Tetrahedron. Vol. 26, pp. 1157 to 1161. Pergamon Press 1970. Printed in Great Britain

PHOTOCHEMISTRY—I

PHOTOLYSIS OF 2-PHENYL-3,1-BENZOXATHIAN-4-ONE AT 3500 Å*

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(*Received in the UK* 3 *November* 1969; *Accepted for publication* 25 *November* 1969)

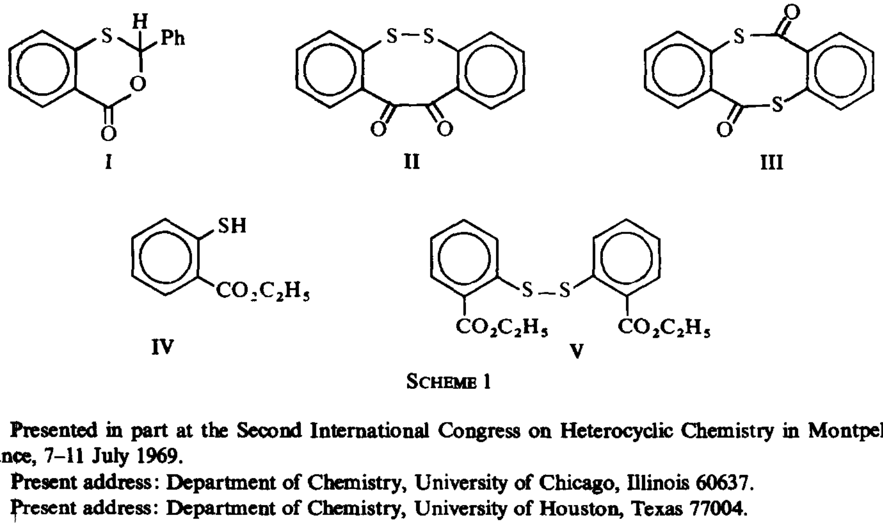
Abstract—Photolysis of 2-phenyl-3,1-benzoxanthian-4-one results in formation of benzaldehyde and dibenzo [*c*,*g*]-[1,2]-dithiocan-5,6-dione. This reaction has been studied in considerable detail—including a low temperature investigation—and a mechanism is presented. In addition 2-hydrogen, 2-methyl, and 2,2-diphenyl-3,1-benzoxathian-4-ones were found to undergo analogous reactions.

As PART of our studies on organosulphur compounds we report a new photofragmentation reaction in the benzoxathianone system.

Photolysis of 2-*phenyl*-3,1-*benzoxathian*-4-*one* (I)

Irradiation of a chloroform solution of 2-phenyl-3,1-benzoxathian-4-one (I) in a Rayonett photoreactor equipped with RUL 3500 Å lamps resulted in the formation of benzaldehyde and a hitherto unknown solid compound. No other products could be detected by TLC, and in fact the amount of the two products accounts for the consumption of starting material.

The quantum yield for disappearance of starting material, which is equal to quantum yield for formation of benzaldehyde and equal to twice the quantum yield for formation of II—in accordance with stoichiometry—was estimated to be 0·05 using a potassium ferrioxalate actinometer.



SCHEME 1

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* Presented in part at the Second International Congress on Heterocyclic Chemistry in Montpellier, France, 7–11 July 1969.

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Elucidation of the structure for the solid photoproduct was based on its spectroscopic and chemical properties. Elemental analysis, molecular weight (MS), IR and NMR spectra left two possibilities for this structure: II or III. Comparison of the photoproduct with the thioester derivative (III), which is a known compound[1] showed that besides a large difference in m.pts, the two compounds clearly differed on TLC. More positive evidence for the disulphide linkage was established by treating the photoproduct with Raney Nickel. This reaction resulted in formation of benzoin and benzil as the main products. We conclude that the photoproduct has the dibenzo[*c*,*g*]-[1,2]-dithiocan-5,6-dione structure (II).

