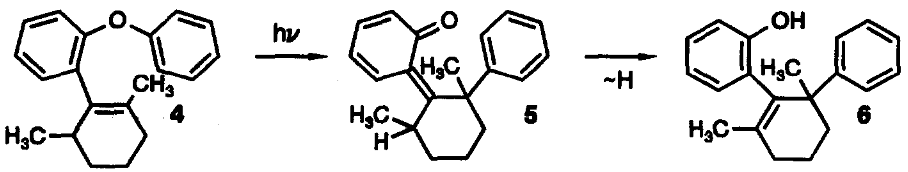
Summary: On irradiation of the *o*-vinyl diaryl ethers **4**, **7**, and the D-labeled derivative **16**, a rearrangement takes place leading to the phenol **6** (from **4**) and the corresponding vinyl-bridged hydroxy stilbenes **8/17** (from **7/16**) as primary products. The latter compounds are further transformed into the phenanthrenes **9** and **18** after 6π-cyclization and subsequent loss of methanol and water, respectively. A mechanism involving inter- or intramolecular diradical pathways is discussed.

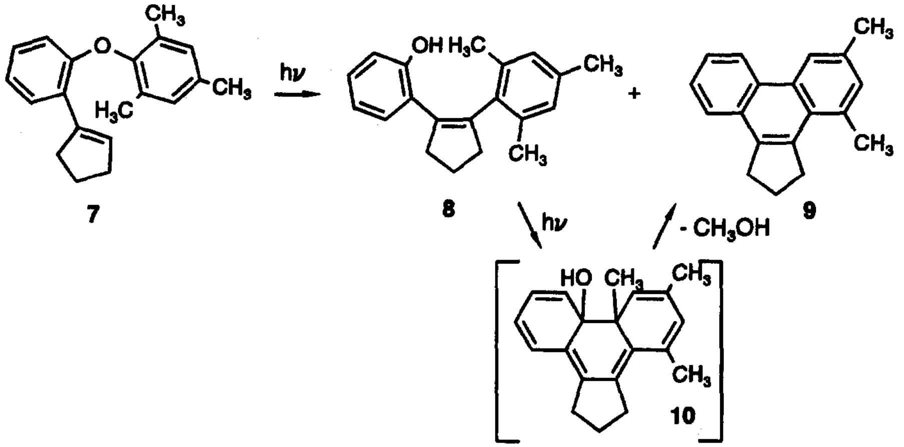
In connection with our long standing interest in the photochemistry of heteroatom containing systems,[1] we have recently studied the light induced transformation of some examples of the title compound into hydroxy stilbene derivatives.[2] Although the results could be explained by a mechanism involving initial 8π-electrocyclization to bridged vinyl carbonyl ylide intermediates (see **1**→**2**→**3**), the failure of detecting any of the originally expected 7-membered heterocycles [*i.e.* dibenzo-(dihydro)-oxepins], shed some doubt on this interpretation. In addition, it is known that simple diaryl ethers not only undergo 6π-photocyclization to furan derivatives[3] but also a second type of photorearrangment leading to aryl phenols which are structurally related to compounds of type **3**; a fragmentation-recombination mechanism is usually discussed for this reaction.[4]



In order to gain a deeper insight into the course of the above photoreaction we made further studies using specifically labeled *o*-vinyl diaryl ethers.[5] First we undertook investigations with compound **4** substituted by two methyl groups at the cyclohexene ring.[6] Direct irradiation of **4** with a high pressure mercury lamp (quarz filter) resulted in the formation of one monomeric product, which was identified as phenol **6** (isolated in 65% yield, IR (CCl_4): ν_{OH}= 3520 cm^{-1}).[7] The outcome may be taken as further indication for the intermediate formation of an *o*-quinodimethane analogue, which (due to the blocked benzylic position) is stabilized in this case by migration of an allylic hydrogen of the cyclohexane ring.[8] Unfortunately no details on the former steps are available.

