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PHOTOLYSIS OF CYCLIC ENOL ESTERS IN THE PRESENCE OR ABSENCE OF A SINGLE ELECTRON TRANSFER PHOTOSENSITIZER

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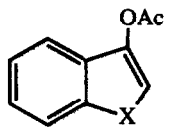
Abstract. The photochemistry of enol esters **1** is dominated by electrocyclic ring opening (**1b** → **3** + **4**), 1,3-acyl migration (**1c,d** → **6c,d**) and [2 + 2] dimerization (**1d** → **11**) Photosensitization with triphenylpyrylium tetrafluoroborate (TPT) enhances formation of oxidation products (**1b** → **5**, **1c,d** → **9c,d** + **10c,d**), presumably through the intermediacy of radical cations **1b-d** +

INTRODUCTION

Some time ago we examined the photochemistry of 4-acetoxy-2H-chromene (**1a**), which was found of interest due to competition between the well established enol acetate, styrene and 2H-chromene photoreactivities [1] The incorporation of oxygen to the structures of several photoproducts pointed to the involvement of oxidation processes in the photochemistry of **1a** In view of these results, we decided to undertake a related study on three cyclic enol acetates with close structural similarities 4-acetoxy-2-phenyl-2H-chromene (**1b**), 4-acetoxy-1,2-dihydronaphthalene (**1c**) and 3-acetoxy-1H-indene (**1d**), in which the variations with respect to compound **1a** were phenyl substitution at C-2, transformation into a carbocyclic analogue and ring contraction, respectively These variations were expected to produce significant changes in the photochemical behaviour, an assumption that was later confirmed by experiment In order to gain a deeper insight into the possible involvement of oxidation processes in the photochemistry of these compounds, we also decided to carry out the irradiation of **1b-d** under single electron transfer (SET) oxidation conditions, using triphenylpyrylium tetrafluoroborate (TPT) as photosensitizer [2] The results obtained in this way were substantially different from those of the direct photolysis, although the isolation of some common products revealed a small degree of coincidence in the reaction pathways