It appeared that the same photoreaction proceeds in hydrocarbon solvent. In this case II precipitates quantitatively due to its extreme insolubility. In another experiment we employed ethanol as solvent. In this solvent the photoreaction proceeds to yield benzaldehyde and diethoxycarbonyl diphenyl disulphide (V) as the main products. Only traces of II were found, but contrary to the photolysis in chloroform and hydrocarbon solvents large amounts of polymer were formed. Extensive TLC analysis of this reaction revealed that the photoproducts in fact were benzaldehyde and the ethyl ester of thiosalicylic acid (IV). Further evidence for the latter compound was based on an IR spectrum of the photolysis mixture, which showed an absorption band near 2540 cm^{-1} due to S—H stretching.[2] The isolated disulphide which—somewhat surprising—could not be detected in the crude reaction mixture must have been formed during the separation procedure (Various thiols are known to undergo S—H bond fission upon irradiation[3]).

For further clarification of this reaction another photolysis experiment was carried out at low temperature (77°K) in hydrocarbon glass. This technique[4] permits trapping of unstable intermediates and offers direct evidence concerning the nature of primary processes.

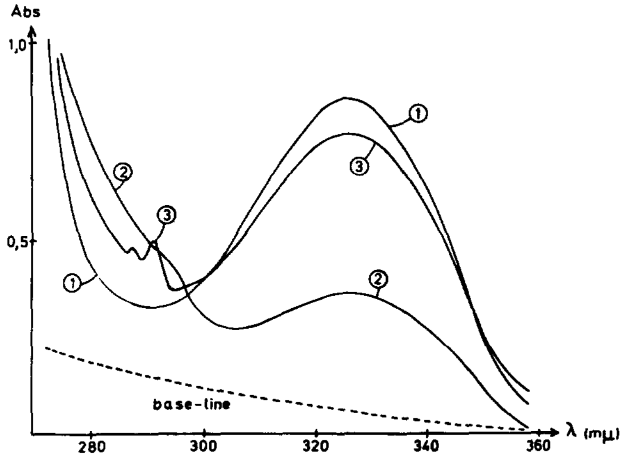
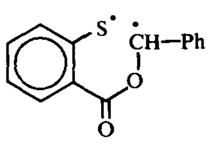


FIG. 1 (1) I (10^{-3} M) in 3-methylpentane at 77°K, 10 mm cell.
(2) The same sample after irradiation with 1 kW Hg–Xe source at 77°K for 30 min. (Corning glass filter No. 9863).
(3) The irradiated sample after warming up to room temperature in the dark and freezing again to 77°K.

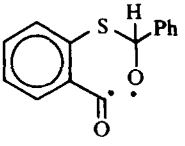
The information from this experiment is obtained from the UV spectra presented in Fig. 1.

The important points are that at the end of the procedure listed in Fig. 1, 90% of the original intensity of the 326 nm band has been restored, and that in the region around 290 nm absorption due to benzaldehyde can be seen (compared with authentic sample). Quite conclusive evidence for the presence of benzaldehyde at this point was given by emission typical for benzaldehyde (bands at 397, 424, 457, and 494 nm, wave lengths of the bands and their relative intensity ratio are the same as corresponding entities measured with authentic sample of benzaldehyde). No such emission was observed after the irradiation at 77°K (see 2, Fig. 1) *without* warming of the sample.

It can thus be concluded that to a high degree the photoinduced bond fission is thermally reversed and that the expulsion of benzaldehyde is also a thermal reaction. We have no conclusive experimental evidence to distinguish between the intermediates VI and VII. It appeared (see below) that the quantum yields for formation of II from 2-hydrogen-(IX), 2-methyl-(X), 2-phenyl-(I), and 2,2-diphenyl-3,1-benzoxathian-4-one (XI) were in the order $\phi(XI) > \phi(I) \gg \phi(IX) > \phi(X)$. This trend gives some evidence for higher probability of VI over VII.

