STRUCTURE OF THE INTERMEDIATE FORMED IN THE SYNTHESIS OF SYMMETRICAL PYRYLIUM IONS

M.-C. GAZEAU†, M. SIMALTY, P. VALAT, V. WINTGENS AND J. KOSSANYI*

CNRS, 2–8 rue Henri Dunant, 94320 Thiais, France

D. DOIZI, G. SALVETAT AND J. JARAUDIAS

DCC–DPE–SPL, CEN Saclay, 91191 Gif sur Yvette, France

B. PERLY

DSM–DRECAM–SCM, CEN Saclay, 91191 Gif sur Yvette, France

J. VIAN AND J.-L. PEGLION

Institut de Recherche SERVIER, 11 rue des Moulineaux, 92150 Suresnes, France

The synthesis of symmetrical blocked pyrylium derivatives by reaction of a cyclic aromatic ketone with ethyl orthoformate goes through an intermediate which can be isolated under certain conditions. This intermediate is unstable when starting from 1-tetralone derivatives but, surprisingly, it can be isolated easily when the synthesis is performed with 1-indanone derivatives. Further, in the latter case, this intermediate cyclizes hardly into the expected blocked pyrylium derivative. Its ionic structure was demonstrated by mass spectrometry and by 500 MHz ^{1}H and ^{13}C NMR techniques including heteronuclear H–C COSY and DEPT polarization transfer experiments. Hydrolysis of this intermediate in aqueous ethanol solution forms, in acidic or basic media, a pseudo-base, which in the latter case presents strong similarities with that obtained by the base-catalysed ring-opening of a blocked pyrylium ion. In both acidic and basic solutions, the pseudo-base obtained by the two sources shows identical UV–visible absorption spectra. The difficulty of the intermediate (g) originating from 1-indanone derivatives in cyclizing into the blocked pyrylium structure, in contrast to the intermediate formed from 1-tetralone derivatives, is tentatively explained.

INTRODUCTION

Pyrylium salts constitute a series of heterocycles which exhibit an important electron acceptor character[1] due to their cationic structure. This property has received a considerable attention with regard to their use as sensitizers toward photoconductors[2] and in electrophotoreprographic techniques[3] where they trap electrons and allow the migration of positive holes towards a negatively charged electrode.

Many of the pyrylium salts show an efficient fluorescence emission,[4] which led them to be proposed as laser dyes[5]. Blocking the rotation of the phenyl substituents at positions 2 and 6 on the heterocycle markedly increases the fluorescence efficiency.[6]

During the preparation of the symmetrical molecules by condensation of ethyl formate with two molecules of 1-indanone or 1-tetralone derivatives, a coloured transient intermediate was formed which was rapidly transformed in air or in the presence of 95% ethanol into the final pyrylium ion. This intermediate, red, blue or green depending on the starting ketone, was observed during the formation of compounds 2–4 and 6.

In the absence of oxygen, and mainly of the alcoholic solvent, this intermediate could be kept several days, and its UV–visible absorption spectrum

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1

2 n = 1 , R = H , X = ClO$_4^-$

3 n = 2 , R = H , X = ClO$_4^-$

4 n = 2 , R = OMe, X = BF$_4^-$

5

6

7

could be recorded in several instances. Crystals isolated during the synthesis were tentatively submitted to an x-ray analysis but, unfortunately, the compound decomposed too rapidly when exposed to the x-ray beam or even before.

The formation of such a coloured intermediate was found to be general with blocked molecules substituted or not by a methoxy group along their long axis. We were fortunate during the synthesis of compound **5** that the reaction stopped at a blue intermediate, and proceeded with difficulty towards **5**, even in the presence of ethanol. The high stability of this intermediate enabled us to measure all the analytical and spectroscopic data for characterizing its structure.

RESULTS AND DISCUSSION

Synthesis

2,6-Di(paramethoxyphenyl)pyrylium ion (**1**) was prepared in one step by the reaction of p-methoxyacetophenone with triethyl orthoformate used as a solvent

in the presence of concentrated sulphuric acid following an extension of the procedure already described.[7]

The same reaction applied to 1-indanone or 1-tetralone, substituted or not by a methoxy group on the aromatic ring in the para position to the carbonyl group, leads to the formation of the symmetrical tetrahydrodibenzo[c,h]xanthylium ions **2–4**, unsubstituted at position 7.

Compound **6**, similar to **4** but without the possibility of rotation of the methoxy substituents, was synthesized following the general procedure from 2,3,7,8-tetrahydronaphtho[2,3b]furan-5(6H)-one (**7**), which was prepared[8] from 4-(2,3-dihydro-5-benzofuranyl)butanoic acid (**8**).

Fluorescence emission

The compounds were excited at the maximum of their long-wavelength absorption band. All of them exhibit (Figure 1) an intense fluorescence in both weakly polar (dichloromethane, $\varepsilon = 9\cdot1$) and strongly polar (acetonitrile, $\varepsilon = 37\cdot5$) solvents (Table 1). The position of the

Table 1. Absorption maxima and fluorescence maxima, decay and quantum yields of compounds **1–6** in different solvents (excitation at the maximum of the absorption band)

| Compound | CH$_3$CN | | | | CH$_2$Cl$_2$ | | | | CH$_3$COOH | | | |
	λ_{max}^{abs} (nm)	λ_{max}^{f} (nm)	τ_s (ns)	Φ_f	λ_{max}^{abs} (nm)	λ_{max}^{f} (nm)	τ_s (ns)	Φ_f	λ_{max}^{abs} (nm)	λ_{max}^{f} (nm)	τ_s (ns)	Φ_f
1	463	546	4·0	0·85	488	536	3·9	0·91				
2	432	480[a]	3·9[a]	0·54[a]	449	485[a]	3·6	0·78				
3	445	492	4·8	1·0	462	499	4·1	1·0				
4	496	567	5·5	0·88	524	566	5·3	0·84	500	567	5·33	1·0
6	520	595	6·0	0·94	547	595	5·8	0·87				

[a] From Ref. 6 and 9.

