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PHOTOCHEMICAL REACTIONS OF BIANTHRONE AND RELATED SUBSTANCES

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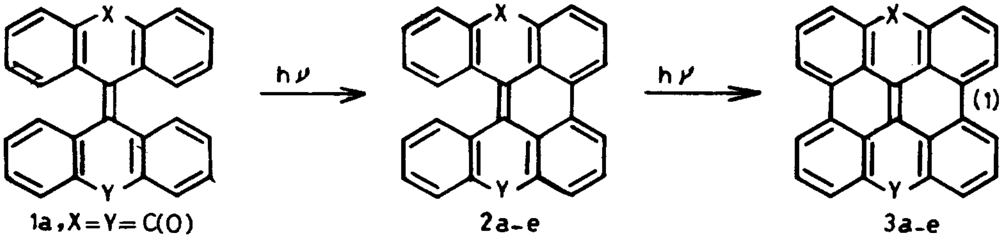
ABSTRACT : Photocleavage reactions of a wide range of ethylene compounds were investigated. Photosensitized oxygenation resulted in formation of their corresponding ketones. On the other hand, photoreaction of these substrates with elemental sulfur yielded the corresponding thioketones. Furthermore, photobehaviour of some ethylene episulfides also was studied. It could be concluded that UV-irradiation provides a rapid and effective desactivation pathway for this class of compounds.

INTRODUCTION

In recent years, there has been an increased interest in the photochemistry of heterocyclic compounds in general[1-4] and in the environmental photochemistry of heterocyclic pesticides in particular.[5-8] In the course of investigations of the photodegradation of pesticides,[9-13] we have turned our attention to photoreactions of some heterocyclic compounds.[14,15] In the present work, we have decided to study the photochemical behaviour and cleavage of bianthrone and analogous compounds as well as their episulfides.

I- PHOTOOXYGENATION OF (1a-c) and (6a,b).

As early as 1912, [16] it was claimed that bianthrone (**1a**) undergoes photochemical cyclization (**1**⟶**2** ⟶**3**) upon UV-irradiation or insolation (eq. 1).



1a, X=Y=C(O)
1b; X=Y=O
1c, X=Y=S
1d, X=Y=NMe
1e, X=O; Y=S

2a-e

3a-e

2 and 3, X and Y as in 1

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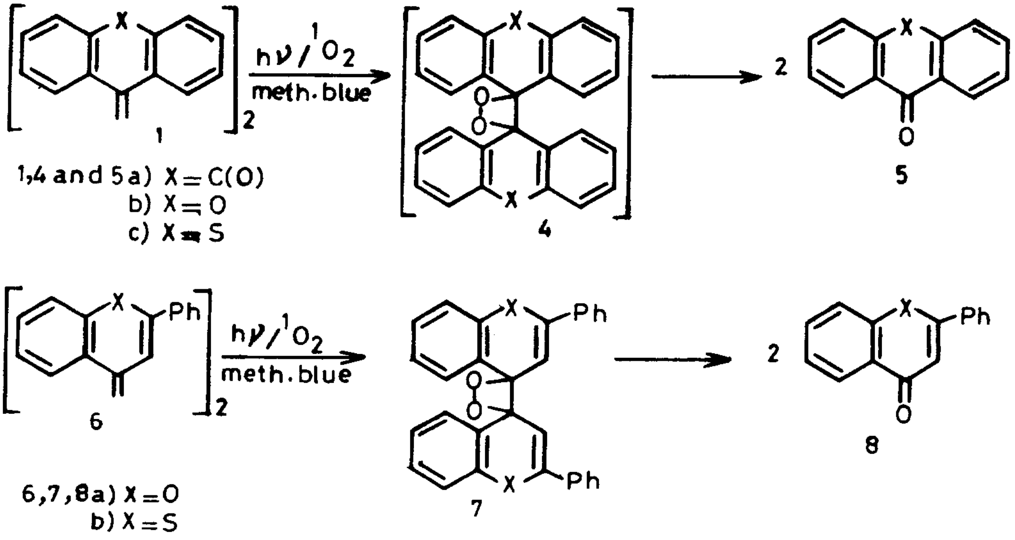
Later on, equation 1 was established[17-19] in the case of irradiation of bianthrone (**1a**) or its related compounds (**1b-e**) in absence of oxygen. In all cases, no cleavage for the ethylene linkage was observed.

