

Photo-oxygenations of bisphenylhydrazones, monophenylhydrazones, bishydrazones and monohydrazones of 1,2-diketones and related systems

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Abstract. Rose Bengal-sensitized photo-oxygenations of several bisphenylhydrazones of 1,2-diketones have been studied. The photo-oxygenation of benzil bisphenylhydrazone (9a) gave a mixture of products consisting of 2,4,5-triphenyl-1,2,3-triazole (10a, 27%), benzil (11a, 16%) benzoic acid (12, 33%) and biphenyl (13, 6%), whereas, biacetyl bisphenylhydrazone (9b), under analogous conditions gave a 2% yield of 4,5-dimethyl-2-phenyl-1,2,3-triazole (10b), a 30% yield of biacetyl monophenylhydrazone (16b) and a 1% yield of biphenyl. Cyclohexane-1,2-dione bisphenylhydrazone (9c) gave likewise, the corresponding triazole, 10c (19%), cyclohexane-1,2-dione monophenylhydrazone (16c, 18%) and a small amount of biphenyl (13, 2%). Photo-oxygenation of acenaphthenequinone bisphenylhydrazone (9d) gave a mixture of products consisting of acenaphthenequinone monophenylhydrazone (16d, 67%), 1,8-naphthoic anhydride (23, 22%) and biphenyl (13, 9%). The photo-oxygenations of both benzil monophenylhydrazone (16a) and acenaphthenequinone monophenylhydrazone (16d) gave rise to products, similar to those obtained from 9a and 9d, respectively.

Photo-oxygenation of 1,2-bisphenylazostilbene (18a) gave a 65% yield of the triazole 10a, whereas, 2,3-bisphenylazo-2-butene (18b) gave a 16% yield of the triazole 10b and a 5% yield of biphenyl. On the other hand, the photo-oxygenation of 1,2-bisphenylazocyclohexene (18c) gave a 77% yield of cyclohexane-1,2-dione (11c). The photo-oxygenation of 1,2-bisphenylazoacenaphthylene (18d) gave a 46% yield of acenaphthenequinone monophenylhydrazone (16d), a 51% yield of 1,8-naphthoic anhydride (23) and a 9% yield of biphenyl.

The photo-oxygenations of both benzil bishydrazone (25) and benzil monohydrazone (27) have been studied. In the case of the former, a mixture of products consisting of a 28% yield of benzil (11a) and a 17% yield of benzoic acid have been isolated, whereas in the case of the latter, a 55% yield of benzoic acid was isolated as the sole product.

Reasonable mechanisms have been suggested for the formation of the various products in the photo-oxygenations of the different substrates that we have examined.

Keywords. Photo-oxygenation; Rose Bengal; bisphenylhydrazones; monophenylhydrazones; singlet oxygen.

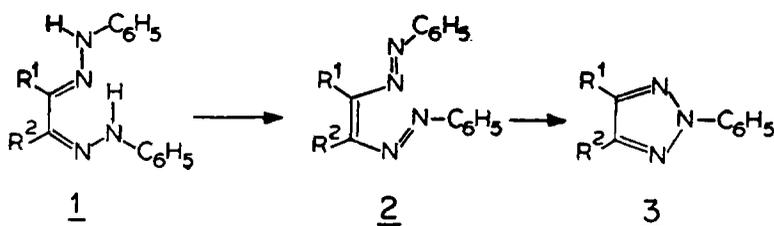
1. Introduction

Numerous studies concerning the oxidation of hydrazones and phenylhydrazones of various 1,2-diketones using different oxidising agents have been reported in

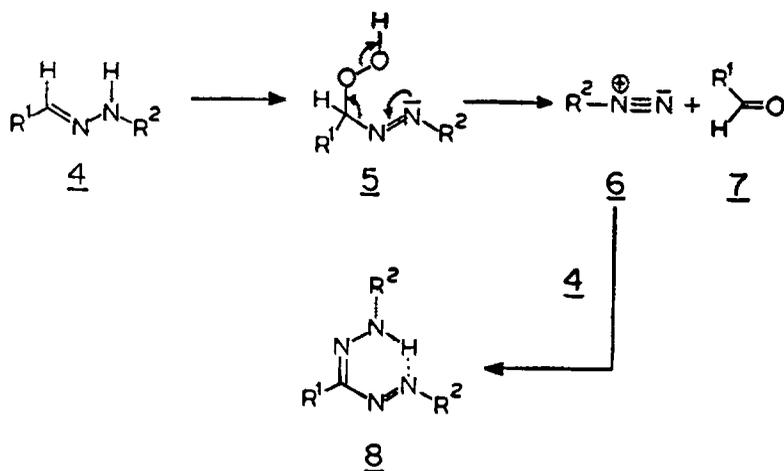
the literature. Thus, it has been shown that reagents like copper sulphate (El Khadem and El-Shafei 1958), manganese dioxide (Morrison *et al* 1961; Wittig and Heyn 1964; Hauptman *et al* 1965; Maier and Heep 1965; Bhatnagar and George 1967), nickel peroxide (Balachandran *et al* 1975; George and Balachandran 1975; Sukumaran *et al* 1974), potassium dichromate (von Pechman 1888; Stolle 1926), alkaline potassium ferricyanide (Curtin and Alexandrou 1966), mercuric oxide (Rinehart 1973) and a mixture of iodine and sodium ethoxide (Spasov and Robev 1953, 1955) bring about the oxidation of these substrates. Nickel peroxide oxidation of bisphenylhydrazones of 1,2-diketones (1), for example, has been reported to give bisphenylazoalkenes (2) as primary products (Balachandran *et al* 1975; George and Balachandran 1975; Sukumaran *et al* 1974). In addition, triazoles (3) have also been reported to be formed in these reactions (scheme 1) (Balachandran *et al* 1975; Angadiyavar *et al* 1971; Sukumaran *et al* 1972). The oxidation of several sugar osazones, likewise, has been shown to give the corresponding osotriazoles (El Khadem 1963, 1965).