Figure 1. Absorption and fluorescence spectra of (solid line) compound **2** $(2 \cdot 5 \times 10^{-6}$ M) and (dashed line) compound **6** $(2 \times 10^{-6}$ M) in dichloromethane solution

fluorescence in these two solvents does not vary markedly (by less than 10 nm) although the absorption is blue-shifted in acetonitrile.

The variation of the difference $\Delta\bar{\nu}$ between the absorption and the fluorescence maxima can be taken as an indication of the change in dipole moment of the molecule in its excited state as compared with its ground state.[10] The higher the variation observed for this difference between a polar and a non-polar solvent, the greater is the change in dipole moment. Lippert's Δf function[11] of the solvent can be used to measure this variation. In the present case, the $\Delta(\bar{\nu}_{abs} - \bar{\nu}_f)$ value measured between acetonitrile and dichoromethane (for which Δf varies from $0 \cdot 305$ to $0 \cdot 218$, respectively) for the different compounds is $1400\ \mathrm{cm}^{-1}$ for **1**, $660\ \mathrm{cm}^{-1}$ for **2**, $505\ \mathrm{cm}^{-1}$ for **3**, $1110\ \mathrm{cm}^{-1}$ for **4** and $950\ \mathrm{cm}^{-1}$ for **5**. Values higher than $4000\ \mathrm{cm}^{-1}$ are usually observed when the change in dipole moment between the ground state and the excited state is large. Hence it can be postulated safely in the present case that the dipole moment of the excited state is not very different from that of the ground state. This is not the case for the derivatives of the tetrahydrodibenzo[c,h]xanthylium ion when they are unsubstituted at positions 3 and 11 but have an anisyl group at pos-

ition 7; then, the dipole moment of the molecule varies by $\Delta\mu = 18$ D between the ground state and the excited state.[12] The small difference found here has been verified with compound **4** by using solvents of various polarities. The following $\Delta\bar{\nu}$ values were obtained: $2000\ \mathrm{cm}^{-1}$ in chloroform $(\varepsilon = 4 \cdot 8)$, $1880\ \mathrm{cm}^{-1}$ in 1-chloropentane $(\varepsilon = 6 \cdot 6)$, $1700\ \mathrm{cm}^{-1}$ in dichloromethane $(\varepsilon = 9 \cdot 1)$, $2360\ \mathrm{cm}^{-1}$ in butyronitrile $(\varepsilon = 19 \cdot 0)$, $2450\ \mathrm{cm}^{-1}$ in ethanol $(\varepsilon = 24 \cdot 6)$ and $2380\ \mathrm{cm}^{-1}$ in acetonitrile $(\varepsilon = 37 \cdot 5)$.

Structure of the intermediate 9 formed during the synthesis of 5

The product crystallizes as blue plates which were unfortunately too thin for correct x-ray analysis. On the other hand, elemental analysis indicated that the species is associated with one equivalent of the hydrogensulphate anion HSO_4^-; therefore, this intermediate must have an ionic character.

No intermediate could be observed during the synthesis of the non-blocked pyrylium ion **1**. In the 5,6,8,9-tetrahydrodibenzo[c,h]xanthylium series, the intermediate formed during the synthesis is transitory, which impedes an extended study. Nevertheless, when

synthesizing **3**, an intermediate can be characterized which absorbs at 532 and 572 nm in methanol and at 530 and 564 nm in 2,2,2-trifluoroethanol. Similarly, the intermediate in the preparation of **4** gives two bands at 560 and 608 nm in methanol and at 580 and 622 nm in dichloromethane solution.

A major difference is observed between the intermediates in the tetrahydrodibenzo[*c,h*]xanthylium series (**3** and **4**) and the bisindeno[1,2*b*;2,1-*c*]pyrylium series (**2** and **5**), in that the absorption of the first two intermediates presents two bands apparently corresponding to a single structure, whereas that of the intermediate formed from **2** shows four well separated bands above 490 nm, which could be attributed to two different structures. The pink intermediate formed during the synthesis of **2** shows four bands at 496, 510, 528 and 548 nm in 2,2,2-trifluoroethanol, which are blue shifted to 500, 520, 540 and 560 nm in dichloromethane.

The long-wavelength UV–visible absorption spectrum of intermediate **9** has a maximum at 594 nm with a less intense band around 550 nm in chloroform solution (Figure 2). This absorption evolves slowly with time in this solvent, being blue shifted by 44 nm, to give two new maxima at 550 and 510 nm, respectively. In trifluoroacetic acid, intermediate **9** is stable and

shows (Figure 2) the same absorption maxima at 550 and 510 nm; evaporation of CF_3COOH and redissolution of the remaining product in chloroform gives back the original spectrum, with two bands at 550 and 594 nm, as was found when **9** was dissolved directly in chloroform. In 2,2,2-trifluoroethanol, **9** absorbs at 535 and 574 nm, while these bands are found at 546 and 586 nm in dichloromethane.

