

CONJUGATE ADDITION OF FURANS TO ENONES OR  
THEIR SYNTHETIC EQUIVALENTS <sup>+</sup>

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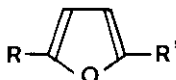
**Abstract** — Conjugate addition of furans **5** to enones **3** in the presence of an alcohol and boron trifluoride etherate is described. A same reaction product is obtained with hemiacetal vinylogs **1**, synthetic equivalents of enones **3**.

Acidic treatment of adducts **6** and **7** leads to tri- and tetraketones **15** and **16**.

The acid-mediated addition of simple furans to enone proceeds in modest yield since this reaction is limited by side reactions such as polymerization of the furans and/or enone. Kraus and Gootschalk <sup>1</sup> have described an elegant way to prepare some of these compounds using furans and  $\gamma$ -iodosilylenol ethers. Nevertheless, with the simplest enone, the methyl vinyl ketone, yields are modest even with the use of high pressure conditions. <sup>2</sup>

We have previously shown that Michael reaction of enol ether to hemiacetal vinylogs **1** in the presence of boron trifluoride etherate gave 1,5-dicarbonyl compounds. <sup>3</sup> The delocalized cation **2** postulated as intermediate may be also produced by the reaction of a mixture of enone **3** and hydroxy compounds **4** in the presence of the same Lewis acid which gives high or quantitative yields. <sup>4</sup>

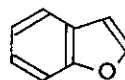
In this report, we describe the reaction of enones **3** and alcohol and of hemiacetal vinylogs **1** with furans **5a-f** yielding adducts in good yields even with methyl vinyl ketone.



**5a** R = R' = H

**5b** R = Me R' = H

**5c** R = OMe R' = H



**5f**

**5d** R = R' = Me

**5e**  $\begin{cases} R = C = CH_2 \\ | \\ OSiMe_2tBu \\ R' = H \end{cases}$

<sup>+</sup> Dedicated to Professor G. STORK for his 65<sup>th</sup> birthday.

With methyl vinyl ketone **3a** and alcohol (ethanol or phenylethanol) the 2,5-disubstituted adduct **6a** is obtained in high yield (entries 1, 2 table 1) from furan **5a**. As previously observed<sup>4</sup> the yield is better than that obtained with hemiacetal vinylog **1a** (entry 3).

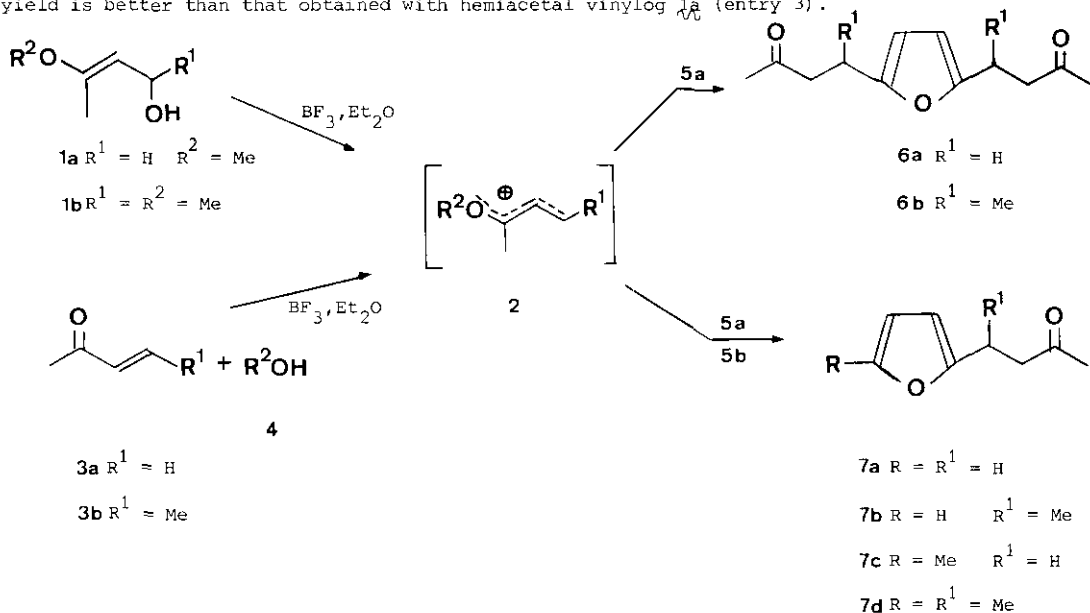
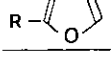


