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Hydrogen Peroxide Oxidation of Polysubstituted Pyrylium Salts : Formation of Enol Esters and Furans

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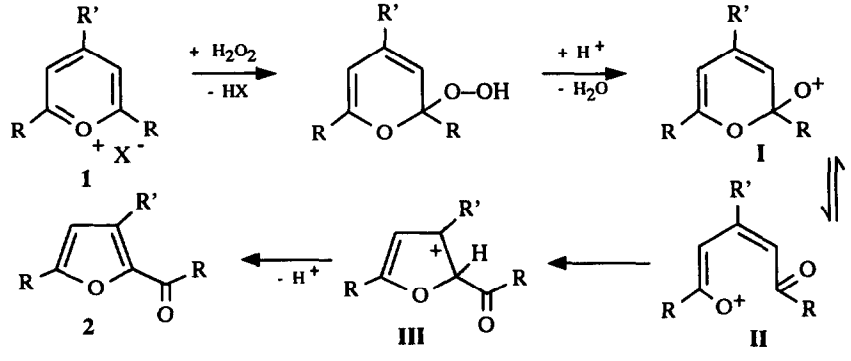
Abstract. *2,4,6-Trialkylsubstituted pyrylium salts* **1** *have been known to afford 2-acyl-3,5-dialkylfurans* **2** *in moderate yields (30 - 45%). Oxidation of these salts in buffer solutions (pH = 3 - 4.5) increased the yields of acylfurans to 75%. In contrast, tetra- and penta-substituted pyrylium salts are mainly converted into enol esters with a δ-keto group and furans all originating presumably by C-O bond cleavages in a common intermediate. This intermediate may result by a C-O acyl shift as inferred from analogous compounds with deuterium labelling.*

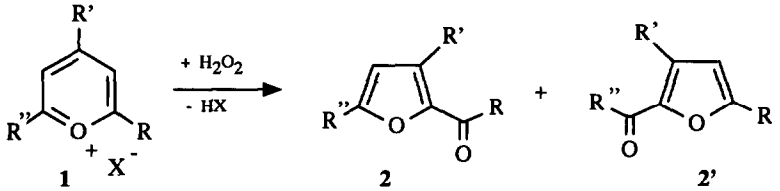
INTRODUCTION

Since the initial report by Balaban and Nenitzescu[1] on the hydrogen peroxide oxidation of 2,4,6-trialkylpyrylium salts **1**, this method has become established for the preparation[2] of 2-acyl-3,5-dialkylfurans **2**, albeit in moderate yields (30-45%). Later applications of this reaction have consisted in the preparation of 2-acylfurans with deuterium labelled substituents[3] or for a conformational study using LSRs.[4] The mechanism (Scheme 1) presumes the formation of an unstable α-hydroperoxide which in the acidic medium leads to the oxocation **I** in equilibrium with its acyclic valence isomer **II**. Cyclisation to the tertiary carbocation **III** and α-proton expulsion with rearomatisation to the 2-acylfuran **2** completes the reaction sequence.



Scheme 1

Dimroth and Mach have shown that even with *t*-butyl substituents the above ring contraction to 2-pivaloylfurans is operative.[5] In this case, beside hydrogen peroxide, hydroxylamine hydrochloride may be employed as oxidising agent, as it forms the same cations **I-III** after expulsion of ammonia. If the 2- and 6-substituents of the pyrylium ring are not identical (Scheme 2), a mixture of 2-acylfurans results and these could be separated in one case (R = R' = Me, R = Et) by preparative GLC[4] :



Scheme 2 **1** **2** **2'**

Products arising from 4- (γ-) addition of the HOO^- nucleophile to the pyrylium ring were not identified. This classifies the HOO^- ion as a hard nucleophile, which similarly to CH_3MgI adds exclusively in the α-position of pyrylium salts,[6] whereas other nucleophiles, including larger Grignard reagents, usually give mixtures of products arising both from α- and γ-addition. α-Phenyl-substituted pyrylium salts, after treatment with weak bases, have been oxidised to 2-benzoylfurans with iodine in acetone.[7] In a classical paper, a tetrasubstituted pyrylium salt, namely 2,3,4,6-tetraphenylpyrylium perbromide was converted to 2-benzoyl--3,4,5-triphenylfuran during the alkaline hydrolysis.[8] Other ring contractions of pyrylium salts to furan derivatives were reported with potassium superoxide[9] or with sulphonium ylides.[10] 2-Acylfurans are of synthetic interest mainly as flavouring agents, perfume components or as intermediates for obtaining a condensed furanic ring which often leads to an enhancement of the biological activity in drugs.

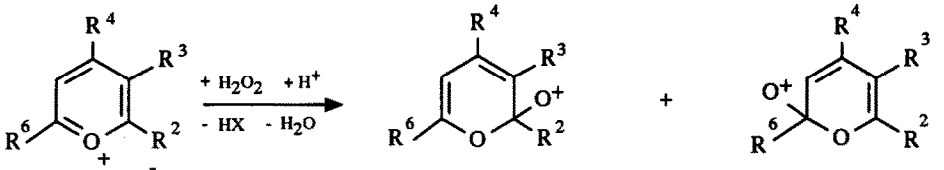
Recently, we have shown that 4-phenyl-2,6-dimethylpyrylium sulfoacetate (**1a**) is oxidised in over 90% yield to the corresponding 2-acetyl-5-methyl-3-phenylfuran (**2a**) which being crystalline was also amenable to an X-ray analysis.[11] In this case, the more than two-fold increase in yield can be ascribed to the greater stability of the benzylic cation **III**, as well as to a resistance against further oxidation of the acetylfuran **2a**. The oxidation of 2-acetylfuran by hydrogen peroxide was indeed investigated by Russian workers who identified acetic, maleic, fumaric and β-formylacrylic acids as the main products of an acid catalysed furan ring cleavage.[12] In the synthesis of acylfurans from pyrylium salts, the further oxidation of 2-acyl-3,5-dialkyl-furans by hydrogen peroxide was partially prevented by short reaction times and rapid steam-distillation of the acylfuran from the strongly acidic and oxidising reaction medium.[1-4] However, as mentioned above, the yields remained at best moderate.

In the present paper we show on one hand that by using aqueous buffers in the pH range 3 to 4.5 for oxidising 2,4,6-trialkylpyrylium salts with hydrogen peroxide, the further oxidation of the 2-acyl-3,5-dialkyl-furans is retarded so that these can be isolated in about 75% yield. On the other hand, we were interested in the fate of type **III** cations, in which the α-hydrogen elimination is not possible, i.e. stemming from tetra- or penta-substituted pyrylium salts. In these cases, interesting enol esters with a δ-keto group and 2-alkylfurans are formed as major products. Two out of the six pyrylium salts (**1d-1i**) which were all oxidised by the same pathway are new (namely **1g** and **1i**), while the pentamethylpyrylium perchlorate (**1h**) was not isolated before, despite several attempts.[13,14] Mechanistic insights into the formation of these products were ascertained by use of a deuterium labelled pyrylium salt **1f**-d_6. This study also shows that the relatively well known pyrylium salt chemistry, which has been repeatedly reviewed,[15] may still furnish unexpected results.

RESULTS AND DISCUSSION

Tempted by the nearly quantitative yields in which 2,6-dimethyl-4-phenylpyrylium sulfoacetate (**1a**) is oxidised with hydrogen peroxide to 2-acetyl-5-methyl-3-phenylfuran[11] we tried to optimise the reaction conditions in which 2,4,6-trialkylpyrylium salts **1b** and **1c** are converted into 2-acylfurans. Addition of radical inhibitors (hydroquinone), or initiators (α,α'-azo-*iso*-butyronitrile), did not alter the reaction course lending support to the cationic mechanism presented above. By using a sodium dihydrogen phosphate buffer (pH = 3), or by addition of disodium hydrogen phosphate (pH = 4-5), the yields in which 2-acetylfurans were isolated after distillation were increased to about 75% (Table). The aqueous buffer has two functions : (*i*) to maintain in equilibrium the pyrylium salt with its hydrolysis product, namely the acyclic 2-ene-1,5-dione[15-18] (pseudobase, *vide infra*), and (*ii*) to prevent the further acid-catalysed oxidation of the 2-acetylfuran. However, minor components (**3-5**) were put into evidence by GC-MS in these reaction mixtures (**4b** being also isolated in 3% yield), thus showing that an alternate pathway to the one presented in Scheme 1 is operative to a small extent.

2,3,4,6-Tetrasubstituted pyrylium salts can be attacked by the hydroperoxide nucleophile in the two nonequivalent α positions, namely in 2 leading to the oxo cation **I** and in 6 leading to the oxocation **I'** (Scheme 3). As Dreux, Royer and coworkers have shown,[6] electronic factors govern the regioselectivity of the α-addition, so that the attack of the nucleophile is expected to occur mainly in the more hindered 2-position of the pyrylium ring, thus favouring the formation of cation **I**. While **I'** can evolve to an acetylfuran **2'**, as depicted in Scheme 1, the rearomatisation of **I** to an acylfuran is inhibited by the 3-substituent which cannot be eliminated.



Scheme 3 **1** **I** **I'**

This expectation was confirmed by the product distribution (Table), as the 2-acetylfurans (**2'**) obtained from tetrasubstituted pyrylium salts, are now minor products, and they were not encountered in the case of pentasubstituted pyrylium salts. The major products are in these cases the enol esters **3** and **4** as well as the alkylfurans **5**. The compositions of the reaction mixtures were determined by GLC and GC-MS and were checked with ^{1}H-NMR integral curves. Yields are of the separated products after column chromatography.

