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Involvement of Oxirane Intermediates in the Electron Transfer Photooxygenation of 1,1- and 1,2-Diarylethylenes Sensitized by 2,4,6-Triphenylpyrylium Tetrafluoroborate

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Abstract: The photooxygenation of *trans*- and *cis*-stilbene (**2a,b**) by means of 2,4,6-triphenylpyrylium tetrafluoroborate (TPT) led to benzaldehyde (**5**) and diphenylacetaldehyde (**6**). Under the same conditions *trans*- and *cis* - 1,2-diphenyloxirane (**4a,b**) afforded **6** as major product, together with minor amounts of **5**, benzophenone (**8**) and, in the case of **4b**, 1,2-diphenylethanone (**7**). These data support the intermediacy of the oxiranes in the photooxygenation of the corresponding stilbenes and reveal that rearrangement of the radical cations **4a,b**$^{+\cdot}$ occurs by two alternative pathways: phenyl migration and H migration. The TPT-photosensitized oxygenation of 5-methylene-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (**9**) produced mainly dibenzosuberone (**10**) and dibenzosuberane (**11**), together with trace amounts of products arising from dehydrogenation of the dimethylene bridge (**14,15,16**) and solvent-derived products (**12,13, 18**). The formation of **10** and **11** is justified *via* the radical cation of the 1,1-diphenylethylene moiety, generated by electron transfer from the olefin to the excited sensitizer. The epoxide **20**, aldehyde **17** and dioxetane **19** appear to be key intermediates. Formation of the minor compounds **14**, **15** and **16** can be explained through the radical cation of the 1,2-diphenylethane substructure.

INTRODUCTION

The photooxygenation of arylolefins with electron transfer (ET) photosensitizers has been intensively studied in recent years.[1] In a number of cases, the formation of oxygenation products has been rationalized through reaction of the olefin radical cations with molecular oxygen. This appears to be the preferred photooxygenation pathway when 2,4,6-triphenylpyrylium tetrafluoroborate (TPT, **1**) is used as photosensitizer, since excited TPT generates neither singlet oxygen nor superoxide radical anion.[2-5]

1,2-Diarylolefins such as *trans*-stilbene (TS, **2a**) and *cis*-stilbene (CS, **2b**) have been oxygenated using TPT[5-7] and a variety of other ET photosensitizers, such as 9,10-dicyaneanthracene (DCA),[8,9] or methylene blue (MB),[10] as well as semiconductor powders (i. e. TiO_2).[11] It is known that irradiation of a mixture of **1** and **2a** or **2b** in methylene chloride solution produces benzaldehyde (**5**) as single product.[6,7] Its formation was thought to occur *via* dioxetane (**3**) and/or oxirane (**4**) intermediates. The involvement of **3** would be in agreement with the obtention of benzaldehyde by reaction of **2a** with singlet oxygen (generated by photosensitization with tetraphenylporphine);[12] however, the proposed intermediacy of **4** did not take into account earlier work on the TPT-photosensitized transformation of *trans*-1,2-diphenyloxirane (**4a**) into diphenylacetaldehyde (**6**).[13] The original work was focused on the rearrangement process and therefore no other byproducts were reported. Since a careful product study might shed some light on the mechanism of TPT-promoted photooxygenation, it appeared interesting to undertake a reinvestigation of the above reactions, trying to correlate the behaviour of the stereoisomeric olefins **2a/2b** with that of the corresponding epoxides **4a/4b**.