1a X= -OCH_2-

1b X= -OCH(Ph)-

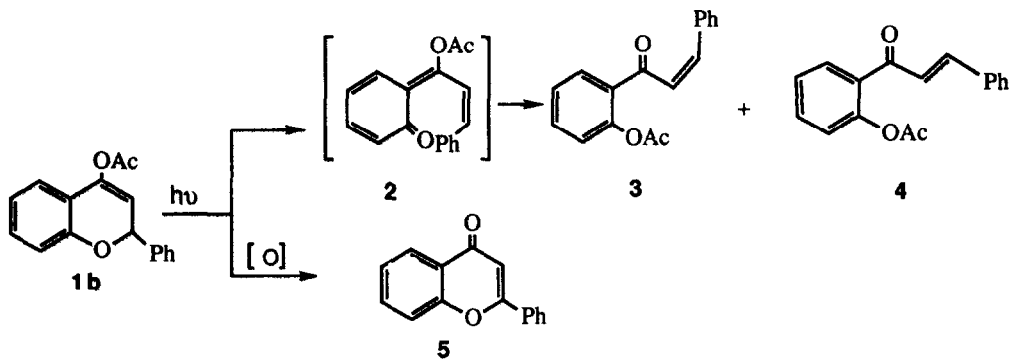
1c X= -CH_2CH_2-

1d X= -CH_2-

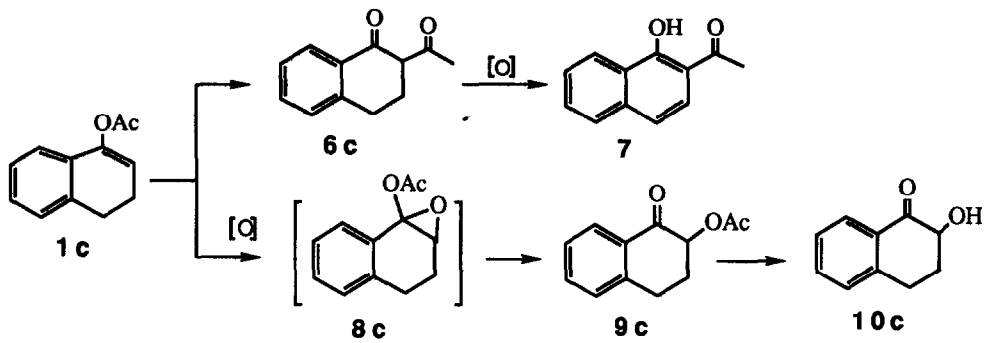
RESULTS AND DISCUSION

The required substrates were obtained by treatment of the corresponding ketonic precursors (flavanone, α-tetralone or 1-indanone, respectively) with isopropenyl acetate, in the presence of p-toluenesulfonic acid as catalyst

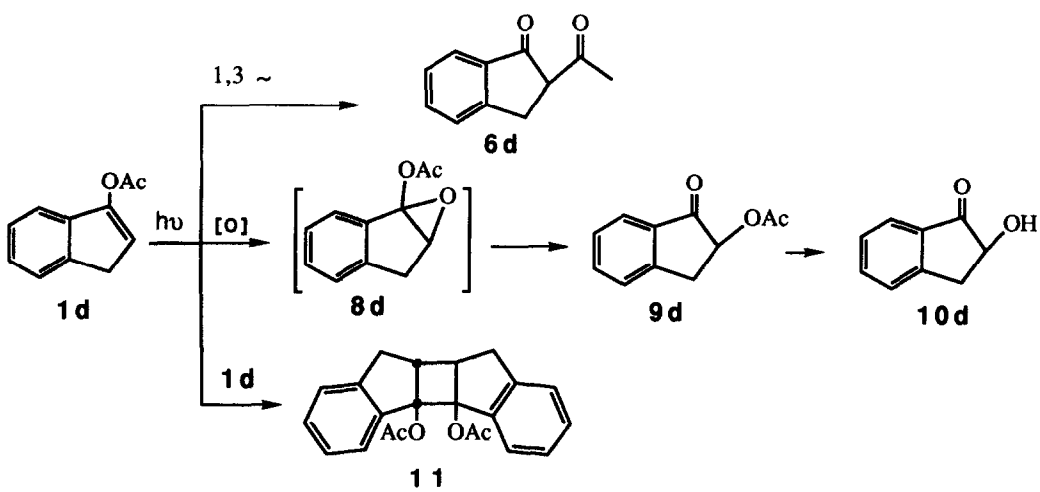
Irradiation of **1b** through quartz in hexane solution led to the formation of cis-2′-acetoxychalcone (**3**) as major product, together with small amounts of the trans-isomer (**4**) and flavone (**5**). Compounds **3** and **4** are the result of electrocyclic opening of the pyran ring, followed by transacylation of the intermediate o-quinoneallide **2** [1] Flavone is evidently an oxidation product, whose formation can be explained through several routes and shall be discussed later, together with the TPT-photosensitized experiment



When the carbocyclic analogue **1c** was irradiated under identical experimental conditions no product of ring opening was detected in the photolisate Instead, three tetralones (**6c**, **9c**, and **10c**) and the naphthol **7** were isolated from the reaction mixture Compound **6c** can be accounted for in terms of a photochemical 1,3-acyl migration of the vinyl ester moiety [3] Aromatization of its enol tautomer easily explains formation of **7** The oxygenated tetralones **9c** and **10c** must arise via a highly reactive oxirane (**8c**), which requires the involvement of air oxygen Although such intermediate was not isolated, the feasibility of this hypothesis was checked by treating **1c** with m-chloroperbenzoic acid in methylene chloride, whereby a mixture of **9c** and **10c** was obtained