Table 1 : Reaction of furans **5** with hemiacetal vinylogs **1** or with enone **3** and alcohol **4** in the presence of  $BF_3, Et_2O$ <sup>a</sup>

Entry	R- 	Reagents <sup>b</sup>	Reagent <sup>c</sup> furan	Reaction products yield % <sup>d</sup>			
1	H	<b>3a</b> + EtOH	1/1	<b>6a</b>	80	<b>7a</b>	7
2	H	<b>3a</b> + Ph-CH-Me   OH	1/1	<b>6a</b>	78	<b>7a</b>	7
3	H	<b>1a</b>	1/1	<b>6a</b>	62	<b>7a</b>	7
4	H	<b>3a</b> + EtOH	1/5	<b>6a</b>	48	<b>7a</b>	16
5	H	<b>1a</b>	1/5	<b>6a</b>	10	<b>7a</b>	21
6	Me	<b>3a</b> + EtOH	1/2			<b>7c</b>	79
7	Me	<b>1a</b>	1/2			<b>7c</b>	71
8	H	<b>1b</b>	3/2	<b>6b</b>	69	<b>7b</b>	11
9	Me	<b>1b</b>	1/2			<b>7d</b>	75
10	Me	<b>3b</b> + EtOH	1/2			<b>7d</b>	80
11	H	<b>3b</b> + EtOH	3/2	<b>6b</b>	22	<b>7b</b>	10
12	H	<b>3b</b> + MeOH	3/2	<b>6b</b>	38	<b>7b</b>	10

a : 0.2 eq. of  $BF_3, Et_2O$  versus enone **3** or hemiacetal vinylog **1**.

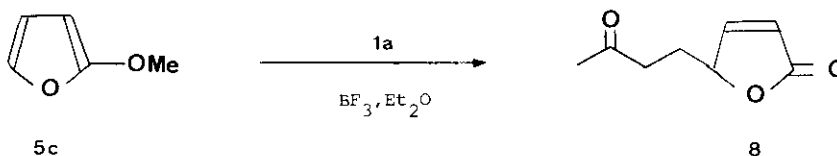
b : Equimolar amount of enone **3** and alcohol **4**.

c : Number of equivalents of reagents versus furan or 2-methylfuran.

d : Yield of isolated product purified by flash chromatography.

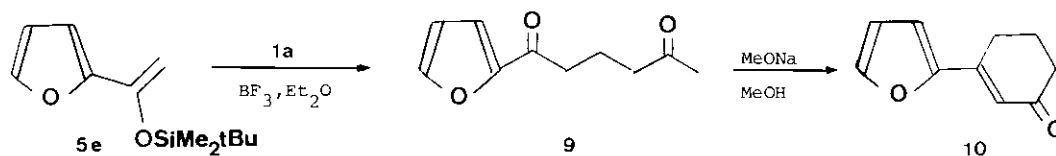
In all cases a small amount (7%) of monosubstituted product **7a** (entries 1 - 3) is obtained. This product may be isolated by flash chromatography.<sup>5</sup> Attempts to produce the monoadduct **7a** always give a mixture of the two compounds **6a** and **7a** even with the use of a large excess of furan (entries 4, 5) but in this case the total yield drops. The reagents enone **3a** + alcohol **4** or hemiacetal vinyllog **1a** also yield the adduct **7c** with 2-methylfuran **5b** (entries 6, 7). In the same reaction conditions, hemiacetal vinyllog **1b** gives the diadduct **6b** with furan (entry 8) or to the monoadduct **7d** with 2-methylfuran (entry 9) in good yields. A comparable yield of compound **7d** is observed with the use of penten-3-one-2 **3b**, ethanol and 2-methylfuran **5b** (entry 10). However this enone **3b** and ethanol or methanol give lower yields with furan **5a** (entries 11, 12). A tentative explanation was based on the rapidity of formation of the postulated cation **2**. From hemiacetal vinyllog **1b**, cation **2** seems to be produced faster than from enone **3b** and alcohol **4**. With the first reagent **1b** a good reaction is obtained whichever of the two furans is used. However, enone **3b** and alcohol **4** only give a good yield when the furan is sufficiently stable in the presence of the Lewis acid.

The butenolide **8** is obtained from 2-methoxyfuran **5c**, in 48% yield.