It results from the Table that only products arising from α addition of the HOO^- nucleophile are encountered and that in the case of 2,3,4,6-tetrasubstituted pyrylium salts (**1d-1h**) the regioselectivity of the 2 addition (*versus* 6-addition which must lead to acetylfurans **2'**) varies between 3.5 and 12. This is in accord with previous findings[6a,b] and calculations.[6c,d]

The formation of the enol esters **4** could be easily explained by assuming as first reaction step the hydrolysis of pyrylium salts which leads to an acyclic 1,5-pentendione **6** (pseudobase), followed in a second step, by a Bayer-Villiger-type oxidation of the latter (Scheme 4). The reaction path *via* the pseudobases is surely encountered in the oxidation of pyrylium salts to 2-acylfurans, in alkaline medium.[7,8] From the oxidation of styrylketones by peracetic acid, Böeseken and coworkers have isolated enol esters and have studied their *E/Z* isomerism.[25] Wenkert and Rubin have later postulated the reaction mechanism.[26]

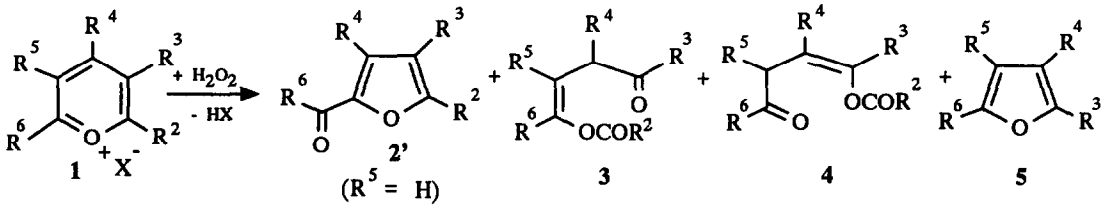


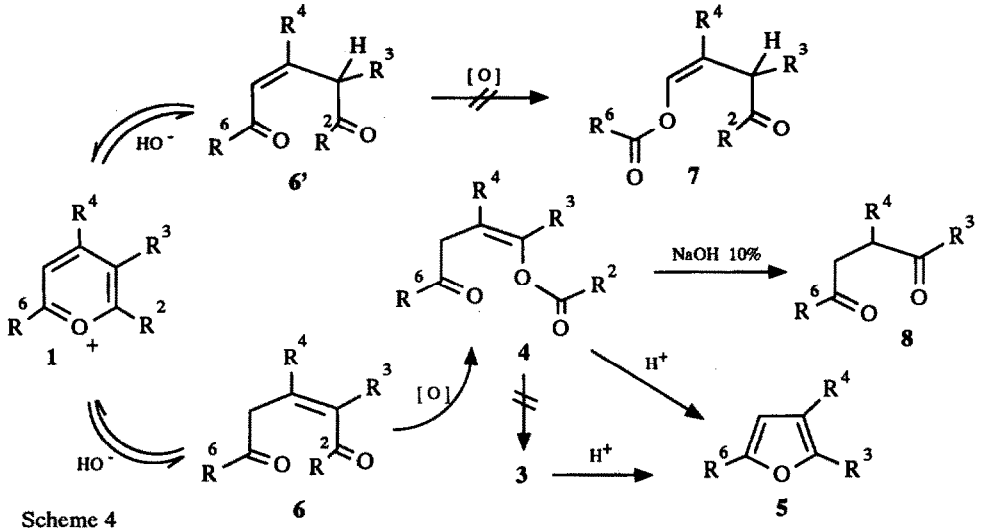
Table. Oxidation of pyrylium salts with hydrogen peroxide in aqueous buffers.[a]

1	R^2	R^3	R^4	R^5	R^6	X	Ref.	Buffer	2 / 2'	3	4	5
a	Me	H	Ph	H	Me	SAC[b]	19	-	94(95)	(1)	(2)	(1)
b	Me	H	Me	H	Me	BF_4	20	NaH_2PO_4	77(90)	-	3(7)	(1)
c	*i*Pr	H	Me	H	*i*Pr	ClO_4	21	NaH_2PO_4	75(92)	-	(3)	(4)
d	Me	Me	Me	H	Me	ClO_4	22	NaH_2PO_4	5(17)	9(10)	27(43)	7(17)
e	Me	*i*Pr	Me	H	Me	ClO_4	23	NaH_2PO_4	5(8)	8(16)	48(50)	15(21)
f	Me	Me	Ph	H	Me	ClO_4	21	NaH_2PO_4	5(12)	15(20)	25(30)	20(25)
								NaH_2PO_4-AcONa	3(12)	15(18)	29(35)	22(33)
								NaH_2PO_4-Na_2HPO_4	16(22)	17(30)	21(35)	6(10)
								NaH_2PO_4/CH_3CN	(13)	(29)	(40)	(12)
								NaH_2PO_4/EtOH	(5)	(4)	(20)	(65)
f-d_6	CD_3	CH_3	Ph	H	CD_3	ClO_4	24	NaH_2PO_4	7(8)	18(23)	30(33)	20(28)
								NaH_2PO_4-AcONa	6(12)	15(22)	30(35)	18(25)
g	*i*Pr	Me	Ph	H	*i*Pr	ClO_4	-	NaH_2PO_4	4(17)	5(20)	26(40)	15(25)
h	Me	Me	Et	H	Me	ClO_4	13,14	NaH_2PO_4	7(8)	18(25)	35(42)	12(20)
i	Me	Me	Me	Me	Me	ClO_4	13,14	NaH_2PO_4	-	26(33)[c]		18(37)
j	Me	Me	Ph	Me	Me	ClO_4	-	NaH_2PO_4	-	33(47)	(9)	14(32)

[a] Figures represent the yields of isolated compounds whereas figures in brackets represent the composition of the reaction mixture (after 20 min at 100°C, or boiling temperature) as determined from GLC or GC-MS ; [b] SAC stands for the sulfoacetate anion, $HOOC\text{-}CH_2\text{-}SO_3^-$; [c] 3i ≡ 4i

Thus, the formation of enol esters from pyrylium pseudobases appears to be probable. However, for 2,3,4,6-tetrasubstituted pyrylium salts, two isomeric pseudobases **6** and **6'** are possible[27] and the latter should lead by the Wenkert-Rubin mechanism to the enol ester **7** and not **3** (Scheme 4). If one presumes that **6** which has a tetrasubstituted double bond, is thermodynamically more stable than **6'**, and that both pseudobases are in equilibrium with the pyrylium salt, then the formation of **7** can indeed be suppressed. The enol ester **3** should then arise *via* **4** by an acid or base catalysed isomerisation during the reaction or its workup. Rio and Fellion have however shown that **6'** (with a trisubstituted double bond) was obtained from a 3-methyl--2,4,6-triphenylpyrylium salt on mild alkaline hydrolysis,[27] and this is in accord with a predominant 2-attack of the HO^- nucleophile and a kinetic control of the reaction.

This isomerisation of **4** into **3** was disproved as **4e** was recovered unchanged either from an aqueous reaction medium (large excess of NaH_2PO_4, presence of H_2O_2, 80 °C, 2 H.) or from a CCl_4 solution which



Scheme 4

was stirred for 12 hours with aqueous $NaHCO_3$. Complete hydrolysis of **4e** occurs easily with 10% NaOH, leading to the expected γ-diketone **8e** (2,4-dimethylheptane-3,6-dione). Both enol esters **3** and **4** are partially transformed into furans **5** on heating with *p*-toluenesulfonic acid. Also the yields in furans **5** are increased at longer reaction times or, especially, by running the reaction in ethanol. These facts may be rationalised by the acid catalysed formation of furans from δ-diketones **8**, which in turn, are hydrolysis and/or trans-esterification products of **3** and **4**. Alternatively, the furans **5** may arise by enolisation of the δ-keto group in **3** or **4**, followed by elimination of R^2COOH.

Interestingly, one can diminish the furan formation in favour of the enol esters, by using aqueous acetonitrile as reaction medium or by using a NaH_2PO_4-Na_2HPO_4 (pH < 5) buffer.

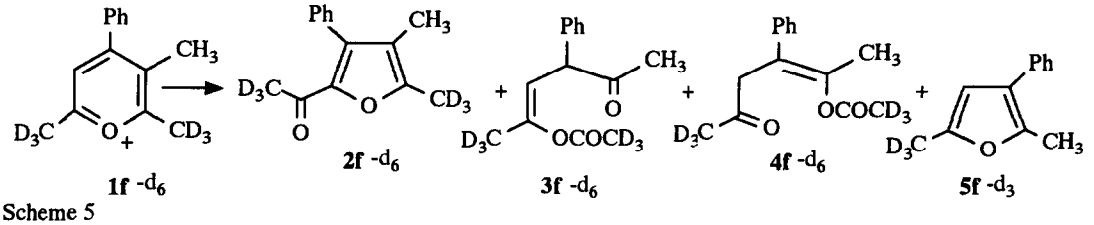
Prolonged contact with silica gel transforms the enol esters **3** and **4** into yellow and impure 2-ene-1,4-diones which in some cases are also present (2-6% by GC-MS) in the crude reaction mixtures and which are known to undergo easily further transformations.[28]

Discussion of the Reaction Mechanism : Pyrylium Salt versus Pseudobase Oxidation

The kinetics of pseudobase formation from 2,4,6-trisubstituted pyrylium salts, in phosphate and acetate buffers, have been investigated thoroughly spectroscopically by UV[16] and ^{13}C-NMR[17]and polarographically.[18] These studies show that at pH ≤ 5, the conversion into pseudobases is slow ($T_{1/2}$ = 58 min. at 25 °C and pH = 3) and reversible, while at pH > 5 the conversion is rapid, complete and associated with a change of colour. By stirring salts **1d** or **1e** with concentrated aqueous NaH_2PO_4 at 100 °C, formation of both pseudobases **6** and **6'** could be monitored by ^{1}H-NMR, the latter being predominant. If hydrogen peroxide was added shortly after admixing the pyrylium salt with the aqueous buffer, the compositions of the reaction mixtures are reproducible and are those given in the Table. If the pyrylium salt was stirred in the aqueous NaH_2PO_4 buffer for more than 30 min, and then hydrogen peroxide was added, the reaction mixtures were more complex, although the products **2-5** were still present. However, with a sodium acetate buffer (at pH = 9 and 100 °C) the addition of hydrogen peroxide after a few minutes led to other products. At higher pH values, when the equilibrium pyrylium salt ⇆ pseudobase is shifted towards the latter, the yields in oxidation

products **2-5** were diminished mainly due to the inter- and intra-molecular condensation of the pseudobases.[15] At low pH values (< 5), oxidation of both the pyrylium salt and its pseudobases may occur. From the fact that the enol esters **3** are formed without the isomerisation of **4** and that no other stereoisomers of both **3** and **4** were encountered, it appears however that the pseudobases **6** or **6'** (which may give rise to E/Z stereoisomers[16,27]) are not oxidised and consequently, the pyrylium ring is the one to be first (or more rapidly) attacked by the HOO^- nucleophile. The geometry of the double bonds in **3** and **4** was unequivocally determined from NOE difference spectra (see the experimental section) as being only the one depicted in the Schemes.

