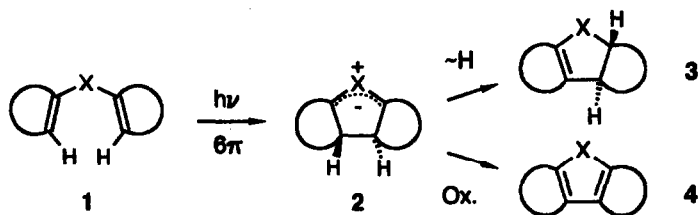


PHOTOCHEMICAL STUDIES WITH *o*-VINYL DIARYL ETHERS A NEW PHOTO-HETEROCYCLIZATION REACTION ?

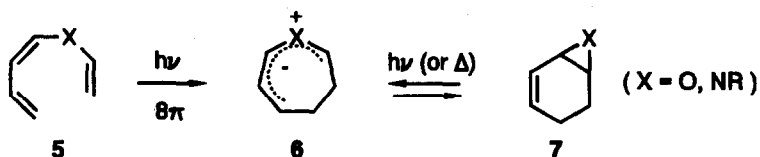
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Summary: On photoexcitation the *o*-vinyl diaryl ethers 10a-d are transformed into *o*-hydroxy stilbenes 11 which preferentially on direct irradiation are further converted affording the annulated phenanthrenes 12.

The 6π -photocyclization is one of the most common excited state reaction which has been successfully performed not only with hexatrienes¹ but also with a great variety of heteroatom-containing systems of the general structure 1 ($X = N, S, O$),² which are isoelectronic with the pentadienyl anion.³ The light induced ring closure of compounds like 1 to the dipolar intermediates 2⁵ is usually followed either by suprafacial 1,4-hydrogen migration or by oxidation leading to the corresponding five-membered heterocycles 3 and 4, respectively.^{2,7}



To the best of our knowledge no analogous ring closure reactions are known for the vinylogous 8π -system, which would result in the formation of terminally bridged 6π -dipoles (see 5 \rightarrow 6). Interestingly enough, the reversible formation of intermediates of type 6 has been unambiguously proved by photochemical (or thermal) excitation of epoxy and epimino cyclohexadienes 7.⁸



Here we report on photochemical results obtained with compounds of type 5. In order to avoid unproductive *cis/trans* isomerizations ("free rotor effect") we started the experiments with *o*-substituted diphenyl ethers 10a-d which bear a bridged vinyl group as part of the 8π -system.

A straightforward synthesis of the bis-conjugated ethers was accomplished by regioselective *ortho*-lithiation⁹ of diphenyl ether (**8**) and subsequent reaction with the corresponding cycloalkanones affording the tertiary alcohols **9**, which on acid treatment were transformed into the required starting materials **10** (over-all yield 53-79%).¹⁰

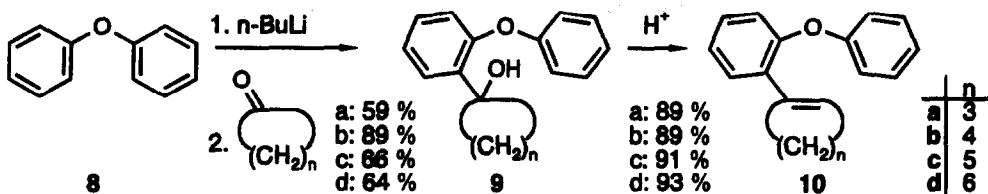
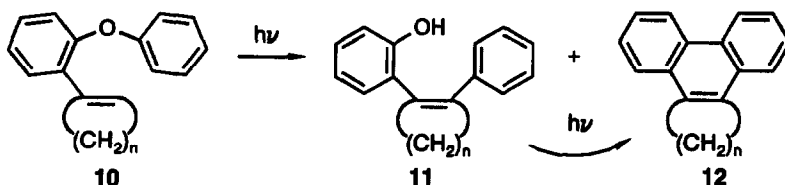


Table 1. UV Data of the Ethers **10a-d** (CH₃CN)

| | λ_{\max} (ϵ) [CH ₃ CN] |
|-------------|--|
| 10 a | 288 (2500), 253 (sh, 13800), 220 (21300) |
| 10 b | 277 (1400), 220 (15000) |
| 10 c | 278 (3300), 241 (sh, 12500), 221 (19500) |
| 10 d | 276 (3300), 235 (sh, 14400), 220 (18800) |

The UV data of **10b-d** are rather similar with long wavelength maxima at approximately 277 nm; only **10a** shows a red shift by 10-12 nm.

Direct irradiation of ca. 10⁻³ M solutions of **10a-d** in ether or methanol has been performed with a high pressure mercury lamp using a vycor filter ($\lambda >$ ca. 240 nm; despite absorption bands at 270-280 nm, solidex filtered light [$\lambda >$ ca. 280 nm] gave extremely slow reactions). Depending on the photolysis conditions one or two products were formed in each case (see Table 2). As exemplified with **10a**, irradiation of 40 mg for 10 min afforded only one compound, namely the cyclopenteno phenanthrene **12a** in almost quantitative yield (run 1). Under the same conditions 100 mg of **10a** were transformed into a 5:1 mixture of **12a** and the phenol derivative **11a** (run 2). On the other hand, an almost selective formation of the latter compound was observed by using acetone as solvent (run 3). Obviously the stilbene **11a** is the primary photoproduct which is converted preferentially from the singlet excited state into the phenanthrene **12a**.¹¹



Compared to **10a** the photoreactivity of the *o*-cyclohexenyl diaryl ether **10b** is considerably reduced. Nevertheless after 3 to 9 fold irradiation times the analogous products, **11b** and **12b**, were formed, yet in slightly smaller yields with the phenol **11b** dominating on both direct and sensitized photolysis (run 4 and 5; in addition to **11b** an isomer is isolated to a minor extent, in which the cyclohexene double bond is only conjugated to the phenol ring). In the case of the cycloheptene and cyclooctene derivatives **10c,d** the phenanthrenes **12** were the sole monomeric products identified by spectroscopic analysis before and after work-up.

