Fries rearrangement of dibenzofuran-2-yl ethanoate under photochemical and Lewis-acid-catalysed conditions

Ana M. A. G. Oliveira, [a] **Ana M. F. Oliveira-Campos**,[a,*] **M. Manuela M. Raposo**,[a] **John Griffiths**[b], and **Antonio E. H. Machado**[c]

[a] *Centro de Química, Universidade do Minho, Campus de Gualtar, 4710 Braga, Portugal.*

[b] *Department of Colour Chemistry, University of Leeds, Leeds LS2 9JT, UK.*

[c] *Universidade Federal de Uberlândia – Instituto de Química, Laboratório de Fotoquímica/GFQM, P.O. Box 593, Uberlândia, 38400-089, Minas Gerais, Brazil.*

Abstract - The Fries rearrangement of dibenzofuran-2-yl ethanoate as a route to *o*-hydroxyacetyldibenzofurans has been investigated, both under thermal Lewis-acid catalysed and non-catalysed photochemical conditions. The reactions were examined theoretically at semi-empirical (PM3 and ZINDO/S) and density functional theory (DFT) levels. The correct selection of reaction conditions provides viable preparative routes to *ortho*-acylated hydroxydibenzofurans**.**

Keywords: Fries rearrangement; Dibenzofuran-2-yl ethanoate; Acetylation.

[*] Corresponding author. Tel. +35 253 604 386; Fax. +35 253 678 983; e-mail: amcampos@quimica.uminho.pt

1. Introduction

Following previous work regarding the preparation of benzopsoralen analogues, [1] the synthesis of derivatives containing an acetyl group in position 4 of the pyran one ring was examined. This required the synthesis of acetyl-substitutedhydroxydibenzofurans, and the readily available dibenzofuran-2-ol (**1**) was chosen as the starting material, as its acetyl ester **2** should undergo Fries rearrangement and potentially afford derivatives of this type (Fig. 1).

The Fries rearrangement of benzene derivatives is well known and can be induced either thermally or photochemically.[2,3] The thermal Fries reaction involves the formation of a solvent caged ion pair, [4] whereas the photoreaction occurs *via* radical intermediates.[2,5] In the latter case, electronic excitation is followed by homolytic cleavage to yield aryloxy and acyl radical pairs, [6] and calculations indicate that this involves the excited singlet state. [7] The photo-Fries rearrangement was first observed by Anderson and Reese, in 1960. [8] In both processes, the resulting pairs of ions or radicals are restrained by the solvent cage, until they combine to form rearrangement products. This can involve reformation of the original ester or formation of several isomeric ketone intermediates. Alternatively, the reactive species can diffuse apart to give other products.

In the present work, the photochemical and the Lewis acid catalysed thermal Fries rearrangements of **2** under a variety of conditions have been investigated and the results compared with theoretical predictions.

2. Experimental results

The synthesis of dibenzofuran-2-yl ethanoate (**2**) was obtained in almost quantitative yield (98 % yield) by reaction of dibenzofuran-2-ol (**1**) with diethylmalonate, in pyridine.[9] The acid catalysed experiments were conducted either without solvent or in dichloromethane solution, using $AlCl_3$ or $TiCl_4$ as Lewis acids, at various temperatures.

The photo-Fries reactions were carried out by sealing solutions of the dibenzofuran (solvents: ethanol, cyclohexane, dichloromethane and acetonitrile) in quartz tubes and exposing them for the appropriate length of time to the radiation from a 16 W low-pressure mercury lamp (principal emission at 254 nm). The main products (Fig. 1) were isolated by column chromatography and characterized by ^{1}H NMR, UV, IR and elemental analysis.

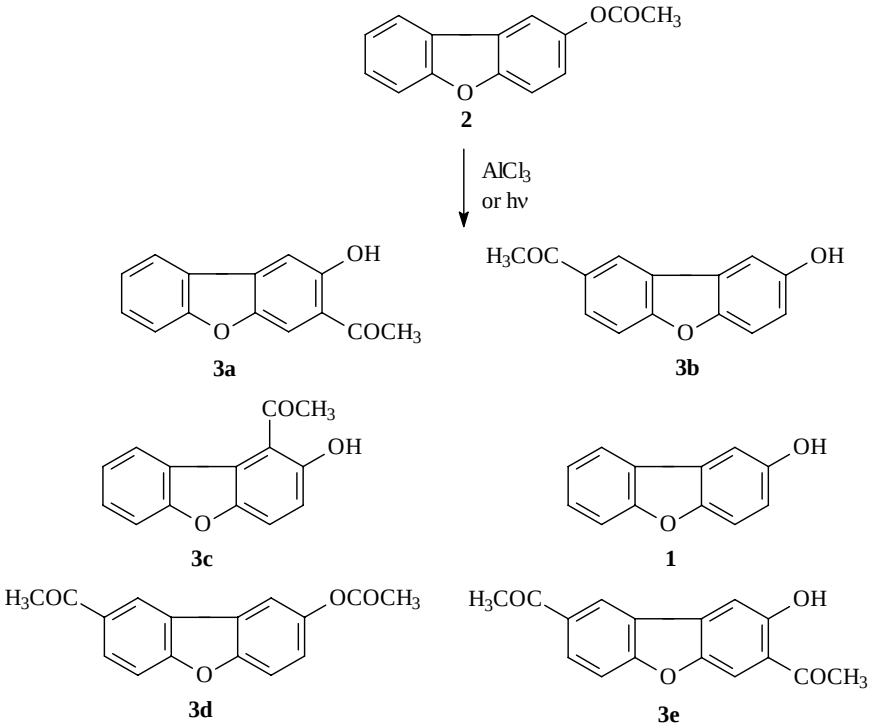

Figure 1. Products obtained in the Fries rearrangements.

The product yields for both the dark and photochemical reactions were estimated by separation of the products by column chromatography or by high performance liquid chromatography (HPLC), using a silica column (Fig. 2). In order to estimate the yields for the main products by HPLC analysis, external calibration was used with solutions of pure reference compounds and the peak height was plotted as a function of the concentration of each compound (peak areas were less useful and difficult to quantify due to the overlap of peaks).