However, among the reactions of singlet oxygen ($^1O_2$) with organic substrates, addition to carbon-carbon double bonds provides methods for the oxygenation of many types of compounds that have had numerous applications in synthesis.[20,21] The reactions of the electrophilic $^1O_2$ take place most readily with electron-rich systems such as enamines,[22,23] enol ethers,[24] and highly substituted olefins,[20b,25] and the oxygenation of these substrates have been extensively investigated. It seems, therefore of interest to examine this sensitized photooxygenation on perylenes (**1a-c** and **6a,b**) to compare the mode of the reaction and the products formed when singlet oxygen is present in the media.

The ethylenes : bianthrone (**1a**), bixanthylene (**1b**), dithioxanthylene (**1c**), diflavylene (**6a**) and dithioflavylene (**6b**) were prepared by treating the corresponding ketones with thionyl chloride followed by the action of copper bronze.[26] A solution of (**1a-c**) or (**6a,b**) in chloroform containing Methylene Blue (or Rose Bengal) as a sensitizer was irradiated with a high pressure mercury lamp for *ca* 15 h, during which time a steady stream of oxygen was bubbled through the solution. The photolysate was evaporated to give the corresponding ketones (**5a-c**) or (**8a,b**), respectively, as the only reaction products in ~80-85%. The identity of products was established by comparison of the m.ps., mass spectra (MS) and IR spectra with those of authentic specimens (*cf.* Table 1).



SCHEME 1

We discuss for the degradation of **1a-c** → **5a-c** as well as **6a,b** → **8a,b** the mechanism shown in scheme 1. Following this, **1** adds $^1O_2$ in a [2 + 2] manner to give an elusive 1,2-dioxetane species (**4**) or (**7**) which cleaves metathetically, i.e. undergoing a displacement reaction, to afford **5** or **8**.

Table 1

Ketones 5 and 8 prepared

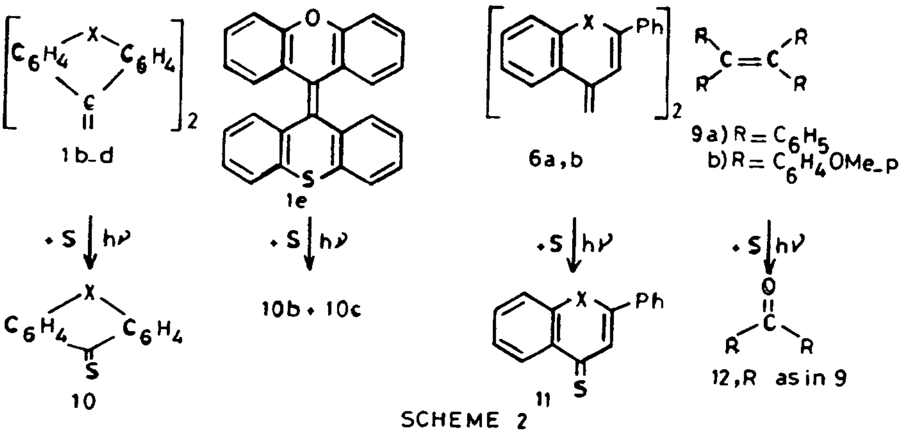
Educt	Irradiation Time (h)	Photooxygenation product	Yield[a] (%)	m.p (°C)
1a	18	**5a**	83	282 - 84
1b	15	**5b**	87	173 - 75
1c	13	**5c**	92	208 - 10
6a	20	**8a**	73	95 - 97
6b	15	**8b**	76	129 - 30

a) Yields are based on consumed starting materials.

II. PHOTOREACTION OF THE ETHYLENE LINKAGE WITH ELEMENTAL SULFUR.

It has been reported that the ethylene linkage in dixanthylene (**1b**), dithiozanthylene (**1c**), NN'-dimethyldiacridine (**1d**), diflavylene (**6a**), and dithioflavylene (**6b**) can be split by the action of sulfur[24,27] under drastic conditions (280°C) or by thionyl chloride[28] followed by water to give the corresponding thioketones or ketones, respectively. It also was pointed out[26,28] that tetraphenylethylene (**9a**) and tetra-p-anisyl-ethylene (**9b**) are unaffected by both sulfur and thionyl chloride.