Table 2. Photoreactions of 10a-d (150 W lamp, Hanau TQ 150)

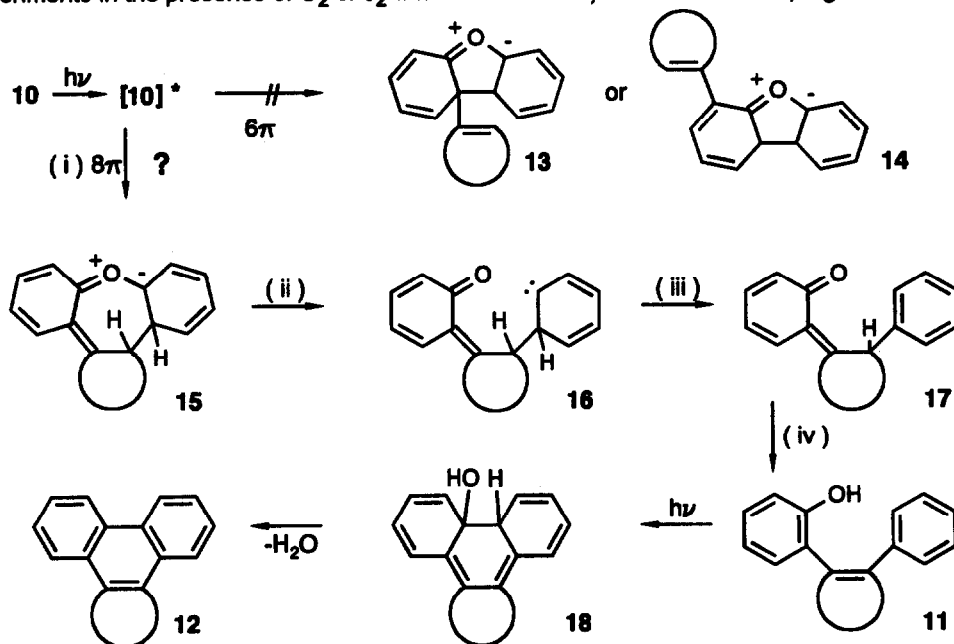
| Run | | mg | Conditions | | | Conversion | Yield (%) ^{a)} | |
|-----|------|-----|-------------------|---------|------------|------------|-------------------------|--------|
| | | | Solvent (100 ml) | Filter | Time (min) | | 11 | 12 |
| 1 | 10 a | 40 | Et ₂ O | Vycor | 10 | 100 | - | 95 |
| 2 | 10 a | 100 | MeOH | Vycor | 10 | 88 | 11(12) | 50(57) |
| 3 | 10 a | 50 | acetone | Solidex | 10 | 95 | 84(88) | <2 |
| 4 | 10 b | 100 | MeOH | Vycor | 90 | 80 | 44(55) | 20(25) |
| 5 | 10 b | 100 | acetone | Solidex | 30 | 79 | 58(73) ^{b)} | 5(7) |
| 6 | 10 c | 100 | MeOH | Vycor | 30 | 50 | - | 20(40) |
| 7 | 10 c | 50 | acetone | Solidex | 30 | 65 | - | trace |
| 8 | 10 d | 100 | MeOH | Vycor | 60 | 55 | - | 40(72) |
| 9 | 10 d | 50 | acetone | Solidex | 30 | 36 | - | <3 |

a) Values in parentheses are referring to conversion b) 9 (11) % of the isomer (see text)

The structure of the photoproducts 11a,b and 12a-d (each isolated in pure form by column and medium pressure chromatography) has been clearly attributed on the basis of the analytical data.¹⁰ 12a¹² and 12b¹³ are known compounds.

A possible - however speculative - mechanism for the formation of the phenol system 11 consists of four steps: (i) 8 π -cyclization of the electronically excited ether 10 leading to the carbonyl ylide 15,¹⁴ (ii) photoinduced (or thermal) cleavage of the C-O bond leading to the carbene 16,¹⁵ which (iii) undergoes rapid 1,2-H-shift to the *o*-quinone methide 17;¹⁶ (iv) 1,5-H migration with formation of the observed phenol derivatives 11.¹⁷ With the exception of (i) all steps have literature precedents.

Surprisingly, no evidence has been obtained for the photochemical 6 π -process involving 13 or 14 which would give rise to dibenzofuran derivatives after subsequent H-shift or oxidation^{2,18} (experiments in the presence of O₂ or J₂ were unsuccessful). This observation, together with the



failure of getting any indication for the formation of dibenzooxepin derivatives prompted further studies on the photochemistry of *o*-vinyl diaryl ethers and related compounds. As shown in the succeeding communication, a different mechanism has been developed on the basis of results with specifically substituted compounds.

The photolability of **11** is easily explained by the well established stilbene-dihydrophenanthrene cyclization¹¹ producing the alcohol **18** which is rapidly transformed under loss of water into the annulated phenanthrenes **12**. In accordance with other results the ring closure process takes place preferentially *via* the singlet excited state.

Acknowledgement: We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this research.

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