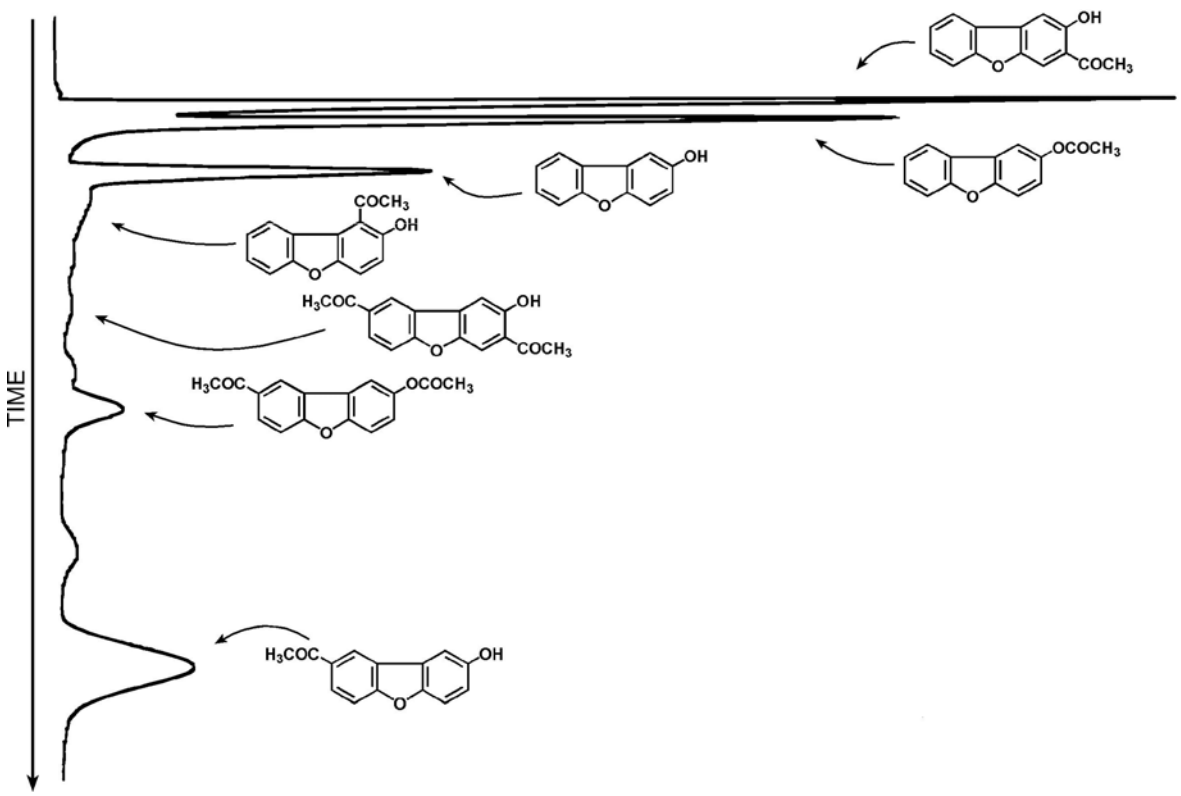

Figure 2. HPLC chromatogram from experiment 4 (see Table 1). Conditions: Column: LichroCART (5 μm, silica 60). Dimensions: 25 cm x 4 mm. Mobile phase: AcOEt / hexane 20:80. Flow rate: 1.6 ml/min. Detector: UV absorption (290 nm, 0.64 AUFs). Sample volume: 5 μl.

2.1. Dark reactions

Solutions of dibenzofuran-2-yl ethanoate in dichloromethane containing aluminium chloride or titanium chloride as catalyst showed no significant rearrangement reaction, either at room temperature or at reflux temperature (Table 1, experiments 1 - 3). In some instances a high level of decomposition of the reactant occurred (e.g. experiment 2). However, when a mixture of reactant and catalyst with no solvent was heated for a short period of time (15 min), rearrangement took place readily, and the main products, apart from the phenol (**1**), formed by hydrolysis, were 2-hydroxydibenzofuran-3-yl methyl ketone (**3a**) and 8-hydroxydibenzofuran-2-yl methyl ketone (**3b**) (see Table I**,** experiments 4 and 5). Only traces of 2-hydroxydibenzofuran-1-yl methyl ketone (**3c**) were observed. Other products were also obtained and two were identified as 8-

acetyldibenzofuran-2-yl ethanoate (**3d**) and 8-hydroxydibenzofuran-2,7-diyl dimethyl diketone (**3e**).

Table 1 – Products obtained from the catalysed Fries rearrangement of **2** under various experimental conditions

		Product / Yield (%)						
Exp.	Conditions	**2**	**3a**	**3b**	**3c**	**3d**	**3e**	**1**
1	$2AlCl_3$, CH_2Cl_2, 7 days, 20 ºC	94	0	0	0	0	0	2
2	$2AlCl_3$, CH_2Cl_2, 30 min, reflux	9	4	0	0	4	0	0
3	$2TiCl_4$, CH_2Cl_2, 3h, reflux [a]	64	0	0	0	0	0	27
4	$2AlCl_3$, 130 ºC, 15 min	17	31	28	3	7	1	10
5	$2AlCl_3$, 130 ºC → 150 ºC, 15 min	19	27	16	3	4	0	11

[a] Yield obtained by column chromatography.

2.2. Photochemical Reactions

The photochemical Fries reaction proved to be more efficient than the thermal acid-catalysed process. In contrast to the thermal reaction, the photochemical process showed that the two rearrangement products were 2-hydroxy-dibenzofuran-1-yl methyl ketone (**3c**) and 2-hydroxydibenzofuran-3-yl methyl ketone (**3a**)**,** with **3c** always present in higher proportion (Table 2). Yields were dependent on solvent and/or reaction time.

Table 2 - Products obtained from the photo-Fries rearrangement of **2** in different solvents

Solvent	Yield, %				Reaction time, min
	2	**3a**	**3c**	**1**	
Dichloromethane	5	19	41	10	300
Cyclohexane	11	21	32	2	1260
Ethanol	13	20[a]	27	12	300
Acetonitrile	37	12[b]	16	12	135

[a] 22 % for 540 minutes of reaction; [b] 14 % for 210 minutes of reaction.

The best results were obtained in dichloromethane (41 % of **3c** and 19 % of **3a**) after 300 min exposure. Roughly similar yields were obtained in ethanol and cyclohexane, but it was noteworthy that significantly longer irradiation time was needed in the latter solvent (Table 2). The reaction was inefficient in acetonitrile and yields of **3a** and **3c** were low. There was a tendency for the primary photoproducts to undergo secondary reactions with increased irradiation time. A similar trend was also observed in dichloromethane and ethanol, but not in cyclohexane. In all cases, the analysis of the products by HPLC showed formation of species with lower retention times than **3a** or **3c** and, in dichloromethane, also some species with higher retention times.