In order to gain more insight on the mechanism, we oxidised 2,6-di-(trideuteriomethyl)-3-methyl-4--phenylpyrylium perchlorate[24] (**1f**-d_6, having a deuterium content of about 96% d_6, by ^{1}H-NMR) with hydrogen peroxide, in an aqueous buffer of NaH_2PO_4 (pH = 3). Almost complete retention of the deuteriomethyl groups in **3** and **4**, was observed and the same result was encountered with a buffer containing beside a 20 molar excess of NaH_2PO_4, one mole (*per* mole **1f**-d_6) of unlabelled sodium acetate (pH = 4.4). The products isolated from both experiments are presented in Scheme 5. Thus, the trideuterioacetyl shift must occur without complete dissociation (which should form the CD_3COO^- anion in the aqueous buffer) and subsequent recombination (which should lead to incorporation of unlabelled acetate ions).



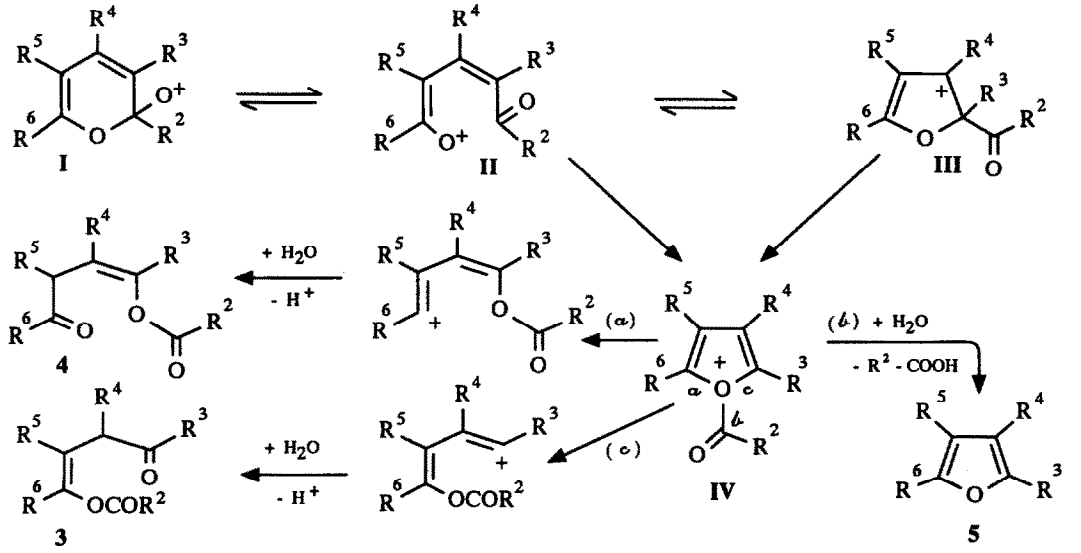
Scheme 5

Formation of the furan **5** is accomplished by expulsion from the pyrylium ring of the 2-carbon atom and its substituent as an acyl moiety. This moiety can be found in the aqueous $NaHCO_3$ washings of the reaction mixture, after acidification, either as isobutyric acid from salt **1g**, or as acetic acid in all other cases.

We present in Scheme 6 a mechanistic explanation which seems to be in accord with all the above findings and which involves an intermediate *O*-acylfurylium ion **IV**. Formation of **IV** from the type **I** cations is in accord with the regioselectivity observed for 2,3,4,6-tetrasubstituted pyrylium salts. Also, the cleavages of the three C-O bonds (denoted *a*, *b* and *c* in Scheme 6) should have comparable probability, leading to products **4**, **5** and **3**, respectively, in comparable amounts. The product distribution shown in the Table again supports this assumption, although enol esters **3** are somewhat less favoured, in all cases except **1j**.

The interesting feature of this reaction is the shift of the acyl moiety (cation **II** or **III** to **IV**). We tried to determine if this acyl shift is 1.2 (i.e. from **III** to **IV**) by attempting to generate cations of type **III** and **IV** by Friedel-Crafts catalysis. Methylation with $CH_3I/AlCl_3$ of the acetylfuran **2a**, (1:1:1 molar ratio) in carbon disulfide, led to almost complete recovery of **2a** after decomposition of the chloroaluminate complex. On the other hand, the acetylation of the furan **5f** with acetyl chloride in carbon disulfide could lead to a type **IV** *O*-acylfurylium ion. Without $AlCl_3$, unreacted **5f** was recovered after decomposition of the reaction mixture and no trace of enol esters was found. With $AlCl_3$, normal acylations occur first in the 4-position of the furan

ring and then, with excess of acetyl chloride, the 3-phenyl ring is *para*-acetylated. Indeed, very few alkylations of 2-acetylfurans have been reported up to now[29] and in the known[30] acylations of alkylfurans, no enol esters have been identified. On the other hand, the acetylation of 2,5-disubstituted furans with $SnCl_4$ in milder conditions is known to lead to 3-acetyl derivatives.[31] On the basis of these experiments we can only speculate that the acyl shift might be 1.5 in cation **II**, leading to **IV**.



Scheme 6

CONCLUSION

Although the oxidation of pyrylium salts with hydrogen peroxide has been known for more than 30 years, there have been no attempts until now either to improve the yields in which 2-acylfurans are obtained from 2,4,6-trisubstituted pyrylium salts, or to study this reaction for tetra- and penta-substituted pyrylium salts. We have shown that by using a sodium phosphate buffer, the yields in which 2-acylfurans can be isolated are almost doubled. On the other hand we have presented a mechanism which is in accord with all previous findings and which leads for the polysubstituted pyrylium salts to enol esters and furans. From the preparative viewpoint, the access to δ-keto-enol esters **3** and **4** with a known geometry, and thus potentially interesting chemistry,[32] may be of use. Also, the preparation of tetrasubstituted furans, which has recently received attention,[33] may be effected by the present reaction if the pyrylium salt is available. In this case use of ethanol as a cosolvent is recommended and chromatographic separations can be avoided as the furans may be obtained by distillation, being the most volatile components. The assigment of the fragmentation patterns of the new enol esters **3** and **4** under EI-MS conditions was facilitated by comparison with the deuterium analogs and will be presented elsewhere.[34]

EXPERIMENTAL

General Methods. Solvents were dried according to standard procedures and distilled before use. Column chromatography was run on silica gel (Merck) using petroleum ether and then increasing amounts of diethyl ether in petroleum ether. For analytical purposes, ready made plates coated with silica gel (Merck, 60F 254, 0.2 mm thick) deposited on aluminium foil were eluted with petroleum ether : ethyl acetate : methanol = 30 : 10 : 1 and from these the R.F. values were measured after UV-visualisation and/or spraying with $Ce(SO_4)_2 : H_3[P(Mo_3O_{10})_4] : H_2SO_4 : H_2O = 1 : 2.5 : 11 : 94$ (by weight). Melting points were determined on a Kofler hot stage melting point apparatus (Reichert, Austria) and are uncorrected. Infrared spectra were run in CCl_4 solution (unless otherwise stated) on Perkin Elmer 1310 and 841 spectrophotometers. Ultraviolet spectra were measured on a Phillips PU 8740 scanning spectrophotometer. Routine GLC analyses were run with a Pye Unicam GCD chromatograph equipped with a FID detector, on a OV17 column (2 m), oven temperature 190 °C, with hydrogen as carrier gas. Electron-impact MS (70 eV) were run on Varian MAT instruments (CH5, CH7 for the GC/MS, and 731 for the HR-MS). Routine ^{1}H-NMR spectra were run at 60 MHz on Varian T60 and at 80 MHz on Bruker WM 80 instruments, while the ^{13}C-NMR (100.62 MHz), DEPT, high field ^{1}H-NMR (400 MHz) and NOE difference spectra were recorded on a Bruker AM 400 instrument. All NMR spectra were run in $CDCl_3$ solution with internal TMS. The δ values are given in ppm while the H-H coupling constants over n bonds (^nJ) are given in Hz ; q stands for quartet.

Oxidation of pyrylium salts in buffered solution. General procedure.