Two hypotheses can be put forward to explain the fact that the absorption of **9** in trifluoroacetic acid is red shifted from 550 to 594 nm after evaporation of the solvent and redissolution in chloroform. First, it could originate[13] from a simple solvent-induced blue shift if the molecule is more polar in the ground state than in the excited state; this would mean that, in the ground-state molecule, the positive charge is localized whereas it is symmetrically delocalized in the excited state; on the other hand, the blue shift of the absorption observed with time in chloroform solution would be initiated by the small quantities of methanol present in the solvent to prevent its oxidation, and oxidized to formic acid. The other hypothesis attributes the change in absorption to an isomerization, e.g. an *E–Z* interconversion around a double bond. In such a case, the six-membered heterocycle of the molecule must be open, and, consequently, it should be possible to perform a photochemical *E–Z*
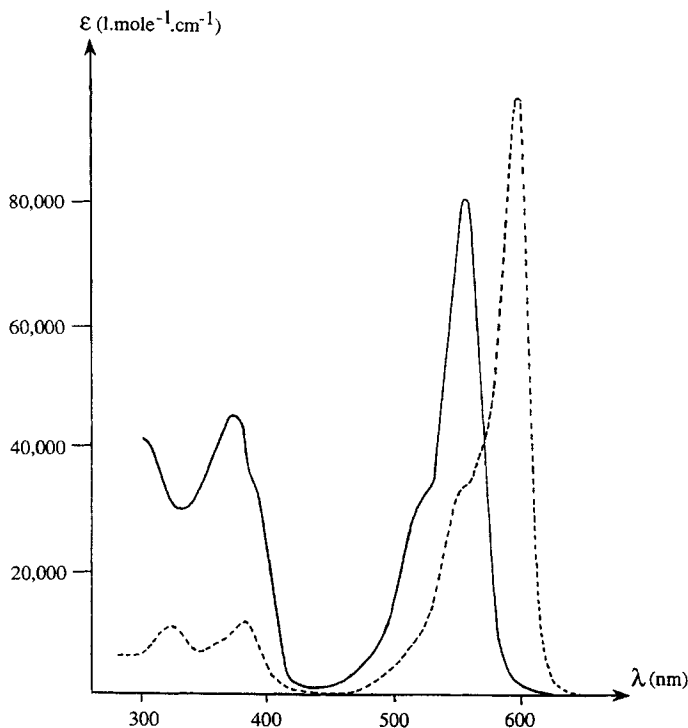

Figure 2. Absorption of intermediate **9** (dashed line) in $CHCl_3$ solution and (solid line) in CF_3COOH solution

conversion if the double bond is not in a ring. However, all attempts to obtain such a transformation failed; therefore, we can exclude this hypothesis and keep the first one.

If the heterocycle is open, the structure of the coloured intermediate should be closely related to that of the pseudo-base obtained by ring-opening of the pyrylium ion under basic conditions. The pseudo-base 10 was synthesized from 2 following the procedure described by Berson[14]. It exists as two different species (Figure 3), depending on the pH of the medium: in acidic or in 2,2,2-trifluoroethanol solution, it has the typical structure of the unsaturated diketone 10a and absorbs at 405 nm, whereas in basic medium (ethanol containing $NaHCO_3$) it has the enolate structure 10b which extends the conjugation over the whole molecule, and red shifts its absorption to 531 nm (the most intense) and 499 nm.

Hydrolysis of intermediate 9 in acidic or basic media

leads to the pseudo-base which presents spectroscopic properties (Figure 3) similar to those of 10: diketone 10a absorbs at 424 nm in a 1:1 ethanol–water mixture containing a small amount of sulphuric acid whereas the keto-enol form is characterized in basic medium (ethanol saturated with Na_2CO_3) by absorption at 490 and 525 nm.

In the dibenzoxanthylium series, the diketo form obtained from 3 absorbs at 424 nm in a 1:1 ethanol–water mixture and the corresponding keto-enol form shows two bands at 520 and 550 nm (in Na_2CO_3-saturated ethanol solution). Similarly, 4 has an keto-enol form which absorbs at 516 and 550 nm in ethanol-water mixtures containing sodium hydroxide.

These results indicate that the methoxy groups attached to the aromatic rings of the keto-enol form of 4 and of intermediate 9 have no net influence on their absorption spectra, as deduced from the comparison of the derivatives originating from 2 and 9 on the one
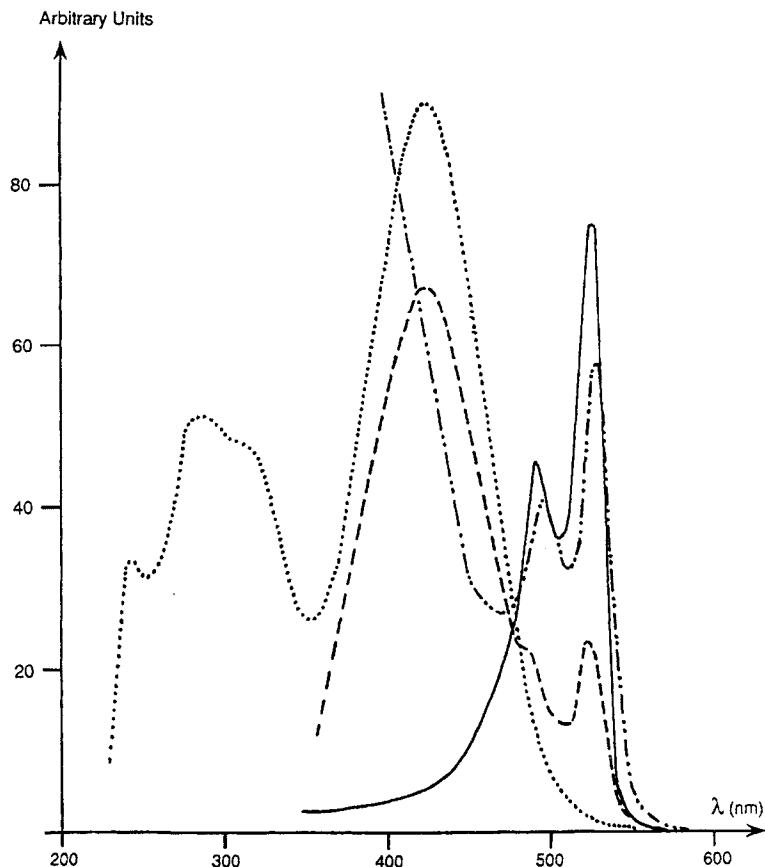
Figure 3. Absorption of the pseudo-base 10 obtained from 2 in (dashed line) H_2SO_4–H_2O–C_2H_5OH and (solid line) Na_2CO_3–H_2O–C_2H_5OH and absorption of the pseudo-base formed from 9 in (dots) H_2SO_4–H_2O–C_2H_5OH and (dashes and dots) Na_2CO_3–H_2O–C_2H_5OH
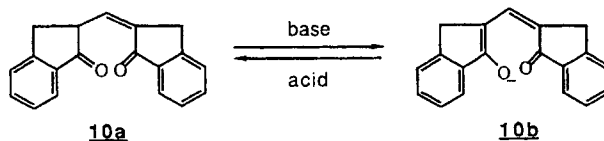
hand, and from **3** and **4** on the other, these derivatives showing very similar absorption spectra in basic medium. Nevertheless, the keto-enols formed from **3** and **4**, themselves derived from 1-tetralones, present a 25 nm bathochromic shift of their absorption when compared with the absorption of their analogues formed from **2** or **9**, which themselves are formed from 1-indanones.

