THERMAL ADDITION REACTION OF AROYLKETENE WITH ETHYL VINYL ETHER: AROMATIC SUBSTITUENT EFFECT ON AROYLKETENE REACTIVITY

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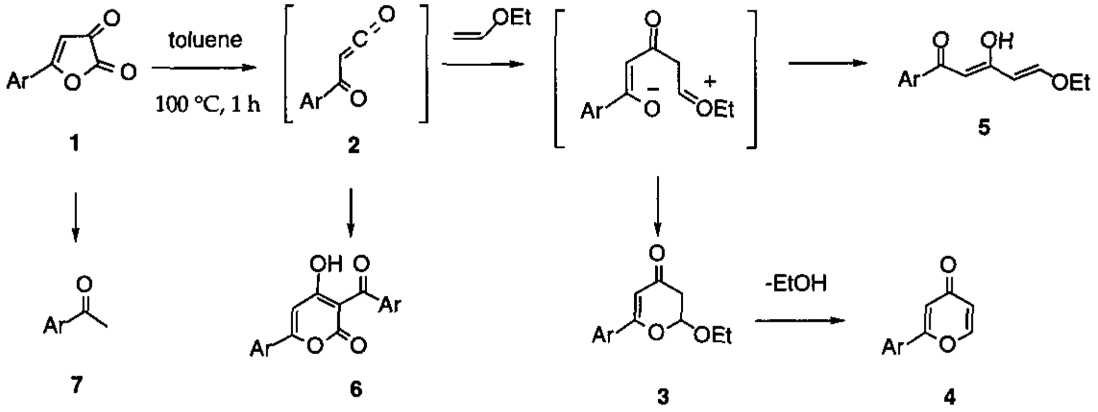
Abstracts —— A series of aroylketenes (**2**) generated by thermolysis of 5-aryl-2,3-dihydrofuran-2,3-diones (**1**) reacted with ethyl vinyl ether under a thermal condition to give 2,3-dihydro-4*H*-pyran-4-ones (**3**) and/or 4*H*-pyran-4-ones (**4**). In this reaction the electron withdrawing substituent (NO_2, Cl) introduced into the aryl part enhanced the ketene reactivity (**2b-e**), while the electron donating one (OMe) did not affect its reactivity (**2f-g**) in a significant extent. The hetero-aroylketenes (**2h**) and (**2i**) showed a fairly good reactivity.

[4+2] Cycloaddition reaction of acylketenes with a variety of hetero-olefins constitutes a method of preparing various heterocyclic compounds.[1] Furthermore, the acylketenes were shown to have good reactivity for electron rich olefins such as enol ethers[2,3] and ketene acetals.[2,4] Recently, we demonstrated that the reaction of aroylketene with 1-aryl-1-trimethylsilyloxyethylene gave 1,5-diarylpentane-1,3,5-trione and/or 2,6-diaryl-4*H*-pyran-4-one and that the introduction of electron withdrawing substituent such as nitro and chloro groups into the aryl part enhanced its reactivity, while that of electron donating group decreased the reactivity.[5] We concluded by detailed analysis of aroylketene molecular orbitals that the addition reaction should proceed in an ionic stepwise way rather than a concerted manner.[5] Furthermore, the results obtained from the reaction with cyclic enol ethers such as dihydrofuran and dihydropyran supported this conclusion.[6] In order to examine further the ketene reactivity we carried out the reaction of aroylketenes (**2**) with ethyl vinyl ether. Although Andreichikov *et al.* already reported a similar reaction, the reaction of benzoylketene (**2a**) with *n*-propyl vinyl ether which gave the 4*H*-pyran-4-one (**4a**) in 30% yield together with the ketene dimer (**6a**),[7] our results were found to be significantly different. Aroylketenes (**2**) used for the reaction were thermally generated *in situ* from 5-aryl-2,3-dihydrofuran-2,3-diones (**1**). Reactions were performed by heating a mixture of **1** and ethyl vinyl ether (2 mol eq) in dry toluene at 100 °C for 1 h in a sealed tube. Thus, dihydro-4*H*-pyran-4-ones (**3**), 4*H*-pyran-4-ones (**4**),



