

Thermal and photochemical transformations of tetraphenyl-*p*-dioxin and tetraphenyl-*p*-dithiin

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Abstract. The thermal transformation of tetraphenyl-*p*-dioxin (1) to 2, 2, 3, 4-tetraphenylbut-3-enolide (5) has been shown to proceed through the intermediacy of cis-dibenzoylstilbene (6) and a reasonable mechanism for this transformation has been suggested. The photolysis of tetraphenyl-*p*-dioxin, on the other hand, has been found to give a mixture of products consisting of mainly benzil and small amounts of tolan. Thermolysis and photolysis of tetraphenyl-*p*-dithiin (31) follow a different pathway giving rise to tetraphenylthiophene, in each case. The photo-oxygenation of tetraphenyl-*p*-dithiin, on the other hand, gave a mixture of products consisting of, tetraphenylthiophene, benzil and benzoic acid.

Keywords. Tetraphenyl-*p*-dioxin; tetraphenyl-*p*-dithiin; thermal transformations; photochemical transformations.

1. Introduction

Six-membered heterocycles like *p*-dioxin and *p*-dithiin, containing two hetero atoms and under the category of eight-electron systems have received considerable attention in recent years (Hafner 1964; Vogel and Gunther 1967; Schmidt *et al* 1971, 1972, 1975). Detailed studies of the uv-spectrum, measurement of bond lengths by electron diffraction method (Connett *et al* 1966) and theoretical calculations, (Tinlan and Decoret 1971) have shown that *p*-dioxin has a nearly planar structure and that the structural features are favourable for electron delocalization in this system. In contrast, *p*-dithiin has been shown to have a non-planar boat configuration (Howell *et al* 1958, 1959).

Berger and Summerbell (1959) have shown that 2, 3, 5, 6-tetraphenyl-*p*-dioxin (1) on heating at 250° is converted to 2, 2, 3, 4-tetraphenylbut-3-enolide (5). These workers have rationalized their observation in terms of an initial intermediate 2, which is then transformed to the product 5, through the furan epoxide, 3 and the dipolar intermediate, 4 as shown in figure 1. The thermal transformation of cis-dibenzoyl-stilbene (6) is known to give the same lactone 5, formed from tetraphenyl-*p*-dioxin and the involvement of the dipolar intermediate 4, has been suggested by earlier workers (Zinin 1872; Japp and Klingerman 1890). In view of our general

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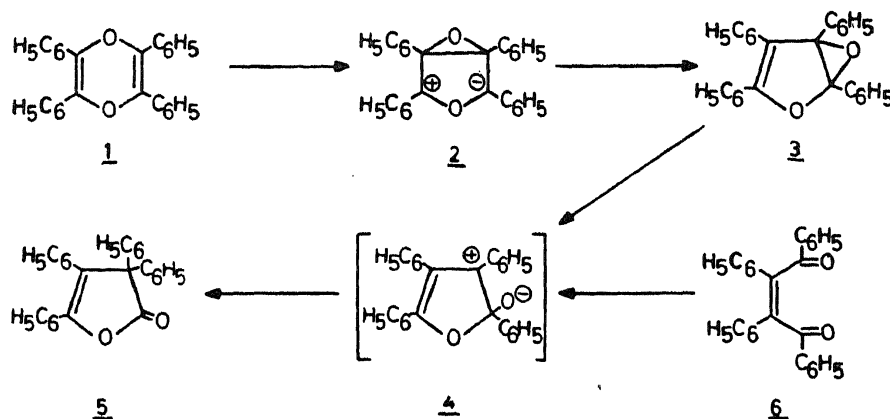


Figure 1.

interest in the thermal and photochemical transformations of *cis*-1, 2-dibenzoylalkenes, we have examined the thermal and photochemical transformations of both tetraphenyl-*p*-dioxin and tetraphenyl-*p*-dithiin, with a view to understanding the details of these transformations. Preliminary results of our studies have been reported in an earlier communication (Lahiri *et al* 1976). The present paper describes the details of our studies in this area of investigation.

2. Results and Discussion

2.1. Preparation of tetraphenyl-*p*-dioxin (1)

Tetraphenyl-*p*-dioxin is reported to be formed in poor yields, along with a complex mixture of products, by refluxing benzoin in ligroin in the presence of *p*-toluenesulphonic acid, (Howell *et al* 1958, 1959). In a reinvestigation of this reaction, Jemmis (1973) has shown that the products formed in this case include, tetraphenyl-*p*-dioxin (1) (6%), *cis*-dibenzoylstilbene (6) (0.5%), benzil (8) (47%), desoxybenzoin (8%) and tetraphenylfuran (9) (12%). A convenient method for preparing tetraphenyl-*p*-dioxin is through the reaction of benzoin with methanol in presence of hydrogen chloride, as reported by Irvine *et al* (Irvine and Weir 1907; Irvine and Mcnicoll 1908) Madelung and Oberwegner (Madelung and Oberwegner 1936a, b) have shown that a mixture of *trans*-6-methoxy-2, 3, 5, 6-tetraphenyl-1, 4-diox-2-ene (10) and *trans, trans*-2, 5-dimethoxy-2, 3, 5, 6-tetraphenyl-1, 4-dioxane (11) is formed on treating benzoin with methanol in presence of hydrogen chloride and that this mixture can be directly treated with zinc chloride in boiling acetic anhydride to give tetraphenyl-*p*-dioxin in good yields (figure 2).

