PHOTOLYSIS OF 2-ARYLOXY- OR 2-ARYLTHIO-1,3-BENZODIOXAN-4-ONES

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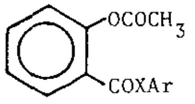
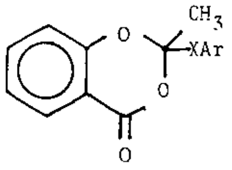
Abstract - Photolysis of 1,3-benzodioxan-4-ones 3b and 4a gives mainly products derived from photorearrangement, photoreduction and/or photosolvolysis. These results closely parallel those obtained by irradiation of the isomeric open-chain compounds 1b and 2a. A mechanism involving the intermediacy of radical pairs A and B, generated by successive homolysis of the aryloxy- or arylthio-carbon and carbonyl-oxygen bonds, is proposed.

We have recently shown[1] that aryl *o*-acetoxybenzoates 1 undergo a photochemical Fries rearrangement, affording benzophenone intermediates useful in the synthesis of xanthones. Previously, it had been reported[2] that S-aryl *o*-acetoxythiobenzoates 2 (sulfur analogues of 1) react in a different way, leading to the formation of disulfides as the only isolable photoproducts.

To extend our knowledge on the photochemistry of acetylsalicylic acid derivatives, and as a part of the search for new entries to condensed γ-pyrones and related structures,[3] we have now investigated the photochemical reactivity of 1,3-benzodioxan-4-ones such as 3 and 4, cyclic isomers of aryl esters 1 and thioesters 2 respectively.



1 X=O
2 X=S



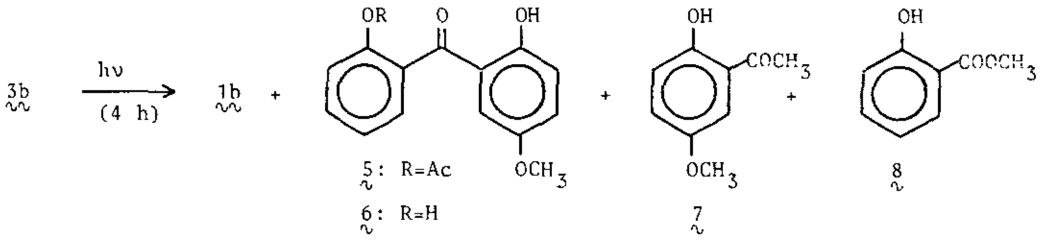
3
4

a: Ar=C_6H_5
b: Ar= *p*-$CH_3OC_6H_4$
c: Ar= *p*-$CH_3C_6H_4$

Compounds of this type are formed in the reaction of o-acetoxybenzoyl chloride with oxygen or sulfur nucleophiles under certain experimental conditions.[4] However, a definitive characterization (including correct combustion analyses) has been achieved in very few cases, due to the poor average yields (about 40 %) and to the difficulty of the separation processes.[5]

Hence, it appeared convenient to look for more suitable conditions for the preparation of the required substrates before undertaking the photochemical study. Specifically, we have found that 3b and 4a can be prepared from o-acetoxybenzoyl chloride and p-methoxyphenol or thiophenol, working at room temperature, in the absence of solvents, under magnetic stirring and continuously removing the evolved HCl through connection to a vacuum line. Operating in this way, yields were high (about 80 %) and products could be purified by conventional techniques (chromatography/crystallization or even direct crystallization of the reaction mixture).

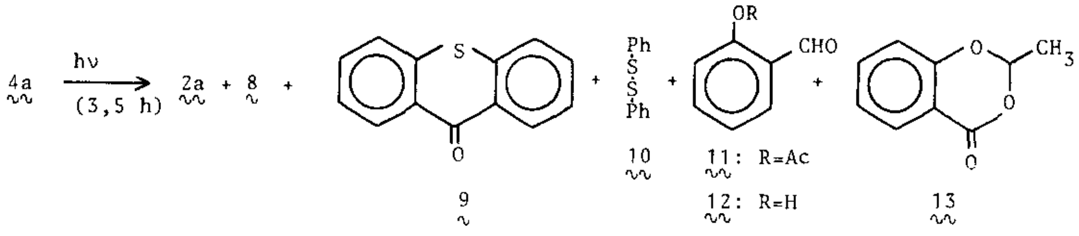
The irradiation of 3b and 4a was carried out in quartz immersion well reactors, using *benzene or methanol as solvents and 125 W medium pressure* mercury lamps as light sources. Under this set of conditions, 3b gave rise to photomixtures, whose composition can be summarized as follows:



Product	Yield (%)	
	Benzene	Methanol
1b	2	-
5	44	10
6	-	traces
7	5	-
8	-	12

Except for the formation of 2-hydroxy-5-methoxyacetophenone 7, these results are closely analogous to those obtained by irradiation of p-methoxyphenyl o-acetoxy-

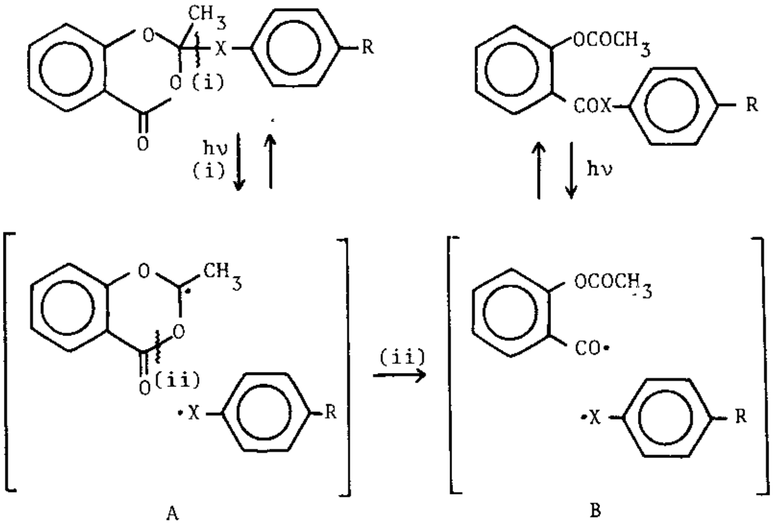
benzoate 1b.[6] Nevertheless, the cyclic isomer 3b requires shorter reaction times for the same degrees of conversion (4 instead 11 h) and in methanol gives lower yields of photo-rearranged products (overall % for 5+6: 10% from 3b, 45% from 1b).
Irradiation of 2-methyl-2-phenylthio-1,3-benzodioxan-4-one 4a in a similar way led to the following pattern of products:



Product	Yield (%)	
	Benzene	Methanol
2a[7]	3	10
8	-	5
9	13	5
10	20	-
11[8]	18	-
12	-	17
13[9]	-	3

In order to establish a valid comparison, it was necessary to have equivalent information about the photolysis of S-phenyl o-acetoxythiobenzoate 2a, open chain isomer of 4a.[10] Work done in our laboratory for this purpose has revealed the formation after 10 h of 9 (10%), 10 (20%) and 11 (50%) in benzene, as well as 8 (10%), 9 (7%), 12 (11%) and S-phenyl thiosalicylate 14[7] (4%) in methanol.
These results make clear a close relationship between the photochemical reactivities of 2a and 4a. As in the case of 1b and 3b, the main peculiarities are the appearance of little amounts of not common products such as 13 and 14, together with the length of irradiation times.
The following scheme could consistently explain the origin of every products isolated

after irradiation of 1,3-benzodioxan-4-ones 3b and 4a :



As a consequence of UV-excitation, successive homolysis of aryloxy- or arylthio-carbon (i) and carbonyl-oxygen bonds (ii) might occur. Recombination of intermediate radical pair B would give benzophenone 5, ester 1b or thioester 2a. Dimerization of phenylthio radical would yield disulfide 10. Acetophenone 7 and thioxanthone 9 could arise from radical pairs A or B[11] through recombination, followed by hydrolysis or acetic acid elimination respectively. Hydrogen abstraction by the same intermediates could explain the isolation of 2-methyl-1,3-benzodioxan-4-one 13 and o-acetoxybenzaldehyde 11. Finally, the appearance of methyl salicylate 8, benzophenone 6 and salicylaldehyde 12 may be attributed to the participation of methanol in photosolvolysis reactions.

EXPERIMENTAL

Melting points are uncorrected. Combustion analyses were performed at the Instituto de Química Orgánica of the C.S.I.C. (Madrid). To obtain the ir-spectra a Perkin-Elmer 577 spectrometer was used; absorptions ($\bar{\nu}$, cm^{-1}) are given only for the main bands. ^{1}H-nmr-spectra were measured with a Hitachi-Perkin-Elmer R-24B instrument; chemical shifts are reported in ppm downfield (δ) from TMS. Mass spectra were recorded with a Hitachi-Perkin-Elmer RMU-6MG spectrometer; the ratios m/e and the relative intensities (%) are listed.