1 - 7
a: Ar = Phenyl
b: Ar = 4-Nitrophenyl
c: Ar = 2-Nitrophenyl
d: Ar = 4-Chlrophenyl
e: Ar = 2-Chlorophenyl
f: Ar = 4-Methoxyphenyl
g: Ar = 2-Methoxyphenyl
h: Ar = 2-Furyl
i: Ar = 2-Thienyl

Scheme 1

Table 1. Reaction of Aroylketenes with Ethyl Vinyl Ether

		Yield (%) of Products				
Run	aroylketene (Ar)	3	4	5	6	7
1	**2a** (Phenyl)	36 (**3a**)	9 (**4a**)	--	--	7 (**7a**)
2	**2b** (4-$NO_2C_6H_4$)	65 (**3b**)	--	--	--	9 (**7b**)
3	**2c** (2-$NO_2C_6H_4$)	50 (**3c**)	12 (**4c**)	--	--	--
4	**2d** (4-ClC_6H_4)	51 (**3d**)	3 (**4d**)	--	--	--
5	**2e** (2-ClC_6H_4)	56 (**3e**)	4 (**4e**)	--	--	--
6	**2f** (4-$MeOC_6H_4$)	--	29 (**4f**)	--	--	--
7	**2g** (2-$MeOC_6H_4$)	--	42 (**4g**)	--	3 (**6g**)	--
8	**2h** (2-furyl)	63 (**3h**)	4 (**4h**)	6 (**5h**)	--	--
9	**2i** (2-thienyl)	49 (**3i**)	--	6 (**5i**)	--	--

5-aryl-1-ethoxypent-1-ene-3,5-diones (**5**), ketene dimers (**6**), and aryl methyl ketones (**7**) were obtained (Scheme 1). The products were readily characterized by ms, ir, uv, and nmr spectral data (see Experimental). The ^{1}H-Nmr of **5** revealed that the stereochemistry of the olefin moiety was *trans* and the 1,3-diketone was completely enolized. The results were summarized in Table 1.

Contrary to Andreichikov's result, all aroylketenes (**2**), except the methoxybenzoylketenes (**2f**) and (**2g**), gave the dihydropyrones (**3**) and the pyrones (**4**) as a major and minor product, respectively. The latter two reactions of **2f** and **2g** gave only the pyrones (**4f**) and (**4g**). Interestingly, in the cases of 2-furoyl-(**2h**) and 2-thenoylketenes (**2i**) the uncyclized products (**5h**) and (**5i**) were yielded. This formation suggested that the addition reaction of **2** with ethyl vinyl ether proceeded in an ionic stepwise manner.

The formation of aroylketene dimer was observed only in the reaction of **2g** which gave **6g** in 3% yield. Aryl methyl ketones (**7**) which may be produced directly from **1** were detected in the reactions of **1a** and **1b**. The occurrence of these side reactions should decreases the efficiency of this addition reaction.

Aroylketenes with a nitro group **2b**, **2c** and a chloro group **2d**, **2e** in the aryl part showed a fairly good reactivity for the olefin. This enhancement in their reactivity when compared with the unsubstituted **2a** is similar to that observed in the reaction of **2** with 1-aryl-1-trimethylsilyloxyethylene.[5] Similarly, the hetero-aroylketenes (**2h**) and (**2i**) showed a fairly good reactivity. However, the methoxybenzoylketenes (**2f**, **2g**) showed a similar or slightly lower reactivity than **2a**. This result was contrast to that of their reactions with the trimethylsilyloxyethylene where the methoxy group considerably decreased the ketene reactivity.[5]

Although the dihydropyrones (**3**) on treatment with *p*-TsOH were quantitatively converted into the corresponding pyrones (**4**), this elimination reaction did not occur in a recognizable rate under a thermal condition (heating at 100 °C in toluene for 10 h).