1,1-Diarylolefins have also attracted considerable attention, owing to the different product selectivities associated to the nature of the involved intermediates (contact ion pairs or free ions).[14-18] In particular, ET photooxygenation of 1,1-diphenylethylene leads to a mixture of benzophenone and dimeric 1,2-dioxanes.[17,18] Likewise, much effort has been devoted to the study of electron transfer reactions of 1,2-diarylethanes in the context of competition between carbon-carbon fragmentation and side chain functionalization.[19-26] In this case, photooxygenation produces C-C bond cleavage, to afford two carbonyl units.[22] Hence, it appeared interesting to investigate the photooxygenation of 5-methylene-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (**9**) under electron transfer conditions (TPT as photosensitizer). This substrate contains the substructures of 1,1-diphenylethylene and 1,2-diphenylethane, and its conformational freedom is severely restricted with respect to both model compounds, which might condition the chemical reactivity of its radical cation $\mathbf{9}^{+\cdot}$.

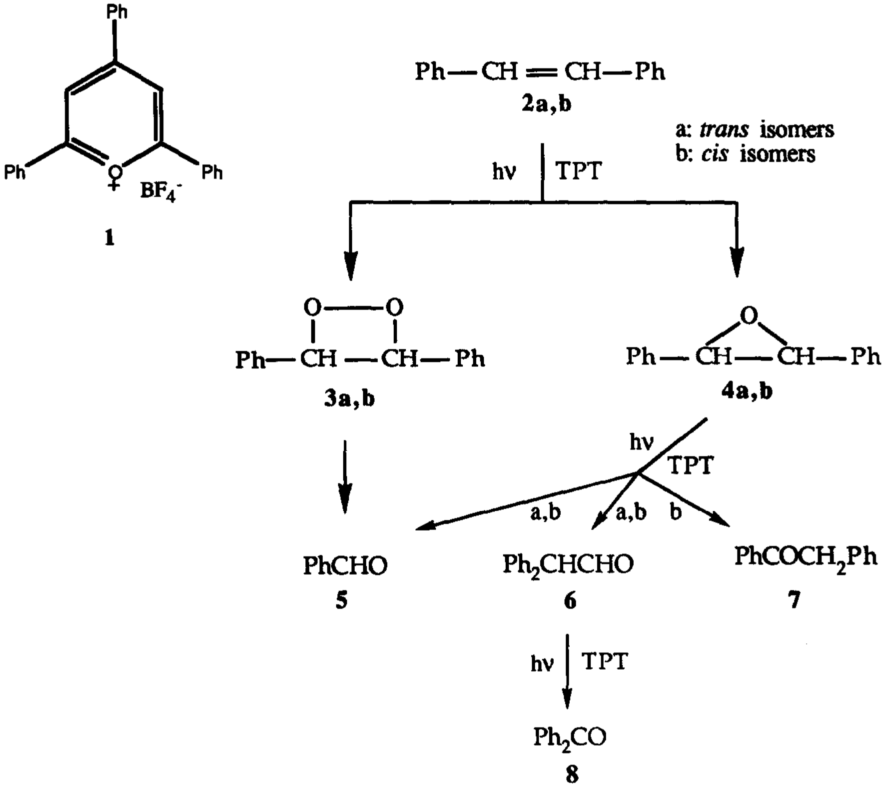
The results obtained in the present work have shown that the TPT-photosensitized oxygenations of diarylolefins such as **2** and **9** follow similar mechanistic pathways and clearly support the involvement of oxirane intermediates in the reactions of radical cations $\mathbf{2}^{+\cdot}$ and $\mathbf{9}^{+\cdot}$ with molecular oxygen.

RESULTS AND DISCUSSION

When TS (10^{-2} M) was oxygenated with TPT (10^{-3} M) as photosensitizer (Table 1, entry 1), under reaction conditions similar to those employed in the literature,[6,7] benzaldehyde was actually obtained, as reported. Besides, diphenylacetaldehyde (**6**) and CS were also formed. On the other hand, ET-photooxygenation of CS (entry 2) using the same procedure afforded a similar mixture consisting of **5**, **6** and TS. The one-way isomerization of $CS^{+\cdot}$ to $TS^{+\cdot}$ is well substantiated in the literature.[27-29] In view of the triplet energies of TS, CS and TPT and the unability of $TS^{+\cdot}$ to undergo the reverse reaction,[27-29] the conversion of TS into CS must have occurred *via* energy transfer from triplet TPT. The obtention of diphenylacetaldehyde (unnoticed in previous work)[6,7] appears to support the epoxidation to **4a** and/or **4b** followed by TPT-photosensitized rearrangement in the reaction medium.