In the present investigation, we have carried out the above reaction photolytically to develop an easier, efficient and general method for the fission reactions of ethylene compounds, affording the products directly, in a purer state and higher yields. Thus, the



SCHEME 2

substrates (**1a-e**) and (**6a,b**) were dissolved or suspended in toluene, and sulfur (>2 equiv.), was added. The reaction mixture was irradiated at the reflux temperature while an inert gas (nitrogen or CO_2) was circulated. Workup of the photolysate results in the formation of the corresponding thioketones as the sole reaction products in good yields, and after a considerably short time (see Table 2).

However, without circulation of nitrogen, photolysis of **1b** and **1c** (as examples) also gave products **10b** and **10c**, respectively, but in lower yields (~68%), accompanied by their oxygen analogues **5b** and **5c** respectively.

Table 2

Reaction Conditions and the Products of the Photoreaction of Ethylene Compounds with Sulfur.

Educts	Irradiation Time (h)[a]	Ethylene cleavage products	Yield (%)[b]	m.p (°C)
(**1a** + S)[c]	6	**10a**, x = C(O)	78	202 - 204
(**1b** + S)[c]	4	**10b**, x = O	85	156 - 58
(**1c** + S)[c]	4	**10c**, x = S	85	168 - 70
(**1d** + S)[c]	6	**10d**, x = NMe	82	261 - 63
(**1e** + S)[c]	4	**10b** + **10c**	38, 44	156, 168
(**6a** + S)[c]	8	**11a**, x = O	63	85 - 86
(**6b** + S)[c]	8	**11b**, x = S	68	110 - 112
(**9a** + S)[c]	12	**12a**, x = O	48	47 - 49
(**9b** + S)[c]	12	**12b**, x = O	46	TLC
(**1b** + S)[d]	4	**5b** + **10b**	14, 66	173, 158
(**1c** + S)[d]	4	**5c** + **10c**	9, 72	212, 168

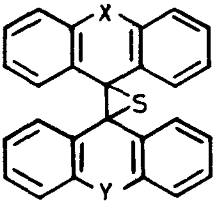
a) Photoreaction was carried out in refluxed toluene.
b) Yields are based on the starting material used.
c) Photoreaction was carried out with inert gas atmosphere.
d) Photoreaction was carried out without inert gas atmosphere

Remarkably, when tetraphenylethylene (**9a**) or tetra-p-anisyl-ethylene (**9b**) was irradiated with sulfur under the same reaction conditions, again the corresponding ketones, and not the thioketones (because of the high sensitivity of thiobenzophenones to moisture), were obtained in *ca.* 48% yield. It is noteworthy that photosensitized oxygenation of **9a** and other aryl-substituted ethylenes with the formation of the corresponding ketones was previously reported.[29]

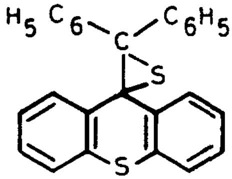
On the other hand, when mixed ethylenes e.g. **1e** was subjected to the above reaction yielded a mixture of **10b** and **10c** in almost equal yields.

III PHOTODEGRADATION OF ETHYLENE SULFIDES

Finally, we became intrigued with the extension of these photostudies to the case of the episulfide of this class of compounds. Thus, the photolysis of a refluxed 1% air-saturated toluene solution of the thiiranes (**13a-c**), **14** and **15**, resulted in the disappearance of the educts (TLC) after *ca* 15 h. The photolysate was separated on silica gel, and a mixture of the corresponding ketones and thioketones were obtained (Scheme 3), Table 3 lists the ethylene sulfides photolyzed, reaction conditions, the products and their percentage yields.



13a) X=Y=O
b) X=Y=S
c) X=O,Y=S



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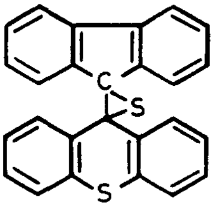

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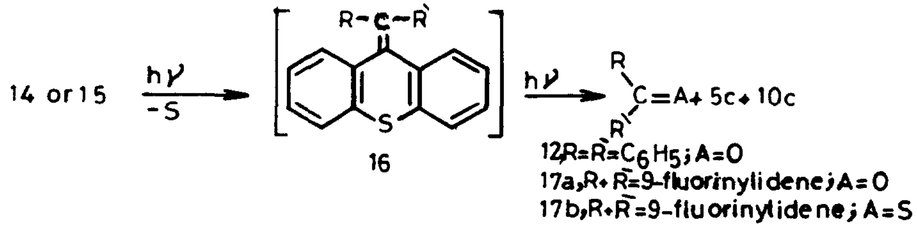