Preparation of the substrates

A mixture of *o*-acetoxybenzoyl chloride (2,18 g, 10,9 mmoles) and *p*-methoxyphenol (1,36 g, 10,9 mmoles) was allowed to react during 4 h, at room temperature and under magnetic stirring, in a flask connected to a water pump. The reaction mixture was applied to preparative tlc plates (Kieselgel Merck PF_{254}) and eluted with CCl_4 (5 parts) and ether (1 part), affording the following products: *p-methoxyphenyl salicylate*[1] (66 mg, 2%), mp 91-92 ºC (hexane), ir (CCl_4) 1690, nmr (CCl_4) 10,40 (s, OH), 8,15-6,70 (m, Ar-H), 3,80 (s, OCH_3); *2-(p-methoxyphenoxy)-2-methyl-1,3-benzodioxan-4-one* **3b** (2,3 g, 72 %), mp 88-90 ºC (cyclohexane), analysis C 67,20 H 4,94 % ($C_{16}H_{14}O_5$ requires C 67,12 H 4,92 %), ir (nujol) 1760, nmr ($CDCl_3$) 8,20-6,56 (m, Ar-H) 3,75 (s, OCH_3), 1,88 (s, CH_3), ms 286 (6), 163 (88), 124 (57), 123 (5), 121 (100), 120 (4), 109 (15), 95,8 (metastable), 93 (6), 92 (6), 89,8 (metastable); *p-methoxyphenyl o-acetoxybenzoate* **1b**[1] (36 mg, 1 %), mp 103 ºC (cyclohexane), ir (CCl_4) 1765 and 1740, nmr 8,17-6,60 (m, Ar-H), 3,70 (s, OCH_3), 2,20 (s, $OCOCH_3$).

Under the same conditions, the reaction between *o*-acetoxybenzoyl chloride (1,1 g, 5,5 mmoles) and thiophenol (0,6 ml, 5,8 mmoles) led, after the chromatographic work-up, to the following products: *diphenyl disulfide* **10**[12] (106 mg, 16 %), mp 56-58 ºC; *2-methyl-2-phenylthio-1,3-benzodioxan-4-one* **4a** (1,24 g, 83 %), mp 71-73 ºC (hexane), analysis C 66,58 H 4,38 S 11,76 % ($C_{15}H_{12}O_3S$ requires C 66,16 H 4,44 S 11,77 %), ir (nujol) 1750, nmr ($CDCl_3$) 8,20-6,38 (m, Ar-H), 2,00 (s, CH_3), ms 272 (1), 163 (80), 121 (100), 120 (4), 110 (4), 109 (6), 93 (4), 89,8 (metastable), 77(2), 71,5 (metastable).

5 ml of CCl_4 containing 0,3 ml (2,9 mmoles) of thiophenol and 240 mg (2,9 mmoles) of pyridine were added dropwise to a solution of *o*-acetoxybenzoyl chloride (550 mg, 2,7 mmoles) in CCl_4 (5 ml), keeping the temperature below 5 ºC during 1 h. After washing with water, the reaction mixture was dried with anhydrous Na_2SO_4 and the solvent was removed in vacuo, to give 620 mg (82 %) of *S-phenyl o-acetoxythiobenzoate* **2a**[7], mp 85-89 ºC (from hexane/ether 1:3), ir (nujol) 1750 and 1670, nmr ($CDCl_3$) 8,21-6,91 (m, Ar-H), 2,23 (s, $OCOCH_3$).

Irradiations

To carry out the irradiations, a 300 ml immersion well reactor, provided with a quartz sleeve and a 125 W medium pressure mercury lamp, was employed. Solvents used for irradiations were previously purified: benzene was azeotropically distilled and methanol was dried over $CaCl_2$, CaO and then distilled. The irradiated solutions were evaporated at reduced pressure and the residues were submitted to preparative tlc chromatography, using hexane (2 parts) and ether (1 part) as eluent, unless otherwise indicated.

Compound **3b** (760 mg, benzene solution, 4 h) gave rise to the following products: *2-hydroxy-5-methoxyacetophenone* **7**[13] (22 mg, 5%), ir (CCl_4) 1640, nmr (CCl_4) 11,61 (s, OH), 7,00-6,54 (m, Ar-H), 3,70 (s, OCH_3), 2,48 (s, $COCH_3$); *2´-acetoxy-2-hydroxy-5-methoxybenzophenone* **5**[1] (334 mg, 44 %), ir (CCl_4) 1770 and 1635, nmr (CCl_4) 11,40 (s,OH) 7,55-6,50 (m, Ar-H), 3,53 (s, OCH_3), 1,92 (s, $OCOCH_3$); *p-methoxyphenyl o-acetoxybenzoate* **1b** (15 mg, 2 %).