Similar experiments were performed on the 1,2-diphenyloxiranes 4a and **4b** (Table 1, entries 3 and 4). In fact, irradiation of a mixture of **4a** and **1** in methylene chloride led to aldehyde **6** , accompanied by benzaldehyde (**5**), and benzophenone (**8**). The formation of benzaldehyde was not reported in the ET-photooxygenation of **4a** by means of TPT, but it is well documented for the analogous processes using related photosensitizers.[8-11] Benzophenone might be a secondary product arising from oxidative decarbonylation of **6**,[30] which is the only product of the TPT-photosensitized reaction of **4a** reported in the literature.[13] This was confirmed by submitting the aldehyde **6** to identical experimental conditions (Table 1, entry 5), whereby benzophenone was obtained (93 %, based on reacted **6**). Likewise, irradiation of *cis*-1,2-diphenyloxirane (**4b**) in the presence of TPT gave rise to a mixture containing **5**, **6**, **8** and 1,2-diphenylethanone (**7**). The latter is

also a rearrangement product (H migration instead of phenyl migration) and its formation indicates a certain degree of steric control, since it is only observed in the case of the *cis*-oxirane 4b.



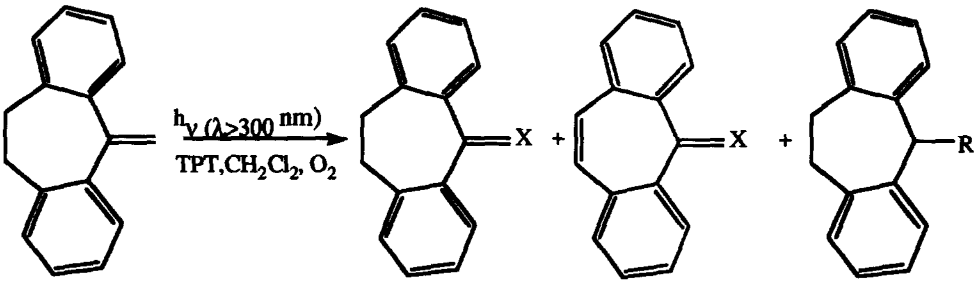
Scheme 1

Table 1. TPT-Photosensitized Oxygenation of Stilbenes and Related Compounds

Entry	Substrate	Conversion (%)	Mass Balance	Product Distribution (%)					
				2a	**2b**	**5**	**6**	**7**	**8**
1	**2a**	21	97		35	34	31		
2	**2b**	28	92	80		12	7		
3	**4a**	100	90			9	75		15
4	**4b**	100	94			13	55	4	28
5	**6**	41	91			5			93

It is worth mentioning that the results presented in Table 1 were obtained under identical experimental conditions, and hence the high conversions obtained for the oxiranes **4** as compared with the stilbenes **2** reflect a dramatic difference in reactivity. This explains why **4a/4b**, in spite of being necessary intermediates in the ET-photooxygenation of **2a/2b** were not even detected in the reaction mixtures.

The aerobic irradiation of **9** in the presence of TPT, using methylene chloride as solvent, led to a mixture of dibenzosuberone **10** (31%) and dibenzosuberane **11** (29%). Some starting material (30%) remained unreacted. Besides, GC-MS analysis allowed to detect additional trace amounts of seven minor products (yields between 1-5 %), whose structures were tentatively assigned as 5-methylene-5*H*-dibenzo[a,d]cycloheptene (**14**) dibenzosuberenone **15**, dibenzosuberene **16**, 5-formyl-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (**17**), 5-chloromethylene-10,11-dihydro-5*H*-dibenzo [a,d]cycloheptene (**12**), 5-dichloromethylene-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (**13**) and 5-(2,2-dichloroethyl)-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (**18**).[31] A control experiment showed that more than 90% of **9** was recovered unchanged when irradiation was performed under argon.



