1291, 1180, 1120, 1070 cm^{-1}; ^1H NMR (CCl_4) δ 3.59 (t, 4 H, J = 4.5 Hz), 3.08 (m, 1 H), 2.78 (m, 2 H), 2.50 (m, 4 H), 2.10 (m, 2 H), 2.00 (s, 3 H), 1.28 (s, 17 H), 0.90 (m, 3 H); mass spectrum, m/e 307 (M^+). Anal. Calcd for $C_{19}H_{33}NO_2$: C, 74.22; H, 10.82; N, 4.56. Found: C, 74.09; H, 10.96; N, 4.50.

Registry No. 4d, 74563-08-9; **8a**, 74563-09-0; **8b**, 74563-10-3; **8c**, 74563-11-4; **9a**, 74563-12-5; **9b**, 74563-13-6; **9c**, 74563-14-7; pyrrolidine, 123-75-1; piperidine, 110-89-4; morpholine, 110-91-8; 2-methyl-5-decylfuran, 74563-15-8.

One-Pot Syntheses of Cyclopent-2-enones from Furan Derivatives

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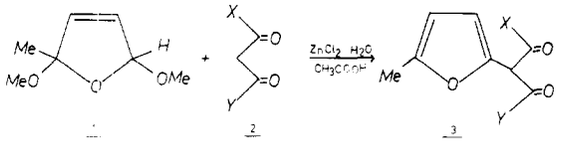
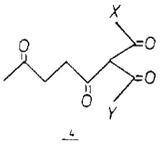
The most versatile method of synthesis of cyclopent-2-enones requires a two-step route: initial preparation of a suitable 1,4-diketone followed by base-catalyzed intramolecular condensation. Furans, which can be considered condensed forms of 1,4-diketones, are often used as starting materials for this sequence.[1]

In a previous paper[2] we reported an efficient synthesis of 2-(5-methyl-2-furyl) 1,3-dicarbonyl compounds **3**, obtained in high yield by intramolecular condensation of 2-methyl-2,5-dihydro-2,5-dimethoxyfuran (**1**) with active methylene compounds.



a: X = Me, Y = OEt
b: X = Ø, Y = OEt
c: X = Me, Y = Me
d: X = Ø, Y = Ø

We now describe a useful application of **3** as starting materials for the direct synthesis of cyclopent-2-enones. These furans are precursors of 1,4-diketones of type **4** and are capable of undergoing cyclization in the same acidic medium in which the opening of the furan ring occurs.



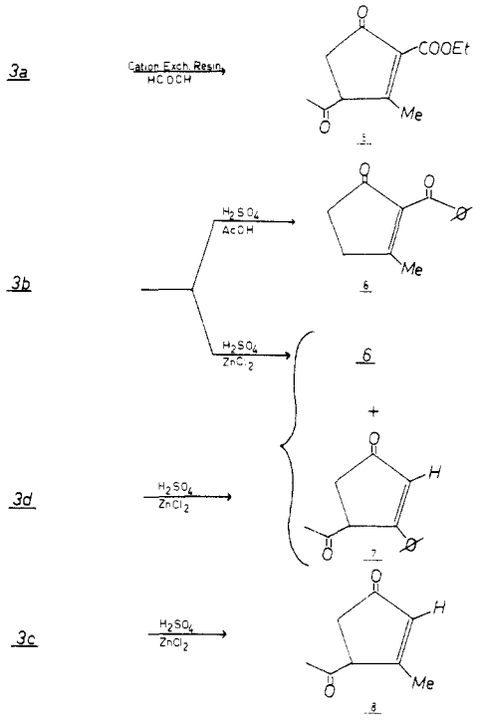
3a–c were prepared by a simplified modification of the previous procedure,[2] using **2** and **1** in a 1.5:1 mol ratio. **3d** was prepared under similar conditions, using **2d** and **1** in 1:1.5 mol ratio and dimethoxyethane as a solvent for **2d**.

Treatment of **3a–d** with acid and $ZnCl_2$ in acetone–water at 70 °C for several hours converted them to the cyclopentenones **5–8**, which had analytical and spectroscopic data in agreement with those reported for similar compounds[3] and consistent with the proposed structures.