SCHEME 3

A plausible mechanism of this reaction shown in Scheme 3. In this case, initial photodesulfuration (e.g. by α-cleavage) may occur to give the corresponding ethylenes followed by photocleavage with the liberated sulfur into the thioketones and the carbenes which could be

Table 3

Reaction Conditions and the Products of the Photodegradation of Thiiranes

Educt	Irradiation Time (h)[a]	Product	Yield[a] (%)
13a	18	**5b, 10b**	33, 45
13b	18	**5c, 10c**	38, 42
13c	15	**5b, 5c, 10b, 10c**	13, 18, 10, 20
14	12	**5c, 10c, 12**	12, 17, 28
15	12	**5c, 10c, 17a**[c], **17b**[d]	10, 17, 18, 22

a) The photolysis was carried out in a saturated air toluene solution at the reflux temperature.
b) Yields are approximated, based on consumed starting material.
c) m.p. of fluorenone (17a) = 81 °C, d) m.p. of thiofluorenone (17b) = 75 °C

oxidized to their ketones, e.g. 3,3'-diphenyl spiro-(thiaxanthene-10,2'-thiiran) (**15**) yielded the intermediate 10-(diphenylmethylene)-thiaxanthene (**16**) on UV-irradiation. **16** cleaves with sulfur to give benzophenone (**12**), thioxanthone (**5c**), and thioxanthione (**10c**), since the sulfur presented in the medium is in 1 : 1 molar ratio.

In conclusion, the singlet oxygen photolysis and the photoreaction of heterocyclic ethylene substrates provide an easy synthetic route to the cleavage of both ethylene linkage and ethylene sulfides. Moreover, it is evident from the above observations that, in contrast to the earlier reports, the ethylene bond in tetraphenylethylene can be cleaved by sulfur, if the reaction is carried out photolytically.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were run on a Perkin-Elmer Infracord Spectrometer Model 197 (Grating). The mass spectra were run at (70 eV) on Kratos MS-50 equipment provided with a data system. Authentic specimens were either available or prepared according to known procedures.

Photolytic reactions were carried out in Pyrex vessel (λ 313 nm) equipped with a high pressure Hg-lamp (Philips HPK 125).

Singlet-Oxygen Photolysis of the Ethylenes (1a-c) and (6a,b), ***General Procedure.*** A solution of the ethylene (**1a-c**) or (**6a,b**) (2.5g) in chloroform (250 ml) containing methylene blue (30 mg) is irradiated while oxygen is circulated through the solution at a moderate rate. The reaction is monitored by TLC. After disappearance of the starting material (irradiation time, see Table 1), the solvent is removed *in vacuo,* and the residue recrystallized from an appropriate solvent in the presence of Norite (to remove traces of sensitizer). The photooxygenation products were identified by comparison, of m.p., MS, and IR spectra of each product with those of the respective authentic specimens. Table 1 lists the perylenes oxidized, reaction conditions, the ketones produced and their percentage yields.

Photoreaction of the Ethylenes (1a-e), (6a,b) and (9a,b) with Elemental Sulfur in the presence of Inert Gas. ***General Procedure.*** A mixture of the ethylene (**1a-e**), (**6a,b**) or (**9a,b**) (2.5g) with elemental sulfur (1.5g) in toluene (or ethyl acetate) (250 ml) is irradiated under reflux while a stream of CO_2 gas was bubbling through the mixture. TLC analysis showed no trace of any starting material. The reaction mixture was worked up in the usual manner to give the photoproducts (**10a-d**), (**11a,b**), and (**12a,b**), identified by m.p. and mixed m.ps. as well as comparative IR and MS spectra. See Table 2 for the irradiation time and the percentage yields.

In the case of the photoreaction of **1e** with sulfur, after irradiation, the solvent was evaporated to dryness in the presence of silica gel (7g), and then the mixture was separated by chromatography on silica gel with light petroleum ether, then with chloroform with increasing amounts of ethyl acetate. Thioketones (**10b**) and (**10c**) were isolated in a pure state, for comparative yields, see Table 2.

Photoreaction of the Ethylenes (1b,c) with Elemental Sulfur in absence of Inert Gas. Irradiation of **1b** or **1c** (as a representative examples) was carried out in toluene, similar to the general procedure, employing the same amounts without using CO_2 gas. After evaporation of the solvent *in vacuo*, **5b** and **10b** or **5c** and **10c**, respectively, were obtained by column chromatography (silica gel/chloroform with increasing amounts of ethyl acetate). For comparative yields, see Table 2.