Thus, a structure similar to **10b**, with substantial conjugation over the whole molecule, including the two methoxy groups which shift the absorption by *ca* 50 nm to the red, could correspond to intermediate **9**.

In addition, the fast atom bombardment mass spectrum gives (Figure 4) a molecular ion as base peak at m/z 391 (100%); it loses successively 28 mass units (C_2H_4) to give an ion at m/z 363 (5%) and 46 mass units (C_2H_5OH) leading to m/z 317 (20%), which now has the structure of the dibenzopyrylium ion. The ion at m/z 363 also loses 2 mass units, forming an ion at m/z 361 (20%) which, in turn, eliminates 28 mass units to give an ion at m/z 333 (46%).

The NMR data give important information about its structure. The ^1H NMR spectrum (Figure 5) indicates a symmetrical structure for intermediate **9** with two CH_3—CH_2—O— chains (6H as a triplet at 1·44 ppm with $J = 7·1$ Hz, and 4H as a quadruplet at 4·78 ppm
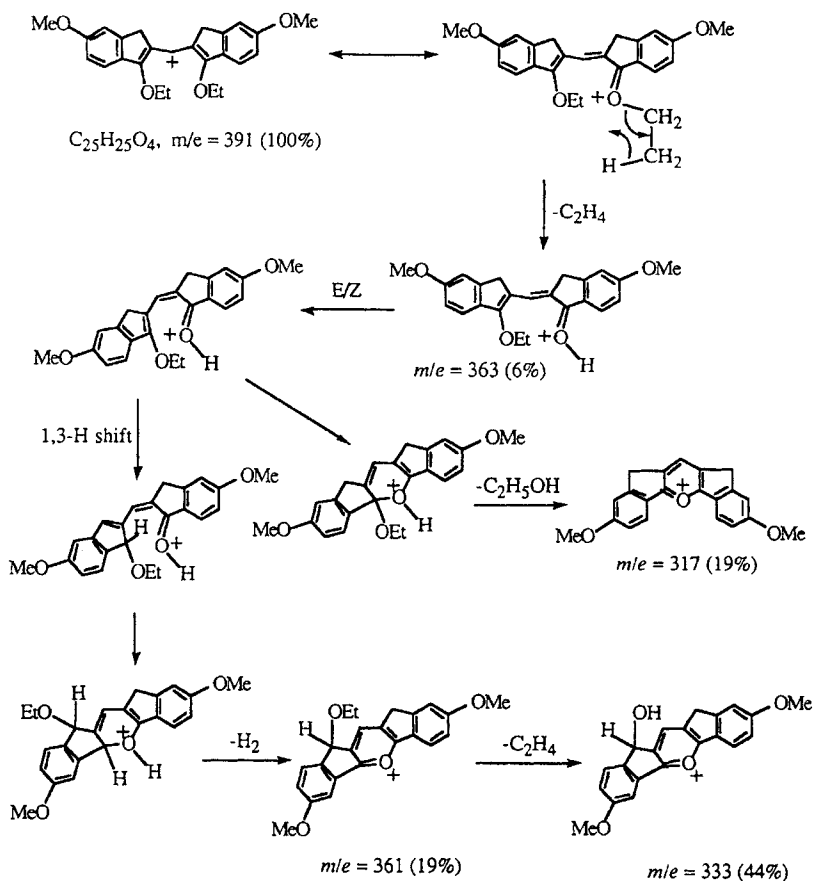
Figure 4. Mass spectrometric fragmentation of intermediate **9**
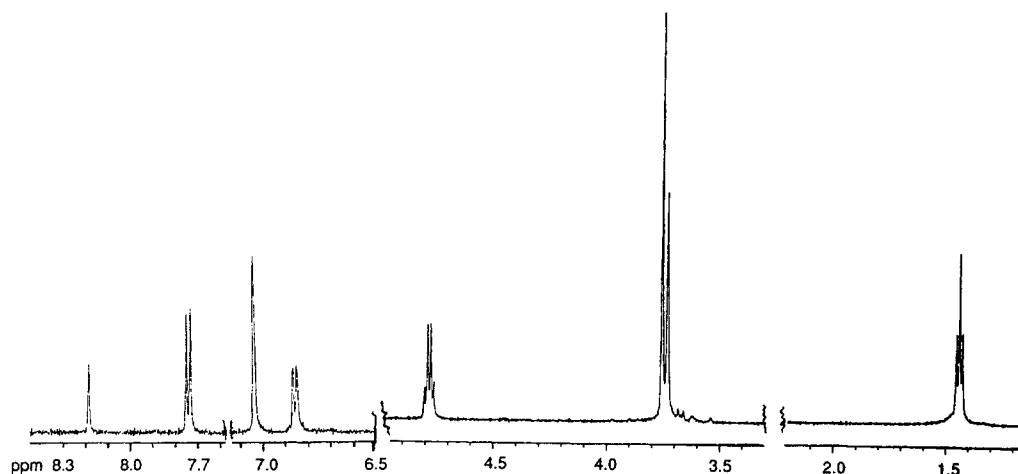
Figure 5. 500 MHz ^{1}H NMR spectrum of intermediate 9 in CD_2Cl_2 solution