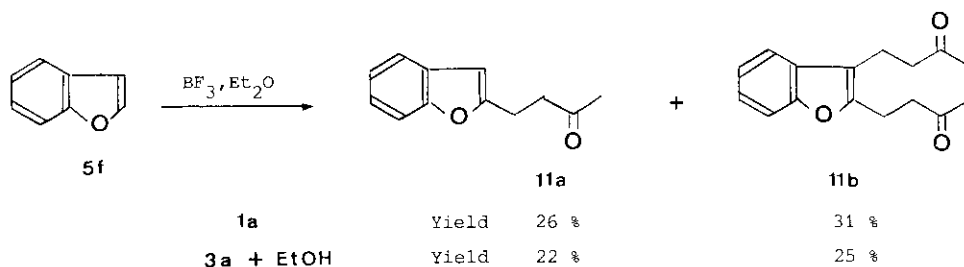


This product is similar to that observed by H. Takei and co-workers<sup>6</sup> from 2-butene-4-olide and methyl vinyl ketone in the presence of a base or from 2-trimethylsilyloxyfuran, methyl vinyl ketone and tin tetrachloride.

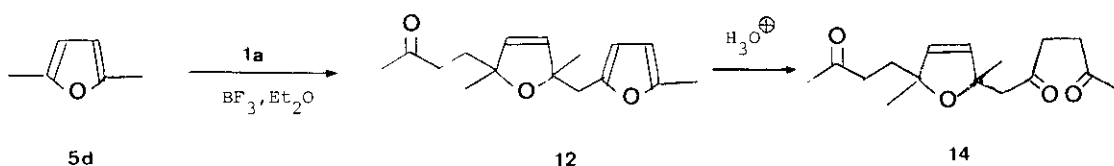
For the silylenol ether of 2-acetylfuran **5e** two competing reaction centers were present. In the same conditions, the enol ether gives dicarbonyl compound **9** in 50% yield. This diketone is classically cyclized in basic medium in quantitative yield.



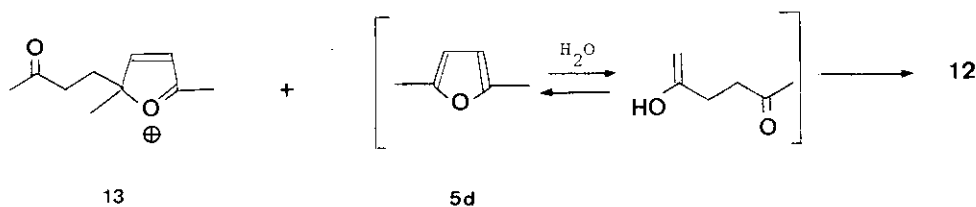
Benzofuran **5f** with hemiacetal vinyllog **1a** or with methyl vinyl ketone **3a** and ethanol always gives a mixture of 2- and 2,3-adducts **11a** and **11b** in quite the same proportion.



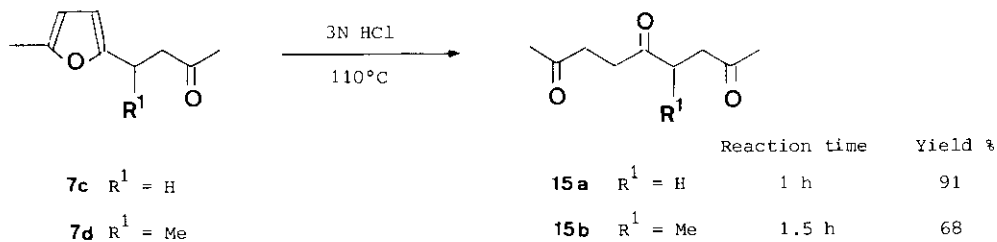
With 2,5-dimethylfuran **5d**, in which the two electron rich positions are substituted, the formation of compound **12** is observed.



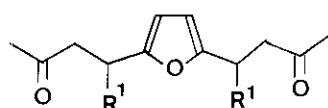
The structure of compound **12** is fully compatible with spectral data and elementary analysis. This result may be explained by the formation of an intermediate oxonium **13** which reacts with the enol of the open form of 2,5-dimethylfuran. Acidic treatment of this compound yields ketone **14** which is in agreement with the proposed structure.



Acidic treatment of compounds **7c-d** leads to the corresponding triketone **15a,b**.

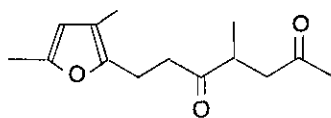


In the same reaction conditions, tetraketone **16a** is obtained in excellent yield from furan **6a**.