2.2. Thermolysis of tetraphenyl-*p*-dioxin

Although the thermolysis of tetraphenyl-*p*-dioxin (1) in the absence of any solvent at 250° has been reported to give exclusively the lactone 5 in a 90% yield, (Berger and Summerbell 1959) we have found in our present studies that actually a mixture of products consisting of both the lactone 5 (84%) and *cis*-dibenzoylstilbene (6, 10%)

is formed on neat heating of 1 at 260° for 45 minutes. When the thermolysis of 1, however, was conducted at lower temperatures and in different solvents under reflux, an increase in the yield of *cis*-dibenzoylstilbene has been observed. In refluxing toluene (110°) for example, a 10% yield of benzil (8) was obtained after 45 hr and most of the starting material (81%) was recovered unchanged. In refluxing *o*-dichlorobenzene (180°), on the other hand, 1 gave mainly *cis*-dibenzoylstilbene. Small amounts of benzil were also formed in all these cases. When 1 was refluxed in nitrobenzene (210°) for 20 hr, a 91% yield of the lactone 5 and a 8% yield of *cis*-dibenzoylstilbene were formed. Table 1 summarizes the results of these studies.

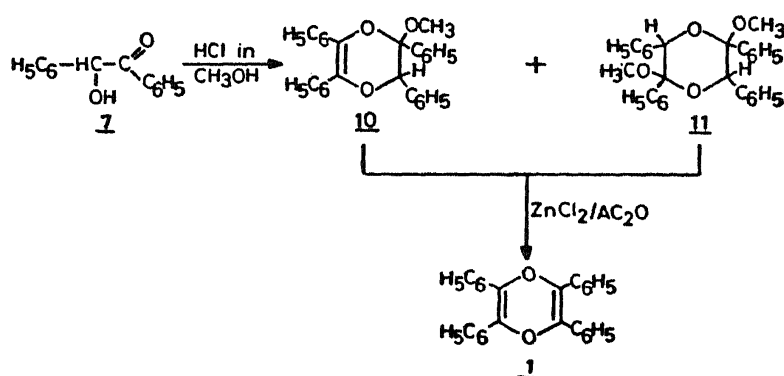


Figure 2.

The results of our studies clearly show that under thermal conditions, tetraphenyl-*p*-dioxin (1) is first converted to *cis*-dibenzoylstilbene (6), which then at higher temperatures is transformed to 2, 2, 3, 4-tetraphenylbut-3-enolide (5). The transformation of 1 to 5, in principle, can proceed through different pathways as shown in figure 3. One of these routes (Path 'a') would involve an initial electrocyclic reaction of 1 through a ($\omega^2s + \pi^2s + \pi^2s$) type of reaction to form the carbonylylid 2, which can subsequently undergo transformation to the furan epoxide, 3. Subsequent conversion of 3 to the lactone 5 can take place either through a dyotropic rearrangement (Reetz 1973) or in a stepwise process involving the zwitterionic intermediate 12. The fact that *cis*-dibenzoylstilbene (6) is formed as an intermediate in the transformation of 1 to 5 would preclude this pathway. However, with a view to ascertaining whether the furan epoxide 3 is formed as an intermediate in the transformation of 1 to 5, we have attempted at preparing this epoxide through the peracid oxidation of tetraphenylfuran

Table 1. Thermolysis of tetraphenyl-*p*-dioxin (1) at different temperatures

Solvent	Temperature (°C)	Time (hr)	Recovered	Products (%)		
				1	5	6 8*
Toluene	110	45	81	—	—	10
<i>o</i> -Dichlorobenzene	180	38	8	—	82	16
<i>o</i> -Dichlorobenzene	180	45	5	—	81	24
<i>o</i> -Dichlorobenzene	180	50	—	3	79	30
Nitrobenzene	210	20	—	91	8	—
No solvent	260	$\frac{3}{4}$	—	84	10	—

*Formed by the air-oxidation of 1.

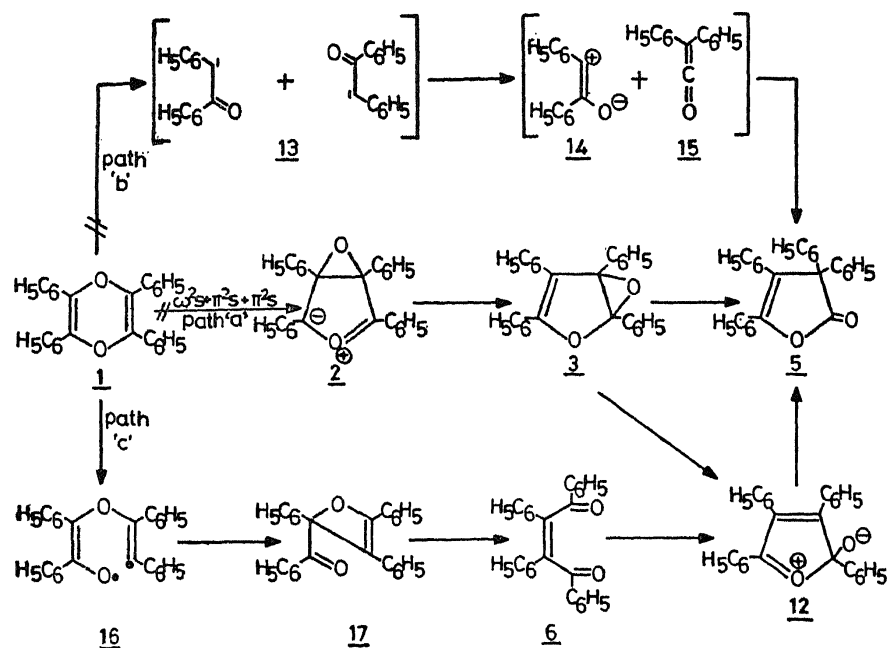


Figure 3.

