131. Synthesis of 2-Cycloalkenones (Parts of 1,4-Diacyl-1,3-butadiene Systems) and of a Heterocyclic Analogue by Metal-Catalyzed Decomposition of 2-Diazoacylfurans

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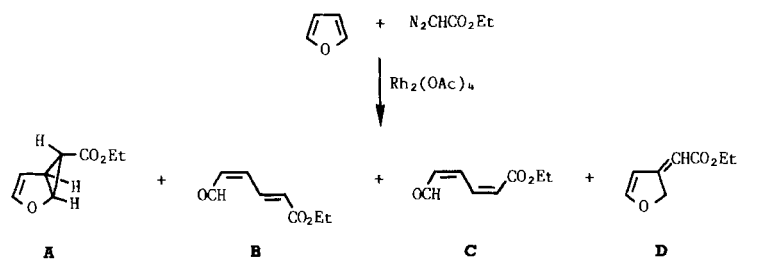
(27. V. 87)

Furans with side-chains at C(2) of various lengths terminating in diazomethyl keto groups are shown to undergo $Rh_2(OAc)_4$-catalyzed furan unravelling with the production of 2-cyclopentenone, 2-cyclohexenone, and 2-cycloheptenone to each of whose olefinic C(β) is attached an acrylaldehyde unit. Interposition of a cyclohexane or a methylaminomethylene moiety between the furan and diazoketo functions leads to the formation of a hydroindenone and pyrrolone, respectively. Replacement of the diazomethylketo terminus by an α-diazoethylketo system or a α-diazo-β-keto-ester function produces 2-substituted 2-cycloalkenones. A furan with a C_4, diazomethylketo-terminating side-chain at C(3) is described to be transformed into a 4-formylmethylidene-2-cyclohexenone.

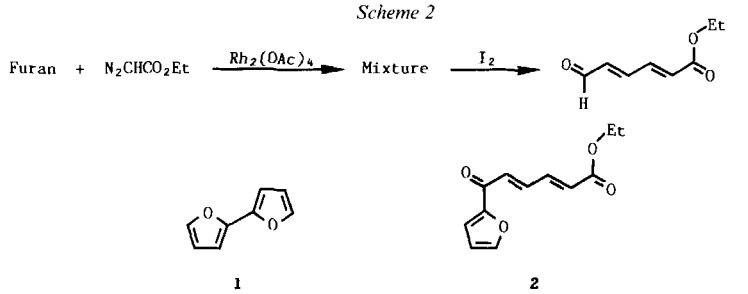
Introduction. – In a recent, broad study of the decomposition of ethyl diazoacetate, ethyl diazopropionate, and various diazomethyl ketones in a variety of furans induced by dirhodium tetraacetate, it was shown that the major products are fused dihydrofuranocyclopropanecarbonyl compounds and/or furan-unravelled, dienic dicarbonyl systems (as illustrated by **A**–**D** for the simplest case in *Scheme 1*) [1]. It, furthermore, was

Scheme 1



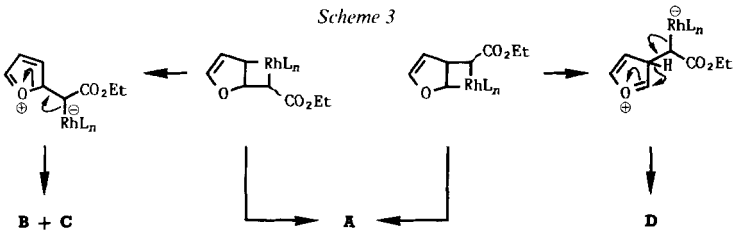
A **B** **C** **D**

Scheme 2



1 **2**

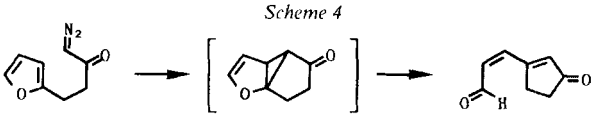
Scheme 3



indicated that treatment of the crude reaction mixture with mild acid led to the isolation of (1*E*,3*E*)-1,4-diacyl-1,3-butadienes usually in high yields. This efficient, new method of dienedione synthesis, illustrated in *Scheme 2* as well as by the new, ready conversion of 2,2'-bifuryl (**1**) [2] into keto ester **2** (see *Exper. Part*)[1]) was formulated mechanistically as shown in *Scheme 3*.

The ease of formation of the acyclic, highly functionalized compounds suggested that an intramolecular version of the furandiazo ketone decomposition might lead to structurally even more interesting, cyclic 1,4-diacyl-1,3-butadienes. This idea was lent credence by a 1974 report depicting the copper-sulfate-induced decomposition of a furan-containing diazomethyl ketone **E** in cyclohexane solution resulting in the production of a cyclopentane-incorporating 1,4-diacyl-1,3-butadiene **G** *(Scheme 4)* [3]. Whereas the structure presented for the product was at odds with the name, '*trans*-3-(cyclopent-2-enone-3-yl)propenal', and no data substantiating the intermediacy of a tricyclic ketone **F** was in evidence, the report, nevertheless, gave a strong impetus to the following general study of metal-promoted decompositions of furan-attached diazo ketones.

