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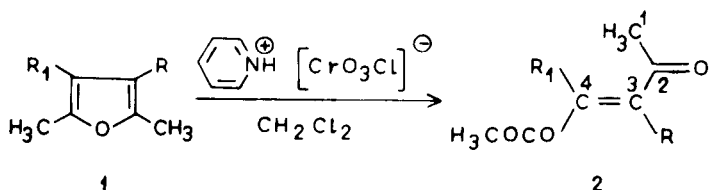
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A novel oxidation of tetrasubstituted furans with pyridinium chlorochromate has been studied and this has led to a convenient synthesis of 4-acetoxy-3-acetyl- or methoxycarbonyl-4-substituted phenylbut-3-en-2-one.

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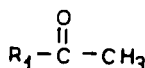
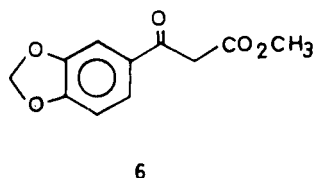
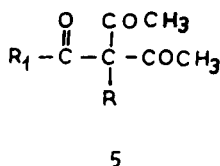
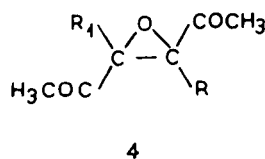
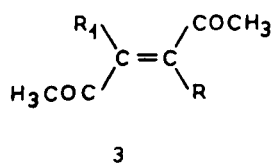
Oxidation of substituted furans have been reported earlier to yield  $\alpha,\beta$ -unsaturated ketones [2,3]. In the present study it was observed that the oxidation of 3-acyl or methoxycarbonyl-2,5-dimethyl-4-substituted phenylfurans **1a-f** with pyridinium chlorochromate gave compounds which were different from the expected  $\alpha,\beta$ -unsaturated ketones **3**. The details of this investigation are presented here.



a - c : R = CO<sub>2</sub>CH<sub>3</sub>

d - f : R = COCH<sub>3</sub>

1, 2	R <sub>1</sub>
a, d	3, 4 - dimethoxyphenyl
b, e	3, 4 - methylenedioxyphenyl
c, f	- 4 methoxyphenyl



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Oxidation of 2,5-dimethyl-3-methoxycarbonyl-4-substituted-phenylfurans **1a-1c**, reported by us earlier [4,5], with pyridinium chlorochromate gave compounds, the mass spectra of which exhibited sixteen mass unit more than the expected mass of the  $\alpha,\beta$ -unsaturated ketones **3**. The IR spectra of these compounds exhibited carbonyl bands at around 1660, 1720 and 1760 cm<sup>-1</sup>. The NMR spectra indicated the presence of two acetyl groups and one methoxy group besides the required aromatic protons. On the basis of these data three tentative structures **2**, **4** or **5** may be proposed for these oxidation products. Structures **4** and **5** were ruled out on the basis of <sup>13</sup>C-NMR spectra of the oxidation products. The two quaternary carbon atoms of the three membered ring in **4** and the quaternary sp<sup>3</sup> carbon atom in **5** are expected to appear between  $\delta$  65-70 ppm but the <sup>13</sup>C-NMR signals for the two quaternary carbon atoms at around 160 ppm and the absence of any peak between 65-70 ppm supported the structure **2**. The reactions of **2a-2c** with aqueous acid or alkali to furnish **7** and the conversion of **2b** on activated surface to **6** provided additional evidence for structure **2**.

Similar to the oxidation of **1a-1c**, compounds **1d-1f** could also be oxidized with pyridinium chlorochromate to **2d-2f**. The spectroscopic data of these compounds were in agreement with the assigned structures. The stereochemistry of **2a-2c** was worked out by comparing the pmr spectra of these compounds with the spectra of **2d-2f** (Table I). The downfield shift of the -OCOCH<sub>3</sub> signals in **2a-2c** is only possible if the acetyl group at C-4 and methoxycarbonyl at C-3 are oriented in a *cis* geometry.

