

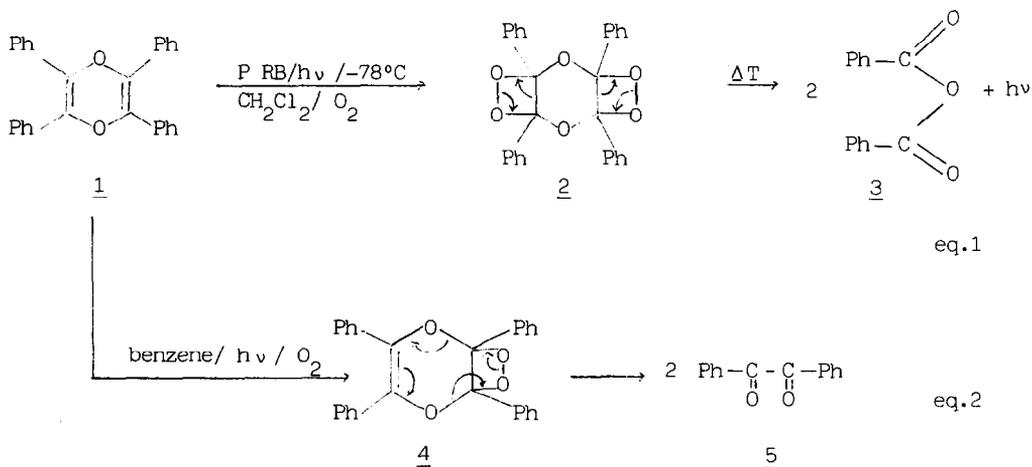
SYNTHESIS OF (Z)-STILBENDIOL DIBENZOATE BY SENSITIZED PHOTOOXYGENATION OF
 2,3,5,6-TETRAPHENYL-p-DIOXIN¹

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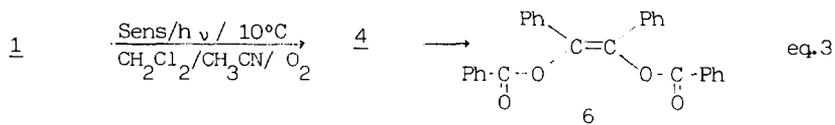
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Summary: Sensitized photooxygenation of 2,3,5,6-tetraphenyl-p-dioxin with singlet and triplet excitable sensitizers yields (Z)-stilbendiol dibenzoate together with benzil. Experimental proofs show that unconnected mechanisms could operate accounting for the 1,2-diketone and the endiol diester formation.

Two recent reports^{2,3} on the singlet oxygenation of 2,3,5,6-tetraphenyl-p-dioxin 1⁴ show two different pathways of fragmentation via the intermediates bisdioxetane 2 and monodioxetane 4 leading respectively to benzoic anhydride 3 and benzil 5 eq. 1,2.



The unusual cleavage of 4, with total retention of the dioxetanyl carbon-carbon bond,⁵ induced us to study the sensitized photooxygenation of 1 with singlet and triplet excited sensitizers with the purposes to isolate the C-C cleavage product from 4 i.e. the (Z)-stilbendioldibenzoate 6 and attempt to define the different mechanisms affording 5 and 6 eq. 3.



Typical experimental conditions are as follows: oxygen-saturated dry acetonitrile/dichloromethane solutions⁸ of 1×10^{-2} M in the presence of sensitizers (6×10^{-4} M) are irradiated at 10°C with a 700W high pressure mercury lamp through a CuSO_4 filter solution. The products 5, 6, isolated by column chromatography on silica gel, have been identified by their spectral properties and by comparison with authentic commercial and/or synthesized samples⁹ (Table 1).

Table 1 PHOTSENSITIZED OXIDATION OF 2,3,5,6-TETRAPHENYL-p-DIOXIN

Run	Conditions ^a	Time of Irr. (h)	Sensitizer	Conversion (% mol)	Products (% yields) ^b	
					<u>5</u> ^c	<u>6</u>
1		0.5	DCA	100	27	70
2	5×10^{-3} M (BQ)	0.7	"	"	30	65
3	5×10^{-3} M (DABCO)	3	"	"	7	90
4	1×10^{-2} M (DABCO)	3	"	50	-	45
5	5×10^{-3} M (KI)	1	"	100	7	90
6	5×10^{-2} (TPE) ^d	2	"	"	65	30
7 ^e		2	"	2	traces	--
8		1.5	Bz ^f	100	75	20
9	5×10^{-3} M (DABCO)	2	"	"	12	85
10		1.5	MB ^g	"	65	30
11	5×10^{-3} M (DABCO)	2	"	"	12	85
12 ^h		2	none	not quoted	not quoted	

^aOxygen was bubbled into a 50 mL Pyrex test tube, except as noted. ^bDetermined by GC with biphenyl (BP) as internal standard. ^csee ref. 8,9. ^dTetraphenyl ethylene (TPE). ^eNitrogen atmosphere. ^fBenzil (Bz). ^gMethylene blue (MB). ^hSeveral dioxins show the same autoxidation ref 15.