The auto-oxidation of several aldehyde and ketone phenylhydrazones has been studied in detail by different groups of workers (Buckingham 1969; Pausacker 1950; Criegee and Lohaus 1951; Chaplin *et al* 1959; Bellamy and Guthrie 1965; Chernova *et al* 1967). It has been shown that phenylhydrazones, in general, undergo air-oxidation to produce the corresponding phenylazohydroperoxides

Scheme -1



Scheme -2



(Buckingham 1969; Pausacker 1950; Criegee and Lohaus 1951; Chaplin *et al* 1959; Bellamy and Guthrie 1965; Chermova *et al* 1967). These phenylazohydroperoxides, in turn, have been reported to undergo spontaneous, slow decomposition to give rise to the corresponding azoalkanes (Chermova *et al* 1967a, b).

Several aldehyde arylhydrazones have been shown to be photochromic materials (Chalkley 1929; Brown and Shaw 1961; Exelby and Grinter 1965), although different views have been advanced to explain this behaviour (Biltz 1899; Chattaway 1906). In a recent investigation, Lewis and Spencer (1975) have shown that the air-oxidation of aldehyde arylhydrazones (**4**) result in the formation of formazans (**8**) in varying yields. The formation of formazans in these reactions has been rationalised in terms of the initial formation of arylazohydroperoxides (**5**) which then cleave to give the diazonium cations **6**. Subsequent coupling of **6** with the starting aldehyde arylhydrazones will lead to the formazans **8**, as shown in scheme 2.

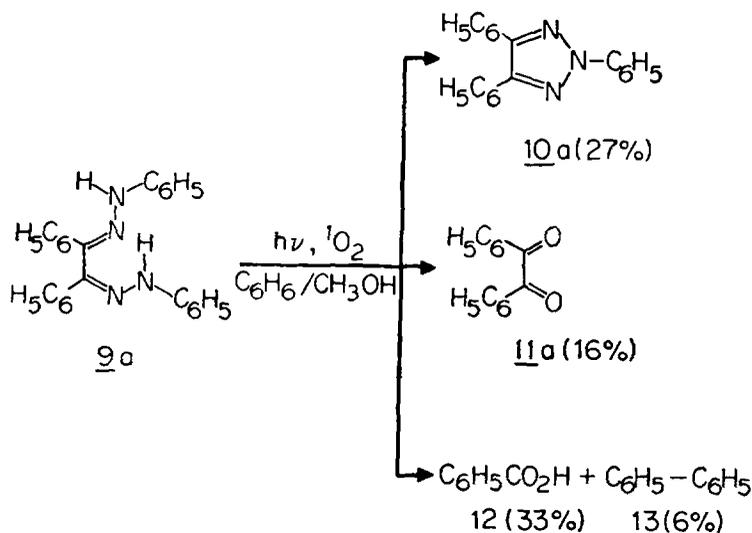
No detailed report concerning the air-oxidation of either bisphenylhydrazones or bishydrazones of 1,2-diketones has so far appeared in the literature. In view of our general interest in the photo-oxygenations of nitrogen-containing organic substrates, we deemed it worthwhile to examine the dye-sensitised photo-oxygenations of a few representative examples of mono- and bisphenylhydrazones and also the mono- and bishydrazones of certain 1,2-diketones.

2. Results and discussion

In the present studies, we have examined the photo-oxygenations of benzil bisphenylhydrazone (**9a**), benzil monophenylhydrazone (**16a**), biacetyl bisphenylhydrazone (**9b**), cyclohexane-1,2-dione bisphenylhydrazone (**9c**), acenaphthenequinone bisphenylhydrazone (**9d**), acenaphthenequinone monophenylhydrazone (**16d**), benzil bishydrazone (**25**) and benzil monohydrazone (**27**). In addition, the photo-oxygenations of a few bisphenylazoalkenes like 1,2-bisphenylazostilbene (**18a**), 2,3-bisphenylazo-2-butene (**18b**), 1,2-bisphenylazo-1-cyclohexene (**18c**) and 1,2-bisphenylazoacenaphthylene (**18d**), were examined with a view to understanding some of the mechanistic details of these oxidations.

Irradiation of a solution of benzil bisphenylhydrazone (**9a**) in a mixture of benzene and methanol and in presence of Rose Bengal as a sensitiser for 90 min resulted in the formation of a mixture of products consisting of 2,4,5-triphenyl-1,2,3-triazole (**10a**, 27%), benzil (**11a**, 16%), benzoic acid (**12**, 33%) and biphenyl (**13**, 6%) (scheme 3). Under analogous conditions, the photo-oxygenation of biacetyl bisphenylhydrazone (**9b**) gave a mixture of 4,5-dimethyl-2-phenyl-1,2,3-triazole (**10b**, 2%), biacetyl monophenylhydrazone (**16b**, 30%) and biphenyl (**13**, 1%). In addition, a 5% yield of the unchanged starting material was also recovered from this run. Similarly, the photo-oxygenation of cyclohexane-1,2-dione bisphenylhydrazone (**9c**) gave a mixture of the triazole (**10c**, 19%), cyclohexane-1,2-dione monophenylhydrazone (**16c**, 18%) and a small amount of biphenyl (**13**, 2%). The photo-oxygenation of acenaphthenequinone bisphenylhydrazone (**9d**), on the other hand, gave a mixture of products consisting of acenaphthenequinone monophenylhydrazone (**16d**, 67%), 1,8-naphthoic anhydride (**23**, 22%) and biphenyl (**13**, 9%).