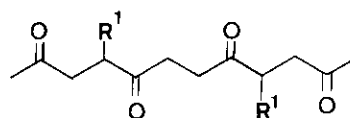


**6a**  $R^1 = H$

**6b**  $R^1 = Me$

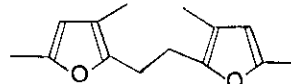


**17**



**16a**  $R^1 = H$

**16b**  $R^1 = Me$



**18**

Starting material					<b>16</b>	<b>17</b>	<b>18</b>
<b>6a</b>	115°C	0.5 h	%	94			
<b>6b</b>	120°C	6 h	%	10		17	68
<b>6c</b>	20°C	5 d	%	57		15	13

The adduct **6c** in similar conditions gives a little tetraketone **16b** accompanied by substituted furans **17** and **18**. Furan **18** is the major product.

On the other hand, acidic treatment at room temperature (5 days) inverses the proportion of tetraketone **16b** and furan **18**. No starting material is observed in either case.

The three products **16-18** are easily separated by flash chromatography.<sup>5</sup> With these two conditions furan **17** is always present in the same proportions. In the reaction conditions the tetraketone **16b** is cyclized in two steps yielding first furan **17** and then **18**. Thus, in this reaction 2,3,5-trisubstituted furan **17** and **18** may be prepared from simple furan.

The synthetic possibilities of these reactions are now in progress.

#### EXPERIMENTAL

<sup>1</sup>H NMR spectra were recorded on a Perkin Elmer 60 MHz R 12 spectrometer and <sup>13</sup>C on a Varian CFT 20 spectrometer. All chemical shifts are reported in  $\delta$  units downfield from internal TMS in CDCl<sub>3</sub> solution otherwise noted. IR spectra (film) were obtained with a Perkin Elmer 237 instrument. Nitromethane is dried on molecular sieves and distilled prior to use. All reactions were conducted under an argon atmosphere.

Example : Reaction of 2-methylfuran **5b** with methyl vinyl ketone **3a** (entry 6)

To 10 mmol of furan **5b** (0.82 g, 2 eq) in 10 ml of nitromethane were added 5 mmol of methyl vinyl ketone (0.35 g) in 5 ml of nitromethane. The mixture was cooled to -20°C and 1 mmol of boron trifluoride etherate solution (123  $\mu$ l, 0.2 eq.) in 5 mmol of ethanol (0.23 g) were added via syringe with stirring. Stirring was continued for 1 h. The reaction mixture was allowed to warm to -10°C and 5 ml of an aqueous saturated solution of sodium hydrogencarbonate were added.

The mixture was extracted with methylene chloride (4 x 10 ml), dried (MgSO<sub>4</sub>) and evaporated.

Adduct 7c was purified by flash chromatography (ether/petroleum ether : 5/100). Yield : 79 %.

Reaction of 2-methylfuran 5b with hemiacetal vinylog 1a<sup>8</sup> (entry 7)

To 10 mmol of furan 5b (0.82 g, 2 eq) in 10 ml of nitromethane were added 5 mmol of hemiacetal vinylog 1a (0.51 g) in 5 ml of nitromethane. The solution was cooled to -20°C. Boron trifluoride etherate (1 mmol, 123 µl, 0.2 eq) mixed with 31 µl of diethyl ether<sup>8</sup> (BF<sub>3</sub>·Et<sub>2</sub>O/Et<sub>2</sub>O = 4/1 volumic ratio) were introduced via syringe. Stirring was continued for 1 h. Work up was the same as above.

All the experiments are as described above except for some molecular ratios (furan/reagents) which are defined when necessary.

2,5-Di(3-oxobutyl)furan 6a

IR : 1720 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR : 2.13 (6 H, s), 2.78 (8 H, s), 5.88 (2 H, s). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) : 22.2 (2 x C<sub>1</sub>'), 29.2 (2 x C<sub>4</sub>'), 41.2 (2 x C<sub>2</sub>'), 105.7 (C<sub>3</sub>, C<sub>4</sub>'), 153.3 (C<sub>2</sub>, C<sub>5</sub>), 206.0 (2 x C<sub>3</sub>').

2,5-Di(1-methyl-3-oxobutyl)furan 6b

IR : 1720 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR : 1.22 (6 H, d), 2.13 (6 H, s), 2.7 (4 H, m), 3.30 (2 H, m), 5.90 (2 H, s). <sup>13</sup>C NMR : 18.1 (CH<sub>3</sub> at C<sub>1</sub>'), 28.2 (C<sub>1</sub>'), 29.4 (C<sub>4</sub>'), 48.4 (C<sub>2</sub>'), 103.4 (C<sub>3</sub> and C<sub>4</sub>'), 156.5 (C<sub>2</sub> and C<sub>5</sub>), 206.0 (C<sub>3</sub>').