Irradiation of the same substrate (630 mg) during 4h in methanol gave: *methyl salicylate* **8**[12] (40 mg, 12 %); *2´ acetoxy-2-hydroxy-5-methoxybenzophenone* **5** (63 mg, 10 %); *2,2´dihydroxy-5-methoxybenzophenone* **6**[1] (10 mg), mp 93 ºC, ir (CCl_4) 1615, nmr (CCl_4) 10,70 (s, 2´OH), 10,10 (s, 2-OH), 7,70-6,60 (m, Ar-H), 3,70 (s, OCH_3).

From compound **4a** (610 mg) the following products were obtained after irradiation during 3,5 h in benzene (eluent, hexane/ether 1:1): *diphenyl disulfide* **10** (49 mg, 20 %); *S-phenyl o-acetoxythiobenzoate* **2a** (18 mg, 3 %); *thioxanthone* **9**[12] (58 mg, 13 %); *o-acetoxybenzaldehyde* **11**[8] (66 mg, 18 %), mp 31-35 ºC, ir (CCl_4) 1760 and 1690, nmr (CCl_4) 9,80 (s, CHO), 7,87-6,88 (m, Ar-H), 2,31 (s, $OCOCH_3$).

Compound **4a** (850 mg) was converted after 2 h in methanol into: *methyl salicylate* **8** (24 mg, 5 %); *2-methyl-1,3-benzodioxan-4-one* **13**[9] (15 mg, 3 %), ir (CCl_4) 1760, nmr (CCl_4) 8,00-6,80 (m, Ar-H), 6,12 (c, C_2-H), 2,30 (d, CH_3); *S-phenyl o-acetoxythiobenzoate* **2a** (85 mg, 10 %); *thioxanthone* **9** (31 mg, 5 %); *salicylaldehyde* **12** (87 mg, 17%). Irradiation of **2a** (850 mg) in benzene afforded after 10 h *diphenyl disulfide* **10** (68 mg, 20 %), *thioxanthone* **9** (62 mg, 10 %) and *o-acetoxybenzaldehyde* **11** (256 mg, 50 %). Finally, when the same substrate (1g) was irradiated during 10 h in methanol the products were *methyl salicylate* **8** (60 mg, 10%), *thioxantone* **9** (51 mg, 7 %), *salicylaldèhyde* **12** (50 mg, 11 %) and *S-phenyl thiosalicylate* **14**[7] (34 mg, 4 %), mp 50-53 ºC, ir (nujol) 1640, nmr ($CDCl_3$) 10,85 (s, OH), 8,15-6,73 (m, Ar-H).

REFERENCES AND NOTES

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4. C. Rüchardt and S. Rochlitz, Liebigs Ann. Chem., 1974, 15.

5. The reaction of *o*-acetoxybenzoyl chloride with five phenols (phenol, *o*-cresol, *p*-cresol, *o*-chlorophenol and *p*-chlorophenol) and benzyl mercaptane has been studied in Ref. 4. The formation of cyclic compounds of the type **3** or **4** was observed in every cases, working in tetrahydrofuran solution and in the absence of pyridine. However, only in the case of 2-(*o*-chlorophenyl)-2-methyl-1,3-benzodioxan-4-one was possible a complete separation from the accompanying *o*-acetoxybenzoate.
6. Photoproducts of **1b**: in benzene **5** (55 %); in methanol **5** (21 %), **6** (24 %) and **8** (9 %) (from Ref. 1).
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9. D.T. Mowry, W.H. Yanko and E.L. Ringwald, *J. Am. Chem. Soc.*, 1974, **96**, 2358.
10. It is worth mentioning that the only product isolated from irradiation of the related compound **2c** in benzene was the corresponding disulfide (30 %), although two fractions accounting for more than 30 % of reacted material remained unidentified (Ref. 2).
11. The evolution of arylthio and aroyl radicals with electron-withdrawing substituents to form thioxanthones has been previously considered. See for example J. Martens and K. Praefcke, *Tetrahedron*, 1974, **30**, 2565 and references therein.
12. Identified by comparison with an authentic sample.
13. R.A. Wayne and E.L. George, *J. Org. Chem.*, 1980, **45**, 501.

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