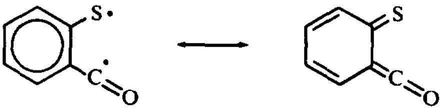


VI



VII

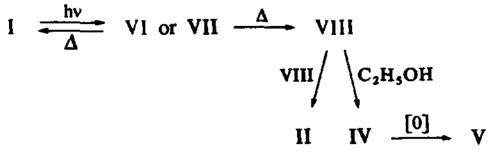
If the thermal character of the benzaldehyde expulsion applies for room temperature, we conclude that the primary intermediate VI or VII unimolecularly fragmentates into benzaldehyde and a second intermediate VIII (Cyclization to I is the competing reaction).



VIII

It has been surprising that no significant colour due to the chromophore VIII could be observed. However, the only way to escape an intermediate of type VIII is to presume that expulsion of benzaldehyde takes place after or at the same time as the further reaction (e.g. dimerization or addition of ethanol) which seems unlikely. Furthermore, the mass-spectra of I, II, and III all show their base-peaks at *m/e* 136 corresponding to an ionized fragment of type VIII, thus inducing some sort of probability in this arrangement of atoms.

Therefore we are summarizing our considerations in the following Scheme 2.



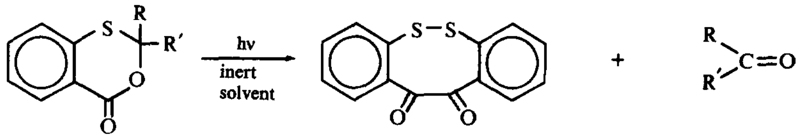
Scheme 2

Recently a very similar mechanism has been shown to be operative in the photodecarbonylation of N-phenyloxindole in the presence of nucleophiles.[5]

Photolysis of other 2-substituted-3,1-benzoxathian-4-ones

Photolysis of 2-H (IX), 2-methyl (X), and 2,2-diphenyl-3,1-benzoxathian-4-one (XI) at 3500 Å in every case yielded dibenzo[*c,g*]-[1,2]-dithiocan-5,6-dione. We did not try to trap formaldehyde and acetaldehyde from IX and X, respectively, but we isolated benzophenone from XI. According to TLC these reactions proceeded as cleanly as that of I.

We can now summarize this general photofragmentation in Scheme 3.



Scheme 3

R	R'	
H	H	IX
H	CH_3	X
H	C_6H_5	I
C_6H_5	C_6H_5	XI

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were determined on either a Perkin–Elmer Infracord or Beckman IR-10 spectrometer and UV spectra on a Bausch and Lomb Spectronic 505 spectrometer. NMR spectra were recorded on a Varian A-60 spectrometer, using TMS as an internal standard. In low-temp absorption and emission work, quartz cells and quartz Dewar equipped with flat windows and containing liquid N_2 were used. Absorption spectra were recorded using Cary 15 spectrometer. For emission work, apparatus described by Becker[6] was used.

Starting materials

2,2-RR'-3,1-Benzoxathian-4-one		Source	UV: λ_{max}
H,H	(IX)	7	228, 254, 323 nm (ethanol
CH_3,H	(X)	7	227, 255, 323 nm (ethanol)
C_6H_5,H	(I)	8	228, 254, 325 nm (ethanol)
C_6H_5,C_6H_5	(XI)	9	233, 265, 330 nm (methanol)

Solvents. Chloroform was washed with water (to remove EtOH), dried over $MgSO_4$, and distilled. Light petroleum (b.p. 40–60°) and Benzene ANALAR, BDH Chemicals Ltd., U.K. were used without purification.

Photolysis of 2-phenyl-3,1-benzoxathian-4-one (I) *in chloroform.* A soln of 12·03 g (0·050 mole) of I in 600 ml $CHCl_3$ stirred by a N_2 flow was irradiated (Pyrex cell) in a Rayonett photoreactor at 3500 Å for 50 hrs.

