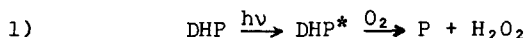


PHOTOCHEMICAL RING OPENING AND TRUE PHOTO-OXIDATION IN THE 4A,4B-DIHYDROPHENANTHRENES

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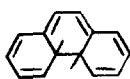
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In an earlier paper<sup>1</sup> we drew attention to the possible existence of true photo-oxidation in the dihydrophenanthrenes (DHP's), equation 1, which may take place in addition to the spontaneous oxidation of DHP's with molecular oxygen, equation 2.

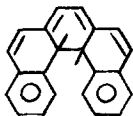


The high efficiency of the latter process in DHP proper, (I), and its derivatives studied at the time made it rather difficult to prove conclusively the existence of process 1.

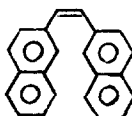
In a recent investigation<sup>2</sup> of the dibenzo derivative of (I), compound (II), formed during u.v. irradiation of *cis* di-(2-naphthyl)ethylene, (III), we showed that this particular DHP exhibits several unusual properties, including a very low quantum yield for (II)  $\xrightarrow{h\nu}$  (III) (photochemical ring opening), a very slow spontaneous oxidation, equation 2, and an appreciable quantum yield of fluorescence even at room temperature.



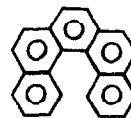
I



II



III



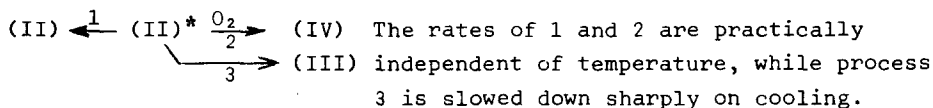
IV

These properties make it possible to investigate the possible photo-oxidation of (II) to 3,4,5,6-dibenzophenanthrene, (IV), without the ambiguities mentioned above.

(III) was converted partly into (II) by irradiation of solutions in methylcyclohexane with 366 nm light at 10°. The solutions were then flushed with Argon containing less than 5 ppm of oxygen, and irradiated at various temperatures with light at 436 nm, causing the photo-reversion (II)  $\xrightarrow{h\nu}$  (III). The quantum yields  $\phi$  of this process were as follows:

Temperature	+15°	0°	-10°	-20°	-30°	-120°
$\phi(\text{DHP} \rightarrow \text{cis})$	0.01	0.005	0.002	0.0012	0.0006	0.00016

When a similar irradiation was carried out with air-flushed solutions, the quantum yield of DHP erasure remained constant at about 0.005 down to -120°. Moreover, spectral analysis of the solutions resulting from this erasure showed them to be identical with similar solutions resulting from oxidation with atomic iodine, i.e. containing (IV). Only at 0° and higher temperatures little or no (IV) is formed during erasure in aerated solutions, because the yield of (II)  $\xrightarrow{h\nu}$  (III) is high enough for this process to compete with photo-oxidation, (II)  $\xrightarrow[\text{O}_2]{h\nu}$  (IV). To summarize, excited DHP can revert to its ground state, or undergo ring opening to give (III), or react with oxygen to give (IV):



Initial experiments had shown that process 2 takes place even with traces of oxygen. Its rate was therefore measured in solutions kept at -30° [where  $\phi(\text{DHP} \rightarrow \text{cis})$  is already sufficiently

low) and flushed with nitrogen containing varying amounts of oxygen. The results, expressed as relative half-lives of DHP erasure with light at 436 nm, were as follows:

Oxygen content (%):	20	2	0.4	0.03	0.0005
Erasure half-life(min.):	1.7	3	4	9	45

Here the value at 0.0005% oxygen represents reaction 3. The photo-oxidation 2 thus takes place already at very low partial oxygen pressures, although the overall quantum yield for  $(II) \xrightarrow{h\nu} (IV)$  is only about 0.005. Thus even the erasure at 0.0005% oxygen may include some oxidation.

This could be due to formation of an oxygen-DHP complex at rather low concentrations of oxygen, which should show up in fluorescence quenching experiments. However, no quenching of DHP fluorescence was observed in solutions flushed with nitrogen containing 2% oxygen, and even under pure oxygen the emission of DHP at  $-30^\circ$  retained 55% of its value under nitrogen. These results seem to exclude static quenching by oxygen.

Earlier experiments had shown that DHP (I) and many of its derivatives are oxidized spontaneously with molecular iodine, just as with oxygen. Both of these oxidations are very slow with (II), and it was of interest to examine the photo-oxidation of (II) with molecular iodine:  $(II) \xrightarrow{h\nu} (II)^* \xrightarrow{I_2} (IV) + HI$ . Small volumes of a concentrated solution of iodine in methylcyclohexane were added to  $1.5 \times 10^{-5}$  M Argon-flushed solutions of (II) in the same solvent at minus  $-30^\circ$ , to give iodine concentrations of about  $2 \times 10^{-4}$  M. Irradiation at 405 nm resulted in rapid oxidation to (IV), at about a hundredfold rate, compared with air-saturated solutions in the absence of iodine. Light at 405 nm is absorbed predominantly by (II)

and not by iodine, so that one may conclude that the reaction  $(II)^* + I_2 \longrightarrow (IV) + 2HI$  occurs, and that its rate exceeds that of the reaction  $(II)^* + O_2 \longrightarrow (IV) + H_2O_2$  by several orders of magnitude.

As already reported, irradiation of a similar mixture of (II) and iodine at 546 + 578 nm, where only iodine absorbs, causes oxidation to (IV) via the reaction  $(II) + 2I \longrightarrow (IV) + 2HI$ .

The common method employed for photocyclodehydrogenation reactions to obtain phenanthrene derivatives involves u.v. irradiation in the presence of air and iodine.<sup>4</sup> In view of the present results it appears plausible that under these conditions the DHP's produced primarily are dehydrogenated by a combination of processes, including spontaneous oxidation with molecular oxygen and iodine, oxidation with atomic iodine, and oxidation involving electronically-excited DHP. It is unlikely that singlet oxygen is also involved, in view of the absence of reports on similar dehydrogenation reactions.

#### References

- <sup>1</sup>K.A. Muszkat and E. Fischer, *J. Chem. Soc. (B)* (1967) 662.
- <sup>2</sup>T. Knittel, G. Fischer and E. Fischer, *Chem. Comm.* (1972) 84.
- <sup>3</sup>H. Stegemeyer and E. Fischer, unpublished results.
- <sup>4</sup>C.S. Wood and F.B. Mallory, *J. Org. Chem.* (1964) 3373.