EXPERIMENTAL

Unless otherwise stated, following procedures were adopted. Melting points (mp) were determined with YANACO MP-S1 melting point apparatus and are uncorrected. Infrared (Ir) spectra were measured with JASCO FT/IR-5000 Fourier transform infrared spectrometer using KBr and are given as cm^{-1}. Ultraviolet (uv) spectra were recorded on HITACHI U-3200 photospectrometer, and are given as nm (ε).

^{1}H-Nmr and ^{13}C-nmr spectra were obtained with a JEOL JNM-EX90 (^{1}H; 90 MHz), ^{13}C; 22.5 MHz) in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. High-resolution Mass (HRms) and Low-resolution Mass (LRms) spectra were obtained on JEOL JMS-D300 or JMS-HX110A spectrometer at 30 eV by the direct inlet system. The 5-aryl-2,3-dihydrofuran-2,3-diones (**1**) were prepared following our published procedure.[5]

Reaction of Aroylketenes with Ethyl Vinyl Ether (General Procedure)

A solution of **1** (500 mg) and ethyl vinyl ether (2 mol eq) in toluene (10 ml) was heated at 100 °C for 1 h in a sealed tube. After concentration *in vacuo*, the residue was purified by column chromatography over SiO_2 (benzene, CH_2Cl_2-hexane = 1:1, or CH_2Cl_2), medium pressure liquid chromatography (hexane-AcOEt = 2-4:1), and recrystallizations to give **3**, **4**, **5**, **6**, and **7**. The yields were listed in Table 1. The dimer (**6g**) was identified by comparison with the reported one.[5]

2-Ethoxy-6-phenyl-2,3-dihydro-4*H*-pyran-4-one (**3a**): Yellow oil. Ir: 1669, 1605, 1574. Uv: 291 (16600). ^{1}H-Nmr: 1.27 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 2.66 (1H, dd, J = 6, 17 Hz, H-3), 2.92 (1H, dd, J = 4, 17 Hz, H-3), 3.81, 4.09 (each 1H, dq, J = 7, 7, 7, 10 Hz, $C\underline{H}_2CH_3$), 5.61 (1H, dd, J = 4, 6 Hz, H-2), 6.07 (1H, s, H-5), 7.4 - 7.8 (5H, m, ArH). LRms *m/z*: 218 (M^+).

2-Phenyl-4*H*-pyran-4-one (**4a**): Pale yellow needles from acetone-ether, mp 102 - 104 °C [lit.,[7] mp 104 °C and lit.,[8] mp 102 - 104 °C].

2-Ethoxy-6-(4-nitrophenyl)-2,3-dihydro-4*H*-pyran-4-one (**3b**): Pale yellow needles from benzene, mp 172 - 173 °C. Ir: 1665, 1589, 1520. Uv: 318 (16700). ^{1}H-Nmr: 1.27 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 2.70 (1H, dd, J = 4, 17 Hz, H-3), 2.98 (1H, dd, J = 5, 17 Hz, H-3), 3.70, 4.01 (each 1H, dq, J = 7, 7, 7, 10 Hz, $C\underline{H}_2CH_3$), 5.67 (1H, dd, J = 4, 5 Hz, H-2), 6.14 (1H, s, H-5), 7.92, 8.29 (each 2H, dt, J = 2, 2, 9 Hz, ArH). LRms *m/z*: 263 (M^+). *Anal.* Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.07; H, 5.11; N, 5.26.