The formation of the rearrangement product **3a** as a function of time in these different solvents is shown in Figure 3. The detail in Figure 3 shows the parallel percentage decrease in concentration of the starting material **2** with time. The highest rate of disappearance of dibenzofuran-2-yl ethanoate (**2**) occurred in dichloromethane, and the lowest rate in cyclohexane. It can be seen from Figure 3 that photodecomposition of **3a** becomes evident after varying irradiation times, depending on the solvent, and is most pronounced in acetonitrile (after ca. 3 h), whereas in cyclohexane formation of **3a** is still increasing after 20 h.

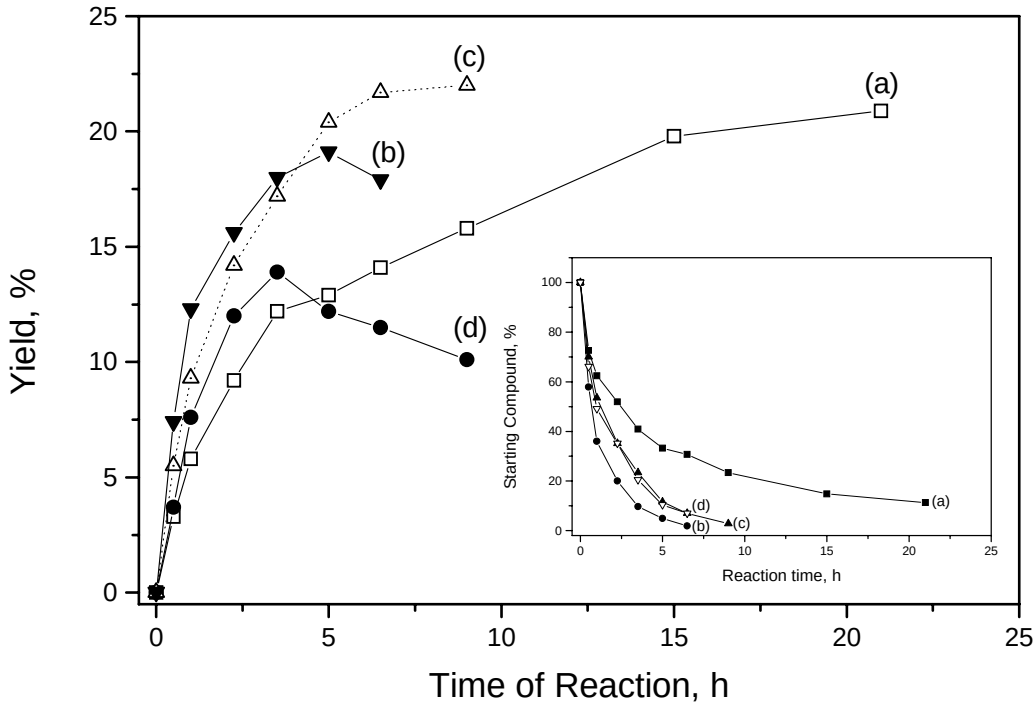

Figure 3. Photo-formation of 2-hydroxydibenzofuran-3-yl methyl ketone (**3a**), in different solvents: (a) cyclohexane, (b) dichloromethane, (c) ethanol, (d) acetonitrile. In detail: consumption of dibenzofuran-2-yl ethanoate (**2**) in the photochemical reaction, using different solvents: (a) acetonitrile, (b) ethanol, (c) cyclohexane, (d) dichloromethane.

Similar results were also observed for formation of **3c,** but its tendency to undergo photodecomposition was higher As the sum of the amounts of **3a, 3c** and unreacted **2** do not reach 100 %, it can be concluded that other species that were not identified, are formed.

The variation of the ratios **3a**/**3c** as a function of the conversion of **2** is shown in Figure 4. The ratio is below unity and it is approximately constant throughout each reaction until a relatively high conversion of 2 has been reached, when the ratio increases sharply. This can be attributed principally to the fact that **3c** decomposes faster than **3a** towards the end of the reaction.

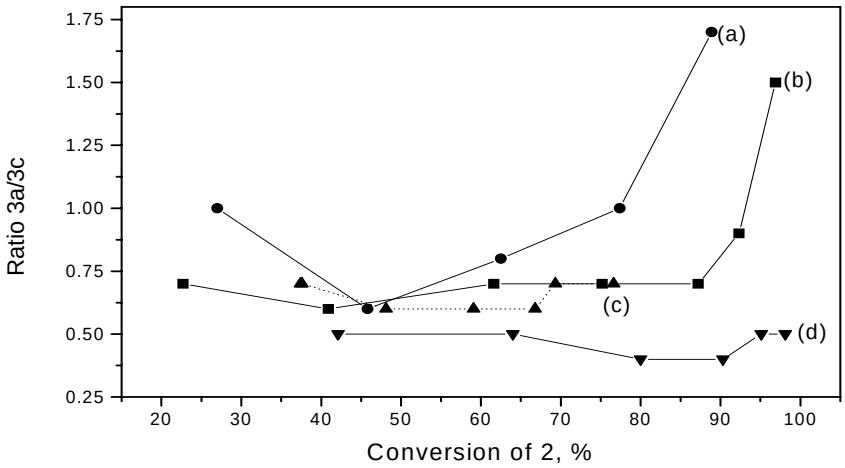

Figure 4. Ratios **3a/3c** as a function of the conversion of **2**.

In order to study the effect of the concentration of starting material on the formation of the reaction products, ethanolic solutions of **2** of three different concentrations (1 x 10^{-3}, 2 x 10^{-3}, and 5 x 10^{-3} mol dm^{-3}) were irradiated, and the percent formation of **3a** determined as a function of irradiation time. The results are shown in Figure 5. It can be seen that for more dilute solutions, decomposition starts earlier and consequently the yield decreases. However the maximum yield obtained is only 22 %.