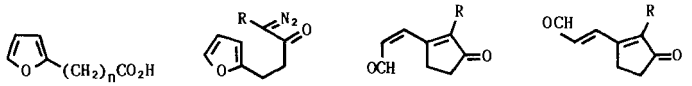
Scheme 4



E **F** **G**

Results and Discussion. – Exposure of diazo ketone **4a** (=**E**) [3], prepared from 3-(2-furyl)propionic acid (**3a**) [4] by reaction with $SOCl_2$ in pyridine/Et_2O and subsequently with ethereal diazomethane, to $Rh_2(OAc)_4$ in CH_2Cl_2 solution at 0° gave, in less than 10 min, a crystalline keto aldehyde **5a** in 80% yield, *i.e.* a substance identical in all respects with compound **G** reported earlier [3]. The spectral data of the cyclic 1,4-diacyl-1,3-butadiene (see *Exper. Part*) and the ready isomerization of the compound (on being kept in $CHCl_3$ solution, presumably containing some HCl, at room temperature) into keto aldehyde **6a** showed compound **G** to possess the (*Z*) configuration in the side-chain. In neither the present Rh-promoted reaction nor in any of those to be discussed have compounds of type **F** been observed (even on early quenching of the reactions), suggesting that cyclopropanes are not intermediates en 'route' to cyclic 1,4-diacyl-1,3-butadienes and that in intramolecular furan/diazo ketone interactions, the strained metallocycle

[1]) Experiment by Mr. *Mitchell Nambu*.

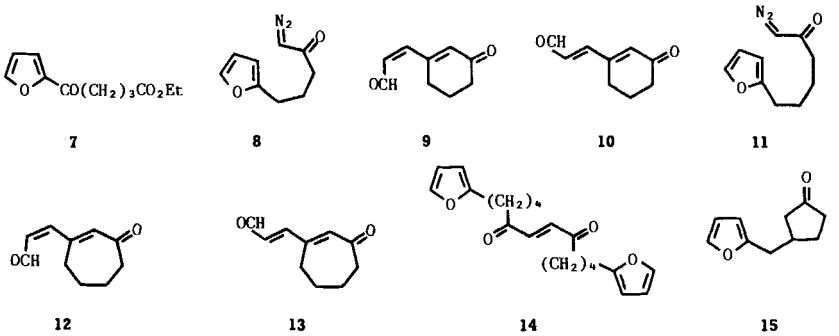


3a $n = 2$ **4a** R = H **5a** R = H **6a** R = H
b $n = 3$ **b** R = Me **b** R = Me **b** R = Me
c $n = 4$ **c** R = COOEt **c** R = COOEt **c** R = COOEt

and/or its bond-cleavage intermediate favor a decomposition route toward products of type **B** and **C** rather than **A.**

In order to ascertain the effect of diazocarbon substituents, the decomposition of diazo ketones **4b** and **4c** was investigated. The diazo compounds were prepared by the interaction of the acyl chloride of **3a** with ethereal diazoethane and ethyl diazoacetate, respectively. Decomposition of diazo ketone **4b** over $Rh_2(OAc)_4$ in CH_2Cl_2 at room temperature led in 5 min to solid keto aldehyde **5b** (95% yield). A similar reaction of diazo keto ester **4c** at 35° for 30 min converted it into ester **5c** (75% yield). Being left in $CHCl_3$ solution for an extended time transformed **5b** and **5c** into their (*E*)-isomers **6b** and **6c**, respectively. The reactions of diazo ketones **4b** and **4c** showed that diazocarbon substitution has no ill effect on the synthetic method, except to reduce somewhat the otherwise high rate of diazo-ketone decomposition.

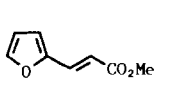
In order to gain some insight into the effect of ring size on the cyclization procedure, the decomposition of the diazo ketones derived from acids **3b** [5] and **3c** (prepared by the stannic-chloride-catalyzed acylation of furan with 4-(methoxycarbonyl)butyryl chloride, alkaline hydrolysis of the resultant keto ester **7**, and *Wolff-Kishner* reduction) [6] was studied next. Exposure of diazo ketone **8** to the Rh catalyst in CH_2Cl_2 at 0° for 70 min afforded liquid keto aldehyde **9** (65% yield) which, by slow chromatography on silica gel, was transformed into its crystalline isomer **10.** On the other hand, the same reaction with diazo ketone **11** in refluxing CH_2Cl_2 for 10 min yielded a complex mixture whose silica-gel chromatography permitted the isolation of liquid keto aldehyde **12** (19% yield), a compound which was converted into its crystalline (*E*)-isomer **13** by I_2 in CH_2Cl_2. The other recognizable diazo ketone decomposition products proved to be enedione **14** and the intramolecular C–H insertion product **15** [7]. These observations indicated the chain-length represented by the cyclopentenone-producing diazo ketone **4a** to be the most favorable one for efficient cyclization[2]).