The nature of substituents on the phenyl ring of **1a-1f** has been found to influence the pyridinium chlorochromate oxidation. The tetrasubstituted furans having electron donating substituents on the phenyl ring yielded the tetrasubstituted olefins and the absence of the substituents or the presence of electron withdrawing substituents on the phenyl ring inhibited the pyridinium chlorochromate oxidation of tetrasubstituted furans. It is likely that the pyridinium chlorochromate oxidation of tetrasubstituted furans possibly yielded oxiranes structurally similar to **4** which after ring opening followed by rearrangement gave **2a-2f**. This presumption is based on the literature precedence in

Table I  
Physical, Analytical and Spectral Data

Compound 1	Mp, °C 2	Yield % 3	Molecular formula 4	Analysis %	
				Calcd./Found 5	H 6
<b>2a</b>	98	70	C <sub>16</sub> H <sub>18</sub> O <sub>7</sub>	59.62 59.90	5.59 5.98
<b>2b</b>	oil	54	C <sub>15</sub> H <sub>14</sub> O <sub>7</sub>	58.80 59.20	4.57 4.98
<b>2c</b>	oil	50	C <sub>15</sub> H <sub>16</sub> O <sub>6</sub>	61.60 62.00	5.47 5.34
<b>2d</b>	oil	63	C <sub>16</sub> H <sub>18</sub> O <sub>6</sub>	62.70 62.50	5.88 5.60
<b>2e</b>	oil	54	C <sub>15</sub> H <sub>14</sub> O <sub>6</sub>	62.06 62.45	4.82 4.84
<b>2f</b>	oil	50	C <sub>15</sub> H <sub>16</sub> O <sub>5</sub>	65.21 65.00	5.79 5.88

## Spectral Data

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ir: 1660, 1720 and 1760 (CO); nmr (deuteriochloroform): 1.80 (s, 3H, COCH<sub>3</sub>), 2.48 (s, 3H, OCOCH<sub>3</sub>), 3.61 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.86 (s, 6H, 2 × OCH<sub>3</sub>), 6.73-6.83 (d, 1H, 5' Ar-H, J<sub>o</sub> = 9 Hz), 7.32-7.44 (dd, 2H, 2' and 6' Ar-H, J<sub>o</sub> = 9b Hz, J<sub>m</sub> = 3 Hz); <sup>13</sup>C-nmr: 19.03 (q, 1-C), 20.57 (q, OCOCH<sub>3</sub>), 52.18 (q, 3-CO<sub>2</sub>CH<sub>3</sub>), 56.09, 56.17 (q, 2 × OCH<sub>3</sub>), 110.40, 110.66, 124.68 (d, Ar-C), 129.59, 149.28, 154.06 (s, Ar-C), 162.07 (s-3-C), 164.58 (s, 4-C), 167.52 (s, 3-CO<sub>2</sub>CH<sub>3</sub>), 189.87 (s, 2-C and OCOCH<sub>3</sub>)

ir: 1660, 1720 and 1765 (CO); nmr (carbon tetrachloride): 1.80 (s, 3H, COCH<sub>3</sub>), 2.42 (s, 3H, OCOCH<sub>3</sub>), 3.58 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 5.93 (s, 2H, OCH<sub>2</sub>O), 6.62-6.73 (d, 1H, 5' Ar-H, J<sub>o</sub> = 9 Hz), 7.20-7.32 (dd, 2H, 2' and 6' Ar-H, J<sub>o</sub> = 9 Hz, J<sub>m</sub> = 3 Hz); <sup>13</sup>C-nmr: 18.99 (q, 1-C), 20.52 (q, OCOCH<sub>3</sub>), 52.14 (q, 3-CO<sub>2</sub>CH<sub>3</sub>), 108.04, 108.20, 126.31 (d, Ar-C), 102.07 (t, OCH<sub>2</sub>O), 131.30, 148.39, 152.48 (s, Ar-C), 162.23 (s, 3-C), 164.44 (s, 4-C), 167.42 (s, CO<sub>2</sub>CH<sub>3</sub>), 189.35 (s, 2-C and OCOCH<sub>3</sub>)

ir: 1660, 1720 and 1760 (CO); nmr (carbon tetrachloride): 1.79 (s, 3H, COCH<sub>3</sub>), 2.45 (s, 3H, OCOCH<sub>3</sub>), 3.60 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 3.81 (s, 3H, OCH<sub>3</sub>), 6.74-6.85 (dd, 2H, 3' and 5' Ar-H, J<sub>o</sub> = 9 Hz, J<sub>m</sub> = 2 Hz), 7.66-7.78 (dd, 2H, 2' and 6' Ar-H, J<sub>o</sub> = 9 Hz, J<sub>m</sub> = 2 Hz)