with $J = 7\cdot1$ Hz) and two methoxy substituents (6H as a singlet at 3·75 ppm); the four protons of the five-membered rings appear as a singlet at 3·72 ppm.

Seven protons are found in the deshielded region, one doublet (2H, $J = 8\cdot8$ Hz) at 6·83 ppm, one singlet (2H) at 7·02 ppm, one doublet (2H, $J = 8\cdot8$ Hz) at 7·75 ppm while the proton attached to the positively charged carbon atom appears as one singlet (1 H) at 8·21 ppm.

The ^{13}C NMR spectrum of this blue intermediate is indicative and, as for the ^{1}H NMR spectra, it favours a symmetrical structure for the molecule. Two ordinary

sp^3 carbon atoms are found (Figure 6), one at 15·9 and the other at 35·3 ppm; the sp^3 carbon atoms bound to the alkoxy oxygen atoms give two signals, one at 57·2 and the other at 72·0 ppm; the sp^2 carbon atoms appear between 112·0 and 166·4 ppm.

The distinction between the CH and CH_3 groups on the one hand and the CH_2 groups on the other, obtained by DEPT polarization transfer technique, corroborates (Figure 7) the assignments made for the different carbon and hydrogen atoms.

The heteronuclear H–C COSY spectrum (Figure 8),
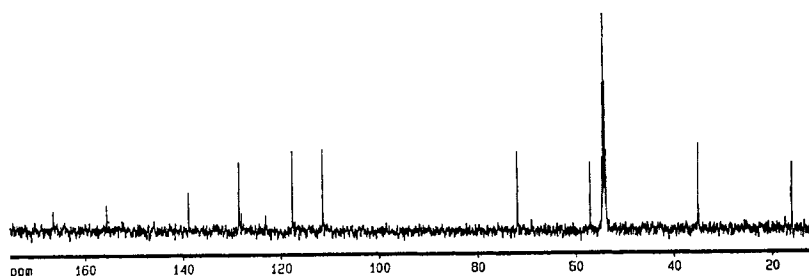
Figure 6. 125 MHz ^{13}C NMR spectrum of intermediate 9 in CD_2Cl_2 solution
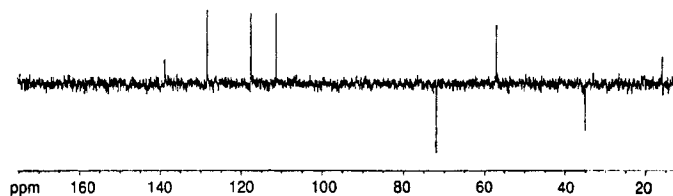

Figure 7. DEPT polarization transfer for CH_n correlation of the 125 MHz ^{13}C NMR peaks of intermediate 9 in CH_2Cl_2 solution
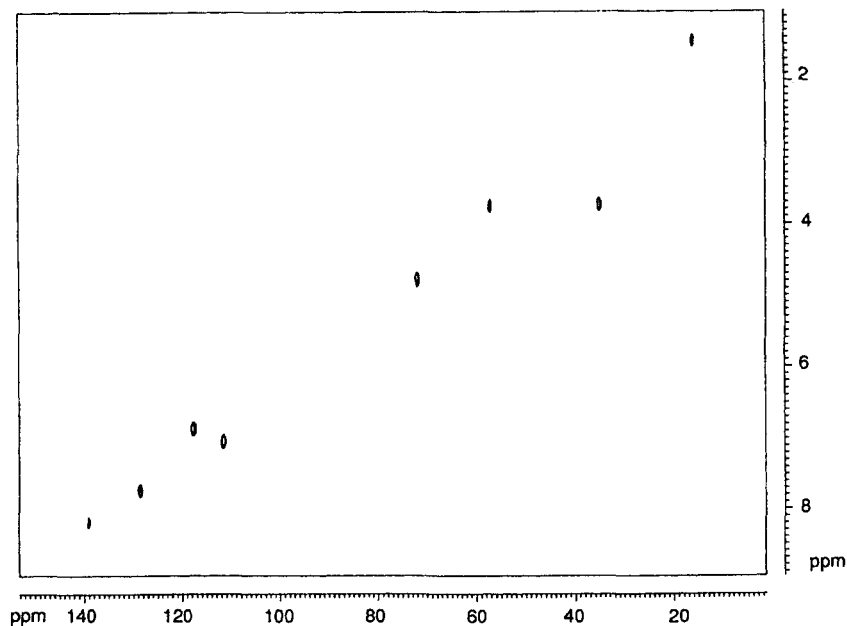
Figure 8. Heteronuclear H–C COSY spectrum of intermediate 9 in CH_2Cl_2 solution

which allows the assignment of all the hydrogen-substituted carbon atoms, corroborates the presence of two methoxy and two ethoxy groups in the molecule. It shows also that there are two series of three aromatic protons arranged in the same manner as in the starting 5-methoxy-1-indanone. Finally, it enables structure 9 to be proposed for this intermediate.