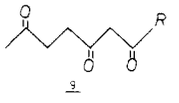
Table I. ^{13}C NMR Data[a]

carbon	6	7	8
C-1	179.1 (s)	171.5 (s)	174.7 (s)
C-2	141.6 (s)	131.7 (d)	132.9 (d)
C-3	204.8 (s)	206.3 (s)[b]	206.8 (s)[b]
C-4	35.3 (t)	39.0 (t)	39.1 (t)
C-5	32.6 (t)	54.9 (d)	57.8 (t)
C-1-CH_3	18.6 (q)		18.2 (q)
C-2-CO	193.5 (s)		
C-5-CO		205.6 (s)[b]	206.0 (s)[b]
$COCH_3$		26.1 (q)	28.1 (q)

[a] Multiplicity in off resonance: s = singlet, d = doublet, t = triplet, q = quartet. [b] Signals within any vertical column may be reversed.



The reaction mechanism may involve the intermediate formation of 1,4-diketones of type **4** by acid fission of the furan ring.[4] The subsequent ring closure depends on the nature of the 1,3-dicarbonyl moiety of **3**; hydrogen bonding may be a factor that determines the reaction path. The strong electrostatic interaction in **3a**, which is completely enolized under the reaction conditions,[5] stabilizes the ester function and prevents acid-catalyzed hydrolysis. This stabilization does not occur in **3b**, which is only 50% enolized;[5] thus, in addition to ring opening this compound undergoes both ester hydrolysis and decarboxylation to a 1,4-diketone **9** (R = Ph). Treatment of **3b** with 1.5%



R = Me
R = Ø

(1) R. A. Ellison, *Synthesis*, 397 (1973).
(2) R. D'Ascoli, M. D'Auria, G. Piancatelli, A. Scettri, *Tetrahedron*, **35**, 2905 (1979).
(3) G. Piancatelli, A. Scettri, G. David, M. D'Auria, *Tetrahedron*, **34**, 2775 (1978), and references therein.
(4) The detection of these intermediates by TLC control was unsuccessful and the interruption of the reactions at various degrees of completion did not allow their isolation.
(5) The degrees of enolization were determined on the grounds of ^1H NMR spectra, recorded in CD_3COCD_3–H_2O (4:1) solution. **3a**: 17.0 ppm (br, 1 H). **3b**: 14.0 ppm (br, 0.5 H), 5.50 (s, 0.5 H).

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aqueous sulfuric acid and glacial acetic acid for 3 h at 130 °C, as described by Büchi and Wuest,[6] gave **6** in 38% yield; under milder conditions it gave a 1:3 mixture of **6** and **7** in 92% yield.

The formation of **6**–**8** can be rationalized by assuming that, during the hydrolysis of the furan ring, **3c** and **3d** undergo an acid-catalyzed β-diketonic fission to intermediates of type **9**, which then cyclize.

The structures of **6**–**8** were confirmed by ^{13}C NMR data (Table I).

This approach provides a flexible sequence for the preparation of substituted cyclopent-2-enones by a simple procedure. The products **5**–**8**, which have not been reported in the literature, are of interest for preparative purposes; for example, **5** could be an intermediate in a synthetic route to modified prostaglandins.[7]

Experimental Section

Melting points were determined on a Kofler block and are uncorrected. ^1H NMR were recorded in CCl_4 solution, unless otherwise indicated, on a Perkin-Elmer R-32 spectrometer at 90 MHz. Chemical shifts are given in parts per million from internal Me_4Si. ^{13}C NMR spectra were recorded at 20 MHz with a Varian CFT-20 Fourier transform spectrometer in $CDCl_3$ solution. Chemical shifts are given in parts per million from internal Me_4Si. IR spectra were taken with a Perkin-Elmer 257 Infracord spectrometer. Commercial Merck silica gel was used for column chromatography. All the reactions were monitored by TLC using Carlo Erba precoated silica gel plates. The chromatograms were developed by spraying with 5 N H_2SO_4 and heating at 110 °C for 10 min. Mass spectra were obtained with an AEI MS-12 spectrometer at 70 eV, using direct insertion at a source temperature of 150 °C.