2-Ethoxy-6-(2-nitrophenyl)-2,3-dihydro-4*H*-pyran-4-one (**3c**): Colorless needles from CH_2Cl_2-ether, mp 92 - 94 °C. Ir: 1526, 1669. Uv: 214 (16400), 262 (12800). ^{1}H-Nmr: 1.25 (3H, t, J = 7 Hz, $CH_2C\underline{H}_3$), 2.78 (2H, d, J = 7 Hz, H-3), 3.69, 3.92 (each 1H, dq, J = 7, 7, 7, 10 Hz, $C\underline{H}_2CH_3$), 5.44 (1H, t, J = 7 Hz, H-2), 5.82 (1H, s, H-5), 7.5 - 8.0 (4H, m, ArH). ^{13}C-Nmr: 14.9 (q, $CH_2\underline{C}H_3$), 42.6 (t, C-3), 66.0 (t, $\underline{C}H_2CH_3$), 104.3 (d, C-2), 106.8 (d, C-5), 124.6 (d, Ar), 129.2 (s, Ar), 130.6 (d, Ar), 131.8 (d, Ar), 133.0

(d, Ar), 148.5 (s, Ar), 166.8 (s, C-6), 192.0 (s, C-4). CIms: *m/z* 264 (MH$^+$). *Anal.* Calcd for $C_{13}H_{13}NO_5$: C, 59.31; H, 4.98; N, 5.32. Found: C, 59.11; H, 5.02; N, 5.29.

2-(2-Nitrophenyl)-4*H*-pyran-4-one (4c): Pale brown prisms from CH_2Cl_2-ether, mp 165 - 167 °C. Ir: 1659, 1518. Uv: 245 (19200). ^{1}H-Nmr: 6.41 (1H, dd, *J* = 2, 6 Hz, H-5), 6.57 (1H, d, *J* = 2 Hz, H-3), 7.5-7.8 (4H, m, ArH), 8.0 - 8.1 (1H, m, H-6). ^{13}C-Nmr: 116.4 (d, C-5), 117.3 (d, C-3), 125.1 (d, Ar), 127.1 (s, Ar), 131.1 (d, Ar), 131.9 (d, Ar), 133.6 (d, Ar), 147.7 (s, Ar), 155.2 (d, C-6), 162.6 (s, C-2), 178.4 (s, C-4). LRms *m/z*: 217 (M$^+$). *Anal.* Calcd for $C_{11}H_7NO_4$: C, 60.83; H, 3.25; N, 6.45. Found: C, 61.02; H, 3.30; N, 6.39.

6-(4-Chlorophenyl)-2-ethoxy-2,3-dihydro-4*H*-pyran-4-one (3d): Colorless needles from CH_2Cl_2, mp 72 - 75 °C. Ir: 1665, 1605, 1562, 1543. Uv: 226 (10000), 249 (8600), 297 (19900), 367 (1500). ^{1}H-Nmr: 1.27 (3H, t, *J* = 7 Hz, $CH_2C\underline{H}_3$), 2.78 (1H, d, *J* = 5 Hz, H-3), 2.80 (1H, d, *J* = 4 Hz, H-3), 3.6 - 4.2 (2H, m, $C\underline{H}_2CH_3$), 5.60 (1H, dd, *J* = 4, 5 Hz, H-2), 6.03 (1H, s, H-5), 7.3 - 7.5 (2H, m, ArH), 7.6 - 7.9 (2H, m, ArH). ^{13}C-Nmr: 15.0 (q, $CH_2\underline{C}H_3$), 42.1 (t, C-3), 65.5 (t, $\underline{C}H_2CH_3$), 101.9 (d, C-2), 102.7 (d, C-5), 127.6 (dx2, Ar), 129.0 (dx2, Ar), 131.2 (s, Ar), 137.7 (s, Ar), 165.1 (s, C-6), 191.3 (s, C-4). HRms *m/z* (M$^+$) Calcd for $C_{13}H_{13}O_3Cl$: 252.0522. Found: 252.0550. *Anal.* Calcd for $C_{13}H_{13}O_3Cl$: C, 61.79; H, 5.19. Found: C, 61.58; H, 5.30.