9

10 $X = O$
11 $X = H, H$
12 $X = CHCl$
13 $X = CCl_2$

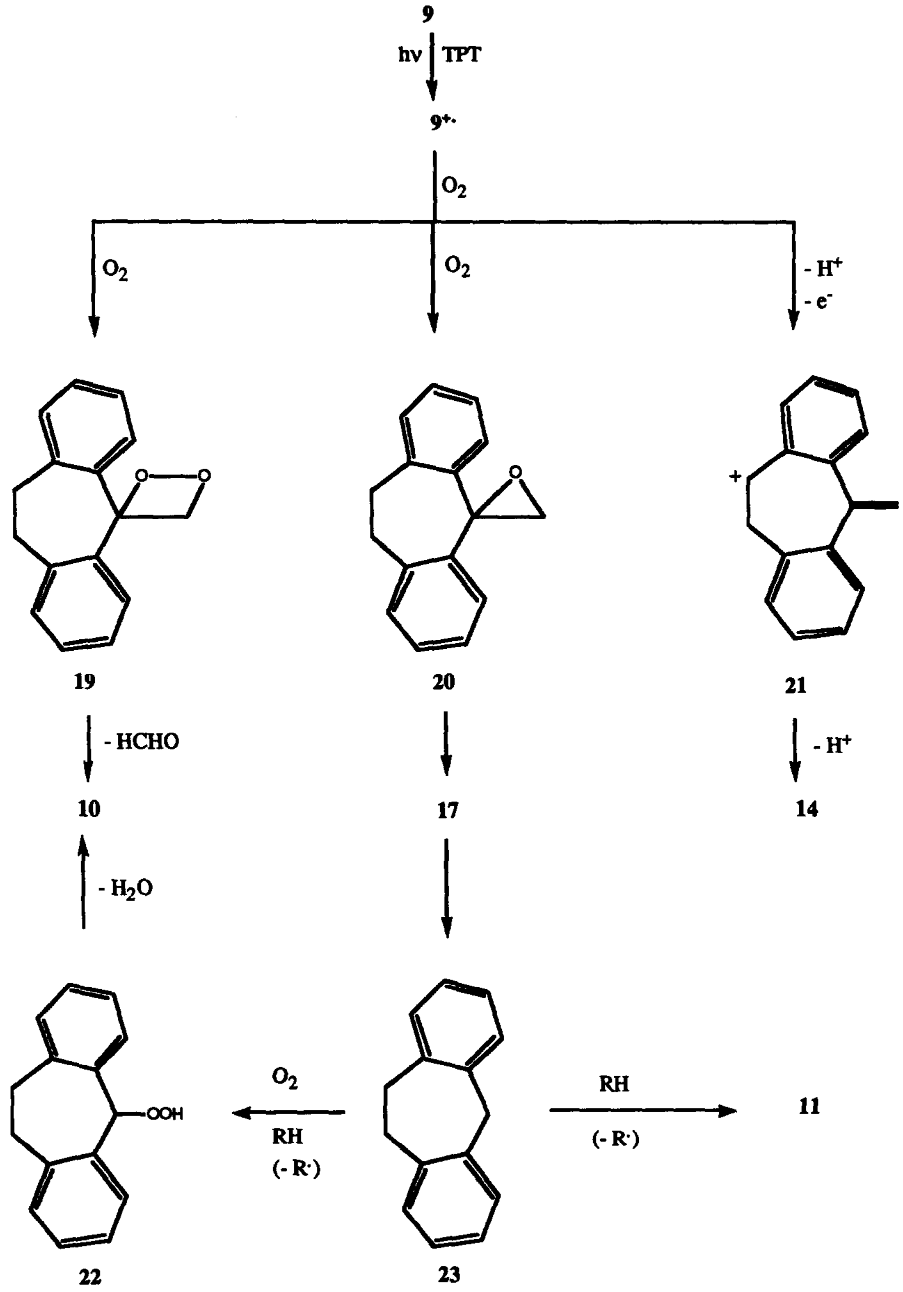
14 $X = CH_2$
15 $X = O$
16 $X = H, H$

17 $R = CHO$
18 $R = CH_2CHCl_2$

Scheme 2

Ketones **10** and **15**, as well as dibenzosuberane **11** were commercially available and the known hydrocarbons **16**[32] and **14**[33] were easily synthesized from ketone **15** by Clemmensen reduction or by addition of methyl magnesium bromide, followed by dehydration, respectively. Mono and dihalogenated derivatives **12**[34] and **13** were prepared from **9** by treatment with sulfuryl chloride in the absence or presence of benzoyl peroxide, respectively. Aldehyde **17**[35] was obtained by treatment of **9** with *m*-chloroperbenzoic acid, followed by acid-catalyzed rearrangement of the resulting epoxide **20**.[35] All the authentic samples presented identical GC retention times and MS fragmentation patterns as the corresponding irradiation products.

A plausible mechanism to explain the obtained results is depicted in Scheme 3. It is evident that the 1,1-diarylethylene moiety is the structural feature which determines the reactivity of compound **9** under electron transfer photooxygenation conditions. Formation of diaryl ketones such as **10** has been justified in similar cases by cycloreversion of dioxetane intermediates of the type **19**. However, the obtention of diarylmethanes


9
hν
TPT
9+·
O2
O2
O2
- H+
- e-
+
19
20
21
- HCHO
- H+
10
17
14
- H2O
O—O
O
OOH
O2
RH
(- R·)
RH
(- R·)
11
22
23

Scheme 3

analogous to **11** in these reactions is unprecedented. A possible route leading to **11** would involve the following steps: epoxidation of the double bond, rearrangement[13] of **20** to the aldehyde **17** and loss of carbon monoxide under the irradiation conditions. In fact, compound **17** was found