(9). It is known that **9** undergoes peroxidation under varying experimental conditions to give different products like *cis*-dibenzoylstilbene (**6**), the enol benzoate of dibenzoylphenylmethane (**18**) and *cis*-dibenzoylstilbene epoxide (**19**), as shown in figure 4 (Lutz *et al* 1962). In the present studies we find that the oxidation of **1** employing an equimolar amount of perbenzoic acid gives a nearly quantitative yield of *cis*-dibenzoylstilbene. Our efforts at isolating the furan epoxide intermediate **3**, even at low temperatures have been unsuccessful.

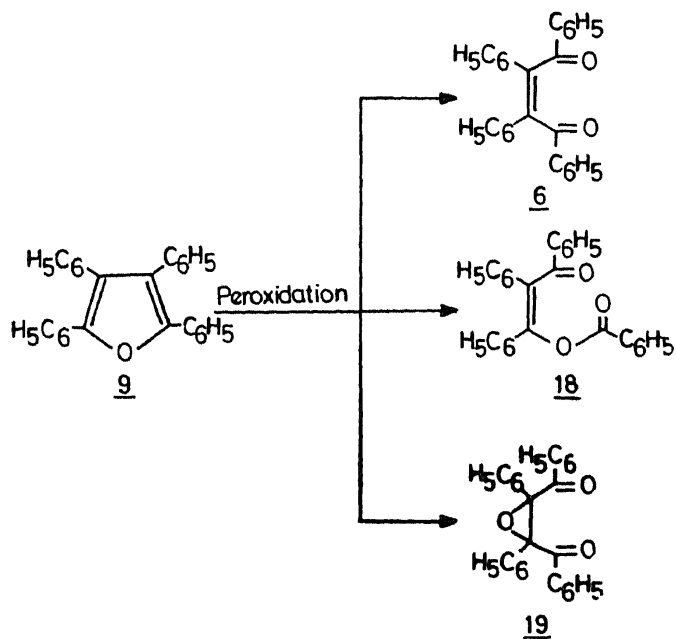


Figure 4.

An alternative mode of transformation of **1** would be through path 'b', involving the initial formation of the ketocarbene **13**. This ketocarbene intermediate, which can exist in the 1,3-dipolar form **14** can undergo a subsequent cycloaddition

reaction with diphenylketene (15), formed by the rearrangement of 13 (figure 3). The fact that the ketocarbene intermediate 13 could not be trapped by dipolarophiles like dimethyl acetylenedicarboxylate and also the intramolecular nature of the transformation of 1 to 5 would rule out path 'b' as a probable pathway for this transformation.

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 15 which can subsequently be transformed to 6 through an oxete intermediate 17. Electrocyclic ring-closure of 6 would give rise to the zwitterionic intermediate 12, which is rearranged to 5 (figure 3).

It has been observed that benzil is formed as a minor product in the thermolysis of 1 and that the yields of benzil increases with increased duration of heating. A reasonable pathway for the formation of benzil in this reaction is through the partial air-oxidation of 1, under thermolytic conditions. The fact that benzil is formed in nearly quantitative yield on treatment of 1 with peracids would support this assumption.

2.3. Photolysis of tetraphenyl-*p*-dioxin (1)

In the thermolysis of 1, if a diradical intermediate like 16 (figure 3) is involved, its formation should be more prominent under photochemical conditions. With a view to examining this possibility we have studied the photolysis of 1 under different conditions.

Photolysis of 1 in *t*-butanol for 15 minutes gave a 56% yield of benzil (8) and 4% yield of tolan (20), besides a 33% of the unchanged starting material. When the photolysis was carried out in benzene for 2½ hr, under nitrogen atmosphere, a mixture of products consisting of benzil (30%), tolan (1%) and trans-dibenzoylstilbene (21, 1.7%) was obtained, besides 53% of the starting material. When the photolysis, however, was carried out in the presence of air, a 70% yield of benzil was obtained besides 20% of the unchanged starting material. The photolysis of 1 in benzene for 10 minutes under oxygen atmosphere gave a 60% yield of benzil. However, when the time of irradiation was increased to 30 minutes, besides a 6% yield of benzil, a complex mixture of products was obtained from which no definite product could be isolated. Examination of this mixture on tlc showed that it closely resembles the products obtained from the photolysis of benzil (Bunbury *et al* 1968, 1969, 1972) and tolan (Buchi *et al* 1962).

From the results of our studies it appears that under photochemical conditions, 1 undergoes homolytic cleavage to give the diradical intermediate 16, which subsequently undergoes either fragmentation to give benzil (8) and tolan (20) or air-oxidation to give benzil via a peroxy intermediate like 22. Both benzil and tolan, under photochemical conditions would undergo further transformations to give the complex mixture of products (figure 5). The formation of small amounts of trans-dibenzoylstilbene (21) in the photolysis of 1 in benzene would suggest that a small fraction of 16 may be getting converted to 17 and subsequently to 21 under these conditions.

In continuation of our studies we have examined the electron-impact fragmentation of tetraphenyl-*p*-dioxin. The mass spectrum of 1 showed the molecular ion peak at *m/e* 388 (16). Other peaks in the spectrum were observed at *m/e* 311 (1), 283 (3),