A concentrated aqueous buffer of pH 3 was prepared from sodium dihydrogen phosphate in 15 to 20 molar excess of the pyrylium salt. Addition of 1 mole of disodium hydrogen phosphate or sodium acetate increased the pH to 4.5. This solution was heated to 100° and was added at once to the pyrylium salt (1 mole) and shortly thereafter, under stirring, aqueous hydrogen peroxide (35 %, 1.4 moles) was added dropwise, fairly rapidly so that within less than one minute the pyrylium salt, buffer and H_2O_2 were all stirred together at 100°. A pertinent change of colour was to be avoided as it indicated pseudobase formation and condensation of the latter to cyanine dyes. This could occur if the pH was over 5. Otherwise, an upper oily layer separated and a slight discolouration from yellow-orange to pale yellow was observed after the first five minutes. After stirring for twenty minutes the reaction mixture was cooled, extracted twice with diethyl ether, the combined ethereal extracts were washed twice with saturated aqueous solutions of sodium hydrogen carbonate and then sodium chloride. By acidification of the aqueous layer and washings, a carboxylic acid could be isolated (acetic acid for salts **1d-f, 1h** and **1i**, or isobutyric acid for **1g**). After drying the ethereal layer over sodium sulfate the crude reaction mixtures were analysed (GLC, GC-MS and NMR) and were transferred to a silica gel column after rotoevaporation of the solvent . The furans **5** were always eluted first (with petroleum ether) after which followed the acylfurans **2'**. The enol esters **3** and then **4** were eluted next with increasing amounts of diethyl ether. In the case of **1g**, the enol esters were eluted in reverse order. Elution with diethyl ether gives yellow fractions in which the *cis/trans* 2-ene-1,4-diones predominate, while final addition of methanol to the eluent gives high molecular mass products which could not be identified. The GLC retention factors are different from the TLC ones. From a OV17 column, the furans **5** were followed by the enol esters **3** and **4** which were however not always separated, and finally by the acylfurans **2'**.

1-(5-Methyl-3-phenylfuran-2-yl)-1-ethanone (2a)[11]. ^{13}C-NMR: 13.62 (5-Me), 27.23 (2-Ac), 111.56 (C-4) 127.83 and 128.88 (C-2',6' and C-3',5'), 128.11 (C-4'), 132.05 (C-3), 134.90 (C-1'), 145.88 (C-5), 155.33 (C-2), 187.03 (C=O). MS (%): 200 (M^+, 64), 199 (M-H, 51), 185 (M-Me, 100), 129 (22), 128 (28), 127 (13), 77 (9), 51 (9), 43 (29).

Oxidation of 2,4,6-trimethylpyrylium tetrafluoroborate **(1b)**.[20]

10.5 g **1b** were oxidised in the presence of 118 g $NaH_2PO_4 \cdot 2H_2O$ with 7.3 ml 35% H_2O_2. The above work-up yielded 6.24 g of yellow oil. Vacuum distillation of 1.89 g of this oil gave 1.59 g (77% yield based on **1b**) of **2b**,[1] m.p. ≈ 10 °C, R_f = 0.48. By column chromatography (150 ml silica gel) of the remaining crude oil, after elution with petroleum ether (300 ml) and then with 100 ml portions containing increasing amounts (1 %, 2 %,...) of diethyl ether in petroleum ether, **2b** was eluted and was followed by **4b**. Other minor components could not be gained in pure form.

***(Z)*-1-(Acetyloxy)-2-methyl-1-penten-4-one (4b)**. Colourless oil isolated in 3% yield (0.235 mg) after vacuum distillation of the combined chromatographic fractions with R_f = 0.32. ^{1}H-NMR (400 MHz): 1.61 (3H, d, ^4J = 1.6, 2-Me), 2.06 (3H, sharp s, 1-OCOMe), 2.09 (3H, s, 5-CH_3), 3.16 (2H, broad s, 3-CH_2), 7.00 (1H, q of t, ^4J = 1.6, ^5J = 0.8, 1-H). Irradiation of the 2-Me d caused a strong, positive NOE effect on 1-H (and on the 3.16 CH_2 group), while irradiation of 1-H (7.00 ppm) caused a weaker positive NOE effect only on the 2-Me doublet. Thus the double bond has *Z* configuration. ^{13}C-NMR: 17.9 (5-CH_3), 20.5 (1-OCOMe), 29.1 (2-Me), 44.9 (CH_2, DEPT), 114.8 (2-C), 132.2 (1-C), 167.5 (1-OCOMe), 205.5 (4-C). IR (PE841): 1754s, 1722s, 1217vs, 1104s. EI-MS (%): 114 (8), 96 (14), 71 (25), 43 (100). Anal. Calcd for $C_8H_{12}O_3$ (156.18): C, 61.52; H, 7.74. Found: C, 61.91; H, 7.97.

Oxidation of 2,6-diisopropyl-4-methylpyrylium tetrafluoroborate (**1c**).[21]

0.666g **1c** and 5.6 g $NaH_2PO_4 \cdot 2H_2O$ in 15 ml water (pH = 3) at 95 °C were oxidised with 0.35 ml H_2O_2 35% affording 0.424 g yellow-orange oil. Vacuum distillation gave 0.362 g (75% yield) **2c**.[1,4]

Oxidation of 2,3,4,6-tetramethylpyrylium perchlorate (**1d**).[22]

3.17 g of **1d** containing less than 3% 4-ethyl-2,6-dimethylpyrylium were oxidised with 1.8 ml 35% H_2O_2 in the presence of 31.4 g $NaH_2PO_4 \cdot 2H_2O$ giving after rotoevaporation (10 °C) 1.43 g of yellow oil which was chromatographed as above. The order of elution was **5d**,[33] **2'd**, **3d**, **4d**, and other unidentified minor components.

1-(3,4,5-Trimethylfuran-2-yl)-1-ethanone (**2'd**). Colourless oil which crystallises at -20 °C, isolated in 5% yield, R_f = 0.51. ^{1}H-NMR (80 MHz): 1.87 (3H, q, $^5J \approx 0.3$, 4-Me), 2.15 and 2.16 (6H, broad s, 2-Ac and 5-Me), 2.36 (3H, s, 3-Me). IR (PE841): 1668vs, 1542s. EI-MS (%): 152 (M^+, 57), 137 (M-Me, 100), 109 (M-Ac, 14), 81 (20), 79 (23), 77 (13), 53 (18), 43 (99), 41 (18), 39 (22). HR-MS: Calcd for $C_9H_{12}O_2$ 152.0837, found 152.0834.

2,4-Dinitrophenylhydrazone of **2'd** : brick red crystals, m.p. 225-8 °C. ^{1}H-NMR (80 MHz): 1.96 (3H, d, $^5J \approx 0.5$, 4-Me), 2.30 (3H, broad s, 5-Me), 2.35 (3H, s, 3-Me), 2.44 (3H, s, MeC=N), 7.86 (1H, d, ^3J = 9, 6'-H), 8.32 (1H, dd, ^3J = 9, ^4J = 2.5, 5'-H), 9.10 (1H, d, ^4J = 2.5, 3'-H). IR (PE841, $CHCl_3$) : 3295mw, 1616s, 1590s, 1333s. UV (EtOH), λ_{max}(log ϵ_{max}): 201 (4.20), 221 (4.18), 266 (4.13), 308 (3.99), 400 (4.41) ; UV (EtOH, NaOH): 213 (4.78), 274 (4.09), 472 (4.37), 575 (sh). Anal. Calcd for $C_{15}H_{16}N_4O_5$ (332.32): C, 54.22; H, 4.81; N, 16.86. Found : C, 53.99; H, 4.67; N, 16.57.

(Z)-**2-(Acetyloxy)-4-methyl-2-hexen-5-one** (**3d**). Colourless oil, isolated in 9% yield, R_f = 0.30. ^{1}H-NMR (400 MHz): 1.09 (3H, d, ^3J = 6.9, 4-Me), 1.89 (3H, d, ^4J = 1.0, 1-CH_3), 2.09 (3H, s, 6-CH_3), 2.14 (3H, sharp s, 2-OCOMe), 3.25 (1H, d of q, ^3J = 9.5, ^3J = 6.9, 4-H), 4.96 (1H, d of q, ^3J = 9.4, ^4J = 1.0, 3-H); ^{13}C-NMR: 16.1 (6-CH_3), 19.6 (4-Me), 20.7 (2-OCO<u>Me</u>), 28.0 (1-CH_3), 44.6 (4-C), 116.1 (3-C), 146.9 (2-C), 168.6 (2-O<u>C</u>OMe), 209.1 (5-C). IR (PE841): 1755s, 1722s, 1370s, 1355s, 1219s, 1178s, 1012s ; EI-MS (%): 127 (14), 110 (51), 86 (22), 85 (88), 659 (11), 67 (56), 43 (100) ; Anal. Calcd for $C_9H_{14}O_3$ (170.21): C, 63.51; H, 8.29. Found: C, 63.69; H, 8.85.

(Z)-**2-(Acetyloxy)-3-methyl-2-hexen-5-one** (**4d**). Colourless oil, isolated in 27% yield, R_f = 0.22. ^{1}H-NMR (400 MHz): 1.66 (3H, q, ^5J = 1.0, 3-Me), 1.86 (3H, sext, ^5J = 1.0 and 0.9, 1-CH_3), 2.05 (3H, s, 6-CH_3), 2.07 (3H, sharp s, 2-OCOMe), 2.95 (2H, broad s, 4-CH_2). ^{13}C-NMR: 16.1 (6-CH_3), 17.4 (3-Me), 20.7 (2-OCO<u>Me</u>), 28.9 (1-CH_3), 46.7 (4-CH_2, DEPT), 116.0 (3-C), 142.4 (2-C), 169.0 (2-O<u>C</u>OMe), 206.2 (5-C). IR (PE841): 1755s, 1716s, 1369s, 1356s, 1201s, 1173s, 1147s. EI-MS (%): 128 (M-CH_2CO, 44), 110 (M-AcOH, 97), 86 (25), 85 (91), 57 (68), 43 (100), 41 (26). Anal. Calcd for $C_9H_{14}O_3$ (170.21): C, 63.51; H, 8.29. Found: C, 63.84 ; H, 8.80.