Photodegradation of the Thiiranes (13a-c), (14), and (15). *General procedure*. The ethylene sulfide (**13a-c**), (**14**) or (**15**) was irradiated in toluene while a stream of air was bubbling in the solution in the way described above. The reaction mixture was worked up as mentioned in the general procedure. The chromatography was carried out with toluene and then toluene containing increasing amounts of ethyl acetate. The photodegradation products with their comparative yields are listed in Table 3.

REFERENCES

1. Rak, J.; Btazejowski, J. *J. Photochem. and Photobiol.* **1992**, *67*, 287.
2. Catalina, F., Tercero, J. M.; Peinado, C.; Sastre, R.; Mateo, J. L.; Allen, N. S. *J. Photochem. and Photobiol.* **1989**, *50*, 249.
3. Coyle, J. D. *Introduction to Organic Photochemistry*, Wiley Chichester (**1986**).
4. Reid, S. T. *Advan. Heterocycl. Chem.* **1983**, *33*, 1; *Ibid.* **1982**, *30*, 239.
5. Pizzocaro, C.; Bolt, M.; Hoffman, M. Z. *J. Photochem. and Photobiol.* **1992**, *67*, 115.
6. Moorman, A. R.; Findak, D. C.; Ku, H. S. *J. Heterocycl. Chem.* **1985**, *22*, 915.
7. Parkanyi, C.; Abdelhamid, A. O. *Heterocycles*, **1985**, 23, 2917.
8. Crank, G.; Mursyidi, A. *Aust. J. Chem.* **1982**, *35*, 775.
9. Abdou, W. M., Mahran, M. R.; Sidky, M. M.; Wamhoff, H. *Chemosphere*, **1985**, *14*, 1343; *Ibid.* **1986**, *15*, 1063.
10. Abdou, W. M.; Born, L.; Hulpke, H.; Mahran, M. R.; Sidky, M. M., Wamhoff, H. *Phos. and Sulf.* **1987**, *29*, 179.
11. Abdou, W. M.; Sidky, M. M.; Wamhoff, H. Z. *Naturforsch.*, **1987**, *42*, 907, and 1153.
12. Mahran, M. M.; Abdou, W. M., Sidky, M. M.; Wamhoff, H. *Synthesis*, **1987**, 506.
13. Abdou, W. M.; Sidky; M. M.; Wamhoff, H. *J. Argic. Food Chem.*, **1988**, 36, 1291.
14. Abdou, W. M.; Mahran, M. R.; Sidky, M. M.; Wamhoff, H. *Phos. and Sulf.* **1988**, *39*, 199.
15. Wamhoff, H.; Abdou, W. M.; Zahran, M. *J. Agric. Food Chem.* **1988**, *36*, 205.
16. Meyer, H.; Rondy, R.; Eckert, A. *Monatsh Chem.* **1912**, *33*, 1447.
17. Attree, G. F.; Perkin, A. G. *J. Chem. Soc.* **1931**, 144.
18. Brockmann, H.; Mühlmann, R. *Chem. Ber.* **1949**, *82*, 348.
19. Agranat, I.; Rabinovitz, M.; Falle, H. R.; Luckhurst, G. R.; Ockwell, J. N. *J. Chem. Soc.* (B), **1970**, 294.
20. a) Wasserman, H. H.; Murray, R. W. Eds. *Singlet Oxygen*, Academic Press, New york, **1979**; b) *Ibid.* Gollnick, K.; Kuhn, H. J., pp 287-427.
21. Wasserman, H. H.; Ives, J. L. *Tetrahedron*, **1981**, *37*, 1825.
22. Foote, C.S.; Lin, J. W. P. *Tetrahedron Lett.* **1968**, 3267.

23. Wasserman, H. H.; Ives, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 7868.
24. Bartlett, P. D., Schaap, A. P. *J. Am. Chem. Soc.* **1970**, *92*, 3223.
25. Wasserman, H. H.; Pickett, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 4695.
26. Schönberg, A.; Asker, W. *J. Chem. Soc.* **1942**, 272.
27. Schönberg A. *Chem. Ber.* **1925**, *58*, 1796; Gleu, K.; Schaarschmidt, R.; *Ibid.* **1939**, *72*, 1246.
28 Schönberg A.; Asker, W. *J. Chem. Soc.* **1942**, 725.
29 Rio, G.; Berthelot, *J. Bull. Soc. Chim. Fr.*, **1969**, 3609.

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