2-(4-Chlorophenyl)-4*H*-pyran-4-one (4d): Colorless prisms from CH_2Cl_2, mp 170 - 172 °C. Ir: 1725, 1622, 1586, 1564. Uv: 274 (11900). ^{1}H-Nmr: 6.43 (1H, dd, *J* = 2, 6 Hz, H-5), 6.82 (1H, d, *J* = 2 Hz, H-3), 7.3 - 7.5 (2H, m, ArH), 7.6 - 8.0 (3H, m, ArH, H-6). ^{13}C-Nmr: 112.2 (d, C-5), 117.0 (d, C-3), 127.3 (d, Ar), 129.3 (d, Ar), 129.4 (s, Ar), 129.5 (dx2, Ar), 140.3 (s, Ar), 155.5 (d, C-6), 163.6 (s, C-2), 180.0 (s, C-4). HRms *m/z* (M$^+$) Calcd for $C_{11}H_7O_2Cl$: 206.0111. Found: 206.0132. *Anal.* Calcd for $C_{11}H_7O_2Cl$: C, 63.94; H, 3.41. Found: C, 63.76; H, 3.62.

6-(2-Chlorophenyl)-2-ethoxy-2,3-dihydro-4*H*-pyran-4-one (3e): Colorless needles from CH_2Cl_2-ether, mp 42 - 45 °C. Ir: 1665, 1605, 1562, 1543. Uv: 226 (10000), 249 (8600), 297 (19900), 367 (1500). ^{1}H-Nmr: 1.28 (3H, t, *J* = 7 Hz, $CH_2C\underline{H}_3$), 2.80 (1H, d, *J* = 6 Hz, H-3), 2.81 (1H, d, *J* = 5 Hz, H-3), 3.75, 4.09 (each 1H, dq, *J* = 7, 7, 7, 9 Hz, $C\underline{H}_2CH_3$), 5.57 (1H, dd, *J* = 5, 6 Hz, H-2), 5.80 (1H, s, H-5), 7.2 - 7.5 (4H, m, ArH). ^{13}C-Nmr: 14.7 (q, $CH_2\underline{C}H_3$), 42.1 (t, C-3), 65.4 (t, $\underline{C}H_2CH_3$), 102.2 (d, C-2), 107.6 (d, C-5), 126.7 (d, Ar), 130.0 (d, Ar), 130.3 (d, Ar), 131.3 (d, Ar), 132.3 (s, Ar), 132.8 (s, Ar), 166.6 (s, C-6), 191.2 (s, C-4). HRms *m/z* (M^+) Calcd for $C_{13}H_{13}O_3Cl$: 252.0563. Found: 252.0553. *Anal*. Calcd for $C_{13}H_{13}O_3Cl$: C, 61.79; H, 5.19. Found: C, 61.52; H, 5.31.

2-(2-Chlorophenyl)-4*H*-pyran-4-one (**4e**): Pale brown oil. Ir: 1655, 1609, 1593, 1545. Uv: 249 (9600). ^{1}H-Nmr: 6.45 (1H, dd, *J* = 2, 6 Hz, H-5), 6.68 (1H, d, *J* = 2 Hz, H-3), 7.3 - 7.6 (4H, m, ArH), 7.86 (1H, d, *J* = 6 Hz, H-6). ^{13}C-Nmr: 117.1 (d, C-5), 117.9 (d, C-3), 127.2 (d, Ar), 130.5 (d, Ar), 130.8 (d, Ar), 131.0 (s, Ar), 131.9 (d, Ar), 132.8 (s, Ar), 155.6 (d, C-6), 163.2 (s, C-2), 179.1 (s, C-4). HRms *m/z* (M^+) Calcd for $C_{11}H_7O_2Cl$: 206.0124. Found: 206.0132.