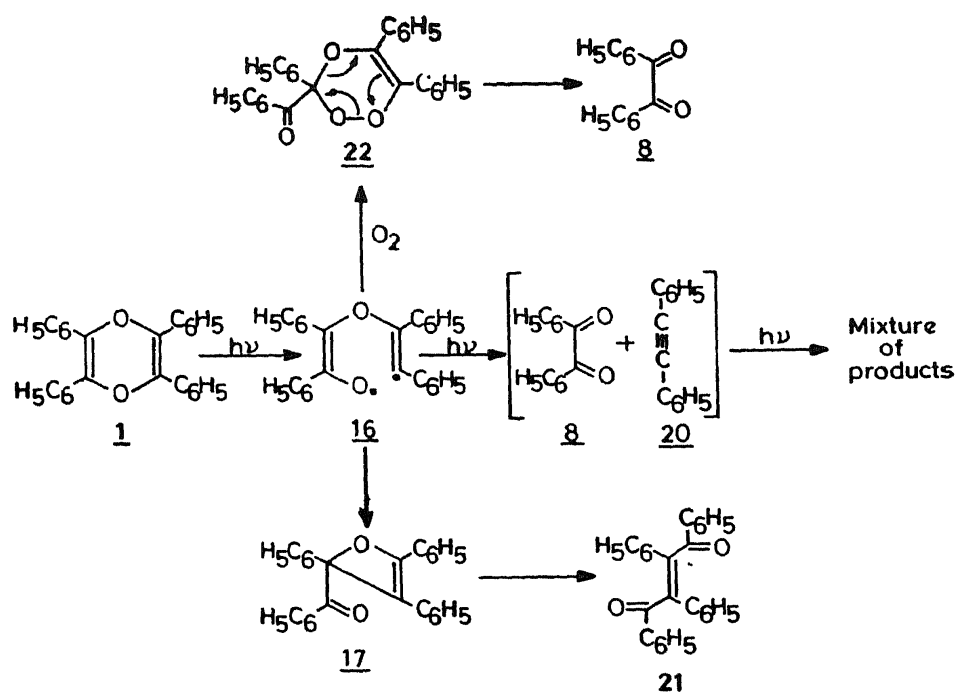


Figure 5.

267 (1), 255 (4), 179 (5), 178 (31), 177 (3), 176 (6), 165 (3), 152 (5), 151 (4), 105 (100), 77 (35), 71 (6), 70 (4), 69 (6), 57 (11), 56 (3), 55 (10), 51 (6), 43 (10) and 41 (6). A comparison of the mass spectrum of 1 with that of *cis*-dibenzoylstilbene (6) (Lahiri *et al* 1977) reveals a striking similarity between the two, which essentially indicates that 1 upon electron impact is transformed to 6, which subsequently undergoes fragmentation to give different ions.

2.4. Thermal and photochemical transformations of tetraphenyl-*p*-dithiin

Thermal transformation of *p*-dithiin derivatives are known to give substituted thiophenes (Parham *et al* 1954, 1955, 1960, 1961). Thus, for example, 2, 3-diphenylthiophene (25) is reported to be the product formed in the thermolysis of 2, 5-diphenyl-*p*-dithiin (23) (figure 6). A probable route to the formation of 25 is through an initial.

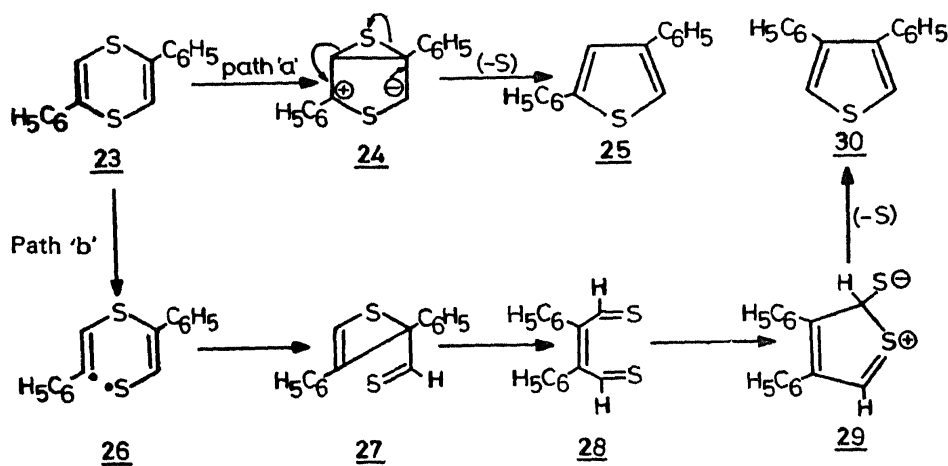


Figure 6.

electrocyclic reaction of 23 by a $[\omega^2s + \pi^2s + \pi^2s]$ type of addition to give the thio-carbonylylid 24, which then loses sulphur to give 25, as shown in figure 6 (path 'a'). An alternative pathway for the thermal transformation of 23 would be through the formation of the diradical intermediate 26, which can then give rise to the thiete derivative 27. The thiete derivative can subsequently undergo ring-opening to give the dithiocarbonyl intermediate 28, which can then give rise to 3, 4-diphenylthiophene (30) through the dipolar intermediate 29, as shown in figure 6 (path 'b'). However, the exclusive formation of 2, 3-diphenylthiophene from 23 and not 3, 4-diphenylthiophene (30) would clearly indicate that path 'a' is followed in the thermal transformation of 23. A similar observation has been made in the thermolysis of 2, 5-diphenyl-3-nitro-*p*-dithiin, which gives exclusively 3, 5-diphenyl-2-nitrothiophene (Parham and Traynelis 1955).

The thermal transformation of a few tetrasubstituted *p*-dithiin derivatives are reported in the literature. Thus, it has been shown that tetracyano-*p*-dithiin undergoes ready thermal transformation, leading to the formation of tetracyanothiophene (Simmons 1968a, 1968b). Similarly, the thermolysis of tetraphenyl-*p*-dithiin (31) is known to give tetraphenylthiophene (33) (Kirmse and Horner 1958). With a view to understanding the mechanistic details of the thermal transformations of *p*-dithiins, we have reinvestigated the reactions of tetraphenyl-*p*-dithiin (31). The thermolysis of 31 at 195° for 30 min and in the absence of any solvent gave rise to a 97% yield of tetraphenylthiophene (33). The same reaction, when carried out in refluxing *o*-dichlorobenzene, gave a 95% yield of 33. No other product could be isolated from these reactions. If the formation of 33 is proceeding through the thio-carbonylylid intermediate 32, as shown in figure 7, then its presence could be detected by trapping experiments. Our attempts to trap the intermediate 32 with dipolarophiles like dimethyl acetylenedicarboxylate have been unsuccessful. It is quite likely that this intermediate undergoes a rapid loss of sulphur to give the thiophene derivative 33 (figure 7).