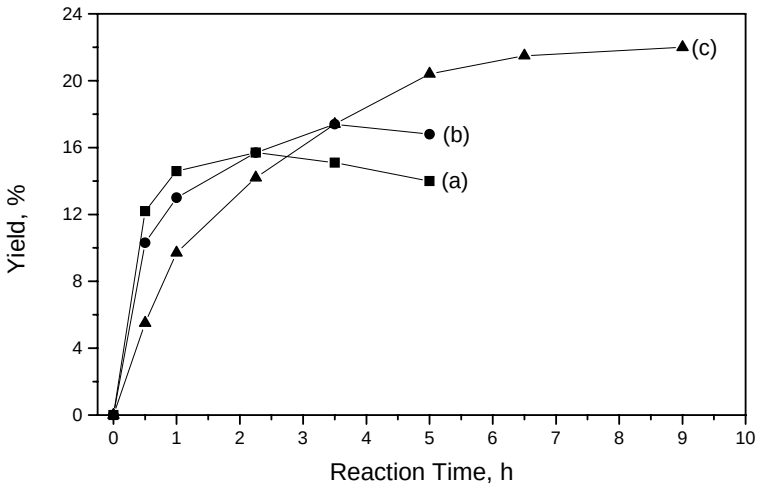

Figure 5. Effect of the dibenzofuran-2-yl ethanoate (**2**) concentration on the photo-formation of 2-hydroxydibenzofuran-3-yl methyl ketone (**3a**) in ethanol: (a) 1 x 10^{-3} mol dm^{-3}, (b) 2 x 10^{-3} mol dm^{-3}, (c) 5 x 10^{-3} mol dm^{-3}.

3. Discussion

3.1. Dark Reaction

The reaction coordinates for the production of 2-hydroxydibenzofuran-3-yl methyl ketone (**3a**), calculated using PM3 for the catalysed reaction and for the hypothetical non-catalysed reaction are shown in Figure 6. The reaction coordinate is the distance between the oxygen atom of dibenzofuran-2-yl ethanoate and the acylium cation as the transition state is approached. For the uncatalysed reaction the coordinate of the reaction is shown until the bond is formed in **3a**. The reaction coordinate for the catalysed reaction ($AlCl_3$) is the bond distance of O – (CO)CH_3 until reaching the transition state. Comparing ΔH_F calculated values for the transition state, a decrease of 172 KJ/mol for the catalysed reaction is indicated. As expected, the activation energy needed for the catalysed reaction is lower. The transition state indicated by the maximum of the uncatalysed curve can be considered to represent the ion pair formed between the acylium cation and the dibenzofuranoxide anion, and similarly, the maximum of the catalysed curve can be considered to represent the complex formed between the dibenzofuranoxide anion and the Lewis' acid. The activation energy for the uncatalysed reaction was calculated to be 306 kJ/mol, whereas for the catalysed reaction the corresponding value was 135 kJ/mol, some 56% lower.

The best practical conditions to effect the thermal rearrangement involve the use of a Lewis acid in combination with heat. The use of a catalyst in refluxing dichloromethane did not result in any significant rearrangement as the boiling point of the solvent (40 ^{o}C) was too low to reach an appropriate reaction temperature, and only decomposition of the starting material was observed.

It is noteworthy that the complex formed between $AlCl_3$ and **2** virtually eliminates the formation of the compound **3c**.

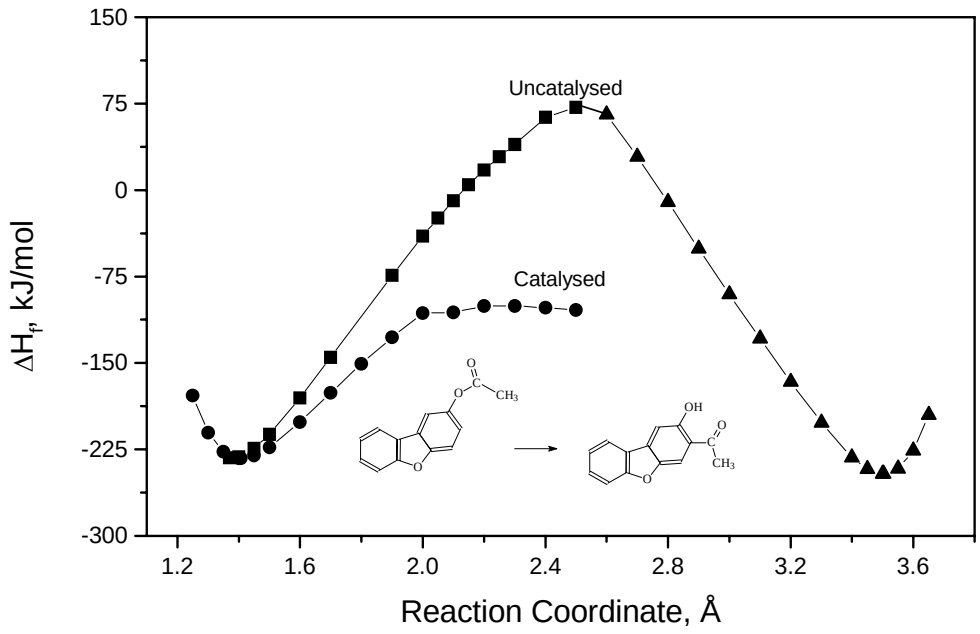

Figure 6. Reaction coordinates, calculated using PM3, considering the formation of 2-hydroxydibenzofuran-3-yl methyl ketone (**3a**), for the catalysed and uncatalysed reactions.

As the ions will possess limited mobility, there will be high tendency for the ion pair to undergo recombination, so regenerating the starting material **2** and preventing rearrangement. This can be overcome by an increase in the reaction temperature, which will tend to displace the transition state (ion pair) in the direction of the products. The concentration of the starting material is also an important parameter, as high concentrations will favour the formation of intermolecular recombination products.

Significant amounts of dibenzofuran-2-ol (**1**) could also be isolated in these Lewis acid catalysed reactions, and this can be ascribed to protonation of the dibenzofuranoxide anion after displacement of the acylium cation. Considering positions in the dibenzofuran ring system that might be attacked by the acylium ion, in an intramolecular process the distance between the acylium cation and that position will play an important role. If one considers the dibenzofuranoxide anion**,** the positions potentially most susceptible to electrophilic attack by the acylium cation may be predicted from the charge densities on the carbon atoms at those positions. Calculated charge densities are shown in Figure 7.

It can be seen that, on this basis, all the unsubstituted carbon atoms in the dibenzofuranoxide anion have the potential to undergo intramolecular acylation, but only products arising from attack at positions 1, 3 and 8 were isolated. Other minor products formed were due to intermolecular reactions, as in the case of 8-acetyldibenzofuran-2-yl ethanoate (**3d**) and 8-hydroxydibenzofuran-2,7-diyl dimethyl diketone (**3e**) and other compounds in small amounts.