Oxidation of 3-isopropyl-2,4,6-trimethyl-pyrylium perchlorate (**1e**).[23]

2.29 g of **1e** and 20.2 g of $NaH_2PO_4 \cdot 2H_2O$ were admixed with 1.38 ml H_2O_2 (35%) at 90 °C and stirred for 40 min at this temperature. After rotoevaporation (10 °C), 1.38 g yellow oil remained out of which 1.28 g were chromatographed as above.

3,5-Dimethyl-2-(1-methylethyl)-furan (**5e**). Isolated in 15% yield as a colourless oil which crystallises at -20 °C, R_f = 0.64. ^{1}H-NMR (60 MHz): 1.20 (6H, d, ^3J = 8, 2-CH<u>Me</u>$_2$), 1.87 (3H, s, 3-Me), 2.18 (3H, d, ^4J = 1, 5-Me), 2.90 (1H, sept. ^3J = 7, 2-<u>C</u>HMe$_2$), 5.50 (1H, broad s, 4-H); IR: 1575, 1460, 1450, 995. EI-MS (%): 138 (M^+, 40), 123 (M-Me, 86), 43 (100), 41 (31), 39 (41). HR-MS: Calcd for $C_9H_{14}O$ 138.1045, found 138.1037.

1-[3,5-Dimethyl-4-(1-methylethyl)furan-2-yl]-1-ethanone (**2'e**). Isolated in 4.5% yield (70 mg) based on **1e**, R_f = 0.43. ^{1}H-NMR (60 MHz): 1.20 (6H, d, ^3J = 7, 4-CH<u>Me</u>$_2$), 2.30 (9H, sharp m, 2-Ac, 3- and 5-Me), 2.80 (1H, sept, 4- <u>C</u>HMe$_2$); upon addition of Eu(fod)$_3$, the 2.30 multiplet is split into three methyl singlets. IR (PE841): 1668s, 1610m, 1536s. EI-MS (%): 180 (M^+, 36), 165 (M-Me, 100), 152 (11), 43 (83), 41 (11), 39 (9). HR-MS: Calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1142.

2,4-Dinitrophenylhydrazone of **2'e** : dark red needles, m.p. 160-170 °C with resolidification, and final m.p. 216-218 °C (from $CHCl_3$). ^{1}H-NMR (60 MHz): 1.27 (6H, d, ^3J = 6.5, CH<u>Me</u>$_2$), 2.33 and 2.38 (3H and 6H, respectively, s, 2-Me-C=N, 3- and 5-Me), 2.90 (1H, sept, 4-C<u>H</u>Me$_2$), 7.70 (1H, d, ^3J = 9, 6'-H), 8.20 (1H, dd, ^3J = 9, ^4J = 2.5, 5'-H), 8.97 (1H, d, ^4J = 2.5, 3'-H), 11.15 (1H, broad s, NH). IR (PE841, $CHCl_3$): 3315w, 1614s, 1593s, 1535m, 1514m, 1420m 1334s, 1312ms, 1274m, 1136m, 1097m. UV (EtOH), λ_{max}(log ϵ_{max}): 196.5 (4.26), 204.9 (4.38), 223.2 (4.41), 264.0 (4.31), 304.4 (4.25), 406.8 (4.64). UV (EtOH, NaOH): 197 (4.36), 206.7 (4.76), 209.2 (4.76), 267.7 (sh, 3.95), 476.5 (4.60), 575 (sh, 4.0). Anal. Calcd for $C_{17}H_{20}N_4O_5$ (360.37): C, 56.66; H, 5.59; N, 15.55. Found: C, 56.42; H, 5.53; N, 15.52.

(*Z*)-**6-Acetoxy-2,4-dimethyl-5-hepten-3-one** (**3e**). Isolated in 8.2% yield (140 mg) based on **1e**, R_f = 0.35. ^{1}H-NMR (400 MHz): 1.011 and 1.065 (6H, two d, ^3J = 6.87, diastereotopical CH<u>Me</u>$_2$), 1.03 (3H, d, ^3J = 7.06, 4-Me), 1.87 (3H, d, ^4J = 1.13, 7-Me), 2.14 (3H, s, OAc), 2.72 (1H, sept, ^3J = 6.87, 2-C<u>H</u>Me$_2$), 3.45 (1H, d of q, ^3J = 9.84, and ^3J = 6.95, 4-H), 4.55 (1H, d of q, ^3J = 9.96 Hz and ^4J = 1.13, 5-H). ^{13}C-NMR: 16.60,

18.14, 18.67, 19.51, 20.76 (five methyl groups), 38.98 (2-C), 41.82 (4-C), 116.46 (5-C), 146.34 (6-C), 168.57 (6-OCOMe), 214.82 (3-C). IR (PE841) : 2976m, 2936m, 2877w, 1759s, 1716s, 1380m, 1370m, 1216s, 1171s, 1012m, 939w. EI-MS (%) : 138 (7), 127 (6.5), 85 (100), 71 (19), 69 (7), 67 (10), 43 (97), 41 (19), 39 (7). Anal. Calcd for $C_{11}H_{18}O_3$ (198.26): C, 66.64; H, 9.15. Found: C, 66.90; H, 9.24.

(*Z*)-3-(Acetoxy)-2,4-dimethyl-3-hepten-6-one (4e). Isolated in 48% yield based on **1e**, R_f = 0.20. ^{1}H-NMR (400 MHz): 0.96 (6H, d, ^3J = 6.84, $CH\underline{Me}_2$), 1.73 (3H, s, 4-Me), 2.05 (3H, s, 7-CH_3CO), 2.11 (3H, sharp s, 3-OAc), 2.85 (2H, s, 5-CH_2), 2.88 (1H, sept, 2-$C\underline{H}Me_2$). ^{13}C-NMR: 17.21, 19.67 ($CH\underline{Me}_2$), 20.31, 28.74, 29.18, 47.46 (CH_2, DEPT), 115.35 (C-4), 149.46 (C-3), 169.19 (O$\underline{C}$OMe), 206.38 (C-6). IR (PE841): 2974ms, 1755s, 1715s, 1367ms, 1199s, 1167ms, 1137m, 1076mw, 1046. EI-MS (%): 156 (23), 138 (91), 123 (84), 113 (86), 95 (51), 69 (39), 43 (100), 41 (82), 39 (27). Anal. Calcd for $C_{11}H_{18}O_3$ (198.26): C, 66.64; H, 9.15. Found: C, 66.48; H, 9.32.

Attempted conversion of **4e** *into* **3e** : 85 mg **4e** dissolved in CCl_4 were heated for 2 h with aqueous NaH_2PO_4 and 5 mg H_2O_2 after which **4e** remained unchanged (by ^{1}H-NMR). The same CCl_4 solution was stirred overnight with aqueous $NaHCO_3$, again without any changes.

2,4-Dimethyl-3,6-heptanedione (8e). Heating a CCl_4 solution of **4e** with 10% NaOH solution for 1 h at 80 °C gave quantitatively **8e** as a colourless fragrant oil. ^{1}H-NMR (60 MHz): 1.05 and 1.08 (6H, two d, ^3J = 7, diastereotopical $CH\underline{Me}_2$), 2.06 (3H, s, 4-Me), 2.67-3.13 (3H, m, 2-$C\underline{H}Me_2$ and 5-CH_2). IR (PE841): 1713s.

Oxidation of 4-phenyl-2,3,6-trimethylpyrylium perchlorate (**1f**)[21] *and of 2,6-di(trideuteriomethyl)-3-methyl-4-phenylpyrylium perchlorate* (**1f**-d_6).[24]

Several oxidations were effected as shown in the Table. The GLC separation of **3f** and **4f** was poor so their relative concentration was approximated as the one which resulted from ^{1}H-NMR integral curves.

2,5-Dimethyl-3-phenylfuran (5f).[35] R_f = 0.60. The 6.64 ppm chemical shift of the 4-proton is probably misprinted in ref.[35]. ^{1}H-NMR (80 MHz): 2.30 (3H, quint ^4J and ^6J < 1, 5-Me), 2.41 (3H, q, $^6J \approx 0.5$, 2-Me), 6.08 (1H, q, $^4J \approx 1$, 4-H), 7.30 (5H, m, 3-Ph). EI-MS (%): 172(M^+, 100), 171 (M-H, 42), 157 (M-Me, 20), 129 (M-Ac, 49), 128 (32), 43 (88).

2-Methyl-3-phenyl-5-trideuteriomethylfuran (5f-d_3). ^{1}H-NMR (80 MHz): 2.40 (3H, s, 2-Me), 6.10 (1H, s, 4-H), 7.32 (5H, m, 3-Ph). EI-MS (%): 175 (M^+, 83), 174 (M-H, 100), 157 (M-CD_3, 29), 129 (M-CD_3CO, 58), 77 (10), 46 (CD_3CO, 16), 43 (Ac, 19). Noteworthy is the small M-CH_3CO peak, 132 (11).

1-(4,5-Dimethyl-3-phenylfuran-2-yl)-1-ethanone (2'f). Colourless oil, R_f= 0.47. ^{1}H-NMR (80 MHz): 1.83 (3H, q, ^5J = 0.6, 4-Me), 2.18 (3H, s CH_3CO), 2.35 (3H, q, ^5J = 0.6, 5-Me), 7.30 (5H, m,Ph). HR-MS: Calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0944.

