

THERMAL AND PHOTOCHEMICAL TRANSFORMATIONS OF TETRAPHENYL-*p*-DIOXADIENE

S. Lahiri, V. Dabral and M. V. George*

Department of Chemistry
 Indian Institute of Technology, Kanpur
 Kanpur 208016, India

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Berger and Summerbell¹ observed that the thermolysis of tetraphenyl-*p*-dioxadiene (1) around 250° gives a 90% yield of 2,2,3,4-tetraphenyl-3-buteno-4-lactone (5). Zinin² had earlier shown that the same lactone 5 is formed a nearly quantitative yield in the thermolysis of *cis*-dibenzoylstilbene (11a). The thermal transformation of 1 to 5 has been assumed to proceed through intermediates like 2, 3 and 4, as per path 'a' in Scheme 1. In the present investigation we have examined the thermal and photochemical transformations of 1 to understand the mechanistic details of these reactions.

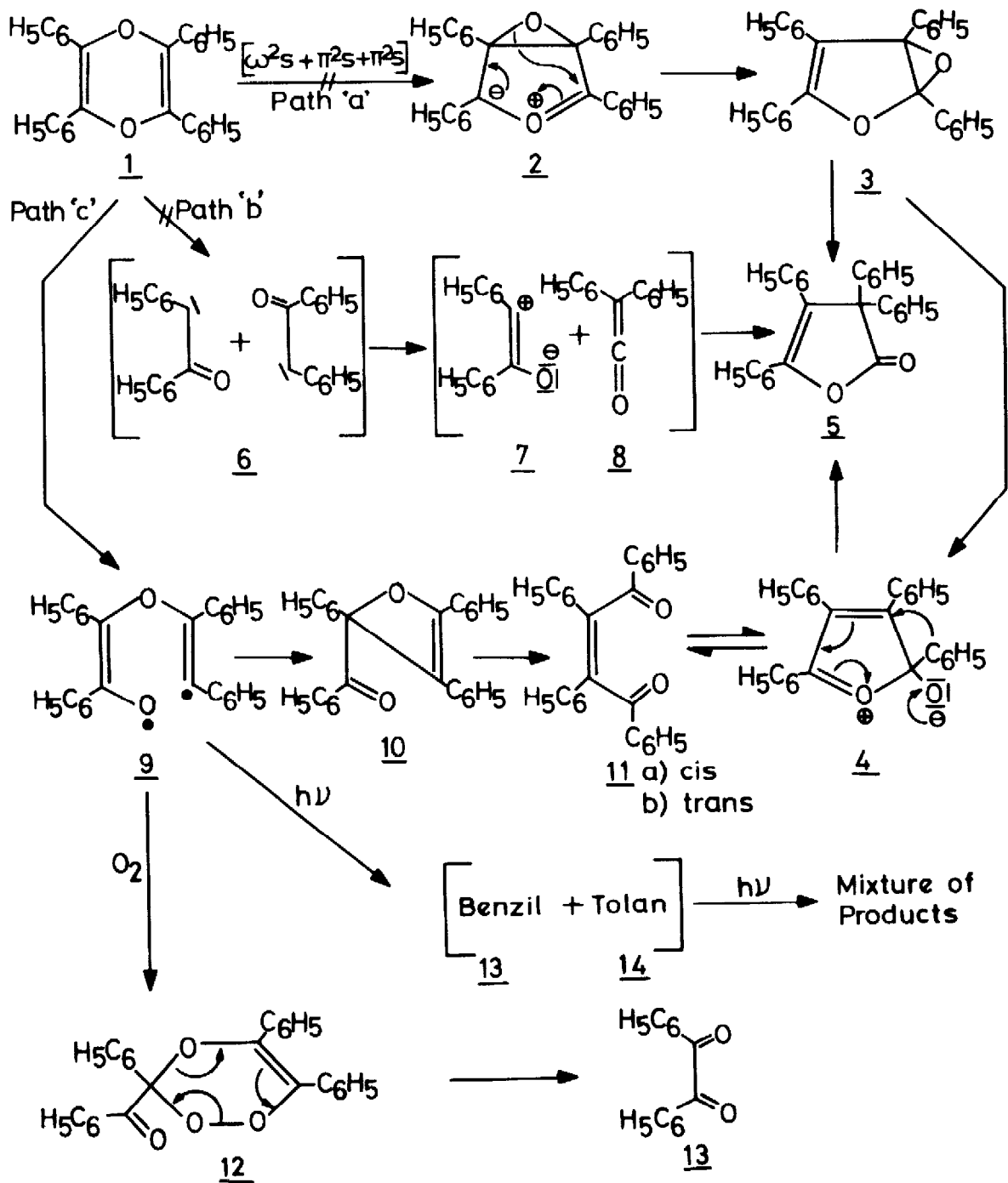
Although the thermolysis of 1 in the absence of any solvent at 250° has been reported to give exclusively the lactone 5 (90%)¹, we have found that actually a mixture of products consisting of both the lactone 5 (84%) and *cis*-dibenzoylstilbene (11a, 10%) is formed on neat heating of 1 at 260° for 45