The non-reactivity of position 4 may be attributed to the fact that 4 is *meta* to the phenoxide group and as with all electrophilic substitution reactions of phenols and phenolate anions, this position will be much less reactive than the two *ortho* positions 1 and 3 on simple resonance grounds. Similar resonance considerations, may explain why there is no reaction in position 7 and 9 in spite of their charge densities. Thus positions 7 and 9 are *meta* to the furan oxygen atom. In the case of position 9 there is also the likelihood of steric inhibition, due the proximity of the Lewis acid moiety. On charge density grounds and their favourable *ortho* or *para* orientation with respect to the furan oxygen, one would expect positions 6 and 8 to be both appreciably reactive to acylation, and yet only the product arising from reaction at position 8 can be detected. Again this may be a steric effect, the furan oxygen making *ortho* attack at position 6 less favourable.

Of the two dominant rearrangement products **3a** and **3c,** the former is by far the most favoured (Table 1), even though the 1-position has a calculated negative charge density about 1.5 times higher than for position 3. This is surprising, as simple electrophilic substitution reactions of 2-hydroxydibenzofuran (e.g. diazo coupling, nitration, bromination) normally strongly favour 1-substitution. This may be due to a steric effect. The Lewis acid moiety at position 2 will exert a large steric effect, so inhibiting reaction at positions 1 and 3. However, position 1 will be additionally hindered to attack because of the proximity of the hydrogen atom in the 9 position of the second benzene ring.

In the most successful reaction (no solvent; $AlCl_3$ catalyst; 130 ºC - experiment 4**,** Table 1), 2-hydroxydibenzofuran-3-yl methyl ketone (**3a**) was the major product.

An estimate of the equilibrium distance between the dibenzofuranoxide and acylium ions in the ion pair in the transition state gave a value of around 2.51 Å. The estimated distance between the nearest reaction centres (positions 1 and 3) and the cation is, respectively, 3.88 Å and 4.58 Å. The formation of the compound 2-hydroxydibenzofuran-3-yl methyl ketone (**3a**) must occur through electrophilic substitution of the acylium cation in the 3-position followed by proton transfer to oxygen. A summary of the reaction sequences taking place in the non-photochemical Lewis acid - catalysed reaction of dibenzofuran-2-yl ethanoate (**2**) is shown in Figure 7.

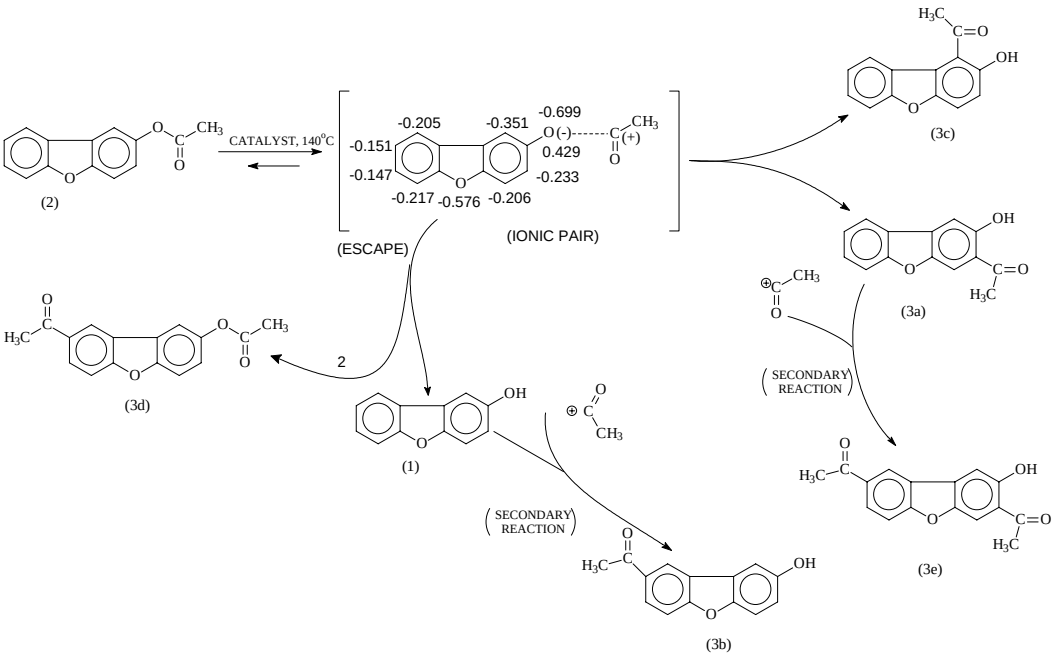

Figure 7. Reaction pathways for the Lewis acid-catalysed Fries reaction of dibenzofuran-2-yl ethanoate (**2**). Total atomic charges over the dibenzofuranoxide anion, estimated using DFT calculation (B3LYP/6-31G*), are also shown.

The calculated standard enthalpies of formation for the isolated compounds, are listed in Table 3 and show that the products **3a**, **3b** and **3c** are thermodynamically more stable than the starting material, **2**, as would be expected.

Table 3 - Calculated ΔH_f values (PM3) for **2** and its various reaction products from the Fries reaction

Compound	ΔH_f, kJ/mol	Observation[a]
Dibenzofuran-2-yl ethanoate (**2**)	- 232.74	Starting reagent
2-hydroxydibenzofuran-3-yl methyl ketone (**3a**)	- 250.11	Major product
8-hydroxydibenzofuran-2-yl methyl ketone (**3b**)	- 255.02	Results from the escape of the cation
2-hydroxydibenzofuran-1-yl methyl ketone (**3c**)	- 245.31	Traces
8-acetyldibenzofuran-2-yl ethanoate (**3d**)	- 406.72	Results from the escape of the cation (intermolecular rearrangement)
8-hydroxydibenzofuran-2,7-diyl dimethyl diketone (**3e**)	- 422.42	From secondary reaction (traces)
Dibenzofuran-2-ol (**1**)	- 81.26	Results from the loss of the acylium cation.

[a] Applies to the dark reactions.

3.2. Photochemical Rearrangement

In contrast to the catalysed dark reaction, in which reaction at position 1 is inhibited by the catalyst, the photochemical rearrangement has no such inhibition and reaction at this position is preferred. This must be due, at least in part, to its higher electronic charge density compared to position 3 (see Fig. 7). The most efficient reaction occurred with dichloromethane as the solvent, when the product **3c** was isolated in 41 % yield after 300 minutes exposure to UV light (Table 2).

