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PHOTOCHEMISTRY OF AROMATIC COMPOUNDS—VI[1]

THE PHOTODECARBONYLATION OF 3,3-DIPHENYL-2-(3*H*)-BENZO[b]THIOPHENONE

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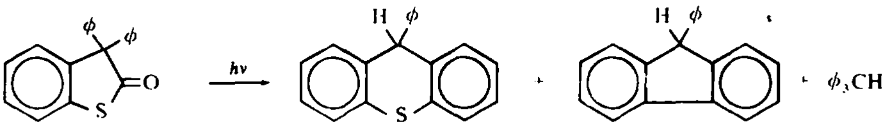
Abstract—The UV irradiation of 3,3-diphenyl-2-(3*H*)-benzo[b]thiophenone (**1**) solutions gives high yields of 9-phenylthioxanthene (**2**) resulting probably from an electrocyclization of an orthoquinoid structure (**8**) containing a S atom followed by a sigmatropic rearrangement.

INTRODUCTION

THE acyl-oxygen[2] and acyl-nitrogen[3] photocleavages are well documented, but there are only a few reports on the cleavage of acyl-sulphur bonds.[4,5] We now describe preliminary data on the photochemistry of the thiolactone 3,3-diphenyl-2-(3*H*)-benzo[*b*]-thiophenone **1**. This substrate was selected because the two phenyl groups may favour the intramolecular scavenging of a probable orthoquinone-like intermediate.[6–8]

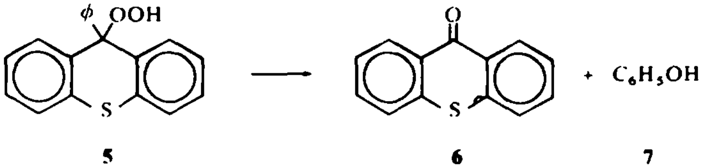
RESULTS AND DISCUSSION

(1) *Direct irradiation.* The irradiation of **1** in methanol, cyclohexane or benzene with a medium pressure mercury arc yields 9-phenylthioxanthene **2**, and small amounts of 9-phenylfluorene **3** and triphenylmethane **4**.



1 **2** **3** **4**

When the solutions were imperfectly deoxygenated, three more products were formed: the hydroperoxide **5**, thioxanthone **6** and phenol **7**, the phenol and the xanthone probably originating from the hydroperoxide:



5 **6** **7**

Two more products, X and Y, are formed in small amounts in all runs, and could not be identified; they appear in appreciable amounts only in cyclohexane solutions. Some fluorene is formed after prolonged irradiation, when most of the starting material has disappeared.

The irradiation of a 10^{-2}M methanol solution of **1** with a 450 W medium pressure arc (quartz well) was monitored by UV spectroscopy. Successive spectra show three clean isosbestic points (as in Fig 1) during the first 40 min: a GLC analysis* after 45 min gives the following composition: 24% of **1**, 75% of **2**, <1% of **3** and ≤1% of **4**, corresponding to 76% conversion and a 99% yield of **2** based on recovered starting material.

In a similar photolysis, carried out in cyclohexane, the isosbestic points are blurred after 20 min; GLC analyses after variable irradiation times give the data collected in Table 1.

TABLE 1. RELATIVE PERCENTAGE YIELD (IN MOLE) IN THE PHOTOLYSIS OF A 10^{-2}M CYCLOHEXANE SOLUTION OF **1**[**]

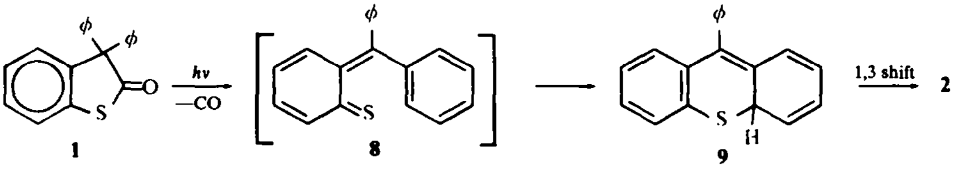
Time (min)	Recovered **1**	**2**[a]	**3**	**4**	X	Y
20	62%	37%	<1%	<1%	—	<1%
40	25%	65%	~1%	<1%	~1%	~7%
60	14%	73%	~2%	~1%	~2%	~7%

[**] Hanovia 450 W medium pressure mercury arc, quartz well.

[a] These amounts correspond to 96%, 85% and 84% yield respectively based on recovered starting material.

(2) *Influence of triethylamine.* Triethylamine is known to accelerate the photofragmentation of aromatic substrates, presumably through a photo-induced electron transfer process.[3a] The reduction potential of the thiophenone **1** was found to be sufficiently high to allow a diffusion controlled exothermic electron transfer. Despite this, triethylamine does not increase the rate of disappearance of **1**, probably because the lifetime of the excited thiophenone is too short.