Table 1. Thermolysis of Tetraphenyl-*p*-dioxadiene at Different Temperatures

Solvent	Temperature (°C)	Time (hr)	Recovered starting material (%)	Products (%)		
				Lactone (<u>5</u>)	<i>cis</i> -Dibenzoylstilbene (<u>11a</u>)	Benzil (<u>13</u>)
Toluene	110	45	81	-	-	10*
<i>o</i> -Dichlorobenzene	180	38	8	-	82	16*
<i>p</i> -Dichlorobenzene	180	45	5	-	81	24*
<i>m</i> -Dichlorobenzene	180	50	-	3	79	30*
Nitrobenzene	210	20	-	91	8	-
No Solvent	260	$\frac{3}{4}$	-	84	10	-

* The higher yields of benzil are due to the air-oxidation of 1.

Scheme 1



minutes. When the thermolysis of 1 however, was conducted at lower temperatures, in different solvents under reflux, an increase in the yield of cis-dibenzoylstilbene has been observed. Table 1 lists the results of these studies. In refluxing toluene (110°) for example, a 10% yield of benzil (13) was obtained after 45 hr. Most of the starting material (81%) was recovered unchanged under these conditions. In refluxing *o*-dichlorobenzene (180°), on the other hand, 1 gave mainly cis-dibenzoylstilbene (11a). Also, small amounts of benzil were formed in these reactions. When 1 was refluxed in nitrobenzene (210°) for 20 hr, a 91% yield of the lactone 5 and a 8% yield of 11a were obtained.

The formation of the lactone 5 in major amounts, both in refluxing nitrobenzene (210°) and on direct heating (250°) would suggest that at higher temperatures, 1 is ultimately converted to 5. If the reaction is proceeding through path 'a', then the carbonyl ylide 2 formed through a [$w^2s + \pi^2s + \pi^2s$] reaction may undergo conversion to the furan epoxide 3, which can subsequently be converted to 5 either directly through a dyotropic rearrangement or in a step-wise process involving the zwitterionic intermediate 4. Our attempts to trap 2, employing dimethyl acetylenedicarboxylate (DMAD) have been unsuccessful. An alternative mode of transformation of 1 would be through path 'b' involving the formation of the ketocarbene 6, followed by the cycloaddition between 7 and 8, intermediates generated from 6. The fact that the ketocarbene 7 could not be trapped by dipolarophiles like DMAD and also the intramolecular nature of the transformation of 1 to 5 would rule out path 'b' for this reaction.

The most reasonable route for the conversion of 1 to 5 seems to be through path 'c', involving the homolytic cleavage of 1 to give the diradical species 9, which can subsequently be transformed to 11a through the oxete intermediate 10. Electrocyclic ring-closure of 11a would give rise to the zwitterionic intermediate 4, which is rearranged to 5.³ The fact that 11a is formed as the major product when 1 is refluxed in *o*-dichlorobenzene would strongly support

this mechanism. Further, we have shown in a separate experiment that 11a is converted to the lactone 5 in a 96% yield, on refluxing in nitrobenzene for 20 hr.

If an intermediate like 9 is involved in the transformation of 1, then its formation should be more prominent under photochemical conditions. Photolysis of 1 in benzene under nitrogen atmosphere for $2\frac{1}{2}$ hr gave a mixture of products consisting of benzil (13, 30%), tolan (14, 1%) and trans-dibenzoylstilbene (11b, 1.7%), besides 53% of the unchanged starting material. When the photolysis of 1 was carried out in presence of air for $\frac{1}{4}$ hr, a 70% yield of benzil was obtained, besides 20% of the unchanged starting material. Photolysis of 1 for 10 minutes under oxygen atmosphere gave a 60% yield of benzil. However, the photolysis of 1 for $\frac{1}{2}$ hr under oxygen bubbling gave a 6% yield of benzil and a complex mixture of products, identical to the products obtained in the photolysis of benzil⁴ and tolan.⁵ Photolysis of 1 in t-butanol for $\frac{1}{4}$ hr however, gave a 56% yield of benzil and 4% tolan, besides 33% of the unchanged starting material. It appears that under photochemical conditions, the initially formed diradical intermediate 9, undergoes fragmentation to give benzil and tolan, which are further transformed to a complex mixture of products.^{4,5} The formation of small amounts of trans-dibenzoylstilbene (11b) in the photolysis of 1 in benzene would suggest that a small fraction of 9 may be getting converted to 10 and subsequently to 11 under these conditions. The increased yield of benzil when the photolysis of 1 is carried out in presence of air may be rationalized in terms of peroxy intermediates like 12 (Scheme 1).

References

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