2,4-Dinitrophenylhydrazones of **2'f** were obtained as a 2:3 mixture of *syn/anti* isomers which after washing with hot ethanol gives an 1:4 mixture with m.p. 235-240 °C. ***Anti***: ^{1}H-NMR (80 MHz): 1.84 (3H, s, 4-Me), 2.29 (3H, sharp s, CH_3C=), 2.36 (3H, s, 5-Me), 6.87 (1H, d, ^3J = 10.2, 6"-H), 7.2-7.4 (5H, m, 3-Ph), 8.02 (1H, dd, ^3J = 10.2 and 2.9, 5"-H), 9.05 (1H, d, ^3J = 2.9, 3"-H), 11.16 (1H, s, NH···O). ***Syn***: 13.09 (1H, broad s, NH). IR: 1610ms, 1575ms, 1330s. UV (EtOH), λ_{max}(log ϵ_{max}): 201 (3.48), 265 (sh), 264.0 (4.31), 303 (2.80), 395 (3.24). UV (EtOH, NaOH): 210.3 (3.98), 265 (sh), 462 (3.28), 570 (sh, 3.07). Anal. Calcd for $C_{20}H_{18}N_4O_5$ (394.39): C, 60.91; H, 4.60; N, 14.21. Found : C, 61.26; H, 4.57; N, 13.84.

2,2,2-Trideuterio-1-(4-methyl-3-phenyl-5-trideuteriomethylfuran-2-yl)-1-ethanone (2f-d_6). ^{1}H-NMR (80 MHz): 1.83 (3H, s, 4-Me), 7.30 (5H, m, Ph).

(*Z*)-2-(Acetoxy)-4-phenyl-2-hexen-5-one (3f). Colourless needles, m.p. 59-61 °C (Et_2O), R_f = 0.35. ^{1}H-NMR (400 MHz): 1.92 (3H, dd, ^4J = 1.2, ^5J = 0.8, CH_3C=), 2.07 (3H, d, ^4J = 0.4, CH_3CO), 2.09 (3H, sharp s, 2-OAc), 4.44 (1H, broad d, ^3J = 8.57, 4-H), 5.58 (1H, d of q, ^3J = 8.62, ^4J = 1.1, 3-H), 7.18 (2H, d of t, ^3J = 7.5, *o*-Ph-H), 7.24 (1H, m, *p*-Ph-H), 7.30 (2H, t of t, ^3J = 7.2, ^4J = 0.9, *m*-Ph-H). ^{13}C-NMR: 19.49 (C-6), 20.52 ($\underline{C}H_3COO$), 28.15 (C-1), 56.07 (C-4), 113.92 (C-3), 127.18 (C-4'), 128.26 and 128.78 (C-3'5' and C-2'6'), 137.79 (C-1'), 147.00 (C-2), 168.05 (2O$\underline{C}$OMe), 205.44 (C-5). EI-MS (%): 189 (15), 172 (4), 148 (12), 147 (100), 131 (4), 129 (15), 103 (6), 91 (2), 77 (7), 51 (3), 43 (77). IR: 1765s, 1725s, 1210s, 1190s, 1155s, 705ms. UV (C_6H_{14}), λ_{max}(log ϵ_{max}): 198 (4.42), 260 (2.18), 267 (2.17), 287 (2.23), 362 (1.02). Anal. Calcd for $C_{14}H_{16}O_3$ (232.28): C, 72.39; H, 6.94. Found: C, 72.99; H, 6.95

(*Z*)-4-Phenyl-6,6,6-trideuterio-2-(trideuterioacetoxy)-2-hexen-5-one (3f-d_6). ^{1}H-NMR (80 MHz): 2.09 (3H, s, CH_3CO), 4.44 (1H, d , ^3J =8.5, CH-Ph), 5.58 (1H, sharp d, ^3J = 8.6, HC=), 7.25 (5H, m, Ph). IR (PE841): 2244w, 1755s, 1721s, 1221s, 1067s, 699s. EI-MS (%): 238 (M^+, 0.1), 195 (14), 175 (5), 151 (100), 132 (14), 130 (11), 103 (7) 77 (9), 46 (67), 43 (28).

(*E*)-2-(Acetoxy)-3-phenyl-2-hexen-5-one (4f), colourless needles m.p. 55-56 °C (C_6H_{14}), R_f = 0.30. ^{1}H-NMR (80 MHz): 1.90 (3H, t, ^5J = 1 , 1-CH_3), 2.04 (3H, s, 6-CH_3), 2.18 (3H, sharp s, 2-OCOCH_3), 3.32 (2H, broad s, 4-CH_2), 7.28 (5H, sharp m, Ph). ^{13}C-NMR: 17.32 (C-6), 20.78 (2-OCO$\underline{C}H_3$), 29.152 (C-1), 47.47 (C-4), 122.559 (C-3), 127.32 (C-4'), 128.37 and 128.76 (C-3'5' and C-2'6'), 138.92 (C-1'), 145.72 (C-2),168.71 (2-O$\underline{C}$OCH$_3$), 205.60 (C-5). MS (%) : 232 (M^+, 0.2), 190 (11), 172 (26), 148 (10), 147 (72), 119 (23), 103 (10), 91 (11), 77 (8), 51 (3), 43 (100). IR : 1758s, 1712s, 1600m (shoulder), 1220s, 1160s,

705ms. UV (C_6H_{14}), $\lambda_{max}(\log \epsilon_{max})$: 194 (4.38), 237 (3.91). Anal. Calcd for $C_{14}H_{16}O_3$ (232.28): C, 72.39; H, 6.94. Found: C, 72.90; H, 7.16

(*E*)-3-Phenyl-6,6,6-trideuterio-2-(trideuterioacetoxy)-2-hexen-5-one (4f-d_6). ^{1}H-NMR (80 MHz): 1.91 (3H, t, ^5J = 1, CH_3C=), 3.36 (2H, q , ^5J = 1, 4-CH_2), 7.25 (5H, sharp m, Ph). EI-MS (%): 238 (M^+, 0.2), 194 (9), 175 (45), 148 (88), 120 (31), 103 (20), 92 (6), 77 (17), 46 (100), 43 (44).

Acetylation of **5f**.

Furan **5f** (0.235 g) in 5 ml CS_2 was added to an ice-cooled suspension of $AlCl_3$ in excess acetyl chloride. The mixture was decomposed with 1% HCl and ice after stirring at room temperature for 90 min. Extraction with diethyl ether, washing of the ethereal extracts with aqueous $NaHCO_3$ and then NaCl solutions, drying and subsequent solvent rotoevaporation, left a 7:3 mixture of mono- (**5f**-Ac) and di-acetylated (**5f**-Ac_2) products which were separated by preparative TLC (3 mm thick silica gel coated plates which were eluted with petroleum ether : diethyl ether : methanol = 30 : 10 : 1).

1-(2,5-Dimethyl-4-phenylfuran-3-yl)-1-ethanone (**5f**-Ac). Colourless oil which crystallised at -20 C, m.p. ≈ 25 °C (CS_2), isolated in 45% yield, R_f = 0.50. ^{1}H-NMR (80 MHz): 1.91 (3H, s, 3-Ac), 2.16 (3H, q, ^6J ≈ 0.6, 5-Me), 2.52 (q, 3H, ^6J ≈ 0.6, 2-Me), 7.33 (5H, m, 4-Ph). IR: 1670s,1559s, 1373s, 1306s, 1210m, 1161m, 700s. EI-MS (%): 214 (M^+, 58), 199 (79), 171 (18), 143 (9), 129 (13), 128 (20), 125 (9), 77 (10), 43 (100). HR-MS: Calcd for $C_{14}H_{14}O_2$ 214.0994, found 214.0985.

1-[2,5-dimethyl-4-(4-acetylphenyl)-furan-3-yl]-1-ethanone (**5f**-Ac_2). Isolated in 20% yield as slightly impure oil, R_f = 0.30. ^{1}H-NMR (80 MHz): 1.98 (3H, s, 3-Ac), 2.19 (3H, q, ^6J ≈ 0.5, 5-Me), 2.54 (3H, q, ^6J ≈ 0.3, 2-Me), 2.63 (3H, s, 4'-Ac), 7.30 (2H, d of small t, ^3J = 8.5, *o*-Ph-H), 7.99 (2H, d of small t, ^3J = 8.5, *m*-Ph-H). IR: 1685vs, 1670vs, 1265s. EI-MS (%): 256 (M^+, 18), 241 (19), 199 (14), 187 (9), 86 (12), 84 (20), 49 (55), 43 (100). HR-MS: Calcd for $C_{16}H_{16}O_3$ 256.1100, found 256.1068.

2,6-Diisopropyl-3-methyl-4-phenylpyrylium perchlorate (**1g**) *and its oxidation.*

The diisobutyrylation of 2-phenyl-2-butene with isobutyric anhydride and perchloric acid gave in 20.5 % yield **1g** which after recrystallisation from *i*PrOH/AcOH (3:1) gave light tan crystals with m.p. 133 °C. ^{1}H-NMR (80 MHz) : 1.48 and 1.49 (6H each, two d, ^3J = 6 and 6.5, respectively, 2- and 6-$CH\underline{Me}_2$), 2.43 (3H, s, 3-Me), 3.46 (1H, sept, 2-$C\underline{H}Me_2$), 3.66 (1H, sept, 6-$C\underline{H}Me_2$), 7.08 (5h, m, Ph). IR (PE841) : 3022m, 2984m, 1618s, 1509s, 1484m, 1094vs, 623m. UV (MeOH) $\lambda_{max}(\log \epsilon_{max})$: 196 (3.61), 208 (4.25), 307 (4.18). Anal. Calcd for $C_{18}H_{23}ClO_5$ (354.83) C, 60.93 ; H, 6.53. Found : C, 61.04, H, 6.83.

Oxidation of 2.37 g **1g** and 10.4 g $NaH_2PO_4 \cdot 2H_2O$ with 1.1 ml H_2O_2 35% in 25 ml water at 100 °C for 35 min, gave after following the same work-up procedure, 1.66 g yellow oil which was separated by column chromatography as above.