From all these data, the ionic structure of intermediate 9 should belong to one of the four possible conformations that can take the ethyl ether of the dienol form of the δ-diketone. The fact that both the ^{1}H and ^{13}C NMR spectra correspond to a symmetrical structure of ion 9 limits these conformations to 9a (R = ethyl) and 9b (R = ethyl).

Interestingly, structure 9a, the one expected to cyclize to the xanthylium ion, has the same overcrowding at the level of the ethoxy groups, whatever the size of the ring (five- or six-membered) attached to the phenyl group. However, 9b has considerable steric hindrance at the level of the saturated carbon atoms for the corresponding six-membered ring, but not for the five-membered ring. Consequently, the most stable conformation of the intermediate formed during the synthesis of 2 and 5 should favour the less crowded conformation 9b. This observation might explain the difference found between the two series of molecules with regard to their cyclization to the pyrylium ion.

EXPERIMENTAL

HPLC analysis was carried out using a Shimadzu liquid phase chromatograph equipped with a single-piston LC-10AS pump and an SPD-10AV UV–visible detector. The Kromasil column was filled with C_{18}-bonded 5 mm silica particules. The injection volume was 2·5 ml, the flow-rate of the solvent was 1 ml min^{-1} and the eluent was 75:25 methanol (for spectroscopy)–water (Waters system). The analyses were carried out at a constant temperature of 30 °C.

9a

9b
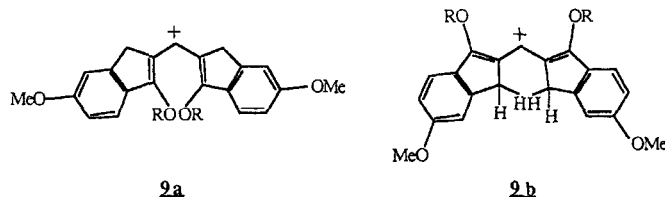
Microanalyses were performed at the Vernaison and Gif-sur-Yvette Centres of the Centre National de la Recherche Scientifique.

UV–visible absorption spectra were obtained with a Varian Cary 219 spectrophotometer and fluorescence spectra were obtained with a Model 44B spectrofluorimeter from Perkin-Elmer equipped with a DCSU2 spectral correction unit. Fluorescence emission was obtained by excitation at the maximum of the long-wavelength absorption band. The optical density at the excitation wavelength was adjusted to a value in the range 0·07–0·1, corresponding to concentrations of the order of 2×10^{-6}–5×10^{-6} M. The quantum yields were measured in various solvents by comparison with the emission from quinine sulphate (in 1 M sulphuric acid solution), for which the value 0·55 was taken.[15] Singlet lifetimes were measured by excitation with a frequency-doubled pulsed YAG laser (B. M. Industries) of 30 ps FWHM. The light was focused through a cylindrical lens on to the sample placed in front of a photodiode. The output from the photodiode was fed into a Tektronix 7912 AD digitized oscilloscope and the data, which were stored in an Apple II+ microcomputer, could be displayed on a Hewlett-Packard Model 7470A graphic plotter. Averaged decays could be analysed directly by the microcomputer.

NMR spectra were obtained at 298 K on a Bruker AMX500 spectrometer operating at 500·13 and 125·77 MHz for ^{1}H and ^{13}C, respectively. Solutions (20 mg ml^{-1}) in deuterated methylene chloride (CEA, France) were used. Chemical shifts are given relative to tetramethylsilane (TMS). ^{13}C NMR spectra were recorded in the presence of composite pulse decoupling of the protons. The multiplicity selection between quaternary, methine, methylene and methyl carbons was derived from a DEPT polarization transfer experiment. The carbon–proton connectivity pattern was derived from a two-dimensional C–H correlation in the direct mode. A BIRD pulse sequence was used to suppress vicinal H–H couplings in the F_1 dimension.

Solvents for spectroscopic measurements, ethanol (Prolabo, RP grade), chloroform (Prolabo, Chromanorm quality) and dichloromethane (Merck, HPLC quality) were used as received. Acetonitrile (Aldrich, HPLC grade) was purified by column chromatography over alumina and distilled before use.

4-(2,3-Dihydro-5-benzofuranyl)-4-oxobutanoic acid (11).

To a suspension of 30 g (0·25 mol) of 2,3-dihydrobenzofuran and 32 g (0·24 mol) of aluminium chloride in 65 ml of 1,2-dichloroethane, cooled to 0 °C, is added a mixture of 24 g (0·24 mol) of succinic anhydride and 65 g (0·49 mol) of aluminium chloride in 130 ml of 1,2-dichloroethane. The addition is such that the temperature is kept below 5 °C. After the addition, the mixture is stirred for 2 h at 5 °C, then poured into 750 ml of water containing 100 ml of concentrated hydrochloric acid. After extraction with methylene chloride, the organic layers are extracted with 1 M aqueous sodium hydroxide until all the product is transferred into the aqueous layer. Acidification of the latter with 6 M HCl releases the expected compound as an oil, which is extracted with methylene chloride. The organic layer is then washed with water and dried (MgSO$_4$). Distillation of the solvent gives 35·7 g of **11** (65% yield), m.p. 138 °C.