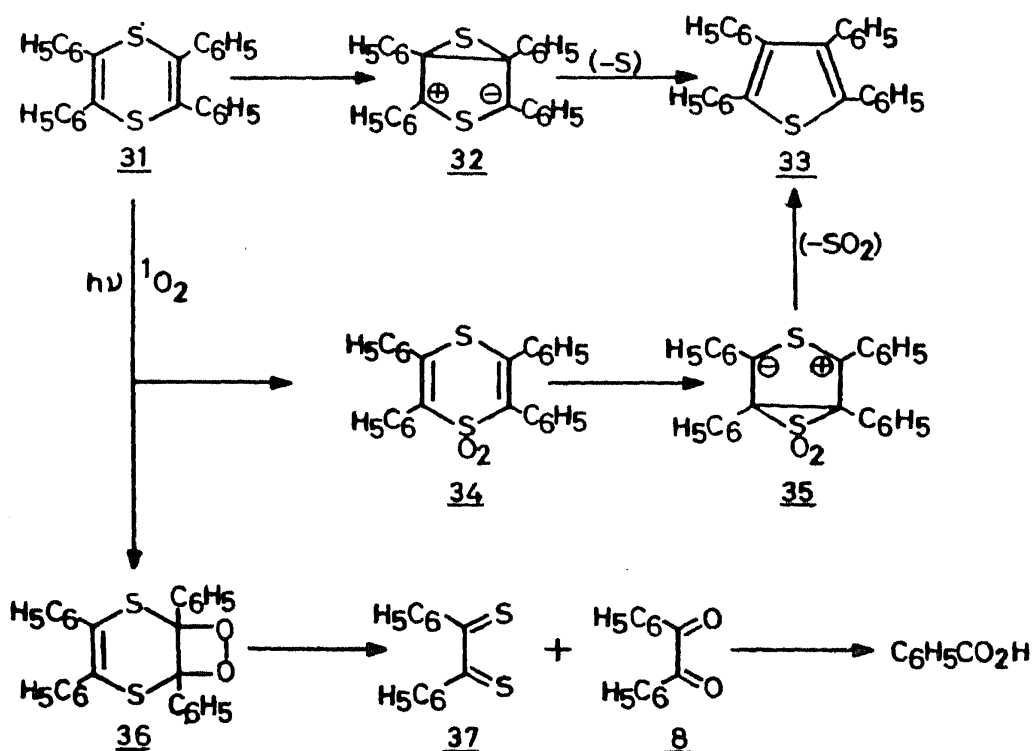


Figure 7.

Further to our studies, we have examined the photolysis of tetraphenyl-*p*-dithiin (31). Photolysis of a benzene solution of 31 resulted in a 15% yield of 33. The formation of 33 in this reaction may be rationalized in terms of a pathway similar to the thermal transformation of 31, as shown in figure 7 or through a diradical pathway similar to path 'b' in figure 6. In contrast, the photo oxygenation of 31 gave rise to a mixture of products consisting of 33 (31%), benzil (8) (15%), benzoic acid (26%) and biphenyl (1%). In addition, the evolution of sulphur dioxide gas, during the reaction, was also detected. The formation of the thiophene 33 and SO₂ in this reaction may be rationalized in terms of the sulphone intermediate 34, which is subsequently transformed to the thiocarbonylylide 35. Loss of sulphur dioxide from 35 will lead to the formation of 33 as shown in figure 7. It might be mentioned in this connection that sulphone intermediates similar to 34 have been postulated in the peracid oxidations of *p*-dithiin derivatives (Parham and Traynelis 1954; Kirmse and Horner 1958). The formation of benzil (8) in the photooxygenation of 31 could be understood in terms of the peroxide intermediate 36, which can subsequently fragment to the dithiocarbonyl derivative 37 and 8. The intermediate 37 itself can undergo further oxidation to give 8, whereas the formation of benzoic acid in this reaction can be attributed to the photooxygenation of benzil itself. A very small yield of biphenyl in this reaction would suggest the involvement of phenyl radicals, perhaps formed through some of the fragmentation modes.

In the present studies, we have also examined the electron-impact induced fragmentation of tetraphenyl-*p*-dithiin (31). The mass spectrum of 31 showed a molecular ion peak at *m/e* 420 (76). The most intense peak in the spectrum of 31 however, was observed at *m/e* 388 (100). Other major peaks in the mass spectrum of 31 were present at *m/e* 310 (5), 309 (11), 308 (7), 307 (7), 277 (4), 267 (7), 266 (5), 221 (3), 210 (5), 178 (67), 165 (12), 155 (4), 154 (3), 152 (3), 151 (2), 121 (63), 77 (9), 64 (3) and 51 (1). It is pertinent to observe that the mass spectrum of 31 shows great similarity to that of tetraphenylthiophene 33, (API Research Project) excepting for the presence of the molecular ion peak in 31 at *m/e* 420. It is apparent from the mass spectrum of 31 that it undergoes ready conversion to tetraphenylthiophene (33), under electron-impact, and in this respect the mass spectral behaviour of 31 is very similar to its thermal and photochemical transformations.