The product distributions obtained in ethanol and cyclohexane showed slightly lower yields. In both solvents the maximum yield of **3c** was around 30 %. However, the reaction time, in cyclohexane, needed to reach this yield was about 4.2 times longer than in ethanol. Despite the longer irradiation period needed to reach a yield of **3c** in cyclohexane comparable to that obtained in ethanol after 300 minutes, secondary reactions of **3a**, **3c,** and even **2,** were less prevalent than in other solvents. As solvent polarity increases, there is an increasing tendency to form other products, including secondary photoproducts from **3a** and (especially) from **3c** (Figs. 3 and 4). This can be explained in terms of increased stabilization of the radical species in more polar solvents, thus favouring the formation of rearrangement products within the solvent cage.[6] Furthermore, the additional stabilization of the dibenzofuranoxy radical, in a polar solvent will increase the probability of this radical escaping from the solvent cage and undergoing hydrogen abstraction to give **1.** As can be seen (Table 2), polar solvents favour this diffusion product. This is in marked contrast to Plank's observations[10], in which he noted that polar solvents such as methanol favoured radical rearrangement, whereas non-polar solvents favoured radical migration followed by hydrogen abstraction.

It is well accepted that the photo-Fries reaction proceeds through radical pairs, formed by excitation of the starting material to a $S_1(n,\pi^*)$ state and subsequent homolytic cleavage of the C – O bond. [6,11] Our theoretical calculations confirm the n,π^* character of the S_1 state of **2**. DFT-TD, PM3 and ZINDO/S calculations (these last two at a configuration interaction level), show that this electronic transition arises from an overlap of excited states involving the carbonyl group and the dibenzofuran ring. As expected, the TD-DFT calculations furnished a more quantitative description of the electronic transitions, presenting an absorption line at 295 nm for the $S_0 \rightarrow S_1$ transition for the isolated molecule, very near to the estimated maximum for this transition observed in ethyl acetate (Fig. 8).

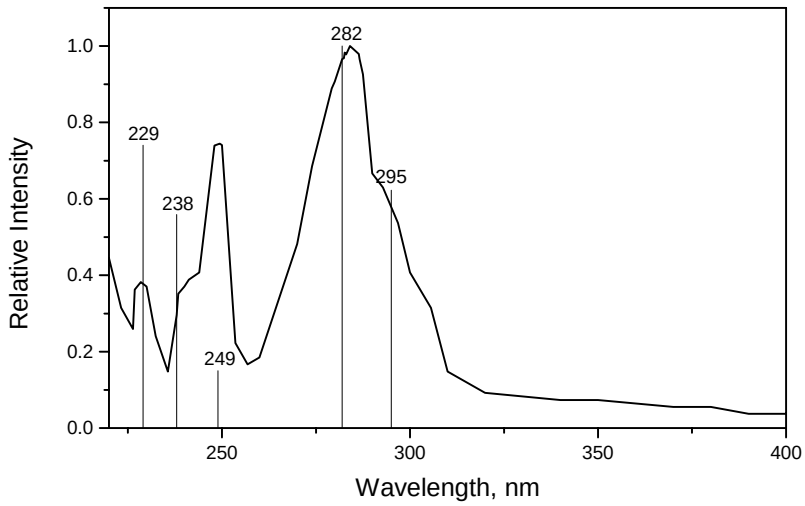

Figure 8 - UV-Vis spectrum of dibenzofuran-2-yl ethanoate(**2**) in ethyl acetate ($1x10^{-5}$ mol dm^{-3}). Vertical lines represent calculated electronic transitions for the isolated molecule (TD-DFT).

The five lines presented in Figure 8 correspond to the first five electronic transitions for **2**, and the band corresponding to the $S_0 \rightarrow S_1$ transition appears as a shoulder in the experimental spectrum, overlapped by the band corresponding to the $S_0 \rightarrow S_2$ transition. The relatively low calculated oscillator strength (0.18 for the isolated molecule) is consistent with the $n \rightarrow \pi^*$ character of this transition.

4. Conclusions

The Fries rearrangement of dibenzofuran-2-yl ethanoate (**2**) as a route to *o*-hydroxyacetyldibenzofurans has been investigated, both under thermal Lewis-acid ($AlCl_3$ and $TiCl_4$) catalysed and non-catalysed photochemical conditions. Reaction products have been isolated and characterized, and the effects of temperature, solvent, type of acid, concentration and time on product distributions have been investigated.

The efficiency of the Lewis – acid catalysed Fries reaction is critically dependent on choice of reaction conditions. The reaction proceeds best at temperatures above about

130 ^{o}C, and in the absence of solvent. The principal rearrangement products are 2-hydroxydibenzofuran-3-yl methyl ketone (**3a**) and 8-hydroxydibenzofuran-2-yl methyl ketone (**3b**). The formation of **3a** possibly occurs by a concerted intramolecular mechanism, mediated by the Lewis' acid, whereas formation of **3b** can still be regarded as intramolecular, but will involve discrete separation of the acylium cation from the complexed dibenzofuranoxide anion within the solvent cage. Minor products are also observed where the separated acylium ion takes part in intermolecular reactions. Steric effects caused by the association between the catalyst and the aryloxy group help explain why 2-hydroxydibenzofuran-1-yl methyl ketone (**3c**) is not formed as the dominant product. A theoretical evaluation of the reaction coordinate, using the PM3 method, shows that the activation energy for rearrangement is about 306 kJ/mol and 135 kJ/mol for the uncatalysed and catalysed processes.

For the photo-Fries reaction, the major products are 2-hydroxydibenzofuran-1-yl methyl ketone (**3c**) and 2-hydroxydibenzofuran-3-yl methyl ketone (**3a**)**,** with **3c** generally dominating. The yields of products in the photochemical reaction are very sensitive to solvent polarity and, as occurs with the dark reaction, the experimental data show that there is a competition between intramolecular and intermolecular mechanisms. The best preparative results were obtained for very low polarity solvents. Photo-rearrangement is also particularly slow in cyclohexane, suggesting that polar solvents favour homolytic cleavage of the ester to give the radical pair.

5. Experimental

5.1. Syntheses

Light petroleum refers to solvent boiling in the range 40 - 60 ºC. Column chromatography (CC) was performed on Merck silica gel 60 (230-400 mesh). Melting points were determined on a Gallenkamp apparatus and are uncorrected. Ultraviolet spectra were recorded in ethyl acetate on a HITACHI 2000 and data are presented in λ_{max} (nm), log ε (mol^{-1} dm^{3} cm^{-1}). Infrared spectra were recorded on a Diffus-IR Bomem

MB-Series FTIR spectrometer in cm^{-1}. ^{1}H-NMR spectra were obtained on a Varian Unity Plus at 300 MHz and the assignments were based on irradiation experiments. The solvent was $CDCl_3$ (if not stated otherwise) and δ is in ppm, relative to internal $SiMe_4$. Elemental analyses were carried out with a LECO CHNS-932.