IR (Nujol): 3000–2500, 1699, 1670, 1603, 1244, 1012 and 939 cm^{-1}. NMR (CDCl$_3$ + DMSO – d_6): δ (ppm) 2·45 (2H, m), 3·16 (4H, m), 3·23 (2H, m), 4·63 (2H, t, $J = 8·8$ Hz), 6·80 (1H, d), 7·8 (2H, m) and 10·9 (1H, s, displaced by D$_2$O).

4-(2,3-Dihydro-5-benzofuranyl)butanoic acid (8).

To a stirred solution of 35·7 g of **11** in a mixture of 60 ml of water, 130 ml of concentrated hydrochloric acid and 7·5 ml of toluene are added slowly 75 g of zinc and 8 g of mercury (II) chloride. The mixture is refluxed for 6 h, 35 ml of concentrated hydrochloric acid are introduced into the reactor and the mixture is stirred overnight. After cooling and decantation, the organic layer is extracted several times with 1 M aqueous sodium hydroxide. The aqueous solutions are collected, acidified with HCl and extracted with methylene chloride. The organic layer is dried (MgSO$_4$) and the solvent is evaporated to give **8**, which is crystallized from diisopropyl ether: 21·4 g (64% yield), m.p. 84–85 °C.

IR (Nujol): 3000–2600, 1709, 1643, 1248, 1045 and 943 cm^{-1}. NMR (CDCl$_3$): δ (ppm) 2·0 (2H, m), 2·4–2·5 (4H, t, $J = 7·4$ Hz), 3·2 (2H, m), 4·55 (2H, t, $J = 8·6$ Hz), 6·7 (1H, m), 6·95 (1H, m), 7·05 (1H, m) and 11·15 (1H, s, acidic).

2,3,6,7-Tetrahydronaphtho[2,3-b]furan-8(5H)-one (12).

A 21·4 g amount of **8** in 220 ml of xylene are added to a hot solution (95–100 °C) of 65 g of polyphosphoric acid in 1 l of xylene. The mixture is maintained at ca 100 °C for 0·5 h, then cooled and poured into 1 l of ice-cold water. The organic layer is separated and the aqueous phase is extracted with 2 × 100 ml of diethyl ether. The organic layers are collected, washed with 10% sodium hydrogencarbonate solution, then with 2 × 100 ml of saturated NaCl solution and dried (MgSO$_4$). The organic solvent is eliminated under reduced pressure to give compound **12**, which is recrystallized from diisopropyl ether: 11·4 g (58% yield), m.p. 67 °C.

IR (Nujol): 1668, 1614, 1265 and 1055 cm^{-1}. NMR (CDCl$_3$): δ (ppm) 2·09 (2H, quintet, $J = 6·3$ Hz), 2·62 (2H, t, $J = 6·5$ Hz), 2·89 (2H, t, $J = 6·1$ Hz), 3·22 (2H, t, $J = 8·6$ Hz), 4·58 (2H, t, $J = 8·6$ Hz), 7·09 (1H, s) and 7·40 (1H, s).

*2,3,5,6,7,8-Hexahydronaphtho[2,3-*b*]furan* **(13)**. A 27 g amount of zinc and 2·7 g of mercury (I) chloride are added to a stirred solution made from 46 ml of concentrated hydrochloric acid, 22 ml of water, 11·4 g of **12** and 30 ml of toluene. The stirred reaction mixture is refluxed for 4 h, then cooled to room temperature. The toluene layer is separated from the aqueous layer, which is extracted twice with 20 ml of toluene. The organic fractions are mixed and washed with dilute sodium hydrogencarbonate solution and with saturated sodium chloride solution. The toluene solution is dried (sodium sulphate) and the solvent is evaporated; the remaining organic liquid is distilled under reduced pressure to give 6·3 g (59% yield) of **13**, b.p. 142–144 °C (16 mmHg).

IR (film) : 1630, 1240 and 1070 cm^{-1}. NMR (CDCl$_3$): δ (ppm) 1·74 (4H, t, $J = 6·3$ Hz), 2·68 (4H, unresolved *triplet*), 3·10 (2H, t, $J = 8·5$ Hz), 4·48 (2H, t, $J = 8·6$ Hz), 6·49 (1H, s) and 6·88 (1H, s).

*2,3,7,8-Tetrahydronaphtho[2,3-*b*]furan-5(6H)-one* **(7)**. A 6·3 g amount of **13** is added to a mixture of 28 ml of acetic acid and 6 ml of propionic acid and cooled to 5 °C. Then, 150 ml of Jones's reagent[16] cooled to 5 °C are added dropwise to the reaction mixture, which is stirred for 1 h and concentrated under reduced pressure (15 mmHg). The mixture is poured into a mixture of diethyl ether (300 ml) and dilute sodium hydrogencarbonate solution (100 ml). The ether layer is separated, concentrated to 100 ml, washed with saturated NaCl solution, dried (sodium sulphate) and the solvent is evaporated. The remaining part is flash distilled (1 mmHg) to give an oil, which crystallizes slowly to give **7**, 5·85 g (88% yield), m.p. 78 °C.

IR (Nujol): 1664, 1616, 1250 and 1055 cm^{-1}. UV (hexane): λ (nm) (ε, 1 mol^{-1}cm^{-1}) 225 (14 950), 232 (15 650), 273 (13 300), 291 (6900), 297 (6500), 303 (7700), 331 (143), 344 (77) and 360 (25). NMR (CDCl$_3$): δ (ppm) 2·08 (2H, *quintet*, $J = 6·2$ Hz), 2·59 (2H, t, $J = 6·2$ Hz), 2·90 (2H, t, $J = 6·0$ Hz), 3·20 (2H, t, $J = 8·6$ Hz), 4·62 (2H, t, $J = 8·6$ Hz), 6·59 (1H, s) and 7·90 (1H, s).