3. Experimental

All melting points are uncorrected and were determined on a Mel-Temp, melting point apparatus. Infrared spectra were recorded either on Perkin-Elmer Model 137 or 521 Infrared Spectrometer. The electronic spectra were recorded on a Beckman DB Spectrometer. The irradiation experiments were carried out using either a 450w Hanovia medium pressure mercury lamp or a 150w Srinivasan-Griffin-Rayonet Photochemical Reactor. Petroleum ether used was of bp 60–80°. The mass spectra were recorded on a Varian Mat CH 7 Mass Spectrometer at 70 eV.

3.1. Starting materials

3.1.1. *Tetraphenyl-p*-dioxin (1) (Madelung and Oberwegner 1936): Through a solution of benzoin (20 g, 0.094 mol) in methanol (500 ml), a stream of dry hydrogen

chloride gas was passed for 1 hr, during which period, a white crystalline solid separated out. After keeping the reaction mixture at room temperature for 12 hr, the solid material was filtered off to give 7 g of a mixture of products consisting of both trans-6-methoxy-2, 3, 5, 6-tetraphenyl-1, 4-diox-2-ene (10) and trans, trans-2, 5-dimethoxy-2, 3, 5, 6-tetraphenyl-1, 4-dioxane (11). This mixture of products (5 g) was subsequently heated with 75 ml of acetic anhydride and 0.5 g of anhydrous zinc chloride till the solution began to boil. On cooling, a bright yellow solid separated out which gave 4 g (22%) of tetraphenyl-*p*-dioxin (1) mp 218° (lit. mp 218°) (Madelung and Oberwegner 1937), on recrystallization from a mixture (1 : 1) of chloroform and petroleum ether.

3.1.2. *Tetraphenylfuran* (9) (Williams 1973): A mixture of benzoin (2g, 9.4 mmol) and anhydrous aluminium chloride (30 mg) was heated in an evacuated sealed tube around 150-200° for 50 hr. The reaction mixture was extracted with carbon tetrachloride. Removal of the solvent from the carbon tetrachloride-extract gave a product mixture. Treatment of this mixture with ethanol gave an ethanol-insoluble product, which on recrystallization from a mixture (10 : 1) of petroleum ether and benzene gave 1.2 g (31%) of tetraphenylfuran (9), mp 173-174° (lit. mp 173°) (Williams 1973).

3.1.3. *Tetraphenyl-p-dithiin* (Mayer and Nitzschke 1963): Benzoin (5g, 0.023 mol) was added to 100 ml of ethanol which had been saturated previously with dry hydrogen chloride gas. A stream of hydrogen sulphide was passed through this suspension. All of the benzoin gradually went into solution and after passing the gas for 1 hr, solid material started precipitating out. After allowing the reaction to proceed for 2 hr, the precipitated material was removed by filtration. The filtered solid was treated with hot ethanol to remove the ethanol-soluble impurities and the residue was recrystallized from chloroform to give 5 g (50%) of tetraphenyl-*p*-dithiin (31), mp 191° (lit. mp 191°) (Mayer and Nitzschke 1963).

3.2. Thermolysis of tetraphenyl-*p*-dioxin

3.2.1. *In toluene*: A sample of tetraphenyl-*p*-dioxin (300 mg, 0.77 mmol) was refluxed in toluene (15 ml) for 45 hr. Removal of the solvent under vacuum gave a product which was extracted with petroleum ether. The residue gave 237 mg (79%) of the unchanged starting material, mp 217-218° (mixture mp), after recrystallization from a mixture (1 : 1) of chloroform and petroleum ether.

The petroleum ether-extract was chromatographed over an alumina column. Elution of the column with petroleum ether gave an additional 7 mg (2%) of the starting material, mp 217-218° (mixture mp) after recrystallization from a mixture (1 : 1) of petroleum ether and chloroform.

Further elution of the column with petroleum ether gave 6 mg (10%) of benzil, mp 91° (mixture mp).

3.2.2. *In o-dichlorobenzene*: A sample of 1 (500 mg, 1.3 mmol) was refluxed in *o*-dichlorobenzene (25 ml) for 38 hr. The solvent was completely removed under vacuum. The reaction mixture was treated with petroleum ether and the insoluble residue was subsequently treated with hot ethanol. The ethanol-insoluble residue gave 40 mg (8%) of unchanged 1, mp 217-218° (mixture mp), after recrystallization

from a mixture (1 : 1) of chloroform and petroleum ether. The ethanol-soluble portions, on cooling gave 335 mg (73%) of cis-dibenzoylstilbene (6), mp 216-217° (mixture mp).

The petroleum ether-soluble portion was chromatographed over an alumina column. Elution of the column with petroleum ether gave 15 mg (16%) of benzil mp 91° (mixture mp).

Further elution of the column with a mixture (3 : 1) of petroleum ether and benzene gave an additional 40 mg (9%) 6, mp 216-217° (mixture mp), after recrystallization from a mixture (1 : 1) of petroleum ether and benzene.

In a repeat run, 1 (500 mg, 1.3 mmol) was refluxed in *o*-dichlorobenzene (15 ml) for 45 hr. Work-up as in the earlier case gave 25 mg (5%) of the starting material, mp 217-218° (mixture mp), 385 mg (81%) of cis-dibenzoylstilbene, mp 216-217° (mixture mp) and 24 mg (24%) of benzil, mp 91° (mixture mp).

In yet another run, 1 (500 mg, 1.3 mmol) was refluxed in *o*-dichlorobenzene for 50 hr. Work-up in the usual manner gave a total amount of 393 mg (79%) of cis-dibenzoylstilbene, mp 216-217° (mixture mp), 30 mg (30%) of benzil, mp 91° (mixture mp) and 15 mg (3%) of 2, 2, 3, 4-tetraphenylbut-3-enolide, mp 136-137° (mixture mp).