2-(3-Oxobutyl)furan 7a

IR : 1720 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR : 2.13 (3 H, s), 2.82 (4 H, 2 t), 5.96 (1 H, m), 6.24 (1 H, m), 7.26 (1 H, d). <sup>13</sup>C NMR (C<sub>6</sub>D<sub>6</sub>) : 21.8 (C<sub>1</sub>'), 29.4 (C<sub>4</sub>'), 41.3 (C<sub>2</sub>'), 104.8 (C<sub>3</sub>), 109.9 (C<sub>4</sub>'), 140.7 (C<sub>5</sub>), 154.2 (C<sub>2</sub>), 206.7 (C<sub>3</sub>').

2-(1-Methyl-3-oxobutyl)furan 7b

IR : 1720 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR : 1.27 (3 H, d), 2.10 (3 H, s), 2.72 (2 H, t), 3.3 (1 H, m), 5.98 (1 H, m), 6.25 (1 H, m), 7.29 (1 H, s broad). <sup>13</sup>C NMR : 18.7 (CH<sub>3</sub> at C<sub>1</sub>'), 28.7 (C<sub>1</sub>'), 30.0 (C<sub>4</sub>'), 49.0 (C<sub>2</sub>'), 103.6 (C<sub>3</sub>), 109.8 (C<sub>4</sub>'), 140.7 (C<sub>5</sub>), 158.7 (C<sub>2</sub>), 207.0 (C<sub>3</sub>').

5-Methyl-2-(3-oxobutyl)furan 7c

IR : 1720 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR : 2.12 (3 H, s), 2.22 (3 H, s), 2.80 (4 H, s), 5.82 (2 H, s). <sup>13</sup>C NMR : 12.5 (CH<sub>3</sub> at C<sub>5</sub>), 21.5 (C<sub>1</sub>'), 28.8 (C<sub>4</sub>'), 40.9 (C<sub>2</sub>'), 105.0 and 105.3 (C<sub>3</sub> and C<sub>4</sub>'), 149.5 (C<sub>5</sub>), 152.0 (C<sub>2</sub>), 206.0 (C<sub>3</sub>').

2-(1-Methyl-3-oxobutyl)5-methylfuran 7d

IR : 1720 cm<sup>-1</sup> (C=O). <sup>1</sup>H NMR : 1.22 (3 H, d), 2.10 (3 H, s), 2.22 (3 H, s), 2.69 (2 H, m), 3.30 (1 H, m), 5.86 (2 H, s). <sup>13</sup>C NMR : 12.6 (CH<sub>3</sub> at C<sub>5</sub>), 18.3 (CH<sub>3</sub> at C<sub>1</sub>'), 28.3 (C<sub>1</sub>'), 29.4 (C<sub>4</sub>'), 48.6 (C<sub>2</sub>'), 103.8 (C<sub>4</sub>'), 105.2 (C<sub>3</sub>), 149.5 (C<sub>5</sub>), 156.5 (C<sub>2</sub>), 206.1 (C<sub>3</sub>').

7-Oxo-2-octene-4-olide 8 (Molar ratio 5c/1a = 1.2/1)

IR : 1750-1770, 1720  $\text{cm}^{-1}$  (C=O), 1605  $\text{cm}^{-1}$  (C=C).  $^1\text{H}$  NMR : 2.0 (2 H, m), 2.17 (3 H, s), 2.68 (2 H, m), 5.15 (1 H, m), 6.16 (1 H, dd), 7.66 (1 H, dd).  $^{13}\text{C}$  NMR : 25.8 ( $\text{C}_5$ ), 29.0 ( $\text{C}_8$ ), 37.1 ( $\text{C}_6$ ), 81.5 ( $\text{C}_4$ ), 120.4 ( $\text{C}_2$ ), 156.1 ( $\text{C}_3$ ), 172.1 ( $\text{C}_1$ ), 206.3 ( $\text{C}_7$ ).