Scheme -3

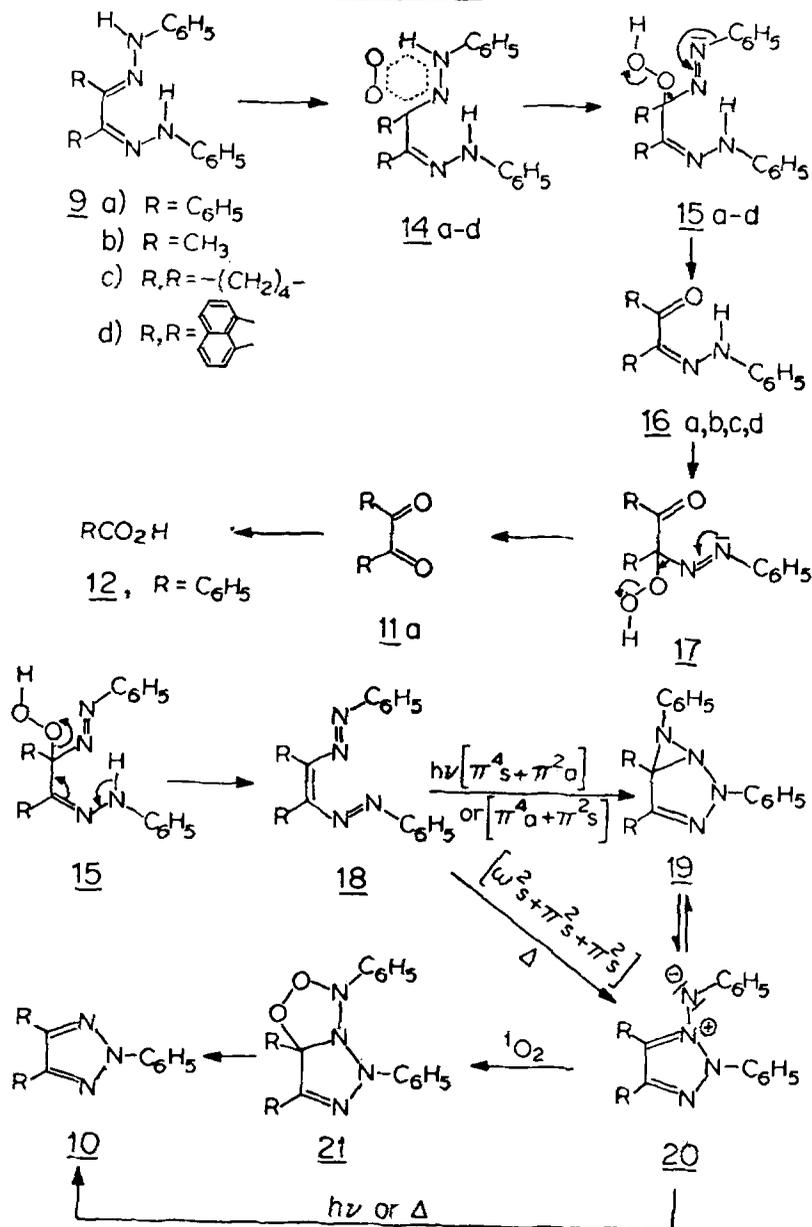


The formation of the various products in the photo-oxygenations of bisphenylhydrazones of 1,2-diketones can be rationalised in terms of the pathway shown in scheme 4. In this scheme, we assume that the initial step in the photo-oxygenation of benzil bisphenylhydrazone (**9a**), for example, involves an "ene-type" of reaction with singlet oxygen to give the hydroperoxide **15a**. One of the possible modes of transformations of **15a** is through an ionic-type of fragmentation leading to the formation of benzil monophenylhydrazone (**16a**), as shown in scheme 4. It is also quite likely that **15a** may undergo a homolytic type of fragmentation to give the monophenylhydrazone **16a** and other fragmentation products like nitrogen and phenyl radicals. In fact, the isolation of a small amount of biphenyl in this reaction may arise through the combination of phenyl radicals with benzene, in an expected manner.

The monophenylhydrazone **16a**, which is assumed to be an intermediate in the photo-oxygenation of **9a**, can itself undergo further reaction with singlet oxygen to give a second hydroperoxide **17a**, which can then cleave to give benzil (**11a**). The formation of benzoic acid (**12**) in the oxidation of **9a** can, however, be rationalised in terms of the photo-oxidation of benzil (**11a**), formed in this reaction. It may be mentioned in this connection that the photolysis of benzil in isopropyl alcohol is reported to give benzoic acid as one of the products (Bunburry and Chuang 1969). The formation of benzoic acid in this reaction has been rationalised in terms of the combination of oxygen with benzoyl radicals, produced from benzil. In the present studies, we have shown that benzil (**11a**) on dye-sensitised photo-oxygenation and under conditions analogous to the transformation of **9a**, is converted to benzoic acid in a 90% yield.