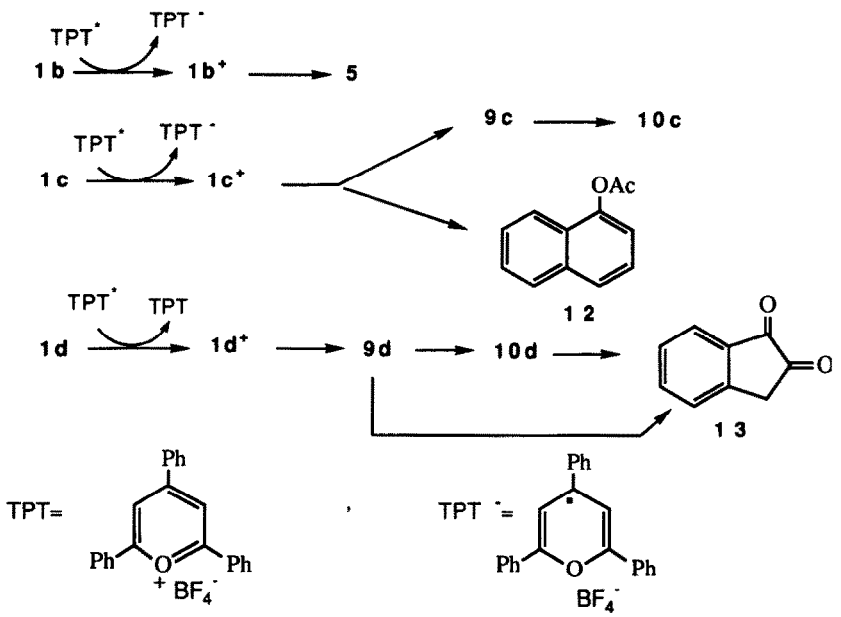
Likewise, irradiation of **1d** also afforded the 1,3-acyl migration product **6d** and the oxygenated indanones **9d** and **10d** but the major product was a 2+2 dimer (**11**) whose structure was tentatively assigned as anti head-to-head according to the following data i) its elemental analysis, satisfactory for a $C_{22}H_{20}O_4$ molecular formula, ii) its mass spectrum with significant peaks at m/z 174 $(M/2)^+$ and 263 (M^+-CH_3CO-CH_2CO), iii) its ir-spectrum, with a carbonyl band at υ=1740 cm^{-1}, iv) its ^{1}H-nmr spectrum with characteristic multiplets in the aromatic and aliphatic regions and, most significantly, an abnormally shielded acetoxy group (δ=1 80 ppm), and v) its ^{13}C-nmr spectrum, also compatible with the proposed structure



Once established the behaviour of enol esters **1b-1d** upon direct irradiation, a series of experiments were carried out using triphenylpyrylium tetrafluoroborate as single electron transfer (SET) photosensitizer To ensure light absorbtion by the latter and prevent direct excitation of the substrates, a potassium chromate solution was used as filter [4] Operating in this way, **1b** gave flavone (**5**) as single product, previously obtained in the absence of TPT in much lower yield (see above) This

result can be explained through initial transfer of one electron from **1b** to excited TPT, to give the corresponding radical cation **1b**$^+$ The subsequent steps would be the same as those accepted to operate in the anodic oxidation of cyclic enol acetates, which also involves analogous radical cations as intermediates and leads to α,β-unsaturated ketones as final products [5] Upon photosensitization with TPT, **1c** gave again the oxygenated tetralones **9c** and **10c**, in addition to α-tetralone (derived from hydrolysis of the starting enol ester **1c**) and, most significantly, a considerable amount of 1-naphthyl acetate (**12**) The latter product obviously involves dehydrogenation of **1c**, its formation being compatible with initial generation of the radical cation **1c**$^+$, followed by a deprotonation /oxidation /deprotonation sequence Analogous aromatization processes have been reported in the single electron transfer oxidation of dihydroaromatics [6]

Finally, the TPT-sensitized irradiation of **1d** produced the acetoxyketone **9d** together with 1-indanone as major products Besides, small amounts of the hydroxyketone **10d** and the diketone **13** were also formed The mechanistic pathways leading to these products would be analogous to those involved in the TPT-sensitized photolysis of **1c**, while the diketone **13** must arise from its hydroxyketone precursor **10d** by way of a second oxidation process