2-(1,5-Dioxohexyl)furan 9

IR : 1715, 1680  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR : 2.0 (3 H, t), 2.15 (3 H, s), 2.58 (2 H, t), 2.88 (2 H, t), 6.62 (1 H, m), 7.3 (1 H, m), 7.68 (1 H, m).  $^{13}\text{C}$  NMR : 17.6 ( $\text{C}_3$ ), 29.4 ( $\text{C}_6$ ), 36.7 ( $\text{C}_2$ ), 41.9 ( $\text{C}_4$ ), 111.7 ( $\text{C}_4$ ), 116.7 ( $\text{C}_3$ ), 146.0 ( $\text{C}_5$ ), 152.0 ( $\text{C}_2$ ), 188.3 ( $\text{C}_1$ ), 207.7 ( $\text{C}_5$ ).

3-(2-Furanyl)-2-cyclohexenone 10

IR : 1660  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR : 2.5 (6 H, m), 6.5 (2 H, m), 6.80 (1 H, m), 7.60 (1 H, s broad).  $^{13}\text{C}$  NMR : 22.1 ( $\text{C}_5$ ), 25.0 ( $\text{C}_4$ ), 37.2 ( $\text{C}_6$ ), 112.0 and 112.3 ( $\text{C}_3$  and  $\text{C}_4$ ), 120.6 ( $\text{C}_2$ ), 144.7 ( $\text{C}_5$ ), 146.9 ( $\text{C}_2$ ), 151.9 ( $\text{C}_3$ ), 199.1 ( $\text{C}_1$ ).

2-(3-Oxobutyl)benzofuran 11a

IR : 1720  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR : 2.15 (3 H, s), 2.95 (4 H, m), 6.4 (1 H, s), 7.1-7.65 (4 H, m).  $^{13}\text{C}$  NMR : 22.8 ( $\text{C}_1$ ), 29.9 ( $\text{C}_4$ ), 42.0 ( $\text{C}_2$ ), 102.6 ( $\text{C}_3$ ), 111.0, 120.7, 122.8 and 123.6 ( $\text{C}_{4-7}$ ), 129.2 ( $\text{C}_8$ ), 155.0 ( $\text{C}_9$ ), 158.1 ( $\text{C}_2$ ), 206.7 ( $\text{C}_3$ ). Anal. Calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2$  : C, 76.57; H, 6.43; Found : C, 77.0; H, 6.4.

2,3-Di(3-oxobutyl)benzofuran 11b

IR : 1720  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR : 2.11 (3 H, s), 2.15 (3 H, s), 2.88 (8 H, m), 7.15-7.6 (4 H, m).  $^{13}\text{C}$  NMR : 16.9 and 19.84 ( $\text{C}_1$  and  $\text{C}_1'$ ), 29.2 and 29.4 ( $\text{C}_4$  and  $\text{C}_4'$ ), 40.7 and 42.4 ( $\text{C}_2$  and  $\text{C}_2'$ ), 112.1 ( $\text{C}_3$ ), 110.9, 118.2, 121.6 and 122.8 ( $\text{C}_{4-7}$ ), 128.5 ( $\text{C}_8$ ), 152.4 ( $\text{C}_9$ ), 153.4 ( $\text{C}_2$ ), 206.3 and 207.0 ( $\text{C}_3$  and  $\text{C}_3'$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{18}\text{O}_3$  : C, 74.40; H, 7.02; Found C 74.1; H, 6.8.

2,5-Dimethyl-2-(3-oxobutyl)-5-(methylene-5(methyl-2-furanyl))dihydrofuran 12

IR : 1725  $\text{cm}^{-1}$  (C=O), 1570  $\text{cm}^{-1}$  (C=C).  $^1\text{H}$  NMR : 1.23 (6 H), 1.80 (2 H, m), 2.10 (3 H, s), 2.26 (3 H, s), 2.47 (2 H, m), 2.84 (2 H, s), 5.76 (2 H, m), 5.90 (2 H, m).  $^{13}\text{C}$  NMR : 13.25 ( $\text{CH}_3$  on furan at  $\text{C}_5$ ), 26.6 and 27.3 ( $\text{CH}_3$  at  $\text{C}_2$  and  $\text{C}_5$ ), 29.6 ( $\text{C}_4$ ), 34.5 ( $\text{C}_1$ ), 38.9 ( $\text{C}_2$ ), 41.4 ( $\text{CH}_2$  at  $\text{C}_5$ ), 88.7 and 88.9 ( $\text{C}_2$  and  $\text{C}_5$ ), 105.8 and 108.0 ( $\text{C}_3$  and  $\text{C}_4$  of furan), 132.2 and 132.8 ( $\text{C}_3$  and  $\text{C}_4$ ), 150.2 ( $\text{C}_2$  and  $\text{C}_5$  of furan), 208.4 ( $\text{C}_3$ ). Anal. Calcd for  $\text{C}_{16}\text{H}_{22}\text{O}_3$  : C, 73.25; H, 8.45; Found C, 73.14; H, 8.55.