The key step in the 9,10-dicyanoanthracene (DCA) [$E^{\text{red}} = -0.98$ V vs SCE; $\Delta E_{\text{O-O}} = 2.94$ eV]-sensitized reaction (run 1) might involve fluorescence quenching of the excited singlet sensitizer by $1 [E^{\text{ox}'} = 0.87$ V vs SCE] leading to the radical ion pair ($\text{DCA}^- 1^+$). The subsequent reduction of molecular oxygen to superoxide anion O_2^- and its coupling with 1^+ would afford 4, ultimately leading to carbonyl products.¹¹ However, the series of experiments (runs 2-7), carried out with (DCA) as photosensitizer, clearly reveal that several unconnected mechanisms could simultaneously operate in this system. In fact, the modest effect exhibited by p-benzoquinone (BQ) [$E^{\text{red}} = -0.67$ V vs SCE], as superoxide anion quencher,¹² seems to leave out the exclusive involvement of O_2^- as oxygen active species. On the other hand, the simple retardation observed in the reactions carried out in the presence of 1,4-diazobicyclo[2,2,2]octane (DABCO)

[$E^{\text{OX}} = 0.64 \text{ V vs SCE}$] and potassium iodide (KI) [$E^{\text{OX}} = 0.37 \text{ V vs SCE}$], singlet oxygen quenchers,¹³ could be due to an easier electron-transfer reaction between (DABCO) and/or (I^-) and the singlet excited sensitizer ($^1\text{DCA}^*$), that would inhibit the formation of the radical cation 1^+ favouring the synthesis of 6 through a singlet oxygenation of 1.

Singlet oxygen, in the (DCA)-sensitized photooxygenations of substrates with low oxidation potentials and in the same time reactive towards $^1\text{O}_2$, has been previously suggested by Foote and co-workers to account for the similar results observed in the (DCA) and Rose Bengal (RB)-sensitized photooxygenation of 1,1-diphenyl-2-methoxyethylene.¹⁴ It might derive from species formed after interception of ($^1\text{DCA}^*$) by the substrate, being unlikely that it derives from direct intersystem crossing of ($^1\text{DCA}^*$) to ($^3\text{DCA}^*$). Our findings are furthermore complicated by the well ascertained autooxidation of 1^{15} , during the irradiation of its oxygenated solutions (run 12) with formation of benzil, which action, as triplet excitable sensitizer ($E_T = 53 \text{ Kcal/mol}$), has been well observed in the photooxygenation of 1 (8,9) [See also the similar results obtained in the methylene blue sensitization: (runs 10,11)]. Triplet excited benzil could add triplet molecular oxygen affording an acylperoxyl radical species, or transfer its energy to O_2 leading to singlet oxygen.¹⁶ Both species appear efficient, through different mechanisms, in the oxidation of 1.^{17,2}

Although our findings do not lead to an inexorable mechanistic conclusion, however they clearly show that the cleavage of 4 must lead to 6, through the usual C-C cleavage,¹⁸ demonstrating at the same time that 5 might arise, mainly, from the intermediate radical cation 1^+ , which formation could be reduced by (DABCO) and (I^-) or enhanced in the indirect tetraphenyl ethylene (TPE)-sensitized photooxygenation (run 6).¹⁴ Preliminary observations on the evolution of the radical cation 1^+ , chemically generated by electron-transfer between 1 and tris-p-bromophenyl-ammoniumyl tetrafluoroborate ($\text{BrC}_6\text{H}_4)_3\text{N}^+\text{BF}_4^-$, leading essentially to 5,¹⁹ provide support for our idea about the different mechanisms affording 5 and 6.

Studies on sensitized photooxygenations of several dioxin with different sensitizers, such as tetrachloro-p-benzoquinone (CA),²⁰ are in progress.

Acknowledgements. We are indebted to the Progetto Finalizzato Chimica Fine e Secondaria for financial support. We also thank Prof. A. P. Schaap for suggestions and Prof. W. Adam for the private preliminary communication of his results.

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- 8) The photooxygenation of 1 in dry acetonitrile, owing to its low solubility, is slower and it affords a complex mixture of 5, (Z) and (E) stilbendiol dibenzoate together with benzoic acid and 3. The isomerization of 6 has been confirmed by (DCA) and/or tetrachloro-p-benzoquinone (CA)-sensitised irradiation of an its solution in nitrogen atmosphere.
- 9) Yields were determined on the isolated products and by GC with biphenyl as internal standard. As two moles of 5 can result from 1 yields are expressed as (mol₅/2xmol 1)x100. The isolated 5 shows the same mp. and spectral data of a pure commercial "Aldrich" sample. 6 mp 158-159°C (lit 159°C ref 10a), shows the following spectral data: ir (KBr pellet); 1725 cm⁻¹, ms 70eV (m/e) 229 (1), 105 (100), 77 (42); ¹Hnmr (CDCl₃ TMS) aromatic protons. The (E) isomer shows similar spectral data but a higher mp. 188°C (lit 189°C ref 10b) and a higher retention time by GC.
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(Received in UK 16 May 1985)