Evaporation of solvent and extraction of the oily residue with light petroleum left 4·4 g (0·016 mole) of a yellow solid, identified as II, dec at 140–5° (chloroform). (Found: C, 61·59; H, 3·17; S, 23·04; M^+ at m/e 272. $C_{14}H_8S_2O_2$, M.W. 272 requires: C, 61·76; H, 2·94; S, 23·52%); IR: 1678, 1185, and 875 cm^{-1}; NMR: only aromatic protons. Concentration, cooling, and filtration of the light petroleum extracts yielded 4·1 g (0·017 mole) of the starting compound (I). The filtrate was concentrated, dissolved in 20 ml EtOH, and added to 500 ml of a 0·12M solution of 2,4-dinitrophenylhydrazine in 30% perchloric acid. Stirring for 1 hr, filtration, and drying yielded 8·1 g (0·028 mole) of the 2,4-dinitrophenylhydrazone of benzaldehyde, m.p. 234–237°.

Reduction of dibenzo[c.g]-[1,2]-*dithiocan-5,6-dione* (II) *with Raney nickel.* 0·4 g of II was refluxed with 8 g of Raney Ni in 65 ml abs EtOH for 90 hr. TLC indicated that, besides unreacted II, benzylalcohol, benzoin, and benzil were present in the crude reaction mixture.

45 mg of benzil, identified as 2,4-dinitrophenyl-hydrazone m.p. 189°, was isolated employing PLC (25 × 45 cm^2 plate covered with 105 g (3 mm layer) of Silicagel, eluation with a 5:45:50 mixture of acetone, light petroleum and benzene).

Photolysis of 2-phenyl-3,1-benzoxathian-4-one (I) *in ethanol.* A soln of 1·00 g (0·0042 mole) of I in 250 ml abs EtOH, stirred by a N_2 flow was irradiated (Pyrex cell) at 3500 Å for 20 hr. Evaporation yielded a red oil with a strong smell of benzaldehyde. PLC separation (105 g Silicagel, eluated 5 times with a 50:50 mixture of benzene and light petroleum) yielded 0·203 g (0·0006 mole) of V, m.p. 118–119° (litt.[10] m.p. 119–120°); IR (KBr): 1705 cm^{-1}; NMR ($CDCl_3$): δ 7·6 (8H, m), δ 4·5 (4H, q), δ 1·5 (6H, t). A few drops of a thick yellow oil with an IR spectrum identical with that of II was also isolated from the plate.

Photolysis of 2-phenyl-3,1-benzoxathian-4-one (I) *in hydrocarbon solvent.* A soln of 0·605 g (0·0025 mole) of I in 250 ml petroleum, stirred by a N_2 flow, was irradiated (Pyrex cell) at 3500 Å for 3 hr. Filtration yielded 0·317 g (0·0012 mole) of II.

Photolysis of 3,1-benzoxathian-4-one (IX) *in hydrocarbon solvent.* A soln of 0·415 g (0·0025 mole) of IX in 250 ml petroleum was irradiated as above for 3 hr. Filtration yielded 0·153 g (0·0006 mole) of II.

Photolysis of 2-methyl-3,1-benzoxathian-4-one (X) *in hydrocarbon solvent.* A soln of 0·450 g (0·0025 mole) of X in 250 ml petroleum was irradiated as above for 3 hr. Filtration yielded 0·057 g (0·0002 mole) of II.

Photolysis of 2,2-diphenyl-3,1-benzoxathian-4-one (XI) *in hydrocarbon solvent.* A soln of 0·330 g (0·0010 mole) of XI in 250 ml benzene was irradiated as above for 1·5 hr. Filtration yielded 0·135 g (0·0005 mole) of II. Evaporation of the filtrate yielded after crystallization from EtOH 0·110 g (0·0006 mole) of benzophenone, m.p. 46–47°.

Acknowledgement—We thank Professor R. S. Becker, University of Houston, for his kind permission to use the low-temperature spectroscopic equipment of his laboratory and for his interest in this work. We appreciate very much a generous gift of 2,2-diphenyl-3,1-benzoxathian-4-one from Professor D. C. Dittmer, Syracuse University. Grants from Statens Almindelige Videnskabsfond and from Carlsbergfondet (to S.-O. Lawesson) are gratefully acknowledged.

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