2,5-Dimethyl-2-(3-oxobutyl)-5-(2,5-dioxohexyl)dihydrofuran 14

IR : 1720  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CCl}_4$ ) : 1.28 (6 H, s), 1.75 (2 H, t), 2.1 (6 H, s broad), 2.4 (2 H, m), 2.62 (6 H, s broad), 5.75 (2 H, m).  $^{13}\text{C}$  NMR : 26.3 and 27.4 ( $\text{CH}_3$  at  $\text{C}_2$  and  $\text{C}_5$ ), 29.5 ( $\text{C}_6$  and  $\text{C}_4$ ), 34.1 ( $\text{C}_1$ ), 36.3, 37.7 and 38.6 ( $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_2$ ), 54.9 ( $\text{C}_1$ ), 87.2 and 88.7 ( $\text{C}_2$  and  $\text{C}_5$ ), 132.1 and 132.6 ( $\text{C}_3$  and  $\text{C}_4$ ), 206.3 and 206.6 ( $\text{C}_2$  and  $\text{C}_5$ ), 208.2 ( $\text{C}_3$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{24}\text{O}_4$  : C, 68.54,

H, 8.62; Found C, 68.41; H, 8.58.

**Hydrolysis** : To 2 mmol of adduct  $\mathbf{6}$  or  $\mathbf{7}$  was added 5 ml of 3N HCl. The reaction mixture was heated to 110°C. The reaction was monitored by TLC. After cooling, ketone was extracted with  $\text{CH}_2\text{Cl}_2$  (4 x 20 ml). The solution was dried ( $\text{MgSO}_4$ ) and ketones  $\mathbf{15}$  and  $\mathbf{16}$  were purified by flash chromatography.

2,5,8-Nonanetrione  $\mathbf{15a}$ <sup>7</sup>

IR : 1720  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR : 2.11 (6 H, s), 2.67 (8 H, s).  $^{13}\text{C}$  NMR : 29.0 ( $\text{C}_1$  and  $\text{C}_9$ ), 35.3, 36.2 ( $\text{C}_3$ ,  $\text{C}_4$ ,  $\text{C}_6$  and  $\text{C}_7$ ), 206.3 ( $\text{C}_2$  and  $\text{C}_8$ ), 207.1 ( $\text{C}_5$ ).

4-Methyl-2,5,8-nonanetrione  $\mathbf{15b}$

IR : 1715  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR ( $\text{CCl}_4$ ) : 1.0 (3 H, d), 1.98 (3 H, s), 2.03 (3 H, s), 2.6 (4 H, s broad), 2.6 (3 H, m).  $^{13}\text{C}$  NMR ( $\text{C}_6\text{D}_6$ ) : 16.5 ( $\text{CH}_3$  at  $\text{C}_4$ ), 29.4 ( $\text{C}_1$  and  $\text{C}_9$ ), 34.9 and 36.7 ( $\text{C}_6$  and  $\text{C}_7$ ), 41.0 ( $\text{C}_4$ ), 46.43 ( $\text{C}_3$ ), 206.0 ( $\text{C}_8$  or  $\text{C}_2$ ), 206.1 ( $\text{C}_2$  or  $\text{C}_8$ ), 211.2 ( $\text{C}_5$ ).

2,5,8,11-Dodecanetetrone  $\mathbf{16a}$ <sup>7</sup>

IR : 1715  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR : 2.12 (6 H, s), 2.68 (8 H, s); 2.70 (4 H, s).  $^{13}\text{C}$  NMR : 29.4 ( $\text{C}_1$  and  $\text{C}_{12}$ ), 35.6 ( $\text{C}_4$ ,  $\text{C}_6$ ,  $\text{C}_7$  and  $\text{C}_9$ ), 36.5 ( $\text{C}_3$  and  $\text{C}_{10}$ ), 206.6 ( $\text{C}_2$  and  $\text{C}_{11}$ ), 207.4 ( $\text{C}_5$  and  $\text{C}_8$ ).