among the minor reaction products. Part of the isolated ketone **10** might also arise from aldehyde **17**, *via* oxygen trapping of the radical **23**. *It is noteworthy that the intermediate hydroperoxide* **22** *was detected in the mixture by GC/MS*,[36] although it was present only as trace amount and was not isolated. A further support in favour of the above rationalization was provided by irradiation of the epoxide **20**, which gave rise to a mixture containing hydrocarbon **11** and ketone **10**, together with traces of aldehyde **17**.

Among the minor products formed upon photooxygenation of **9**, compounds **14**,**15** and **16** presented as common feature a double bond between the carbons at positions 10 and 11. The origin of **14** can be explained by deprotonation of the radical cation $\mathbf{9}^{+\cdot}$ and subsequent oxidation of the resulting radical to the cation **21**. Formation of the other 10,11-dehydrogenated products **15** and **16** can be justified in a similar way. Thus, this type of chemistry related to the behaviour of 1,2-diarylethanes constituted a minor reaction pathway.

Finally, the halogenated derivatives **12**, **13** and **18** are obviously solvent-derived products, which were present in the photooxygenation mixture in very small amounts. Their formation involves chlorination of the olefin at the terminal position (to give **12** and **13**) or solvent addition (to give **18**). Although several routes can be envisaged to explain these results, with the available experimental data it is not possible to decide the actual operating mechanism. However, irradiation of the substrate **9** through quartz, in the absence of sensitizer, also produced the above halogenated derivatives, which indicated that they were not specific of a TPT-mediated photoreaction.

