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193. An Efficient Photosensitizer: O-Ethyl-1-Thionaphthoate

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(2. VII. 75)

Summary. The title compound is recommended as a photosensitizer for excitation by visible light of up to 500 nm due to the following properties: high triplet yield, low singlet-triplet splitting (E_T = 55 kcal/mol), low photochemical reactivity.

The choice of a suitable compound to sensitize photochemical reactions of a given acceptor **A** by triplet energy transfer is not always a trivial matter. The list of requirements to be met by the sensitizer **S** typically includes the following: (1) To allow for selective excitation of **S**, its absorption spectrum should preferably extend to longer wavelengths than that of **A**, (2) intersystem crossing to the triplet state of **S** should be rapid and efficient, (3) the triplet energy E_T of **S** must be high enough and the triplet lifetime long enough to ensure efficient energy transfer to **A**, and (4) **S** must be photochemically and thermally inert.

In the course of our studies of the photoreduction of 2-phenylnaphtho[1,8-*b*,*c*]-furan-5-one [1] we had to find a sensitizing dye absorbing above 450 nm and having a triplet energy in excess of 47 kcal/mol. Tris(2,2′-bipyridine)ruthenium(II)chloride has recently been advocated [2] as a photochemical sensitizer (absorption extending to *ca.* 550 nm, E_T *ca.* 49 kcal/mol); however, its application is limited to polar solvents for reasons of solubility and stability. Biacetyl and other α-diketones have very little absorption above 450 nm and are prone to undergo photoreduction by hydrogen abstraction. We have found that O-ethyl-1-thionaphthoate (**1**) (absorption up to *ca.* 500 nm, E_T *ca.* 55 kcal/mol) satisfied all our demands. In this note we provide the photophysical data necessary for the general use of **1** as a photochemical sensitizer.

Results. – The thioester **1** is readily obtained by the two-step synthesis recently developed by *Barton et al.* [3].

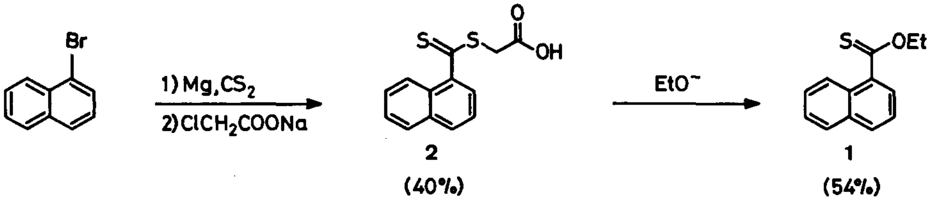

Fig. 1 displays the UV./Vis. absorption and low-temperature phosphorescence emission spectrum of **1**. No luminescence arising from **1** was detected with solutions at room temperature.

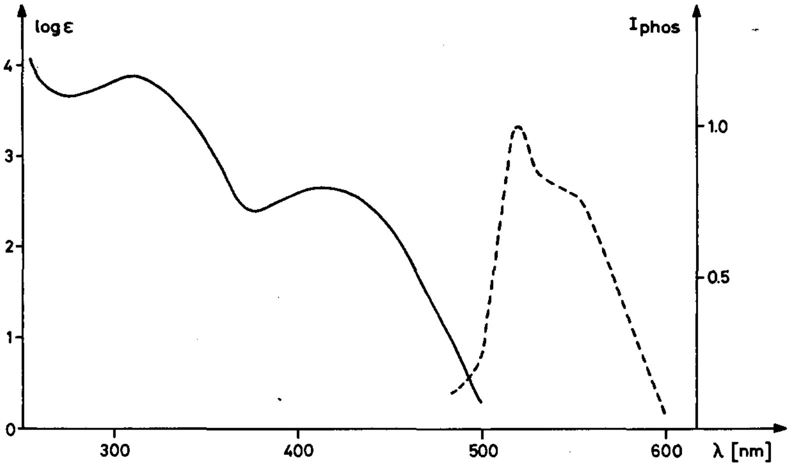

Fig. 1. (———): *UV/VIS absorption spectrum of* **1** *in cyclohexane; solution at room temperature.* (– – – –): *Uncorrected phosphorescence emission spectrum of* **1** *in alcoholic glass solution at 77 K* (I_{phos} in arbitrary units)

The lowest triplet state of the 1-thionaphthoate chromophore has been characterized [4] as predominantly $\pi\pi^*$ in character, thus explaining its low photochemical reactivity and low rate of phosphorescence as compared with other aromatic thioesters. The triplet energy estimated from the high-energy phosphorescence maximum is equal to 55 kcal/mol. In order to ascertain that the weak emission of *ca.* 1 ms lifetime observed from alcoholic glass solutions of **1** at 77 K does arise from the lowest triplet state T (**1**), we have determined the triplet energy of **1** by a second independent method, namely, the direct observation of triplet energy transfer to and from **1** by flash photolysis.