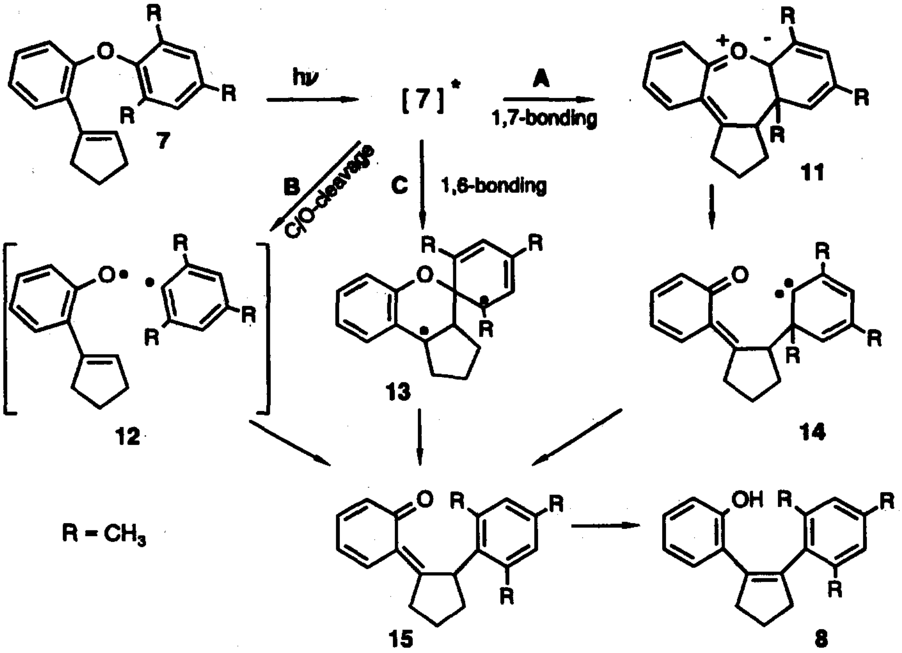


Therefore we turned next to a system bearing methyl substituents at one of the aromatic rings, namely the trimethyl derivative **7** .[6] With regard to the steric more unfavorable situation for vinyl-aryl bonding it was not unexpected that the photoreaction proceeded less efficient; however, again a phenol derivative **8** turned out to be an important primary product (IR (CCl_4): $\tilde{\nu}_{OH}$= 3600 cm^{-1}). Using acetone as solvent (100 ml, solidex filter), 110 mg of **7** was irradiated for 2 h affording **8** in 50% yield (referring to 37% conversion). Under direct excitation conditions (85-100 mg of **7**, 100 ml of solvent, 1 h, vycor filter) the outcome depended on the solvent: whereas the reaction in ether led to a mixture of **8** and the phenanthrene **9** (27 and 12%, respectively, 75% conversion), illumination in methanol resulted in the formation of **9** as the only detectable product (34% after 50% conversion).[7]



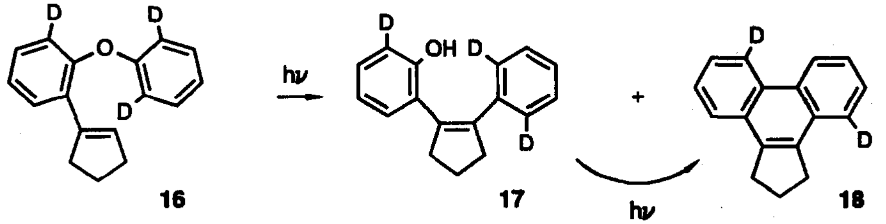
As shown by independent photolysis experiments, **9** is a secondary product formed on direct photolysis (preferentially in methanol as solvent) of the phenol derivative **8**. This transformation deserves interest because the final aromatization step can neither proceed by oxidation (the most common way for stilbene-phenanthrene transformations)[9] nor by simple elimination (*e.g.* of water).[2,10] It is shown by the ^{1}H-NMR data, and in particular by MS spectroscopy [M$^+$ (m/z) = 247], that this product was formed instead by loss of a HO-CH_3 unit (see reaction **8**→**10**→**9**).