Ethyl 2-(5-Methyl-2-furyl)-3-oxobutyrate (3a). $ZnCl_2$ (7.5 mmol) was added to a stirred solution of **1** (5 mmol) and ethyl acetoacetate (7.5 mmol) in AcOH (1–1.5 mL) and H_2O (0.5 mL). After 24 h the mixture was poured into water and extracted several times with Et_2O. The combined extracts were washed with saturated aqueous $NaHCO_3$ and water and dried over Na_2SO_4, and the ether was removed in vacuo. The crude product was chromatographed on SiO_2 and eluted with *n*-hexane–Et_2O (9:1) to give 0.84 g (80%) of **3a** as an oil.

3b and **3c** were prepared under the same conditions from **2b** and **2c** in yields of 85 and 80%, respectively.

Analytical and spectroscopic data for **3a–c** agreed with those reported previously.[2]

(5-Methyl-2-furyl)dibenzoylmethane (3d). $ZnCl_2$ (1.5 g) was added to a stirred solution of **1** (13.2 mmol) and dibenzoylmethane (8.8 mmol) in dimethoxyethane (10 mL), AcOH (3 mL), and water (0.7 mL), and stirring was continued for 24 h. The mixture was worked up as for **3a**, and elution of the chromatogram with benzene–*n*-hexane (4:1) gave 2.3 g (85%) of **3d** as needles from *n*-hexane: mp 101–103 °C; ^1H NMR ($CDCl_3$) δ 18.80 (s, 1 H), 7.25 (m, 10 H), 5.62 (m, 2 H), 2.10 (s, 3 H); IR (1% $CHCl_3$) ν_{max} 3045, 1700, 1675, 1601, 1435, 1385, 1315, 1175, 1065, 1015, 895 cm^{-1}; mass spectrum, *m/e* 304 (M^+). Anal. Calcd for $C_{20}H_{16}O_3$: C, 78.93; H, 5.30. Found: C, 79.01; H, 5.26.

4-Acetyl-2-(ethoxycarbonyl)-3-methylcyclopent-2-enone (5). Acid cation-exchange resin (Merck-Ionenanstaucher I; 1 g) was added to a stirred solution of **3a** (320 mg) in 15 mL of 4:1 acetone–water at 70 °C. After 6 h 0.5 mL of HCO_2H was added and the mixture was refluxed for 24 h. The ion-exchange resin was removed by filtration through SiO_2 under anhydrous conditions, the solvent was removed in vacuo, and the product was chromatographed on SiO_2. Elution with benzene–Et_2O (1:1) gave 95 mg of **5** (50%) as an oil (130 mg of **3a** was recovered): ^1H NMR (CCl_4) δ 4.81 (dd, 1 H, J_1 = 8 Hz, J_2 = 3 Hz), 4.24 (q, 2 H), 3.00 (dd, 1 H, J_1 = 18 Hz, J_2 = 3 Hz), 2.67 (dd, 1 H, J_1 = 18 Hz, J_2 = 8 Hz), 2.54 (s, 3 H), 2.18 (s, 3 H), 1.32 (t, 3 H); IR (1% CCl_4) ν_{max} 2980, 1710, 1600, 1420, 1375, 1350, 1150, 1080, 1050 cm^{-1}; mass spectrum, *m/e* 210 (M^+). Anal. Calcd for $C_{11}H_{14}O_4$: C, 62.95; H, 6.71. Found: C, 62.93; H, 6.66.

2-Benzoyl-3-methylcyclopent-2-enone (6). A solution of **3b** (200 mg) in a mixture of AcOH (4 mL) and 10% H_2SO_4 (0.2 mL) was refluxed at 130 °C for 3 h and worked up as for **3a**. Elution of the chromatogram with benzene–Et_2O (9:1) gave 56 mg (38%) of **6** as an oil: ^1H NMR (CCl_4) δ 7.50 (m, 5 H), 2.62 (m, 2 H), 2.48 (m, 2 H), 2.10 (s, 3 H); IR (1% CCl_4) ν_{max} 3080, 2940, 1720, 1670, 1610, 1460, 1390, 1340, 1300, 1185, 1170, 1080 cm^{-1}; mass spectrum, *m/e* 200 (M^+). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 77.89; H, 5.98.