2-(4-Methoxyphenyl)-4*H*-pyran-4-one (**4f**): Colorless prisms from benzene, mp 115 - 116 °C. Ir: 1653, 1607, 1580, 1516. Uv: 212 (18900), 290 (23100). ^{1}H-Nmr: 3.87 (3H, s, $OC\underline{H}_3$), 6.35 (1H, dd, *J* = 3, 6 Hz, H-5), 6.70 (1H, d, *J* = 3 Hz, H-3), 7.0 - 7.1 (2H, m, ArH), 7.6 - 7.8 (2H, m, ArH), 7.80 (1H, d, *J* = 6 Hz, H-6). ^{13}C-Nmr: 55.3 (s, $O\underline{C}H_3$), 110.7 (d, C-5), 114.3 (dx2, Ar), 116.6 (d, C-3), 123.2 (s, Ar), 127.3 (dx2, Ar), 154.5 (dC-6), 162.1 (s, Ar), 163.8 (s, C-2), 179.0 (s, C-4). LRms *m/z*: 202 (M^+). *Anal*. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99. Found: C, 71.11; H, 5.12.

2-(2-Methoxyphenyl)-4*H*-pyran-4-one (**4g**): Pale yellow prisms from CH_2Cl_2-ether, mp 46 - 48 °C. Ir: 1651. Uv: 261 (14000). ^{1}H-Nmr: 3.91 (3H, s, $OC\underline{H}_3$), 6.34 (1H, dd, *J* = 2, 6 Hz, H-5), 7.08 (1H, d, *J* = 2 Hz, H-3), 7.09 (1H, d, *J* = 6 Hz, H-6), 7.1 - 7.9 (4H, m, ArH). ^{13}C-Nmr: 55.6 (q, $O\underline{C}H_3$), 111.7 (d, C-5), 116.6 (d, Ar), 117.4 (d, C-3), 120.1 (s, Ar), 120.7 (d, Ar), 128.9 (d, Ar), 132.3 (d, Ar), 155.0 (d, C-6), 157.6 (s, Ar), 161.4 (s, C-2), 179.6 (s, C-4). LRms *m/z*: 202 (M^+). *Anal*. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.99. Found: C, 71.25; H, 5.23.

2-Ethoxy-6-(2-furyl)-2,3-dihydro-4*H*-pyran-4-one (**3h**): Pale yellow oil. Ir: 1671, 1626, 1549. Uv: 216 (4000), 307 (21800). ^{1}H-Nmr: 1.25 (3H, t, *J* = 7 Hz, $CH_2C\underline{H}_3$), 2.66 (1H, dd, *J* = 5, 17 Hz, H-3), 2.88 (1H, dd, *J* = 4, 17 Hz, H-3), 3.71, 3.96 (each 1H, dq, *J* = 7, 7, 7, 10 Hz, $C\underline{H}_2CH_3$), 5.56 (1H, dd, *J* = 4, 5 Hz, H-2), 5.99 (1H, s, H-5), 6.53 (1H, dd, *J* = 2, 4 Hz, ArH), 6.93 (1H, dd, *J* = 1, 4 Hz, ArH), 7.56 (1H, dd, *J* = 1, 2 Hz, ArH). ^{13}C-Nmr: 15.1 (q, $CH_2\underline{C}H_3$), 42.5 (t, C-3), 65.5 (t, $\underline{C}H_2CH_3$), 101.0 (d, Ar), 101.9 (d, Ar), 112.5 (d, C-2), 113.4 (d, C-5), 145.8 (d, Ar), 147.6 (s, Ar), 157.7 (s, C-6), 190.8 (s, C-4). LRms *m/z*: 208 (M^+).