As a conclusion, the photochemistry of the cyclic enol esters **1b**, **1c** and **1d** is dominated by electrocyclic ring opening, 1,3-acyl migration and [2+2] dimerization, respectively Other minor products are obtained, whose formation involves oxidation of the starting enol esters These products are obtained in much higher yield when triphenylpyrylium tetrafluoroborate (TPT) is employed as single electron transfer photosensitizer, presumably through the intermediacy of the radical cations **1b**$^+$, **1c**$^+$ or **1d**$^+$

EXPERIMENTAL

General. M ps were determined with a Buchi 510 apparatus and are uncorrected Ir-spectra were obtained in CCl_4 solns with a Perkin Elmer Model 781 spectrometer, υ max (cm^{-1}) is given only for the carbonyl absorption bands ^{1}H-nmr were measured in CCl_4 with a 60-MHz Varian 360 EM instrument, chemical shifts are reported in δ(ppm) values, using TMS as internal standard The ^{1}H-nmr and ^{13}C-nmr spectrum of **11** was recorded with a 300 MHz Varian Model Gemini spectrometer, the signals are reported in δ(ppm) referenced to TMS Mass spectra were determined using a Hewlett-Packard 5988 A spectrometer, the ratios m/z and the relative intensities (%) are indicated for the significant peaks The combustion analyses were performed at the Instituto de Química Bio-Orgánica of C S I C in Barcelona Isolation and purification were done by flash column chromatography on silica gel Merck 60, 70-230 mesh, using hexane as eluent, or alternatively by means of a Waters isocratic HPLC equipment provided with a semipreparative microporasil column, using hexane-ethyl acetate as eluent

Preparation of cyclic enol esters.

The required enol esters **1b-d** were prepared by heating 4 46 mmol of flavanone, α-tetralone or 1-ndanone with 25 ml of isopropenyl acetate and 100 mg (0 58 mmol) of p-toluenesulphonic acid, under continuous removing of the resulting acetone by distillation

4-Acetoxy-2-phenyl-2H-chromene (**1b**) (600 mg, 60%), oil, ir 1765 (ester), ^{1}H-nmr 8 10-6 55 (m, 9H, Ar-H), 6 01 (d, J=2 Hz, 1H, H at C-3), 5 57 (d, J=2 Hz, 1H, H at C-2), 2 30 (s, 3H, COCH_3), Ms 266(17), 223(100), 207(28), 165(17), 147(79), 121(28), 120(24)

4-Acetoxy-1,2-dihydronaphthalene [7] (**1c**) (620 mg, 74%), m p 54-56 °C, analysis C 76 28 H 6 27% (Calcd for $C_{12}H_{12}O_2$ C 76 17 H 6 15%) ir 1765 (ester), ^{1}H-nmr 7 30-7 00 (m, 4H, Ar-H), 5 65 (t, 1H, H at C-3), 3 12-2 32 (m, 4H, H at C-2 and C-1), 2 25 (s, 3H, COCH_3)

3-Acetoxy-1H-indene (**1d**) (550 mg , 71%), m p 45-46 °C, analysis C 75 94 H 5 96% (Calcd for $C_{11}H_{10}O_2$ C 75 85 H 5 78%); ir 1760 (ester), ^{1}H-nmr· 7 25 (s, 4H, Ar-H) , 6 32 (t, 1H, H at C-2), 3 37 (d, J=2 Hz, 2H, H at C-1), 2 20 (s, 3H, $COCH_3$)

General Irradiation Procedure

A soln of 500 mg of the substrate in 300 ml of distilled hexane was placed in an immersion well photoreactor, provided with a quarz sleeve and a 125 W medium presure Hg lamp, and irradiated for 6 h

TPT sensitized photolysis of the substrate (500 mg) was accomplished in CH_2Cl_2 solution (300 ml) in the presence of catalytic amounts of TPT (40 mg) The solution was irradiated during 1 h inside a pyrex immersion well photoreactor, using an aqueous K_2CrO_4 solution (100 mg/ml) as filter

The photoproducts were isolated, after removal of the solvent, with silica gel flash-column chromatography, using hexane as eluent