Triethylamine has however a profound influence on the course of the photolysis: Fig 1 shows that the irradiation of **1** does not proceed directly to the thioxanthene **2** (Fig 2: curve **d**) but that the addition of the amine after photolysis transforms the intermediate into the product (Fig 2) We assume that the new spectrum shown by



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* These amounts of **1** and **2** are found from standardized integrated GLC peaks: the other components were estimated assuming similar catharometers responses.

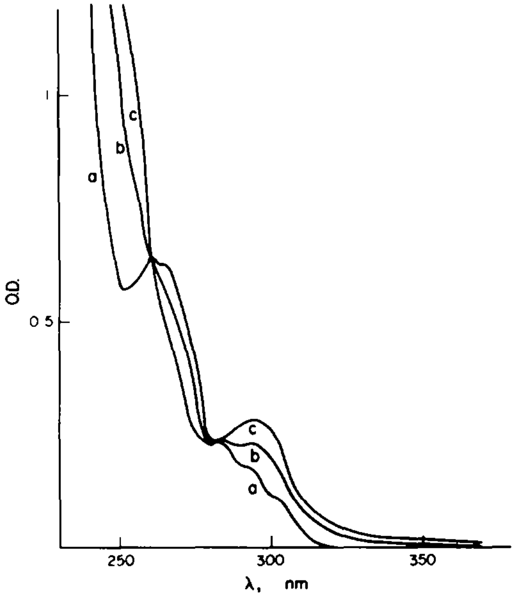


FIG 1. Irradiation of 1 in methanol in spectrophotometer cell with a Philips HPK 125 W medium pressure mercury arc (room temperature) a: 1·2 × 10^{-4}M solution of 1. b: after 15 sec irradiation. c: after 45 sec irradiation. There is a third isosbestic point at $\lambda = 237$ nm

Fig 1 (curve c) is that of 9-phenylisothioxanthene **9**, formed from a transient with an orthoquinoid structure **8**, and which then undergoes a hydrogen shift to yield **2**. The iso-thioxanthene **9** is also a good potential precursor to the hydroperoxide **5**.

(3) *The isothioxanthene* **9**. When **1** in degassed C_6D_6 is irradiated directly in a sealed NMR tube, the NMR spectrum shows new lines, but the peaks characteristic of **2** are weak during the first few hours; after quasi total disappearance of the starting product, the new bands obtained by substraction of **2** show a complex multiplet extending from $\delta = 6{\cdot}7$ to 7·6 ppm, compatible with **9**.

After photolysis in cyclohexane, chromatography through a silicagel column (petroleum ether/benzene: 85/15) gives a fraction whose UV spectrum shows the absorptions of 9-phenylthioxanthene (Fig 2: curve d) and of the first photoproduct (Fig 2: curve a) superimposed. After removal of the solvent, the product is quantitatively transformed into pure 9-phenylthioxanthene after 100 hr at −18°, or after 280 hr in benzene at the same temperature; dilute ($\sim$1·3 × 10^{-4}M) methanol solutions of this product appear to be unexpectedly stable.

The isomerisation of **9** to **2** raises the question of the mechanism of the sigmatropic rearrangement. Ignoring the S atom in a first approximation, one sees that the relevant system is the triphenylmethyl radical. In the ground state, the highest occupied molecular orbital is the non-bonding MO whose coefficients at the reaction centers are of opposite sign; since the cyclic structure of the reactant **9** precludes any antarafacial 1,3-shift, it is concluded that a concerted hydrogen transfer is forbidden.[9] This would explain the very slow uncatalyzed isomerisation of **9** to **2**. The situation is

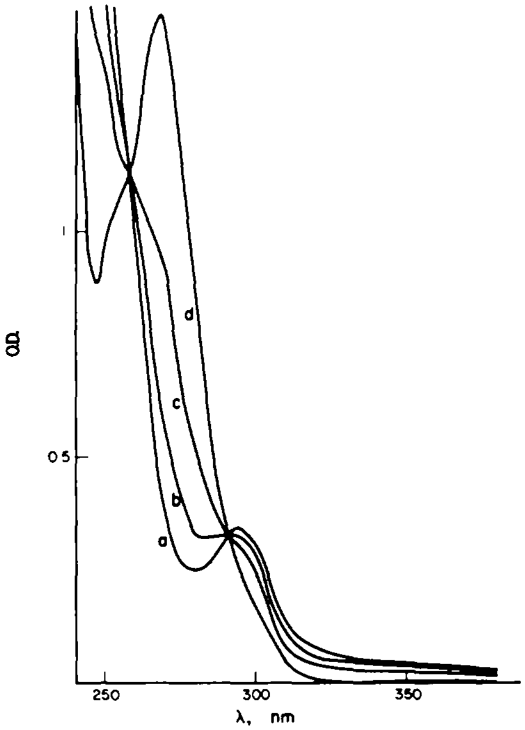
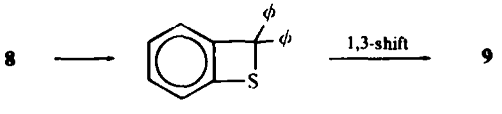