With a view to examining whether benzil monophenylhydrazone (**16a**) is involved as an intermediate in the photo-oxygenation of **9a**, we have studied the dye-sensitised photo-oxygenation of **16a**, in a separate experiment. Photo-

Scheme - 4



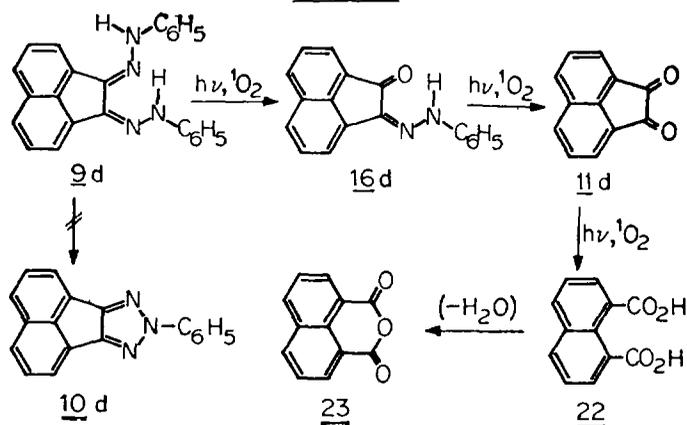
oxygenation of a solution of **16a** in a mixture of benzene and methanol and in presence of Rose Bengal, under conditions analogous to those employed in the case of **9a** gave, a mixture of products consisting of benzil (**11a**, 36%), benzoic acid (**12**, 51%) and biphenyl (**13**, 13%). The fact that products like benzil (**11a**), benzoic acid (**12**) and small amounts of biphenyl are formed in the oxidation of **16a** also would indirectly imply that **16a** could be a plausible intermediate in the photo-oxygenation of benzil bisphenylhydrazone (**9a**).

The involvement of monophenylhydrazones (16) in the photo-oxygenation of bisphenylhydrazones of 1,2-diketones (9) has been further confirmed by the actual isolation of biacetyl monophenylhydrazone (16b), cyclohexane-1,2-dione monophenylhydrazone (16c) and acenaphthenequinone monophenylhydrazone (16d) in the photo-oxygenations of biacetyl bisphenylhydrazone (9b), cyclohexane-1,2-dione bisphenylhydrazone (9d), respectively.

The photo-oxygenation of acenaphthenequinone bisphenylhydrazone (9d) is of interest in that the products formed in this reaction include a 67% yield of acenaphthenequinone monophenylhydrazone (16d) and a 22% yield of 1,8-naphthoic anhydride (23), besides a small yield of biphenyl (13, 9%). None of the triazole 10d could be isolated from this run (scheme 5). In a separate experiment, it has been shown that the photo-oxygenation of acenaphthenequinone monophenylhydrazone (16d) itself gives a mixture of products consisting of 1,8-naphthoic anhydride (23, 41%) and biphenyl (13, 17%). The formation of 1,8-naphthoic anhydride (23) in the photo-oxygenation of acenaphthenequinone bisphenylhydrazone (9d) and acenaphthenequinone monophenylhydrazone (16d) can be understood in terms of the photo-oxidation of acenaphthenequinone (11d) (Maruyama *et al* 1972), which is presumed to be an intermediate in these reactions. In support of this view it has been shown that the photo-oxygenation of 11d, under conditions analogous to the photo-oxygenations of 9d and 16d, gave a mixture of products consisting of 1,8-naphthoic acid (22, 54%) and 1,8-naphthoic anhydride (23, 35%).

The initial step in the photo-oxygenation reaction of a bisphenylhydrazone like benzil bisphenylhydrazone (9a) has been assumed to be an "ene-type" of reaction, involving singlet oxygen and proceeding through a concerted pathway to give the hydroperoxide 15a, as shown in scheme 4. It might be pointed out, however, that even the air-oxidation of 9a, involving triplet oxygen, may also lead to the same hydroperoxide intermediate (15a). In support of this view, it has been observed that the photolysis of a benzene solution of 9a for 90 min, under oxygen bubbling and in the absence of any sensitizer, gave a 44% yield of benzoic acid (12), as the only isolable product. In addition, a 28% yield of the unchanged starting material (9a) could also be recovered from this reaction. The formation of benzoic acid in this reaction could be rationalised in terms of the pathway shown

Scheme-5



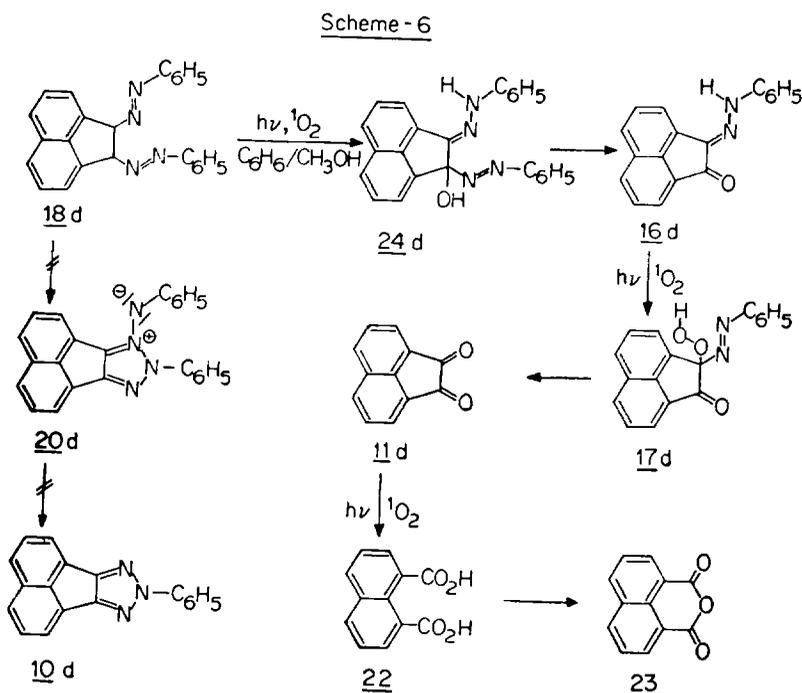
in scheme 4, excepting for the initial step involving the formation of the hydroperoxide 15a. The initial step in this case may involve the formation of the hydroperoxide 15a, through a multi-step process, involving triplet oxygen.