4-Acetyl-3-phenylcyclopent-2-enone (7). Concentrated H_2SO_4 (1.4 mL) and $ZnCl_2$ (600 mg) were added to a stirred solution of **3b** (400 mg) in 25 mL of 4:1 acetone–water. After the mixture was refluxed for 6 h 0.6 mL of concentrated H_2SO_4 was added and the mixture was refluxed for 17 h. The mixture was diluted with AcOEt and washed several times with saturated aqueous NaCl. The neutral organic layer was dried over Na_2SO_4, the solvent was removed in vacuo, and the product was chromatographed on SiO_2. Elution with benzene–Et_2O (9:1) gave 270 mg (92%) of a mixture of **6** and **7**. Separation of the components was achieved by fractional crystallization in CCl_4–*n*-hexane (1:1.5) solution. The pure crystalline **7** (200 mg, 69%) was obtained as needles: mp 85–87 °C; ^1H NMR (CCl_4) δ 7.51 (m, 5 H), 6.58 (m, 1 H), 4.21 (dd, 1 H, J_1 = 7 Hz, J_2 = 3 Hz), 2.70 (dd, 1 H, J_1 = 18 Hz, J_2 = 7 Hz), 2.35 (dd, 1 H, J_1 = 18 Hz, J_2 = 3 Hz), 1.90 (s, 3 H); IR (1% CCl_4) ν_{max} 1715, 1660, 1600, 1450, 1360, 1330, 1180, 920 cm^{-1}; mass spectrum, *m/e* 200 (M^+). Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.08; H, 6.12. Evaporation to dryness of the mother liquors in vacuo gave pure **6** (67 mg, 23%) as an oil.

Similar treatment of **3d** gave a 50% yield of a 1:3 mixture of **6** and **7**.

4-Acetyl-3-methylcyclopent-2-enone (8). Concentrated H_2SO_4 (0.4 mL) and $ZnCl_2$ (400 mg) were added to a stirred solution of **3c** in 25 mL of 4:1 acetone–water at 70 °C. After 18 h 0.2 mL of concentrated H_2SO_4 was added and the mixture refluxed for 18 h. The mixture was worked up as for **3a**, and elution of the chromatogram with benzene–Et_2O (2:1) gave 270 mg (70%) of **8** as an oil: ^1H NMR (CCl_4) δ 5.95 (m, 1 H), 3.61 (dd, 1 H, J_1 = 7 Hz, J_2 = 3 Hz), 2.65 (dd, 1 H, J_1 = 15 Hz, J_2 = 3 Hz), 2.38 (dd, 1 H, J_1 = 15 Hz, J_2 = 3 Hz), 2.10 (s, 3 H), 2.08 (s, 3 H); IR (CCl_4) ν_{max} 2980, 2930, 2875, 1710, 1622, 1430, 1375, 1355, 1290, 1175, 1115, 940, 910 cm^{-1}; mass spectrum, *m/e* 138 (M^+). Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69.70; H, 7.18.

Registry No. 1, 22414-24-0; **2a**, 141-97-9; **2b**, 94-02-0; **2c**, 123-54-6; **2d**, 120-46-7; **3a**, 74684-39-2; **3b**, 74684-40-5; **3c**, 74684-41-6; **3d**, 74684-42-7; **5**, 74684-43-8; **6**, 74744-22-2; **7**, 74684-44-9; **8**, 73923-20-3.

(6) (a) G. Büchi and H. Wuest, *J. Org. Chem.*, **31**, 977 (1966); (b) Under these conditions, a complex mixture of red unidentified products (50–55%), due to decomposition of the materials, was also obtained.
(7) K. Inoue, *Chem. Lett.*, 1747 (1978).

Transaminations Using 9-Fluorenone-1-carboxylic Acid[1]

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In 1978, one of us (C.A.P.) reported some unusual examples of amino acid transamination with *o*-formylbenzoic acid.[2] L-Alanine and L-glutamic acid were converted into pyruvic and α-ketoglutaric acids, respectively, in low yields while *o*-formylbenzoic acid was aminated and further

(1) Most of the work described in this note was presented at the 179th ACS National Meeting, Houston, TX, March 26, 1980.
(2) Panetta, C. A.; Miller, A. L. *J. Org. Chem.* **1978**, *43*, 2113.

0022-3263/80/1945-4503$01.00/0