From the above data, the following conclusions can be drawn: a) diphenylacetaldehyde (**6**) is formed in the TPT-photosensitized oxygenation of *trans* and *cis* -stilbene (**2a** and **2b**) which supports the intermediacy of the oxiranes **4a** and **4b**; b) rearrangement of the radical cation of *cis*-1,2-diphenyloxirane ($\mathbf{4b}^{+\cdot}$) occurs by two alternative pathways: phenyl migration or H migration; the latter affords 1,2-diphenylethanone (**7**) and is not observed with the *trans*-isomer $\mathbf{4a}^{+}$; c) the active moiety of 5-methylene-10,11-dihydro-*5H*-dibenzo[a,d]cycloheptene (**9**) under electron transfer photooxygenation conditions is the 1,1-diarylethylene substructure, and d) the product distribution suggests the involvement of both dioxetane **19** and epoxide **20** intermediates, which is supported by complementary experiments. Dehydrogenation of the dimethylene bridge (related to the behaviour of 1,2-diarylethanes) is a minor pathway.

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EXPERIMENTAL

Melting points are uncorrected and were measured using a Büchi 510 apparatus. ^{1}H- and ^{13}C-nmr spectra were recorded in $CDCl_3$ with a 400 MHz Varian mod Unity; chemical shifts are reported as δ values (ppm) using TMS as internal standard. Mass spectra were determined with a Hewlett-Packard 5988 A spectrometer; m/z ratios and relative abundances (percentages, in brackets) are given only for the main peaks.

5-Methylene-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (**9**),[33] its epoxide **20**[35] 5-methylene-5*H*-dibenzo[a,d] cycloheptene (**14**)[33] 5-formyl-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (**17**)[35] and 2,4,6-triphenylpyrylium tetrafluoroborate[37] (TPT) were prepared according to published procedures. Stilbenes **2a,b**, their oxides **4a,b**, diphenylacetaldehyde (**6**), diphenylethanone (**7**), dibenzosuberone (**10**), dibenzosuberenone (**15**) and dibenzosuberane (**11**) were commercially available. Dibenzosuberene (**16**)[32] was prepared from its corresponding ketone **15**.

General Irradiation Procedure

Aerated 10^{-2} M solutions of stilbenes (**2a,b**), 1,2-diphenyloxiranes (**4a,b**) or diphenylacetaldehyde (**6**) in methylene chloride (5 ml) containing TPT (2 mM) were irradiated for 4 h with the acenaphthylene-filtered light ($\lambda > 400$ nm) of a medium pressure mercury lamp, to ensure selective absorption by the sensitizer.A solution of the substrate **9** (2×10^{-2} M) in methylene chloride (25 ml) was irradiated through Pyrex ($\lambda > 300$ nm), in the presence of TPT (2 mM) for 10 h. The reactions were controlled by TLC and GC. The structures of photoproducts were assigned by GC/MS and confirmed by comparison of their GC retention times and MS fragmentation patterns with those of authentic samples.

5,5-Dichloromethylene-10,11-dihydro-5H-dibenzo[a,d]cycloheptene 13. A solution of substrate **9** (130 mg) and sulfuryl chloride (0.04 ml) in dichloromethane (20 ml) in the presence of benzoyl peroxide (10 mg) was refluxed for 6 h. After evaporation of the solvent, the residue was chromatographed with hexane-ethyl acetate (4:1). Compound **13** (90 mg) was recrystalized from hexane. Mp 80-81 °C; analysis C 69.84 H 4.36 % (Calcd. for $C_{16}H_{12}Cl_2$: C 69.83 H 4.39); ^{1}H-nmr ($CDCl_3$): 2.86 (m, 2H), 3.58 (m, 2H), 7.16-7.24 (m, 6H), 7.33-7.39 (d, J=7 Hz, 2H); ^{13}C-nmr: 140 (s), 138 (s), 137 (s), 130 (d), 129 (d), 128 (d), 126 (d), 120 (s), 32 (t).

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