It has been suggested in scheme 4 that the initial product in the photo-oxygenation of 9a is the hydroperoxide 15a, which in turn fragments to give 16a and ultimately products like benzil (11a) and benzoic acid (12). An alternative mode of fragmentation of 15a would be through the loss of elements of hydrogen peroxide to give 1,2-bisphenylazostilbene (18a). The formation of 2,4,5-triphenyl-1,2,3-triazole (10a) in the photo-oxygenation of 9a can be rationalised in terms of the photo-transformations of 18a, as shown in scheme 4. It is assumed that the bisphenylazostilbene (18a), undergoes a photo Diels-Alder reaction of the $[\pi^4 s + \pi^2 a]$ or $[\pi^4 a + \pi^2 s]$ type to give the bicyclic intermediate 19, which then can lead to the zwitterionic intermediate 20. An alternative mode of transformation of 20 is through a symmetry allowed, thermal pericyclic reaction of the $[\omega^2 s + \pi^2 s + \pi^2 s]$ type, although it is unlikely that this mode may be operative under our reaction conditions (room temperature). Further transformation of the zwitterionic intermediate 20 to the triazole 10 may proceed through the direct loss of phenylnitrene, occurring under either thermal or photochemical conditions. An alternative mode of transformation of 20 is through the adduct 21, formed through the cycloaddition of 20 with singlet oxygen, as shown in scheme 4. It might be mentioned in this connection that the thermal and photochemical transformations of bisphenylazoalkenes like 18 are reported to give the corresponding triazoles (10) (Sukumaran *et al* 1974; Angadiyavar and George 1971; Wintner 1970). The photolysis of 1,2-bisphenylazostilbene (18a), in benzene, for example, is reported to give 61% of the triazole 10a (Sukumaran 1974).

With a view to finding out whether the bisphenylazostilbene 18a is involved as an intermediate in the photo-oxygenation of 9a and whether 18a undergoes transformation to the triazole 10a, under these conditions, we have examined the photo-oxygenation of 18a in a separate experiment. Photo-oxygenation of a solution of 18a in a mixture of benzene and methanol and in presence of Rose Bengal, under conditions analogous to the photo-oxygenation of 9a, gave a 65% yield of the triazole 10a. It is pertinent to observe that the yields of the triazole 10a, formed in the direct photolysis of 18a and also under the dye-sensitised photo-oxygenation conditions appear to be comparable. It is therefore difficult to surmise at present, on the basis of available data, whether the photo-oxygenation of 18a proceeds through the cycloaddition product 21a or not.

The photo-oxygenation of 2,3-bisphenylazo-2-butene (18b), likewise, gave the triazole 10b (10%). In addition, a small yield of biphenyl (13, 5%) could also be isolated from this run. The dye-sensitised photo-oxygenation of 1,2-bisphenylazoacenaphthylene (18d), on the other hand, gave a mixture of products consisting of acenaphthenequinone monophenylhydrazone (16, 46%), 1,8-naphthoic anhydride (23, 51%) and biphenyl (13, 9%). Under analogous conditions, the photo-oxygenation of 1,2-bisphenylazocyclohexene (18c) gave a 77% yield of cyclohexane-1,2-dione (11c). The formation of products like the monophenylhydrazone 16d and the anhydride, 23 in the photo-oxygenation of 1,2-bisphenylazoacenaphthylene (18d) can be rationalised in terms of the reaction sequences shown in scheme 6. In this scheme, we assume that the initial reaction involves

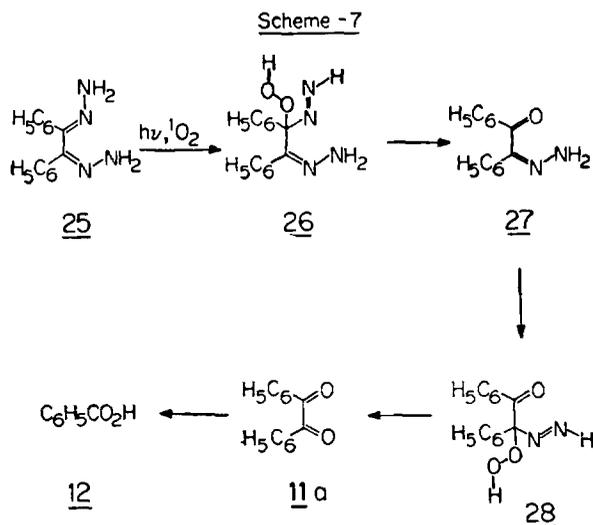
the photo-addition of the elements of water to **18d** to give an intermediate **24d**, which in turn will fragment to the monophenylhydrazone, **16d**. Further transformation of **16d** to give the anhydride **23**, will go through an expected pathway and involving intermediates like **17d**, **11d** and **22** as shown in scheme 6. It is



pertinent to observe that none of the triazole, **10d**, is formed in the photo-oxygenation of **18d**, which is suggestive of the fact that severe angle strains will be encountered in the formation of the zwitterion **20d** and the triazole, **10d**.

Similarly, the formation of cyclohexane-1,2-dione (**11c**) in the photo-oxygenation of **18c** can be rationalised in terms of the initial addition of water, followed by further transformations, analogous to those of **24d**, as shown in scheme 6.