3.2.3. *In nitrobenzene*: A sample of 1 (500 mg, 1.3 mmol) was refluxed in nitrobenzene (25 ml) for 20 hr. The solvent was removed under reduced pressure and the residue was chromatographed over alumina. Elution of the column with a mixture (5 : 1) of petroleum ether and benzene gave 455 mg (91%) of 2, 2, 3, 4-tetraphenylbut-3-enolide, mp 136-137° (mixture mp) after recrystallization from a mixture (4 : 1) of petroleum ether and benzene. Further elution with a mixture (3 : 1) of petroleum ether and benzene gave 40 mg (8%) of cis-dibenzoylstilbene, mp 216-217° (mixture mp), after recrystallization from a mixture (1 : 1) of petroleum ether and benzene.

3.2.4. *In the absence of any solvent*: A sample of 1 (776 mg, 2 mmol) was heated around 260° for 45 minutes. The residue was chromatographed over alumina. Elution of the column with a mixture (5 : 1) of petroleum ether and benzene gave 653 mg (84%) of 2, 2, 3, 4-tetraphenylbut-3-enolide, mp 137° (mixture mp), after recrystallization from a mixture (4 : 1) of petroleum ether and benzene.

Further elution of the column with a mixture (3 : 1) of petroleum ether and benzene gave 78 mg (10%) of cis-dibenzoylstilbene, mp 216-217° (mixture mp), after recrystallization from a mixture (1 : 1) of petroleum ether and benzene.

3.3. Reaction of tetraphenylfuran with perbenzoic acid

A mixture of tetraphenylfuran (1 g, 2.7 mmol) and perbenzoic acid (3 mmol, 34 ml) in chloroform (30 ml) was kept at room temperature for 24 hr. The reaction mixture was washed repeatedly with a 5% solution of sodium bicarbonate and then with water and subsequently dried over anhydrous sodium sulphate. Removal of the solvent under reduced pressure gave 1 g (96%) of cis-dibenzoylstilbene, mp 216° (mixture mp), on recrystallization from a mixture (1 : 1) of petroleum ether and benzene.

The bicarbonate-extract was acidified with 1% hydrochloric acid and was then extracted with ether. Removal of the solvent under vacuum gave 300 mg (92%) of benzoic acid, mp 121° (mixture mp), after recrystallization from hot water.

3.4. Attempted thermolysis of tetraphenyl-*p*-dioxin in presence of dimethyl acetylene-dicarboxylate (DMAD)

A mixture of 1 (200 mg, 0.52 mmol) and dimethyl acetylene-dicarboxylate (148 mg, 1.04 mmol) was refluxed in *o*-dichlorobenzene (15 ml) for 38 hr. Both the solvent and unchanged acetylenic ester were removed under vacuum and the reaction mixture was extracted with petroleum ether. The petroleum ether-insoluble product was extracted with hot ethanol to give 40 mg (8%) of unchanged 1 as ethanol-insoluble material, which melted at 217-218° (mixture mp). The ethanol soluble portion, on work-up gave 372 mg (82%) of cis-dibenzoylstilbene, mp 216-217° (mixture mp).

The petroleum ether-extract was chromatographed over alumina. Elution of the column with petroleum ether gave 40 mg (16%) of benzil, mp 91° (mixture mp). Further elution of the column with a mixture (3 : 1) of petroleum ether and benzene gave an additional crop of cis-dibenzoylstilbene (38 mg, 8%), mp 216-217° (mixture mp), after recrystallization from a mixture (1 : 1) of petroleum ether and benzene.

3.5. Reaction of tetraphenyl-*p*-dioxin with perbenzoic acid

A mixture of 1 (200 mg, 0.52 mmol) and perbenzoic acid (6.8 ml, 0.52 mmol) in chloroform (15 ml) was kept at room temperature for 1 hr. The reaction mixture was washed several times with a 5% solution of sodium bicarbonate and then with water. Removal of the solvent from the chloroform solution gave a residue which was chromatographed over alumina. Elution with petroleum ether gave 104 mg (93%) of benzil, mp 91° (mixture mp). Further elution of the column with petroleum ether gave 90 mg (45%) of unchanged starting material, mp 217-218° (mixture mp).

In a repeat run, 70 mg (0.18 mmol) of 1 and excess of perbenzoic acid (5 ml, 0.38 mmol) in chloroform (10 ml) was kept at room temperature for 1 hr. Work-up of the mixture as in the earlier case gave 72 mg (95%) of benzil, mp 91° (mixture mp), after recrystallization from a mixture (10 : 1) of petroleum ether and benzene.

3.6. Photolysis of tetraphenyl-*p*-dioxin

3.6.1. *In t*-butanol: A solution of 1 (750 mg, 1.95 mmol) in *t*-butanol (210 ml) was irradiated for 15 min under nitrogen atmosphere. Removal of the solvent under vacuum gave a product which was chromatographed over alumina. Elution with petroleum ether gave 10 mg (4%) of tolan, mp 61-62° (mixture mp). Further elution with petroleum ether gave 250 mg (33%) of the unchanged starting material, mp 218° (mixture mp), after recrystallization from a mixture (1 : 1) of petroleum ether and chloroform. Continued elution of the column with petroleum ether gave 150 mg (56%) of benzil, mp 91° (mixture mp), which was recrystallized from a mixture (10 : 1) of petroleum ether and benzene.

3.6.2. *In benzene*: A solution of 1 (600 mg, 1.56 mmol) in dry benzene (700 ml) was photolysed under a dry nitrogen atmosphere for 2½ hr. The photolysis was repeated several times until 1.9 g (4.94 mmol) of the starting material was used up and the combined product mixture was chromatographed over alumina.

Elution of the column with petroleum ether gave 12 mg of a viscous material which

was rechromatographed over a small silica-gel column to give 4 mg (1%) of tolan, mp 61-62° (mixture mp).