2-Methyl-5-(1-methylethyl)-3-phenylfuran (**5g**). Isolated in 15% yield based on **1g**, as colourless oil which darkens on standing at room temperature, RF = 0.60. ^{1}H-NMR (80 MHz): 1.26 (6H, d, ^3J = 7, 5-$CH\underline{Me}_2$), 2.40 (3H, s, 2-Me), 2.91 (1H, sept, ^3J = 7, 5-$C\underline{H}Me_2$), 6.10 (1H, d, ^4J = 1, 4-H), 7.2-7.45 (5H, m, Ph). IR: 1600ms, 1220ms, 700ms. EI-MS (%): 200 (M^+, 39), 185 (M-Me, 100), 141 (7.2), 128 (10), 115 (12), 77 (4) 43 (28). HR-MS: Calcd for $C_{14}H_{16}O$ 200.1201, found 200.1169.

2-Methyl-1-[4-methyl-5-(1-methylethyl)-3-phenyl-2-furanyl]-1-propanone (**2'g**). Isolated in 4% yield as colourless oil, R_f = 0.56. ^{1}H-NMR (400 MHz): 1.11 (6H, d, ^3J = 6.89, 2-COCH$\underline{Me}_2$), 1.34 (6H, d, ^3J = 6.99, 5-$CH\underline{Me}_2$), 1.87 (3H, s, 4-Me), 3.12 (1H, sept, ^3J = 7.0, 5-$C\underline{H}Me_2$), 3.28 (1H, sept, ^3J = 6.9, 2-COC$\underline{H}Me_2$), 7.3-7.6 (5H, m, 3-Ph). Irradiation of the low field septet (3.28 ppm) collapsed the high field *i*Pr doublet (1.11 ppm) while in a NOE difference spectrum, by irradiation of the 4-methyl group (1.87 ppm). positive effects were measured for the high field *i*Pr septet (3.12 ppm) and *ortho* phenyl protons (d, at 7.33 ppm). MS (%): 270 (M^+, 16), 227 (M-C_3H_7, 100), 169 (5), 156 (7), 155 (7), 141 (8), 128 (7), 115 (11), 91 (6), 77 (5), 43 (17), 41 (9). HR-MS: Calcd for $C_{18}H_{22}O_2$ 270.1620, found 270.1605.

(*E*)-6-Methyl-2-(2-methylpropanoyloxy)-3-phenyl-2-hepten-5-one (**4g**). Isolated as colourless oil in 26% yield, R_f = 0.45. ^{1}H-NMR (400 MHz): 0.99 (6H, d, ^3J = 6.92, COC$\underline{H}Me_2$), 1.25 (6H, d, ^3J = 6.96, 2-OCOC$\underline{H}Me_2$), 1.89 (3H, broad s, 1-CH_3), 2.63 (1H, sept, ^3J = 6.87, COC$\underline{H}Me_2$), 2.68 (1H, sept, ^3J = 6.99, 2-OCOC$\underline{H}Me_2$), 3.43 (2H, q, ^5J = 0.8, 4-CH_2), 7.25 and 7.33 (5H, m, 3-Ph). Irradiation at 2.63 ppm sharpened the high field (0.985 ppm) *i*Pr doublet while irradiation at 2.68 sharpened the low field *i*Pr doublet. Irradiation of the 4-CH_2 signal shows positive NOE effects : a doublet (^3J = 8.8) at 7.20 ppm (*o*-Ph protons) and the 2.63 ppm septet. Irradiation of the 1.886 signal (1-CH_3) again shows as positive NOE effects the *o*-Ph protons (doublet, 7.20 ppm), thus the methyl and phenyl group are *cis*, i.e. the 2-3 double bond has the *E* configuration. ^{13}C-NMR: 17.11 (1-C), 18.12 and 18.80 (two $CH\underline{Me}_2$), 33.98 (6-C), 39.70 (2-OCO$\underline{C}HMe_2$), 44.05 (4-CH_2, DEPT), 122.42 (3-C), 127.09 (4'-C), 128.43 and 128.76 (2',6'-C and 3',5'-C), 139.24 (1'-C), 145.37 (2-C), 174.74 (2-$O\underline{C}OCHMe_2$), 210.96 (5-C). IR: 1744s, 1710m, 1690w, 1130s, 700m. EI-MS (%): 288 (M^+, 0.1), 218 (3.6), 200 (23), 185 (10), 147 (33), 105 (17), 77 (12), 71 (43), 43 (100). Anal. Calcd for $C_{18}H_{24}O_3$ (288.39): C, 74.97; H, 8.39. Found C, 74.30; H, 7.95.

(Z)-2-Methyl-3-(2-methylpropanoyloxy)-5-phenyl-3-hepten-6-one (3g). Isolated in 5% yield as colourless oil which crystallises at -20 °C, R_f = 0.41. ^{1}H-NMR (400 MHz): 1.061 and 1.070 (6H, two d, ^3J = 6.84 and 6.85, diastereotopical C-CHMe$_2$), 1.232 and 1.254 (6H, two d, ^3J = 7.02 and 6.99, diastereotopical 3-OCOCHMe$_2$), 2.10 (3H, s, 7-CH$_3$), 2.45(1H, broad sept, ^3J = 6.8, C-CHMe$_2$), 2.65 (1H, sharp sept, ^3J = 6.98, 3-OCOCHMe$_2$), 4.36 (1H, d, ^3J = 8.9, 5-H), 5.61 (1H, d of d, ^3J = 8.8 and ^4J = 0.95, 4-H), 7.20 (2H, m, *o*-Ph), (1H, m, *p*-Ph), 7.31 (2H, m, *m*-Ph). Irradiation pf the 2.65 septet changes the low field *i*Pr dd, while irradiation at 2.49 collapses into a triplet the high field *i*Pr dd and in a NOE difference spectrum shows strong positive effects at the 4-H (5.6 ppm, now a sharp d), thus the 3-4 double bond has *Z* configuration. ^{13}C-NMR: 18.952, 18.995, 20.01 and 20.12 (both CHMe$_2$ groups), 28.35 (7-CH$_3$), 32.29 and 34.00 (3-OCOCHMe$_2$ and C-CHMe$_2$), 56.04 (5-C), 111.47 (4-C), 127.19 (4'-C), 127.98 and 128.79 (2',6'-C and 3',5'-C), 137.92 (1'-C), 155.27 (3-C), 174.35 (3-OCOCHMe$_2$), 205.76 (6-C). IR: 1750s, 1720s, 1685ms, 1600w, 1220s, 700ms. EI-MS (%): 245 (M-Ac, 4), 200 (M-Me$_2$CHCOOH, 14), 185 (8), 175 (57), 131 (13), 103 (15), 91 (12), 77 (10), 71 (Me$_2$CHCO$^+$, 55), 43 (100). Anal. Calcd for $C_{18}H_{24}O_3$ (288.39): C, 74.97; H, 8.39. Found C, 74.50; H, 8.10.

4-Ethyl-2,3,6-trimethylpyrylium **(1h)** *and 2,3,4,5,6-pentamethylpyrylium* **(1i)** *perchlorates and their oxidation*

The diacetylation of 3-methyl-3-pentanol (80g) with acetic anhydride (370 ml) was effected by adding slowly, dropwise, 67% perchloric acid (48 ml) and letting the temperature rise to 110 °C. Heating at 80 °C was continued for two h after completion of addition. After cooling and stirring with diethyl ether, an amorphous solid is obtained which after boiling with charcoal in *i*PrOH containing 1% $HClO_4$, on cooling deposits 99 g (50% diacetylation yield) of a 1:4 mixture of pyrylium perchlorates **1h** and **1i** , m.p. 75-85 °C. Recrystallisation from ethyl acetate gives colourless plates of **1i** which contain less than 5% **1h** (by ^{1}H-NMR), m.p. 104-106 °C and which upon exposure to sunlight become pink. Previous attempts[13,14] to obtain a crystalline 2,3,4,5,6-pentamethylpyrylium salt apparently failed, although better yields were obtained by means of an optimised diacetylation procedure.[14] **1i**: ^{1}H-NMR (80 MHz): 2.40 (6H, s, 3,5-Me$_2$), 2.55 (3H, s, 4-Me), 2.81 (6H, s, 2,6-Me$_2$). ^{13}C-NMR : 14.42 (3,5-Me$_2$), 19.05 (4-Me), 20.01 (2,6-Me$_2$), 131.25 (C-3,5), 170.39 (C-4), 172.10 (C-2,6). IR (PE841, $CHCl_3$): 3026m, 1618m, 1489m, 1097vs, 625m. UV (MeOH), $\lambda_{max}(\log \epsilon_{max})$: 198 (4.41), 245 (3.63), 299 (4.12). Anal. Calcd for $C_{10}H_{15}ClO_5$ (250.68): C, 47.91; H, 6.03; Cl, 14.14. Found C, 47.87; H, 6.09; Cl, 13.5.

In order to have access to products arising both from **1h** and **1i**, 8.1 g of a mixture of the two perchlorates, enriched in **1h** (29%) was oxidised with 4.7 ml 35 % H_2O_2 in 75 ml water containing 76.4 g $NaH_2PO_4 \cdot 2H_2O$ at 100 °C. After the usual workup, 4.22 g of yellow oil with the following composition was obtained: by GLC: **5h** (11.0), **5i** (33.0), **3i ≡ 4i** (23.3), **3h** (7.4), **4h** (12.4), **2'h** (2.5); by GC-Ms **5h** (10.5), **5i** (20.3),**9h** (1.5), **9i** (1.3), **3h** (5.2), **3i ≡ 4i** (20.3), **4h** (20.3), **2'h** (5.5); by ^{1}H-NMR : **5h** (10), **5i** (42), **3i 4i** (23), **3h** (5), **4h** (5). This mixture (3.12 g) was chromatographed as above on 170 ml silica gel. **3-Ethyl-2,5-dimethylfuran**[36] **(5h)** and **2,3,4,5-tetramethylfuran**[36] **(5i)** had R_f = 0.62 and 0.53, respectively.