2-(2-Furyl)-4*H*-pyran-4-one (**4h**): Colorless prisms from CH_2Cl_2-ether, mp 135 - 136 °C. Ir: 1659, 1632, 1589, 1545. Uv: 222 (9700), 289 (20700). ^{1}H-Nmr: 6.32 (1H, dd, *J* = 3, 6 Hz, H-5), 6.57 (1H, dd, *J* = 2, 4 Hz, ArH), 6.69 (1H, d, *J* = 3 Hz, H-3), 6.95 (1H, dd, *J* = 1, 4 Hz, ArH), 7.58 (1H, dd, *J* = 1, 2 Hz, ArH), 7.71 (1H, d, *J* = 6 Hz, H-6). ^{13}C-Nmr: 110.1 (d, Ar), 112.4 (dx2, Ar), 117.2 (d, C-3), 145.5 (d, Ar), 145.7 (s, Ar), 154.1 (d, C-2), 155.9 (s, C-6), 178.5 (s, C-4). *Anal*. Calcd for $C_9H_6O_3$: C, 66.67; H, 3.73. Found: C, 66.30; H, 3.92.

***trans*-1-Ethoxy-5-(2-furyl)pent-1-ene-3, 5-dione (5h)**: Yellow prisms from CH_2Cl_2-ether, mp 67 - 68 °C. Ir: 1632, 1580. Uv: 244 (4700), 273 (6500), 358 (30900). ^{1}H-Nmr: 1.36 (3H, t, *J* = 7 Hz, $CH_2C\underline{H}_3$), 3.99 (2H, q, *J* = 7 Hz, $C\underline{H}_2CH_3$), 5.43 (1H, d, *J* = 13 Hz, H-2), 5.97 (1H, s, H-4), 6.52 (1H, dd, *J* = 2, 4 Hz, ArH), 7.11 (1H, dd, *J* = 1, 4 Hz, ArH), 7.5-7.7 (1H, m, ArH), 7.62 (1H, d, *J* = 13 Hz, H-1). ^{13}C-Nmr: 14.6 (q, $CH_2\underline{C}H_3$), 67.4 (t, $\underline{C}H_2CH_3$), 94.8 (d, C-4 or 2), 102.4 (d, C-2 or 4), 112.4 (d, Ar), 114.7 (d, Ar), 145.5 (d, Ar), 151.2 (s, Ar), 159.8 (d, C-1), 176.1 (s, C-3), 182.7 (s, C-5). LRms *m/z*: 208 (M^+). *Anal*. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81. Found: C, 63.21; H, 5.90.

2-Ethoxy-5-(2-thienyl)-2,3-dihydro-4*H*-pyran-4-one (3i): Yellow oil. Ir: 1661, 1595. Uv: 237 (4200), 260 (5500), 317 (18000). ^{1}H-Nmr: 1.27 (3H, t, *J* = 7 Hz, $CH_2C\underline{H}_3$), 2.67 (1H, dd, *J* = 5, 17 Hz, H-3), 2.89 (1H, dd, *J* = 4, 17 Hz, H-3), 3.73, 4.01 (each 1H, dq, *J* = 7, 7, 7, 10 Hz, $C\underline{H}_2CH_3$), 5.59 (1H, dd, *J* = 4, 5 Hz, H-2), 5.97 (1H, s, H-5), 7.12 (1H, dd, *J* = 4, 5 Hz, ArH), 7.53 (1H, dd, *J* = 1, 5 Hz, ArH), 7.56 (1H, dd, *J* = 1, 4 Hz, ArH). ^{13}C-Nmr: 15.0 (q, CH_2CH_3), 42.2 (t, C-3), 65.5 (t, $\underline{C}H_2CH_3$), 101.3 (d, C-5 or 2), 102.0 (d, C-2 or 5), 128.3 (d, Ar), 128.5 (d, Ar), 130.3 (d, Ar), 136.7 (s, Ar), 161.6 (s, C-6), 190.7 (s, C-4). LRms *m/z*: 224 (M^+).