5.1.1. Dibenzofuran-2-yl ethanoate (2). A mixture of dibenzofuran-2-ol (1) (2.78 g, 15.1 mmol), pyridine (25 ml) and acetic anhydride (7.1 ml, 75.3 mmol) was refluxed for 3 h. Crushed ice (100 g) was added and the mixture was stirred until a formation of a beige precipitate is observed. The mixture was filtered and the solid was recrystallized from ethanol.

Dibenzofuran-2-yl ethanoate (**2**) was obtained as colourless crystals (3.35 g, 94 %); m.p.: 113.5 – 114.5 ºC (ethanol) (lit.[12] 115-116 ºC, *n*-propanol). UV: 284, (4.30). IR (Nujol): 1755 (C=O), 1224, 1158, 1112, 929, 892, 834, 745, 724. ^{1}H NMR: 7.91 (1H, br d, *J* = 7.8 Hz, H-9); 7.69 (1H, d, *J* = 2.7 Hz, H-1); 7.58 (1H, br d, *J* = 8.1 Hz, H-6), 7.56 (1H, d, *J* = 9.0 Hz, H-4); 7.49 (1H, dt, *J* = 1.5, 7.8 Hz, H-7); 7.35 (1H, dt, *J* = 0.9, 7.5 Hz, H-8); 7.17 (1H, dd, *J* = 2.4, 8.7 Hz, H-3); 2.37 (3H, s, CH_3). Anal. calc. for $C_{14}H_{10}O_3$: C, 74.32; H, 4.46 %. Found: C, 74.04; H, 4.68 %.

5.2. Lewis – acid catalysed reaction

A- With solvent. To a solution of dibenzofuran-2-yl ethanoate (2) (0.23 g, 1.0 mmol) in dichloromethane (10 ml) was added the Lewis acid (2.0 mmol of $AlCl_3$, solid, or $TiCl_4$, 1 mol dm^{-3}, in CH_2Cl_2). The mixture was stirred at room temperature or refluxed. Hydrochloric acid (2 M) and crushed ice were added and the mixture was stirred for 15 min. The aqueous layer was extracted with CH_2Cl_2 (3 x 25 ml) and the combined organic extracts were dried ($MgSO_4$). The solvent was evaporated and a solid was obtained. A solution of the final solid, in ethyl acetate, was prepared and diluted to a known volume for HPLC analysis.

B- Without solvent. A mixture of dibenzofuran-2-yl ethanoate (**2**) (0.45 g, 2.0 mmol) and $AlCl_3$ (0.53 g, 4.0 mmol) was heated under argon for 15 min, at the temperature indicated in Table 1. After cooling, crushed ice and conc. HCl (5.0 ml) were added. The resulting mixture was stirred for 15 min and extracted with diethyl ether (3 x 30 ml). The combined organic extracts were dried ($MgSO_4$) and the solvent removed under reduced pressure. A solution of the final solid, in ethyl acetate, was prepared and diluted for analysis by HPLC.

The remaining solids of several experiments were combined and submitted to column chromatography (silica, ethyl acetate / light petroleum ether, 4 - 60 %).

5.2.1. 2-Hydroxydibenzofuran-3-yl methyl ketone (3a), was the first compound eluted and was obtained as intense yellow crystals, m.p.: 170.0-172.0 ºC (ethanol) (lit[12] 168-169 ºC, ethanol / *n*-propanol / water). UV: 365 (3.71), 315 (4.44), 280 (4.01). IR (KBr): 1650, 1631 (strong, C=O), 1609, 1590, 1459, 1426, 1370, 1328, 1218, 865, 817, 749, 660 . ^{1}H NMR: 12.25 (1H, s, OH); 7.95 (1H, br d, *J* = 7.8 Hz, H-9); 7.90 (1H, s, H-4); 7.57-7.53 (1H, m, H-7); 7.48 (1H, s, H-1); 7.41 - 7.31 (2H, m, H-6 and H-8); 2.74 (3H, s, CH_3). Anal. calcd. for $C_{14}H_{10}O_3$: C, 74.32; H, 4.46 %. Found: C, 74.09; H, 4.70 %.

5.2.2. Dibenzofuran-2-yl ethanoate (2). The second compound eluted, was obtained as colourless crystals; mp and spectroscopic data were identical to those of an authentic sample of 2.

5.2.3. Dibenzofuran-2-ol (1). The third compound eluted, was obtained as beige crystals; m.p.: 133.5 – 134.5 ºC (lit[13] 134 ºC, ethanol) UV: 324 (3.73), 290 (4.19). IR (KBr): 3272 (OH), 1600, 1482, 1447, 1361, 1334, 1308, 1282, 1214, 1191, 1168, 1150, 1017, 869, 842, 801, 743. ^{1}H NMR: 7.89 (1H, br d, *J* = 7.5 Hz, H-9); 7.55 (1H, br d, *J* = 8.1 Hz, H-6); 7.46 (1H, dt, *J* = 1.2, 8.2 Hz, H-7); 7.44 (1H, d, *J* = 9 Hz, H-4); 7.38 (1H,

d, *J* = 2.4 Hz, H-1); 7.32 (1H, dt, *J* = 1.2, 7.8 Hz, H-8); 6.97 (1H, dd, *J* =2.4, 8.7 Hz, H-3); 5.01 (1H, br s, OH) .

5.2.4. 2-Hydroxydibenzofuran-1-yl methyl ketone (3c). The fourth compound eluted, was obtained as pale yellow crystals, m.p.: 154.5-155.5 ºC (ethanol / hexane) (lit[12] 105-110 ºC). UV: 302 (4.02). IR (KBr): 3177(OH), 1654 (C=O), 1592, 1454, 1432, 1368, 1277, 1263, 1079, 889, 809, 739, 730. ^{1}H NMR: 11.25 (1H, s, OH); 8.03 (1H, br d, *J* = 8.4 Hz, H-9); 7.69 (1H, d, *J* = 9.0 Hz, H-4); 7.62 (1H, br d, *J* = 8.4 Hz, H-6); 7.51 (1H, dt, *J* = 1.2, 7.2 Hz, H-7); 7.36 (1H, dt, *J* = 1.2, 8.4 Hz, H-8); 7.12 (1H, d, *J* = 9.0 Hz, H-3); 2.91 (3H, s, CH_3). Anal. calcd. for $C_{14}H_{10}O_3$: C, 74.32; H, 4.46 %. Found: C, 74.52; H, 4.81 %.