In continuation of our studies, we have examined the photo-oxygenation of a representative bishydrazone of 1,2-diketone like benzil bishydrazone (**25**), to examine the nature of the products formed in this reaction. Photo-oxygenation of **25** in a mixture of methylene chloride and methanol and in presence of Rose Bengal for 30 min gave a mixture of products consisting of benzil (**11a**, 28%) and benzoic acid (**12**, 17%). The formation of products like benzil and benzoic acid in the photo-oxygenation of **25** can be rationalised in terms of the pathway shown in scheme 7. It has been assumed that benzil monohydrazone (**27**) is involved as an intermediate in the photo-oxygenation of **25**. In support of this assumption, we have observed that the photo-oxygenation of benzil monohydrazone (**27**) itself for 45 min gave a 55% yield of benzoic acid (**12**) as the only isolable product. The absence of any benzil (**11a**) in this reaction may be due to its further oxidation to give benzoic acid. The increased yield of benzoic acid in the photo-oxygenation of **27**, as compared to the case of **25**, is in support of this assumption.



3. Experimental

All melting points are uncorrected and were determined on a Mel-Temp, melting point apparatus. The infrared spectra were recorded on Perkin-Elmer, Model 137 and Model 521 Infrared Spectrometers. All photo-oxygenation experiments were carried out using a 450 W, medium pressure, mercury lamp in a quartz-jacketed immersion well.

3.1. Starting materials

Benzil bisphenylhydrazone (9a) (Spasov *et al* 1951, 1953), m.p. 236°, biacetyl bisphenylhydrazone (9b) (von Pechmann 1888), m.p. 245°, cyclohexane-1,2-dione bisphenylhydrazone (9c) (Godt and Quinn 1956), m.p. 150–151°, acenaphthenequinone bisphenylhydrazone (9d) (Craebe and Gfeller 1893), m.p. 219°, acenaphthenequinone (11d) (Allen and Van Allan 1955), m.p. 259–260°, benzil monophenylhydrazone (16a) (Bamberger and Grab 1901) m.p. 135°, acenaphthenequinone monophenylhydrazone (16d) (Craebe and Gfeller 1893), m.p. 177–178°, 1,2-bisphenylazostilbene (18a) (Balachandran *et al* 1975) m.p. 179°, 2,3-bisphenylazobut-2-ene (18b), (Balachandran *et al* 1975) m.p. 159° (d), 1,2-bisphenylazocyclohexene (18c) (Sukumaran *et al* 1974), m.p. 127–128°, 1,2-bisphenylazoacenaphthylene (18d) (Balachandran 1972), m.p. 180°, benzil bishydrazone (25) (Cope *et al* 1963), m.p. 150–151.5° and benzil monohydrazone (27) (Vogel 1973) m.p. 149–161° (d), were prepared by reported procedures. Dry benzene and absolute methanol were used for photo-oxygenation experiments. Petroleum ether used was the fraction, b.p. 60–80°.

3.2. Photo-oxygenation of benzil bisphenylhydrazone (9a)

3.2a. *In benzene.* A benzene solution of benzil bisphenylhydrazone (1.2 g, 3 mmol in 1200 ml) was mixed with a methanol solution of Rose Bengal (0.03 in 30 ml) and was saturated with oxygen gas. This mixture was irradiated for

90 min under a slow stream of oxygen bubbling. Removal of the solvent under reduced pressure gave a product mixture, which was chromatographed over silica-gel. Elution of the column with petroleum ether gave 0.05 g (6%) of biphenyl (**13**), m.p. 69–70° (mixture m.p.).

Further elution of the column with petroleum ether gave 0.25 g (27%) of 2,4,5-triphenyl-1,2,3-triazole (**10a**), m.p. 123–124° (mixture m.p.) (Biltz and Weiss 1902).

Further elution of the column with a mixture (1 : 1) of petroleum ether and benzene gave 0.1 g (16%) of benzil (**11a**), m.p. 95° (mixture m.p.).

Continued elution of the column with benzene afforded 0.25 g (33%) of benzoic acid, (**12**), m.p. 121–122° (mixture m.p.).

3.2b. *In methylene chloride.* A solution of **9a** (1.2 g, 3 mmol) in dry methylene chloride (1200 ml) was mixed with a methanolic solution of Rose Bengal (0.03 g in 30 ml) and was irradiated for 90 min, under oxygen bubbling. Removal of the solvent under vacuum resulted in a viscous residue, which was chromatographed over silica-gel. Elution of the column with petroleum ether gave 0.3 g (56%) of **10a**, m.p. 123–124° (mixture m.p.).

Further elution of the column with benzene gave 0.02 g (9%) of benzoic acid (**12**), m.p. 121–122° (mixture m.p.).

3.3. *Photo-oxygenation of benzil bisphenylhydrazone (9a) without any sensitiser*

A solution of benzil bisphenylhydrazone (0.14 g, 1 mmol) in benzene (450 ml) was irradiated for 90 min under oxygen bubbling. Removal of the solvent under vacuum gave a viscous material which was dissolved in 30 ml of chloroform. The chloroform solution was treated with a saturated solution of sodium bicarbonate (25 ml) and the aqueous layer on acidification gave 0.08 g (44%) of benzoic acid (**12**), m.p. 121–122° (mixture m.p.) after recrystallisation from a mixture (3 : 1) of petroleum ether and benzene.

The chloroform layer was dried over anhydrous sodium sulphate and removed the solvent under reduced pressure to give a viscous material, which was chromatographed over silica-gel. Elution with a mixture (1 : 1) of benzene and petroleum ether gave 0.11 g (28%) of the unchanged starting material, **9a**, m.p. 236° (mixture m.p.) after recrystallisation from ethanol.