1-(3-Ethyl-4,5-dimethylfuran-2-yl)-1-ethanone (2'h). Isolated in 7% yield based on **1h** (50 mg), R_f = 0.48. ^{1}H-NMR (60 MHz): 1.07 (3H, t, ^3J = 7, 3-CH$_2$CH$_3$), 1.87 (3H, s, 4-Me), 2.22 (3H, s, 5-Me), 2.27 (3H, sharp s, 2-COCH$_3$), 2.65 (2H, q, ^3J = 7, 3-CH$_2$CH$_3$). IR: 1680s. EI-MS (%): 166 (M$^+$, 30), 151 (M-Me, 83), 43 (100), 41 (14), 39 (17).

(Z)-2-(Acetyloxy)-4-ethyl-2-hexen-5-one (3h) : Isolated as pale yellow oil, in 18% yield based on **1h** (120 mg), R_f = 0.26. ^{1}H-NMR (400 MHz) : 0.81 (3H, t, ^3J = 7.4, 4-CH$_2$CH$_3$), 1.4 and 1.6 (2H, m, diastereotopic 4-CH$_2$CH$_3$), 1.90 (3H, d, ^4J = 1.1, 1-CH$_3$), 2.07 (3H, s, 6-CH$_3$), 2.12 (3H, s, 2-OCOMe), 3.04 (1H, d of t ^3J = 9.6, ^3J = 7.9, 4-H), 4.90 (1H, d of q, ^3J = 9.7, ^4J = 1.2, 3-H). ^{13}C-NMR: 11.2 (4-CH$_2$CH$_3$), 16.4 (6-CH$_3$), 19.6 (2-OCOMe), 24.3 (4-CH$_2$CH$_3$), 28.5 (1-CH$_3$), 52.0 (4-CH), 114.7 (3-CH), 147.8 (2-C), 169.3 (2-OCOMe), 208.9 (5-C). IR (PE841): 1756s, 1718s, 1215s. EI-MS (%): 141 (2), 124 (13), 99 (62), 81 (6), 43 (100). Anal. Calcd for $C_{10}H_{16}O_3$ (184.23): C, 65.19; H, 8.75. Found C, 65.40; H, 8.43.

(Z)-2-(Acetyloxy)-3,4-dimethyl-2-hexen-5-one (3i ≡ 4i). Isolated as colourless oil after vacuum distillation (2 Torr) in 25% yield based on **1g**, (450 mg), R_f = 0.32. ^{1}H-NMR (400 MHz): 0.97 (3H, d, ^3J = 6.89, 4-Me), 1.50 (3H, ^5J = 1.18, 3-Me), 1.83 (3H, q, ^5J = 1.10, 1-CH$_3$), 1.98 (3H, s, 6-CH$_3$), 2.07 (3H, sharp s, 2-OCOMe), 3.35 (1H, q, ^3J = 6.91, 4-H). ^{13}C-NMR: 12.73 and 13.39 (3- and 4-Me), 16.32 (6-CH$_3$), 20.61 (2-OCOMe), 27.91 (1-CH$_3$), 48.20 (4-CH), 120.92 (3-C), 141.59 (2-C), 169.06 (2-OCOMe), 208.68 (C-5). IR (PE841): 1754s, 1717s, 1212ms, 1150m. EI-MS (%): 124 (18), 99 (88), 81 (7), 55 (12), 43 (100), 41 (7), 39 (7). Anal. Calcd for $C_{10}H_{16}O_3$ (184.23): C, 65.19; H, 8.75. Found C, 65.29; H, 9.02.

(Z)-2-(Acetyloxy)-3-Ethyl-2-hexen-5-one (4h). Isolated as pale yellow oil in 35% yield based on **1h**, R_f = 0.33. ^{1}H-NMR (400 MHz): 0.93 (3H, t, ^3J = 7.55, 3-CH$_2$CH$_3$), 1.86 (3H, m, ^5J = 0.62, 1-CH$_3$), 2.04 (3H, s, 6-CH$_3$), 2.05 (3H, sharp s, 2-OCOMe), 2.94 (2H, q, ^5J = 0.38, 4-CH$_2$). ^{13}C-NMR: 12.17 (3-CH$_2$CH$_3$), 15.73 (6-CH$_3$), 20.62 (OCOMe), 22.85 (3-CH$_2$CH$_3$, DEPT), 28.80 (1-CH$_3$), 44.47 (4-CH$_2$, DEPT), 121.67 (C-3), 142.61 (C-2), 168.83 (OCOMe), 206.50 (C-5). MS (%): 142 (5), 124 (23), 99 (80), 55(5), 43 (100). Anal. Calcd for $C_{10}H_{16}O_3$ (184.23): C, 65.19; H, 8.75. Found C, 64.89; H, 8.67.

4-Phenyl-2,3,5,6-tetramethylpyrylium perchlorate (**1j**) *and its oxidation.*

The diacetylation of 3-phenyl-2-butene (obtained in turn by the iodine catalysed dehydration of 3-phenyl--3-pentanol) with acetic anhydride and perchloric acid gave **1j** in 9% yield, m.p. 223-4 °C (from 1% $HClO_4$). ^{1}H-NMR (80 MHz) : 2.13 (6H, s, 3,5-Me_2), 2.89 (6H, s, 2,6-Me_2), 7.25 (2H, m, *m*-Ph-H), 7.51 (3H, m, *o,p*-Ph-H). IR ($CHCl_3$, PE841): 3025s, 1611s, 1471m, 1443m, 1096vs, 700m, 623ms. UV (MeOH), λ_{max} (log ϵ_{max}): 202 (4.53), 306 (4.12). Anal. Calcd for $C_{15}H_{17}ClO_5$ (312.75): C, 57.61; H, 5.48; Cl, 11.33. Found: C, 57.09; H, 5.42; Cl, 11.5.

Oxidation of **1j** (0.765 g) in 10 ml water containing 5.73 g $NaH_2PO_4 \cdot 2H_2O$ with 0.35 ml H_2O_2 35%, gave after work-up 0.483 g yellow oil which was separated by column chromatography as above.

3-Phenyl-2,4,5-trimethylfuran (**5j**). Isolated in 14% yield, R_f = 0.61. ^{1}H-NMR (80 MHz): 1.85 (3H, q, ^{5}J = 0.75, 4-Me), 2.20 (3H, q, ^{5}J = 0.75, 5-Me), 2.24 (3H, s, 2-Me), 7.15-7.50 (5H, m, Ph). ^{13}C-NMR: 9.11, 11.39 and 12.20 (2-, 3- and 5-Me) 113.90 (4-C), 122.54 (3-C), 126.21 (4'-C), 128.23 and 129.20 (2',6'- and 3',5'-C), 134.30 (1'-C), 145.03 and 145.35 (2- and 5-C). IR: 1605s, 1260s, 1200m, 1010m, 995m, 700s.EI-MS (%): 186 (M^+, 100), 185 (M-H, 33), 171 (M-Me, 22), 143 (M-Ac, 36), 128 (M-Ac-Me, 25), 115 (11), 93 (5), 77 (4), 43 (17). HR-MS: Calcd for $C_{13}H_{14}O$ 186.1045, found 186.1036.

(*Z*)-2-(Acetyloxy)-3-methyl-4-phenyl-2-hexen-5-one (**3j**). Isolated as pale yellow oil in 33% yield, R_f = 0.35. ^{1}H-NMR (400 MHz): 1.59 (3H, quint, ^{4}J = 1.0, 3-Me), 1.94 (3H, q, ^{5}J = 0.87, 1-CH_3), 2.14 (3H, sharp s, 2-OCOMe), 2.17 (3H, s, 6-CH_3), 4.69 (1H, broad s, 4-H), 7.12 (2H, dd, *o*-Ph-H), 7.22 (1H, d, *p*-Ph-H), 7.29 (2H, t, *m*-Ph-H). Irradiation of the 3-Me signal at 1.59 ppm causes a positive NOE effect on the *o*-Ph protons (7.12 ppm), 4-H proton (4.69 ppm) and 5-Me group, thus the two methyl groups are *cis* i.e. the 2-3 double bond has a *Z* configuration. ^{13}C-NMR: 15.03 and 16.56 (6-CH_3 and 3-Me), 20.77 (2-OCOMe), 29.65 (1-CH_3), 59.42 (4-C), 119.86 (3-C), 127.05 (4'-C), 128.43 and 129.05 (2',6'- and 3',5'-C), 136.56 (1'-C), 142.25 (2-C), 169.06 (2-OCOMe), 206.33 (5-C). IR (PE841): 1755s, 1720s, 1213s, 1161m, 1140m, 700s. MS (%): 186 (86), 162 (26), 161 (96), 143 (87), 128 (24), 115 (24), 91 (19), 43 (100). Anal. Calcd for $C_{15}H_{18}O_3$ (246.31): C, 73.15; H, 7.37. Found C, 73.43; H, 7.88.

(*E*)-2-(Acetyloxy)-4-methyl-3-phenyl-2-hexen-5-one (**4j**). Could not be separated from **3j**, being obtained as a 2:3 mixture, R_f = 0.40. ^{1}H-NMR (80 MHz): 1.10 (d, ^{3}J = 7, 4-Me), 1.80 (s, 1-CH_3), the 6-CH_3 and 2-OCOMe signals are obscured by signals of **3j**, 3.32 (q, 4-H). ^{13}C-NMR: 13.8 (4-Me), 17.7 (6-CH_3), 20.7 (2-OCOMe), 28.2 (1-CH_3), 50.7 (4-CH), 138.1 (1'-C), 144.7 (2-C), 169.0 (2-OCOMe), 207.7 (5-C); other aromatic signals are obscured by **3j**. GC-MS (%): 246 (M^+,1), 204 (1), 186 (38), 161 (71), 105 (17), 91 (11), 43 (100).

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