5.2.5. 8-Hydroxydibenzofuran-2,7-diyl dimethyl diketone (3e). The fifth compound eluted, was obtained as yellow crystals, m.p.: 224.5-226.0 ºC (ethanol). UV: 365 (3.70), 275 (4.67). IR (KBr): 1679 (C=O), 1651, 1628 (strong, C=O), 1423, 1359, 1324, 1239, 1213, 1128, 944, 823, 785. ^{1}H NMR: 12.27 (1H, s, OH), 8.57 (1H, d, *J* = 2.1 Hz, H-1); 8.20 (1H, dd, *J* = 1.8, 8.7 Hz, H-3); 7.94 (1H, s, H-6); 7.60 (1H, d, *J* = 8.7 Hz, H-4); 7.54 (1H, s, H-9); 2.76 (3H, s, 3-$COCH_3$ or 9-$COCH_3$); 2.73 (3H, s, 9-$COCH_3$ or 3-$COCH_3$). Anal. calc. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.52 %. Found: C, 71.71; H, 4.67 %.

5.2.6. 8-Acetyldibenzofuran-2-yl ethanoate (3d). The sixth compound eluted, was obtained as yellow crystals, m.p.: 145.0-147.0 ºC (ethyl acetate - hexane). UV: 292 (4.04), 249 (4.52). IR (Nujol): 1745 (C=O), 1672 (C=O), 1634, 1596, 1287, 1245, 1216, 1155, 1015, 904, 823, 807. ^{1}H NMR: 8.52 (1H, d, *J* = 1.2 Hz, H-9); 8.12 (1H, dd, *J* = 2.1, 8.7 Hz, H-7); 7.73 (1H, d, *J* = 2.4 Hz, H-1) 7.59 (1H, d, *J* = 8.4 Hz, H-6); 7.57 (1H, d, *J* = 8.7 Hz, H-4); 7.22 (1H, dd, *J* = 2.4, 9.0 Hz, H-3); 2.71 (3H, s, $COCH_3$); 2.38 (3H, s, $OCOCH_3$). Anal. calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.52 %. Found: C, 71.61; H, 4.75 %.

5.2.7. 8-Hydroxydibenzofuran-2-yl methyl ketone (3b). The last compound to be eluted, was obtained as brownish yellow crystals, m.p.: 223.5-225.5 ºC (ethyl acetate - hexane). UV: 326 (3.70), 248 (4.62). IR (Nujol): 3193 (OH), 1660 (C=O) 1596, 1580,

1304, 1286, 1263, 1185, 1169, 1113, 1019, 864, 824, 723 . ^{1}H NMR (D_6 - acetone): 8.73 (1H, d, *J* = 2.1 Hz, H-1); 8.62 (1H, br s, OH); 8.18 (1H, dd, *J* = 1.8, 9.0 Hz, H-3); 7.68 (1H, d, *J* = 9.0 Hz, H-4); 7.64 (1H, d, *J* = 2.4 Hz, H-9); 7.54 (1H, d, *J* = 9.0 Hz, H-6); 7.11 (1H, dd, *J* = 2.4, 9.0 Hz, H-7); 2.72 (3H, s, CH_3). Anal. calcd. for $C_{14}H_{10}O_3$: C, 74.31; H, 4.46 %. Found: C, 74.32; H, 4.50 %.

5.3. Photochemical experiments

The photochemical experiments were conducted using a 16 W low-pressure mercury lamp (emission at 254 nm) positioned in the center of a merry-go-round setup (Annular Photoreactor, Model APQ 40 – PhotoChemical Reactors Limited). Solutions of dibenzofuran-2-yl ethanoate (**2**) (5.0 x 10^{-3} mol dm^{-3}), in the appropriate solvent, were sealed in stoppered quartz tubes (23 ml, 1 cm diameter), and placed at 4 cm from the lamp. The samples were rotated about throughout the irradiation period. Samples (0.5 ml) of the solutions were withdrawn at different photolysis times for HPLC analysis, until the concentration of the main products started to decrease after reaching a maximum value.

In order to study the effect of concentration, several ethanolic solutions of **2** of different concentrations (5.0 x 10^{-3} mol dm^{-3}, 2.0 x 10^{-3} mol dm^{-3} and 1.0 x 10^{-3} mol dm^{-3}) were also irradiated.

5.4. HPLC Analyses

High performance liquid chromatography (HPLC) analyses of the reaction mixtures were carried out using a JASCO PU-980 pump with a RHEODYNE – 7725i (20 μl) loop valve, a JASCO UV-975 UV-Vis variable wavelength detector, without scanning capability, and a Shimadzu C-R6A Chromatopac recorder. The column was a Merck LichroCART, 250 mm x 4 mm (Lichrospher Si 60, 5 μm). The analyses were conducted at constant flow rate (1.6 ml/min), with monitoring at λ = 290 nm and with 0.64 AUFs.

All the samples were prepared in ethyl acetate and 5 μl aliquots were injected for each analysis. The standards were obtained by column chromatography and solutions of different concentrations were prepared in order to obtain an external calibration from peak height plotted as a function of the concentration for each compound. The mobile phase was a mixture of ethyl acetate/hexane of analytical grade, in the proportion 20:80.

5.5. Theoretical calculations

The quantum-mechanical calculations were carried out at the semi-empirical (PM3 and ZINDO/S) and Density Functional Theory (DFT) levels. The DFT B3LYP method was employed, using a Gaussian basis-function (6-31G*), to refine the structure of the compound dibenzofuran-2-yl ethanoate (**2**) after its modelling using the PM3 method (UHF calculation, gradient 0.1000 kcal/Å mol, Polak-Ribiere optimisation algorithm)[14] and to evaluate the charge distribution in the ground state of the 2-dibenzofuranoxide anion and radical.

The Berny analytical gradient was used in the optimization using DFT. The requested convergence limit on RMS density matrix was 1 x 10^{-8} and the threshold values for the maximum force and the maximum displacement were 0.000450 and 0.001800 a.u. respectively.

Using time-dependent DFT calculations (B3LYP/6-31G*), the electronic spectrum of the compound dibenzofuran-2-yl ethanoate (**2**) was predicted[15] and compared with experiment.

The reaction coordinates for the formation of the principal product of the dark - Fries reaction under the catalysed and the uncatalysed conditions were calculated using PM3.[16] PM3 was also used to estimate the standard ΔH_f for the starting reagent and all isolated products.

The methods used are available in HYPERCHEM 5.11 Pro, [14] AMPAC 6.56 PC[16] and GAUSSIAN 98W, [15] suites of programs, installed in PC-compatible computers.

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