FIG 2. a: after 1 min irradiation in the same conditions as Fig 1. b: 30 min after the addition of triethylamine (resulting concentration: 2×10^{-2} M). c: 2 hr after the addition of triethylamine d: 89 hr after the addition of triethylamine. Spectrum d is similar to that of 9-phenylthioxanthene **2**.

less clear in the excited state, because the lowest antibonding MO in the triphenylmethyl radical is fivefold degenerate, and the coefficient of the central atom in all five is zero, suggesting that the orbital symmetry requirements will be far less stringent than in the ground state, and a photoinduced 1,3-shift might well occur. This is then probably the origin of the blurring of the isosbestic points after prolonged irradiations, where appreciable amounts of 9-phenylisothioxanthene are able to photoisomerize.

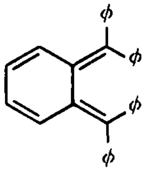
Triethylamine accelerates the isomerisation probably through a base-catalyzed prototropic shift. The isothioxanthene **9** must indeed have a much higher acidity than the triphenylmethane-like 9-phenylthioxanthene **2**, and should be able to give off a proton to the relatively weak base triethylamine.

In the formation of the isothioxanthene, the assumed quinoïd precursor **8** may behave as a triene and cyclise in one step (thermal or photochemical) to **9**; or it could ring-close like a diene to give a thiacyclobutene **10**, which might then undergo a 1,3-sulphur-shift leading to **9**:



10

Quinkert[7] assumes a non planar structure for the carbon analog **11**, and gives good evidence that it behaves like a diene in the ground state and like a triene under irradiation; in the case of the oxygenated ortho-quinoïd structure **12**, Porter[8] has shown that its isomerisation to the dihydroanthrol **13**, is photoinduced.



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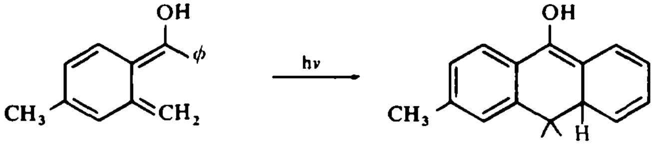

12 **13**

At present, our experiments do not distinguish between mono- and biphotonic processes, and consequently the thermal or photochemical character of the cyclization from **8** to **9** cannot be defined.

EXPERIMENTAL

Compound **1** was synthesized by known procedures[10] and purified by chromatography through a silicagel column (light petroleum/benzene: 75/25) followed by a cristallization from MeOH: m.p.: 148–149° (corr); UV (MeOH): λ_{max}: 261 nm, ε_{max}: 5400; IR (KBr) ν cm^{-1}: 1720, 1500, 1450, 1100, 1020, 820, 770, 760, 710; NMR: CD_3COCD_3, $\delta = 7–7·7$ ppm (complex multiplet); C_6D_6, $\delta = 6·75–7·5$ ppm (complex multiplet).

Compounds **3**, **4**, **6** and **7** isolated by GLC, were found to be identical with authentic samples on the basis of the following criteria: TLC and GLC behaviour, m.p., UV, IR, and mass spectra. 9-Phenylthioxanthene had physical properties identical to literature data[11] (m.p. and UV, IR and NMR spectra). The structure of **5** is based on its mass spectrum (parent peak at $m/e = 306$; loss of O_2: 306 to 274), an IR band at 3450 cm^{-1} (ν OH) and on the nature of products formed (**6** and **7**).[12]

Methanol (MERCK "pro analysis") and perdeutero benzene (99·5% purity, C.E.A.) were used as such. Cyclohexane was freed from benzene by percolation through silicagel.

Irradiations on a preparative scale were performed with 10^{-2}M solns in an immersion well (quartz or pyrex) apparatus with a medium pressure Hanovia 450 W mercury arc or a low pressure Hanau NK6 lamp.

Small scale photolysis were run in cylindrical spectrometer cells on $1·2 \times 10^{-4}$M solns, with a medium pressure Philips HPK 125 W mercury lamp.

In all cases the solns were first deoxygenated by bubbling pure N_2, and then kept under a gentle N_2 flow during the irradiation. The experiments in NMR tubes were run on solns degassed by freeze-pump-thaw cycles down to a residual pressure of about 10^{-4} Torr.

The spectra were recorded with a Cary 14 (UV), Perkin-Elmer 237 (IR), Hitaschi-Perkin-Elmer RMU-6D (mass), and Varian A-60 or T-60 (NMR) spectrometers. The Gas chromatograph was from F. & M.

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