4,9-Dimethyl-2,5,8,11-dodecanetetrone  $\mathbf{16b}$

IR : 1715  $\text{cm}^{-1}$  (C=O).  $^1\text{H}$  NMR : 1.10 (6 H, d), 2.11 (6 H, s); 2.2-3.2 (10 H, m).  $^{13}\text{C}$  NMR : 16.2 (2  $\text{CH}_3$  at  $\text{C}_4$  and  $\text{C}_9$ ), 29.4 ( $\text{C}_1$  and  $\text{C}_{12}$ ), 34.1 ( $\text{C}_6$  and  $\text{C}_7$ ), 40.5 ( $\text{C}_4$  and  $\text{C}_9$ ), 46.1 ( $\text{C}_3$  and  $\text{C}_{10}$ ), 206.6 ( $\text{C}_2$  and  $\text{C}_{11}$ ), 211.5 ( $\text{C}_5$  and  $\text{C}_8$ ).

2-(4-Methyl-3,6-dioxoheptyl)-3,5-dimethylfuran  $\mathbf{17}$

IR : 1715  $\text{cm}^{-1}$  (C=O), 1585  $\text{cm}^{-1}$  (C=C).  $^1\text{H}$  NMR : 1.04 (3 H, d), 1.86 (3 H, s), 2.11 (3 H, s), 2.18 (3 H, s), 2.8 (4 H, s), 2.4-3.1 (3 H, m), 5.7 (1 H, s).  $^{13}\text{C}$  NMR : 9.4 ( $\text{CH}_3$  at  $\text{C}_3$ ), 13.0 ( $\text{CH}_3$  at  $\text{C}_5$ ), 16.1 ( $\text{CH}_3$  at  $\text{C}_4'$ ), 19.7 ( $\text{C}_1'$ ), 29.5 ( $\text{C}_1'$ ), 39.4 ( $\text{C}_2'$ ), 40.9 ( $\text{C}_4'$ ), 46.0 ( $\text{C}_5'$ ), 108.5 ( $\text{C}_4$ ), 114.4 ( $\text{C}_3$ ), 147.3 ( $\text{C}_2$  or  $\text{C}_5$ ), 148.9 ( $\text{C}_2$  or  $\text{C}_5$ ), 206.8 ( $\text{C}_6'$ ), 212.0 ( $\text{C}_3'$ ).

1,2-[Di(3,5-dimethyl-2-furanyl)]ethane  $\mathbf{18}$

IR : 1585  $\text{cm}^{-1}$  (C=C).  $^1\text{H}$  NMR : 1.79 (6 H, s), 2.22 (6 H, s), 2.78 (4 H, s), 5.78 (2 H, s).  $^{13}\text{C}$  NMR : 9.2 ( $\text{CH}_3$  on  $\text{C}_3'$  of furan), 13.1 ( $\text{CH}_3$  on  $\text{C}_5'$  on furan), 25.1 ( $\text{C}_1$  and  $\text{C}_2$ ), 108.5 (2  $\text{C}_3'$ ), 114.8 (2  $\text{C}_4'$ ), 148.0 ( $\text{C}_2'$  or  $\text{C}_5'$ ), 148.9 ( $\text{C}_2'$  or  $\text{C}_5'$ ).

REFERENCES

1. G. A. Kraus and P. Gottschalk, Tetrahedron Lett., 1983,  $\mathbf{24}$ , 2727.
2. C. Jenner, J. Rimmelin, F. Antoni, S. Libs and E. Schleifer, Bull. Soc. Chim. France, 1981 65 and references cited.
3. P. Duhamel, J. M. Poirier and G. Tavel, Tetrahedron Lett., 1984,  $\mathbf{25}$ , 43; P. Duhamel, J. M. Poirier and L. Hennequin, Tetrahedron Lett., 1984,  $\mathbf{25}$ , 1471; C. Vottero, D.E.A.



Rouen 1985.

4. P. Duhamel, L. Hennequin, N. Poirier and J. M. Poirier, Tetrahedron Lett., 1985, 26, 6201.
5. W. C. Still, M. Kahn and A. Mitra, J. Org. Chem., 1978, 43, 2923.
6. M. Asaoka, N. Yanagida, N. Sugimura and H. Takei, Bull. Chem. Soc. Jpn., 1980, 53, 1061.
7. H. Stetter, W. Basse, H. Kuhlmann, A. Landscheidt and W. Schlenker, Chem. Ber., 1977, 110, 1007.
8. J. M. Poirier, M. Fomani and L. Hennequin, Bull. Soc. Chim. France, in press.

Received, 19th May, 1986