Irradiation of *4-acetoxy-2-phenyl-2H-chromene* (**1b**) Irradiation of **1b** (500 mg, 1,87 mmol) in hexane afforded the following products starting material (50 mg, 10%), *flavone* [2d] (**5**) (30 mg, 7%), *cis -2'-acetoxychalcone* (**3**) (300 mg, 61%), oil, analysis C 76 76 H 5 32% (Calcd for $C_{17}H_{14}O_3$ C 76 66 H 5 31%), ir 1760 (ester), 1670 (ketone), ^{1}H-nmr 8 09-7 02 (m, 9H, Ar-H), 7 02 (d, J=12 Hz, 1H, CH=CH-Ph), 6 52 (d, J=12 Hz, 1H, CO-CH=CH), 2 29 (s, 3H, $COCH_3$), Ms 266 (5), 224 (59), 223 (100), 207 (33), 165 (21), 147 (99), 121 (46), 120 (50), *trans-2'-acetoxychalcone* (**4**) (94 mg, 19%), m p 66-67 °C, analysis C 76 80 H 5 30% (Calcd for $C_{17}H_{14}O_3$ C 76 66 H 5 31%), ir 1760 (ester), 1670 (ketone), ^{1}H-nmr 8 02-7 05 (m, 10H, Ar-H +CH=CH-Ph), 6 85 (d, J=18 Hz, 1H, CO-CH=CH), 2 10 (s, 3H, $COCH_3$), Ms 266 (8), 224 (57), 223 (100), 207 (29), 165 (20), 147 (99), 121 (39), 120 (54)

Irradiation of *4-acetoxy-1,2-dihydronaphthalene* (**1c**). Irradiation of **1c** (500 mg, 2 65 mmol) in hexane gave rise to the following products starting material (35 mg, 7%), *2-acetyl-1-tetralone* [8a] (**6c**) (79 mg,16%), *1-hydroxy-2-acetonaphthone* [9] (**7**) (42 mg, 9%), *2-acetoxy-1- tetralone* [10] (**9c**) (70 mg, 13%), *2-hydroxy-1-tetralone* [10] (**10c**) (94 mg, 22%)

Irradiation of *3-acetoxy-1H-indene* (**1d**) Irradiation of **1d** (500 mg, 2 87 mmol) in hexane afforded the following products starting material (100 mg, 20%), *2-acetylindanone* [8] (**6d**) (83 mg, 16%), *2-acetoxyindanone* [11] (**9d**) (56 mg, 10%), *2-hydroxyindanone* [11] (**10d**) (21 mg, 5%), *anti-1,2-diacetoxydibenzo [c,i] tricyclo [5 3 0 0 ^{2,6}] decane* (**11**) (309 mg, 31%), m p 97-99 °C, analysis C 75 84 H 5 78%

(Calcd for $C_{22}H_{20}O_4$ C 75 70 H 5 55%), ir 1740 (ester), ^{1}H-nmr 7 68-7 22 (m, 8H, Ar-H), 3 86 (d, J=15 Hz, 1H, H at C-5), 3 55 (dd, J=15 Hz, and J=5 Hz, 1H, H at C-5), 2 33 (d, J=5 Hz, 1H, H at C-6), ^{13}C-nmr 169 75, 146 53, 140 33, 129 89, 127 72, 126 95, 126 11, 91 68, 45 70, 38 47, 20 89, Ms 264 (1), 263 (3), 174 (23), 132 (100), 43 (71)

TPT-sensitized photolysis of enol esters **1b-d**

TPT-sensitized photolysis of **1b** afforded *flavone* (**5**) (283 mg, 68%)

TPT-sensitized photolysis of **1c** afforded **9c** (94 mg, 35%), **10c** (25 mg, 6%) and *1-naphthyl acetate* [9] (**12**) (33 mg, 26 %)

TPT-sensitized photolysis of **1d** afforded **9d** (219 mg, 40 %), **10d** (17 mg, 4%) and *1,2-indandione* [12] (**13**) (20 mg, 5%)

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