3.4. *Photo-oxygenation of benzil monophenylhydrazone (16a)*

A solution of Rose Bengal in methanol (0.01 g in 10 ml) was added to a benzene solution of benzil monophenylhydrazone (**16a**, 0.6 g, 2 mmol in 200 ml) and the mixture was saturated with oxygen gas. This mixture was then irradiated for 45 min, under a slow stream of oxygen bubbling. Removal of the solvent under vacuum resulted in a product mixture, which was chromatographed over silica-gel. Elution of the column with petroleum ether gave 0.05 g (13%) of biphenyl, m.p. 69–70° (mixture m.p.).

Further elution of the column with a mixture (3 : 1) of petroleum ether and benzene gave 0.15 g (36%) of benzil (**11a**), m.p. 95° (mixture m.p.), after recrystallisation from ethanol.

Subsequent elution of the column with benzene afforded 0.25 g (51%) of benzoic acid (**12**), m.p. 120–121° (mixture m.p.), after recrystallisation from petroleum ether.

3.5. Photo-oxygenation of benzil (**11a**)

A solution of benzil (0.21 g, 1 mmol) in dry benzene (150 ml) was mixed with a methanol solution of Rose Bengal (0.01 g in 10 ml) and the mixture was irradiated for 90 min, under oxygen bubbling. Removal of the solvent under vacuum gave a viscous material, which was dissolved in 30 ml of methylene chloride and afterwards extracted with a saturated solution of sodium bicarbonate.

Work-up of the aqueous layer by acidification with dilute hydrochloric acid and subsequent extraction with chloroform gave 0.21 g (90%) of benzoic acid (**12**), m.p. 121–122° (mixture m.p.), after recrystallisation from a mixture (3 : 7) of benzene and petroleum ether.

Work-up of the organic layer after removal of benzoic acid by treatment with sodium bicarbonate solution did not give any isolable product.

3.6. Photo-oxygenation of biacetyl bisphenylhydrazone (**9b**)

A solution of biacetyl bisphenylhydrazone (1 g, 4 mmol) in dry benzene (360 ml) was mixed with a methanol solution of Rose Bengal (0.02 g in 20 ml) and the mixture was irradiated for 30 min, under oxygen bubbling. Removal of the solvent under vacuum gave a product mixture, which was chromatographed over silica-gel. Elution with petroleum ether gave 0.15 g (13%) of biphenyl, m.p. 69–70° (mixture m.p.).

Further elution of the column with a mixture (1 : 4) of benzene and petroleum ether gave 15 mg (2%) of 4,5-dimethyl-2-phenyl-1,2,3-triazole (**10b**), identified through a comparison of its infrared spectrum with that of an authentic sample (von Pechmann 1888, 1897).

Subsequent elution of the column with a mixture (3 : 1) of petroleum ether and benzene gave 0.05 g (5%) of the unchanged starting material, **9b**, m.p. 254° (mixture m.p.).

Further elution of the column with a mixture (3 : 1) of petroleum ether and benzene gave 0.15 g (30%) of a product, identified as biacetyl monophenylhydrazone (**16b**), m.p. 134–135° (mixture m.p.) (von Pechmann 1888).

3.7. Photo-oxygenation of cyclohexane-1,2-dione bisphenylhydrazone

A methanol solution of Rose Bengal (0.02 g in 20 ml) was added to a benzene solution of cyclohexane-1,2-dionebisphenylhydrazone (1.17 g, 4 mmol in 360 ml) and the mixture was irradiated for 15 min, under oxygen bubbling. Removal of the solvent under vacuum gave a product mixture which was chromatographed over silica-gel. Elution with petroleum ether gave 20 mg (2%) of biphenyl (**13**), m.p. 69–70° (mixture m.p.).

Further elution of the column with a mixture (3 : 1) of petroleum ether and benzene gave 0.15 g (19%) of 2-phenyl-4,5-tetramethylene-1,2,3-triazole (**10c**), m.p. 90° (mixture m.p.) after recrystallisation from petroleum ether.

Subsequent elution of the column with a mixture (1 : 1) of petroleum ether and benzene gave 0.15 g (18%) of cyclohexane-1,2-dione monophenylhydrazone

(16c), m.p. 184–185° (mixture m.p.) (Shredov *et al* 1964, 1965) after recrystallisation from petroleum ether.

3.8. Photo-oxygenation of acenaphthenequinone bisphenylhydrazone (9d)

A solution of acenaphthenequinone bisphenylhydrazone (1.086 g, 4 mmol) in benzene (600 ml), containing a small amount of Rose Bengal (0.03 g in 30 ml of methanol) was irradiated for 30 min, under oxygen bubbling. Removal of the solvent under vacuum gave a product mixture, which was chromatographed over a silica-gel column. Elution with petroleum ether gave 0.08 g (9%) of biphenyl, m.p. 69–70° (mixture m.p.).

Further elution of the column with benzene gave 0.5 g (67%) of an orange-red crystalline solid, characterised as acenaphthenequinone monophenylhydrazone (16d), m.p. 178° (mixture m.p.) (Allen and van Allan 1955) after recrystallisation from benzene.

Subsequent elution of the column with benzene gave 0.12 g (22%) of a crystalline white compound, m.p. 271° (d) and identified as 1,8-naphthalic anhydride (23). There was no depression in the melting point of 23, when mixed with an authentic sample of 23.