ir: 1650, 1690, 1755 (CO); nmr (carbon tetrachloride): 1.74 (s, 3H, COCH<sub>3</sub>), 2.05 (s, 3H, 3-COCH<sub>3</sub>), 2.36 (s, 3H, OCOCH<sub>3</sub>), 3.85 (s, 6H, 2 × OCH<sub>3</sub>), 6.71-6.81 (d, 1H, 5' Ar-H, J<sub>o</sub> = 9 Hz), 7.30-7.42 (dd, 2H, 2' and 6' Ar-H, J<sub>o</sub> = 9 Hz, J<sub>m</sub> = 3 Hz); <sup>13</sup>C-nmr: 19.35 (q, 1-C), 20.50 (q, OCOCH<sub>3</sub>), 30.44 (q, 3-COCH<sub>3</sub>), 56.04, 56.14 (q, 2 × OCH<sub>3</sub>), 110.51, 124.87 (d, Ar-C), 130.37, 149.41, 154.34 (s, Ar-C), 160.09 (s, 3-C), 167.59 (s, 4-C), 191.63 (s, 3-COCH<sub>3</sub>), 195.35 (s, 2-C and OCOCH<sub>3</sub>)

ir: 1640, 1680, 1745 (CO); nmr (carbon tetrachloride): 1.70 (s, 3H, COCH<sub>3</sub>), 1.98 (s, 3H, 3-COCH<sub>3</sub>), 2.26 (s, 3H, OCOCH<sub>3</sub>), 5.95 (s, 2H, OCH<sub>2</sub>O), 6.64-6.74 (d, 1H, 5' Ar-H, J<sub>o</sub> = 9 Hz), 7.27-7.40 (dd, 2H, 2' and 6' Ar-H, J<sub>o</sub> = 9 Hz, J<sub>m</sub> = 3 Hz); <sup>13</sup>C-nmr: 19.35 (q, 1-C), 20.54 (q, OCOCH<sub>3</sub>), 30.44 (q, 3-COCH<sub>3</sub>), 108.17, 108.50, 126.68 (d, Ar-C), 131.56, 148.66, 152.82 (s, Ar-C), 160.18 (s, 3-C), 167.51 (s, 4-C), 191.88 (s, 3-COCH<sub>3</sub>), 195.23 (s, 2-C and OCOCH<sub>3</sub>)

ir: 1650, 1685, 1750 (CO); nmr (carbon tetrachloride): 1.69 (s, 3H, COCH<sub>3</sub>), 1.98 (s, 3H, 3-COCH<sub>3</sub>), 2.28 (s, 3H, OCOCH<sub>3</sub>), 3.78 (s, 3H, OCH<sub>3</sub>), 6.73-6.86 (dd, 2H, 3' and 5' Ar-H, J<sub>o</sub> = 9 Hz, J<sub>m</sub> = 3 Hz), 7.68-7.82 (dd, 2H, 2' and 6' Ar-H, J<sub>o</sub> = 9 Hz, J<sub>m</sub> = 2 Hz); <sup>13</sup>C-nmr: 19.34 (q, 1-C), 20.45 (q, OCOCH<sub>3</sub>), 30.45 (q, 3-COCH<sub>3</sub>), 55.59 (q, OCH<sub>3</sub>), 114.20, 114.42, 129.73, 130.55 (d, Ar-C), 131.65, 132.19 (s, Ar-C), 160.03 (s, 3-C), 167.53 (s, 4-C), 192.38 (s, 3-COCH<sub>3</sub>), 195.43 (s, 2-C and OCOCH<sub>3</sub>)

which the substituted pyrrole, on oxidation with chromic acid, have been reported to furnish substituted oxiranes [6].

## EXPERIMENTAL

Melting points were determined on an electrically heated block and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 157 grating instrument. The <sup>1</sup>H nmr spectra were recorded on a Perkin-Elmer R-32 spectrometer using tetramethylsilane as internal reference and <sup>13</sup>C-nmr spectra on CFT-20 spectrometer.

4-Acetoxy-3-acetyl or Methoxycarbonyl-4-substituted-phenylbut-3-en-2-ones **2a-2f**. General Procedure.

To a well stirred solution of **1** (0.01 mole) in dry dichloromethane (50 ml) was added pyridinium chlorochromate (0.04 mole) and the reaction mixture was stirred at room temperature (30°) for 10 hours. It was then diluted with ether and the organic layer was passed through a column of silica gel. The column was finally eluted with chloroform-hexane (1:2). Removal of the solvent yielded the desired compounds as oils, except **2a** which was recrystallized from chloroform and petroleum benzene.

Substituted Acetophenones **7a-7c**. General Procedure.

To a solution of **2a-2c** (0.5 g) in methanol (1.5 ml) was added 10% aqueous hydrochloric acid (0.5 ml) or 10% aqueous sodium hydroxide (0.5 ml) and refluxed for 2 hours. After removal of solvent it was extracted with chloroform and the usual work up of organic layer gave the required acetophenones. These were identical in all respects with the authentic acetophenones.

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