Continued elution of the column with petroleum ether gave 1 g (53%) of the unchanged starting material, mp 217-218° (mixture mp), after recrystallization from a mixture (1 : 1) of petroleum ether and chloroform. Further elution with the same solvent gave 150 mg (30%) of benzil, mp 91° (mixture mp) which was recrystallized from a mixture (10 : 1) of petroleum ether and benzene.

Subsequent elution of the column with a mixture (20 : 1) of petroleum ether and benzene gave 15 mg (1.7%) of trans-dibenzoylstilbene, mp 239° (mixture mp).

3.6.3. *In presence of air:* A solution of 1 (100 mg, 0.26 mmol) was photolysed in dry benzene (210 ml) for 15 min. Removal of the solvent gave a product mixture which was chromatographed over alumina. Elution with petroleum ether gave 61 mg (70%) of benzil, mp 91° (mixture mp). Further elution of the column with petroleum ether gave 20 mg (20%) of the unchanged starting material, mp 217-218° (mixture mp).

3.6.4. *In presence of oxygen:* A solution of 1 (150 mg, 0.39 mmol) in dry benzene (210 ml) was photolysed for 30 min, under oxygen bubbling. Removal of the solvent gave a product which was chromatographed over alumina. Elution with petroleum ether gave 10 mg (6%) of benzil, mp 91° (mixture mp).

Further elution of the column gave 100 mg of a complex mixture from which no definite compound could be isolated.

In a repeat run, a sample of 1 (150 mg, 0.39 mmol) was photolysed for 10 min in dry benzene (210 ml) under oxygen bubbling. Work-up of the mixture as in the earlier case gave 90 mg (60%) of benzil, mp 91° (mixture mp), after recrystallization from a mixture (10 : 1) of petroleum ether and benzene. No other product could be isolated from this run.

3.7. Photolysis of a mixture of benzil and tolan

A mixture of benzil (105 mg, 0.5 mmol) and tolan (89 mg, 0.5 mmol) was taken in dry benzene (210 ml) and was photolysed for 2½ hr, under nitrogen atmosphere. Thin layer chromatography comparison of this photolysed mixture with the complex mixture obtained from the photolysis of tetraphenyl-*p*-dioxin under identical conditions, showed similarity in many respects.

3.8. Thermolysis of tetraphenyl-*p*-dithiin (31)

3.8.1. *Without any solvent:* Tetraphenyl-*p*-dithiin (100 mg, 0.24 mmol) was heated in a test tube around 195° for 30 minutes. The reaction product was recrystallized from a mixture (3 : 1) of petroleum ether and chloroform to give 90 mg (97%) of tetraphenylthiophene (33), mp 190-191° (mp 184-185°) (Kirmse and Horner 1958).

Anal. Calcd for C₂₈H₂₀S : C, 86.5; H, 5.15; Mol. Wt., 388. Found: C, 86.94; H, 4.9; Mol. wt., 388 (Mass spectrometry).

Ir spectrum (KBr) ν_{\max} : 3200 and 2425 cm⁻¹ ($\nu_{\text{C--H}}$), 1610, 1500 and 1485 cm⁻¹ ($\nu_{\text{C=C}}$).

Uv spectrum (CHCl_3) λ_{max} : 245 nm (ϵ , 25,100), 255 (20,000) and 315 (16,000).

3.8.2. *In o*-dichlorobenzene: A solution of 31 (100 mg, 0.24 mmol) in *o*-dichlorobenzene (10 ml) was refluxed for 4 hr. After removal of the solvent, the residual product was recrystallized from a mixture (3 : 1) of petroleum ether and chloroform to give 88 mg (95%) of 33, mp 190-191° (mixture mp).

3.9. Attempted reaction of tetraphenyl-*p*-dithiin with dimethyl acetylenedicarboxylate

A mixture of 31 (100 mg, 0.24 mmol) and dimethyl acetylenedicarboxylate (67 mg, 0.47 mmol) was refluxed in *o*-dichlorobenzene (10 ml) for 4 hr.

Removal of the solvent and recrystallization of the residue from a mixture (3 : 1) of petroleum ether and chloroform gave 88 mg (95%) of 33, mp 190-191° (mixture mp). No other product could be isolated from this run.

3.10. Photolysis of tetraphenyl-*p*-dithiin

A solution of 31 (250 mg, 0.6 mmol) in dioxan (225 ml) was photolysed for 8 hr under nitrogen atmosphere. Removal of the solvent gave a product which was chromatographed over silica-gel. Elution with petroleum ether gave 33 mg (15%) of 33, mp 190-191° (mixture mp).

Elution of the column with a mixture (4 : 1) of petroleum ether and benzene gave 15 mg (6%) of the unchanged starting material, mp 190-191° (mixture mp).

3.11. Photo-oxygenation of tetraphenyl-*p*-dithiin

A solution of 31 (195 mg, 0.46 mmol) in benzene (175 ml) was irradiated in presence of Rose-Bengal (25 mg in 15 ml of CH_3OH) and under oxygen bubbling for $\frac{3}{4}$ hr. Removal of the solvent under vacuum gave a product mixture which was chromatographed over silica-gel. Elution with petroleum ether gave 7 mg (1%) of biphenyl, mp 69-70° (mixture mp).

Further elution of the column with petroleum ether gave 55 mg (31%) of 33, mp 188-189° (mixture mp).

Subsequent elution of the silica-gel column with a mixture (9 : 1) of petroleum ether and benzene gave 30 mg (15%) of benzil, mp 91° (mixture mp).

Continued elution of the column with a mixture (4 : 1) of petroleum ether and benzene gave 15 mg (26%) of benzoic acid, mp 120-121° (mixture mp).

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