3.9. Photo-oxygenation of acenaphthenequinone monophenylhydrazone (16d)

A solution of acenaphthenequinone monophenylhydrazone (0.5 g, 2 mmol) in benzene (200 ml) containing a small amount of Rose Bengal (0.01 g in 10 ml of methanol) was irradiated, under oxygen bubbling for 45 min. Work-up of the mixture as in the earlier cases, by chromatographing over silica-gel and elution with petroleum ether, gave 0.05 g (17%) of biphenyl (13), m.p. 69–70° (mixture m.p.).

Further elution of the column with benzene gave 0.15 g (41%) of 1,8-naphthalic anhydride (23), m.p. 271° (mixture m.p.).

3.10. Photo-oxygenation of acenaphthenequinone (11d)

A solution of acenaphthenequinone (0.364 g, 2 mmol) in benzene (400 ml) was mixed with a methanol solution of Rose Bengal (0.02 g in 20 ml) and irradiated under oxygen bubbling for 30 min. Removal of the solvent under vacuum gave a product, which was fractionally crystallised from ethanol to give 0.2 g (54%) of 1,8-naphthalic acid (22), m.p. 269–270° (mixture m.p.).

Removal of the solvent from the mother liquor gave a product which was chromatographed over silica-gel. Elution with petroleum ether gave 10 mg (3%) of biphenyl, m.p. 69–70° (mixture m.p.).

Subsequent elution of the column with benzene gave 0.14 g (35%) of 1,8-naphthalic anhydride, m.p. 269–271° (mixture m.p.).

3.11. Photo-oxygenation of 1,2-bisphenylazostilbene (18a)

A solution of 1,2-bisphenylazostilbene (18a) (0.4 g, 1 mmol) in benzene (200 ml) was mixed with a methanol solution of Rose Bengal (0.015 g in 10 ml) and the mixture was irradiated under oxygen bubbling for 1 hr. Removal of the solvent under reduced pressure gave a product mixture which was chromatographed

over silica-gel. Elution of the column with petroleum ether gave 0.2 g (65%) of 10a, m.p. 123–124° (mixture m.p.), after recrystallisation from petroleum ether.

3.12. Photo-oxygenation of 2,3-bisphenylazo-2-butene (18b)

A small amount of Rose Bengal (0.015 g in 10 ml of methanol) was added to a benzene solution of 2,3-bisphenylazo-2-butene (18b) and the mixture was irradiated, under oxygen bubbling for 8 hr. Work-up of the mixture by removal of the solvent under vacuum and chromatographing the residue over silica-gel gave 0.03 g (5%) of biphenyl (13), m.p. 69–70° (mixture m.p.).

Further elution of the column with a mixture (9 : 1) of petroleum ether and benzene gave 0.05 g (16%) of 4,5-dimethyl-2-phenyl-1,2,3,- triazole (10b), b.p. 160°/60 mm. The identity of 10b was established by comparison of its infrared spectrum with that of an authentic sample (von Pechmann 1888, 1897).

3.13. Photo-oxygenation of 1,2-bisphenylazocyclohexene (18c)

A benzene solution of 1,2-bisphenylazocyclohexene (1 g, 3.4 mmol in 350 ml) containing a small amount of Rose Bengal (0.02 g in 20 ml of methanol) was irradiated under oxygen bubbling for 90 min. Work-up of the mixture as in the earlier cases by chromatographing over silica-gel and elution with benzene gave 0.3 g (77%) of cyclohexane-1,2-dione (11c) identified through a comparison of its infrared spectrum with that of an authentic sample.

3.14. Photo-oxygenation of 1,2-bisphenylazoacenaphthylene (18d)

A solution of 1,2-bisphenylazoacenaphthylene (0.62 g, 2 mmol) in benzene, (200 ml) was mixed with a methanol solution of Rose Bengal (0.01 g in 10 ml) and the mixture was irradiated, under oxygen bubbling for 6 hr. Removal of the solvent under vacuum gave a product mixture, which was chromatographed over a silica-gel column. Elution with petroleum ether gave 0.05 g (9%) of biphenyl, m.p. 69–70° (mixture m.p.).

Further elution of the column with a mixture (3 : 1) of petroleum ether and benzene gave 0.25 g (46%) of acenaphthenequinone monophenylhydrazone (16d), m.p. 178° (mixture m.p.), after recrystallisation from benzene.

Subsequent elution of the column with a mixture (1 : 1) of benzene and petroleum ether gave 0.2 g (51%) of 1,8-naphthalic anhydride (23), m.p. 270–271° (mixture m.p.).

3.15. Photo-oxygenation of benzil bishydrazone (25)

A solution of benzil bishydrazone (0.952 g, 4 mmol) in methylene chloride (400 ml) was mixed with a solution of Rose Bengal (0.02 g) in methanol (20 ml). Oxygen was passed through the solution for 10 min and then it was irradiated for 30 min, under a slow stream of oxygen bubbling. Removal of the solvent under vacuum gave a product mixture, which was chromatographed over silica-gel. Elution of the column with a mixture (3 : 1) of petroleum ether and benzene gave 0.2 g (28%) of benzil (11a), m.p. 95° (mixture m.p.), after recrystallisation from ethanol.

Further elution of the column with benzene gave 0.07 g (17%) of benzoic acid (12), m.p. 121–122° (mixture m.p.), after recrystallising it from petroleum ether.

3.16. Photo-oxygenation of benzil monohydrazone (27)

A solution containing a mixture of benzil monohydrazone (1.32 g, 6 mmol) in methylene chloride (600 ml) and Rose Bengal (0.03 g) in methanol (30 ml) was irradiated under oxygen bubbling for 45 min. Removal of the solvent under vacuum and work-up of the product mixture by chromatographing over silica gel and elution with benzene gave 0.3 g (55%) of benzoic acid (12), m.p. 121–122° (mixture m.p.).

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