For considering the mechanism of the transformation **7**→**8** it is most important to note that in the primary photoproduct the substitution pattern of the methyl groups remained the same as in **7**, *i.e.* at the 2,4,6-positions. Based on this fact the originally suggested ylide route with 1,7-bonding as the first step becomes unlikely (path **A**, see below): after 7-ring cleavage of the carbonyl ylide **11** the intermediate carbene **14** would have to rearrange by exclusive 1,2-allyl shift in order to give structure **15** with a symmetrical substitution of the aromatic ring. Since no indication for products deriving from a competitive CH_3-shift have been obtained, this result is not compatible with the known migratory aptitude in such carbene rearrangements.[11]



If the o-quinodimethane structure **15** is accepted as direct precursor of **8**, the transformation **7**→**15** can be formally regarded as a 1,5-shift of the methylated phenyl ring to the terminus of the olefinic bond. Apart from a less probable concerted process, especially two pathways have to be discussed: (i) C/O-cleavage of [**7**]* to give the radical pair **12** which recombines to **15** (see route **B**). A similar sequence has been proposed for a related reaction of a substituted *o*-phenyl diaryl ether.[12] However, in our case homolysis of the other ether bond should at least compete with this reaction, and hence give rise to the formation of isomeric products. (ii) 1,6-bonding with formation of the diradical **13**, which is easily deactivated by bond reorganisation to give **15** (see route **C**).[13]

Conclusive evidence against the ylide route **A** was obtained with the trideuterio diaryl ether **16**, which was synthesized from bis-*o*,*o*'-tetradeuterio diphenyl ether.[6,14] Acetone sensitized irradiation of **16** led in almost quantitative yield to the trideuterio phenol **17**, whereas the direct photolysis of **16** (or of **17**) produced the annulated dideuterio phenanthrene **18**.[15] The retention of the deuterium in the positions 2 and 6 of the photoisomer **17**[16] clearly excludes the intermediacy of a carbene like **14**;[11] as a consequence the diradicals routes **B** or **C** have gained further support.



Although a clear decision between the inter- and intramolecular radical pathways is not possible, the high selectivity of the reactions with respect to the cleavage of only one of the ether bonds as well as the exclusive aryl-vinyl recombination during the reaction is explained more convincingly by route C. As an alternative, the intermediates **12** and **13** might represent points on the reaction coordinate of this transformation.

Further studies with other derivatives of **1** as well as with the corresponding amines and sulfides are under investigation.

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6. The starting materials were synthesized following the procedure described in the preceding communication. 2,4,6-Trimethyl diphenyl ether is obtained by Ullmann reaction of trimethyl phenol and bromo benzene. **4**: oil, ^{1}H-NMR (250 MHz, $CDCl_3$): δ = 0.82 (d, J=7 Hz, CH_3), 1.38 (s, CH_3); UV (CH_3CN) $\lambda_{max}(\varepsilon)$ = 275 nm (1300); **7**: oil, ^{1}H-NMR: δ = 2.21 (s, 4-CH_3), 2.14 (s, 2,6-CH_3); UV (CH_3CN) $\lambda_{max}(\varepsilon)$ = 290 nm (3600).
7. All new compounds are characterized by spectroscopic data as well as by elemental analysis and/or mass spectra.
8. 8a. E. Hoshimoto, S. Yamauchi, N. Hirota, S. Nagaoka, *J. Chem. Phys.* **1991**, *95*, 10229, and references. 8b. A subsequent phenanthrene cyclization is, of course, not possible in this case.
9. 9a. For a recent review on the photochemistry of stilbenes see: H. Meier, *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1399. 9b. Although there seems to be no precedent for HO-CH_3 elimination, aromatization of dihydrophenanthrenes by loss of H-Hal, H-CN, H-OAlk and H-CH_3, respectively, are known: H. Meier, *Houben Weyl*, *IV/5a*, part 1, 511, Thieme, Stuttgart, **1975**.
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13. Taken a helical geometry of the electronically excited, syn arranged vinyl dienyl ethers the stereoelectronic situation is quite favorable for an antarafacial 1,6-orbital overlap.
14. Obtained by refluxing a solution of diphenyl ether in Et_2O with 2 eq. *n*-butyl lithium for 20 h, and subsequent quenching by D_2O. After four cycles the deuteration grade was > 90%.
15. As in case of the non-deuterated series[2] the isolated phenanthrene is the result of bond formation which involves the OH substituted position of the phenol ring.
16. The position of the deuterium atoms was unambiguously determined by ^{1}H-NMR and ^{13}C-NMR spectroscopy techniques including simulation experiments.[5] ^{13}C-NMR (100 MHz, $CDCl_3$): **17**: 115.5 (C-3', $J_{C,D}$= 24.6 Hz), 127.0 (C-2,6, $J_{C,D}$= 24.0 Hz); **18**: 122.8 ($J_{C,D}$= 24.0 Hz), 124.8 ($J_{C,D}$= 24.8 Hz).

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