T (**1**) exhibits an intense, structureless absorption in the visible ($\lambda_{\max}$ 490 nm) with a lifetime of *ca.* 5 μs in highly dilute, deaerated solutions at room temperature. However, as noted previously [4], the triplet lifetime depends on the concentration of the parent compound **1** owing to the self-quenching process

$$\mathrm{T}\,(\mathbf{1}) + \mathbf{1} \xrightarrow{k_{sq}} \mathbf{1} + \mathbf{1}$$

The observed self-quenching rates k_{sq} are close to the diffusion controlled limit. Since exothermic triplet energy transfer is also a diffusion controlled process, it will prevail over the self-quenching as long as the acceptor concentration exceeds that of **1**. After flash excitation of **1** ($\lambda_{\max} > 400$ nm) in deaerated, 10^{-4}M benzene solutions, efficient energy transfer takes place with the following acceptor molecules: Tetracene (E_T 29.4 kcal/mol [5]), anthracene (42.0), pyrene (48.3), 1,2,3,4-dibenzanthracene (50.8), and 1,2,5,6-dibenzanthracene (52.3). The transfer was monitored by the appearance of the well-known, characteristic triplet absorption spectra [6] of the above hydrocarbons. The triplet state of chrysene (57.1) is not appreciably populated by sensitization but is quenched by **1** with a bimolecular rate constant of *ca.* $10^9 \mathrm{M}^{-1}\mathrm{s}^{-1}$ when generated by direct flash excitation. Energy transfer both to and from coronene (54.6) are slower than the rate of diffusion by at least an order of magnitude as expected [7] for molecules with nearly equal triplet energies. The triplet energy of **1** is thus bracketed in the range of 54.7 ± 2 kcal/mol.

The quantum yield Φ_T of triplet formation of **1** was estimated by comparing the intensities of the initial triplet absorption by 1,2-benzanthracene after flash sensitization with biacetyl and **1**, respectively. The experimental conditions were chosen such that (1) only a small fraction of the sensitizer and acceptor present in the solution were excited, (2) the amount of light absorbed by the two sensitizers was equal, (3) quantitative energy transfer took place within the lifetime of the excitation flash (5 μs), and (4) the acceptor triplet decayed by first order kinetics. Using Φ_T (biacetyl) $= 0.998$ as a reference value [8] we obtained $\Phi_T\,(\mathbf{1}) = 1 \pm 0.1$, where the considerable systematic errors possibly arising from deviations from condition (2) above and from an error of the reference value are not accounted for. This result supports our earlier conclusion [4] that intersystem crossing in aromatic thioesters is very fast and efficient.

Quantum yields of disappearance of **1** in the absence of triplet energy acceptors were estimated for 436 nm excitation using a split-beam apparatus described earlier [1]. Values of $<10^{-4}$, $<6 \cdot 10^{-5}$, and *ca.* $2 \cdot 10^{-3}$ were obtained with 10^{-4}M solutions of **1** at room temperature in cyclohexane, benzene, and 2-propanol, respectively.

Conclusion. – O-Ethyl-1-thionaphthoate (**1**) provides a convenient photochemical sensitizer with a spectrum of properties not previously available [9]:

absorption up to 500 nm; near unit quantum yield of intersystem crossing; relatively high triplet energy of 55 ± 1 kcal/mol; low photochemical and thermal reactivity.

The diffusion-controlled self-quenching of triplet excited **1** by parent **1** should be of no consequence in preparative experiments. When dealing with highly dilute samples suitable for UV.-spectrophotometric monitoring, however, it must be kept in mind that energy transfer will be efficient only as long as the acceptor concentration exceeds that of **1**.

Experimental Part

In cooperation with Mr. *R. Eggenberger*, Mr. *H.-J. Grass*, and M. *E. Rommel*.

The flash photolysis equipment has been described [1]. The aromatic hydrocarbons used in the energy transfer experiments were purified by column chromatography, recrystallization and sublimation until their triplet absorption spectra were in agreement with literature [6].

Synthesis of O-ethyl-1-thionaphthoate **1**. Sodium hydride (9.6 g, *Fluka, pract.*) was suspended in dry dimethoxyethane (50 ml) cooled to 0°. Abs. ethanol (3 ml) in dimethoxyethane (10 ml) was added dropwise. When the evolution of hydrogen had ceased the solution was heated to reflux for ten minutes. After recooling to 0° a solution of carboxymethyl-1-dithionaphthoate (**2**) [10] (2.62 g) in dimethoxyethane (50 ml) was slowly added. Again the solution was refluxed for ten minutes and cooled down to room temperature. After careful addition of 300 ml of water the reaction mixture was extracted with three 100 ml portions of diethyl ether. The extract was dried over calcium chloride. Evaporation of the solvent yielded 1.8 g of raw **1** as a yellow oil. Chromatography on alumina (*Merck*, neutral) with petroleum ether and crystallization from pentane at – 78° gave pure **1** (1.16 g, 54%) as bright yellow crystals, m.p. 41°. – NMR. ($CDCl_3$, int. TMS): δ 1.57 (*t*, $J = 7$ Hz, 3 H); 4.86 (*q*, $J = 7$ Hz, 2 H); 7.5 (*m*, 3 H); 7.9 (*m*, 3 H), and 8.28 ppm (*m*, 1 H).

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