***trans*-1-Ethoxy-5-(2-thienyl)pent-1-ene-3, 5-dione (5i)**: Pale yellow prisms from CH_2Cl_2-ether, mp 47 - 51 °C. Uv: 262 (8600), 362 (20300). ^{1}H-Nmr: 1.36 (3H, t, *J* = 7 Hz, $CH_2C\underline{H}_3$), 3.99 (2H, q, *J* = 7 Hz, $C\underline{H}_2CH_3$), 5.40 (1H, d, *J* = 12 Hz, H-2), 5.90 (1H, s, H-4), 7.11 (1H, dd, *J* = 4, 5 Hz, ArH), 7.55 (1H, dd, *J* = 1, 5 Hz, ArH), 7.60 (1H, d, *J* = 12 Hz, H-1), 7.65 (1H, dd, *J* = 1.4 Hz, ArH). ^{13}C-Nmr: 14.0 (q, $CH_2\underline{C}H_3$), 61.6 (t, $\underline{C}H_2CH_3$), 110.8 (d, C-4), 117.0 (d, C-2), 127.9 (d, Ar), 128.4 (d, Ar), 129.8 (d, Ar), 133.2 (s, Ar), 154.3 (d, C-1), 159.7 (s, C-3), 178.8 (s, C-5). LRms *m/z*: 224 (M^+). *Anal*. Calcd for $C_{11}H_{12}O_3S$: C, 58.92; H, 5.40. Found: C, 59.03; H, 5.42.

Deethoxylation of 3 with TsOH.

The dihydropyrones (**3a**, **b**, **c**, **d**, **e**, **h**, **i**) (50 mg) in CH_2Cl_2 (10 ml) was treated with *p*-TsOH (10 mg) under reflux for 3-4 h to give the corresponding pyrones (**4a**, **b**, **c**, **d**, **e**, **h**, **i**) in a quantitative yield.

2-(4-Nitrophenyl)-4*H*-pyran-4-one (4b): Colorless prisms from CH_2Cl_2-ether, mp 207 - 211 °C. Ir:

1653, 1613, 1518. Uv: 241 (12200), 299 (15200). ^{1}H-Nmr: 6.45 (1H, dd, *J* = 2, 6 Hz, H-5), 6.89 (1H, d, *J* = 2 Hz, H-3), 7.9 - 8.0 (3H, m, H-6, ArH), 8.3 - 8.4 (2H, m, ArH). ^{13}C-Nmr: 114.5 (d, C-5), 117.6 (d, C-3), 124.3 (dx2, Ar), 126.8 (dx2, Ar), 136.9 (s, Ar), 149.4 (s, Ar), 155.0 (d, C-6), 161.2 (s, C-2), 178.4 (s, C-4). LRms *m/z*: 217 (M$^+$). *Anal.* Calcd for $C_{11}H_7NO_4$: C, 60.83; H, 3.25; N, 6.45. Found: C, 61.05; H, 3.28; N, 6.49.

2-(2-Thienyl)-4*H*-pyran-4-one (4i): Colorless needles from CH_2Cl_2-ether, mp 71 - 72 °C. Ir: 1651, 1574. Uv: 225 (7700), 260 (15700). ^{1}H-Nmr: 6.34 (1H, dd, *J* = 2, 6 Hz, H-5), 6.65 (1H, d, *J* = 2 Hz, H-3), 7.15 (1H, dd, *J* = 4, 5 Hz, ArH), 7.53 (1H, dd, *J* = 1, 5 Hz, ArH), 7.57 (1H, d, *J* = 1, 4 Hz, ArH), 7.75 (1H, d, *J* = 6 Hz, H-6). ^{13}C-Nmr: 110.8 (d, C-5), 117.0 (d, C-3), 127.9 (d, Ar), 128.4 (d, Ar), 129.9 (d, Ar), 134.2 (s, Ar), 154.4 (d, C-6), 159.6 (s, C-2), 178.5 (s, C-4). LRms *m/z*: 178 (M$^+$), HRms *m/z* (M$^+$) Calcd for $C_9H_6O_2S$: 178.0088. Found: 178.0118. *Anal.* Calcd for $C_9H_6O_2S$: C, 60.68; H, 3.40. Found: C, 60.39; H, 3.34.

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