General procedure for the preparation of **1–4** *and* **6**. A 0·03 mol (1·75 ml) amount of 96% concentrated sulphuric acid (sp. gr. 1·84) is added dropwise to a solution of 0·06 mol of *p*-methoxyacetophenone or of the cyclic ketone in 60 ml of ethyl orthoformate. The stirred solution becomes strongly coloured (blue or green depending on the starting material). After 2 h, 100 ml of 95% ethanol are added to the solution, the colour of which changes to orange. The pyrylium or xanthylium salt is precipitated by addition of 500 ml of diethyl ether. The mixture is filtered and the precipitate is washed with diethyl ether, then dried. The solid is dissolved in 200 ml of 95% ethanol and an equimolar proportion of lithium tetrafluoborate is added while

stirring. The pyrylium or xanthylium ion precipitates as the tetrafluoborate. The solid is collected, washed with diethyl ether and recrystallized from acetic acid. A few millilitres of nitromethane are added when the solid dissolves with difficulty.

*2,6-Di(*p*-anisyl)pyrylium tetrafluoborate* **(1)**. Compound **1** is obtained in 62% yield as described above, m.p. 251 °C.

UV (CH$_2$Cl$_2$): λ (nm) (ε, 1 mol^{-1}cm^{-1}) 285 (7900), 322 (10 500), 367 (5900) and 488 (22 700). Lit.:[17] 488 nm (22 700).

*Bisindeno[1,2-*b*;2,1-*e*]pyrylium perchlorate* **(2)** *and 5,6,8,9-tetrahydrodibenzo[*c,h*]xanthylium perchlorate* **(3)**. These two compounds are prepared following the procedure already described.[6]

*3,11-Dimethoxy-5,6,8,9-tetrahydrodibenzo[*c,h*]xanthylium tetrafluoborate* **(4)**. Compound **4** is prepared in 61% overall yield from 10·57 g of 6-methoxy-1-tetralone and 1·47 g of concentrated sulphuric acid in 60 ml of ethyl orthoformate. Recrystallization from 100 ml of acetic acid gives 7·56 g of **4**, m.p. 307 °C (with decomposition).

Analysis: calculated (C$_{23}$H$_{21}$O$_3$BF$_4$), C 63·88, H 4·86, B 2·50, F 17·58; found, C 63·95, H 4·80, B 2·52, F 16·95%. IR (KBr): 2960, 2910, 2830, 1600, 1590, 1565, 1545, 1495, 1465, 1445, 1390, 1375, 1315, 1260, 1240, 1205, 1190, 1135, 1095, 1075, 1045, 1025, 1005, 920, 860, 820, 750 and 640 cm^{-1}. NMR (CDCl$_3$): δ (ppm) 3·18 (8H, s), 4·02 (6H, s), 7·00 (2H, d, $J = 2·6$ Hz), 7·17 (2H, dd, $J = 8·6$ and 2·6 Hz), 8·16 (2H, d, $J = 8·6$ Hz) and 8·18 (1H, s).

*5,6,8,9-Tetrahydrobisbenzo-2,3-dihydrofuro[6,5-*c*; 5',6'-*h*]xanthylium tetrafluoborate* **(6)**. The general procedure indicated above is used to obtain this compound from 1 g of 2,3,7,8-tetrahydronaphtho[2,3*b*]furan-5(6*H*)-one **(7)** and 0·26 g of concentrated sulphuric acid in 30 ml of ethyl orthoformate. The final tetrafluoborate **6** is isolated in 51% overall yield (0·73 g), m.p. 316 °C.

Analysis: calculated (C$_{25}$H$_{25}$O$_5$BF$_4$), C 65·81, H 4·64, B 2·37; found, C 64·62, H 4·62, B 2·27. IR (KBr): 2980, 2900, 1760, 1740, 1620, 1570, 1560, 1460, 1400, 1330, 1275, 1245, 1220, 1190, 1180, 1020, 980 and 760 cm^{-1}. NMR (CDCl$_3$–CF$_3$COOD, 1:1): δ (ppm) 3·10–3·65 (12H, unresolved *m*), 4·75 (4H, t, $J = 8·9$ Hz), 6·75 (2H, s) and 6·13 (1H, s).

Intermediate **9**. Intermediate **9** is obtained in 68% yield from 5-methoxyinden-1-one following the general procedure described above, m.p. 179 °C.

Analysis: calculated (C$_{25}$H$_{28}$O$_8$S), C 61·49, H 5·78, S 6·56; found, C 59·45, H 6·09, S 6·28; corrected for 3%

water, C 61·31, H 5·93, S 6·48%. IR (KBr): 2970, 2935, 2850, 1604, 1526, 1481, 1419, 1394, 1350, 1307, 1271, 1230, 1208, 1149, 1113, 1075, 1019, 975, 925, 751, 699, 669, 604 and 545 cm^{-1}.

Pseudo-base **10**. A 0·20 g (7 × 10^{-4} mol) amount of bisindeno[1,2-*b*;2,1-*e*]pyrylium perchlorate (**2**) is dissolved in 100 ml of 95% ethanol and heated on a water-bath; 3 ml of a 0·55 M (50 gl^{-1}) solution of sodium acetate are added dropwise to this solution while stirring. The fluorescence of the solution vanishes immediately. The product precipitates on cooling; the precipitate is filtered, washed with an excess of water and recrystallized from 95% ethanol to give 164 mg (85% yield) of the pseudo-base **10**.

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