7 **8** **9** **10** **11**

12 **13** **14** **15**

[2]) The decomposition of diazo ketones derived from furoic acid (**3**, n=0) and homofuroic acid (**3**, n=1), *i.e.* compounds designed to form substituted cyclopropenones and cyclobutenones, respectively, led only to intractable material.



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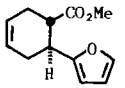

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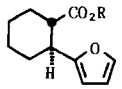
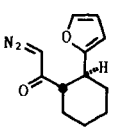


18a R = Me
b R = H



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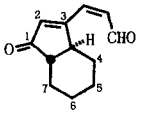

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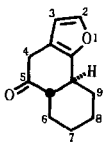

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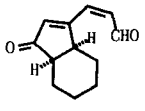

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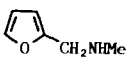
The following example of another diazo ketone decomposition is a cyclopentenone-producing process, but one introducing greater structural complexity. Heating a xylene solution of 1,3-butadiene and the methyl ester **16** of 3-(2-furyl)acrylic acid [4] at 195° for 18 h yielded (70%) ester **17** whose hydrogenation over Pd afforded (92%) the dihydro derivative **18a**. Base hydrolysis of the latter gave (91%) acid **18b**. Stirring a mixture of diazo ketone **19** (derived from acid **18b**) and the Rh catalyst in CH_2Cl_2 at room temperature for 5 min led to crystalline keto aldehyde **20** in 75% yield as well as to a small quantity (8%) of keto furan **21** (*i.e.* a product of type **D**, see *Scheme 3*). Interestingly, silica-gel-catalyzed isomerization of the aldehyde **20** affected only the α-keto bridgehead of the bicycle (→**22**), leaving the (*Z*) side-chain untouched. No attempt was made to force a modification of the side-chain configuration of isomer **22**.

As a test for formation of heterocyclic 1,4-diacyl-1,3-butadienes, the decomposition of a diazocarbonyl compound with a N-containing, furan-terminating chain was investigated. The starting material was prepared by application of the *Westheimer* method of diazoacetamide production [8] on *N*-furfuryl-*N*-methylamine (**23**) [9], *i.e.* interaction of the latter with *p*-nitrophenyl diazoacetate (**24**). Decomposition of the resultant diazoacetamide **25** over the Rh catalyst in CH_2Cl_2 at room temperature for 5 min gave a complex mixture from which there could be isolated a *ca.* 2:1 mixture (14%) of aldehydes **26** and **27**. Upon being left in a $CHCl_3$ solution at room temperature for 12 h, this mixture was transformed nearly quantitatively into crystalline isomer **27**.



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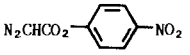

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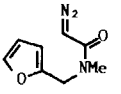

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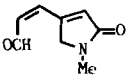

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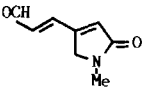

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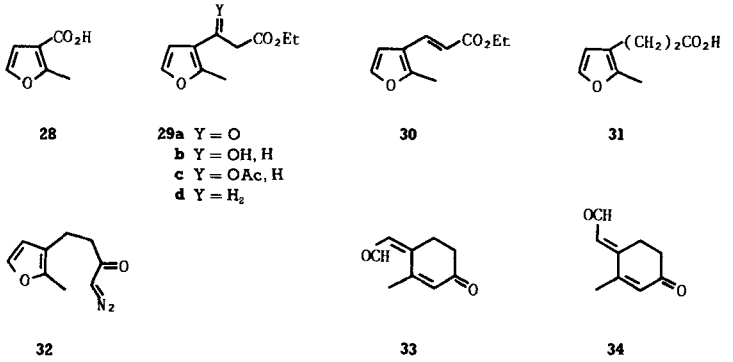
Finally, it was of interest to determine, whether the reaction under present consideration would take place, were the diazo-ketone-containing side-chain of the furan nucleus radiating from the β-position. For this reason, the following procedure for the synthesis of an appropriate diazo ketone was pursued. Conversion of 2-methyl-3-furoic acid (**28**) [10] into its acyl chloride, condensation with lithium ethyl lithiomalonate, and decarboxylation gave keto ester **29a**. $NaBH_4$ reduction of the latter at 5°[3]), acetylation of the

[3]) Reduction at room temperature gave a diol.



28 **29a** Y = O; **b** Y = OH, H; **c** Y = OAc, H; **d** Y = H_2 **30** **31**

32 **33** **34**

resultant hydroxy ester **29b**, and base-induced elimination of acetic acid from diester **29c** yielded ester **30**. Pd-promoted hydrogenation of the acrylic ester afforded propionic ester **29d** whose alkaline hydrolysis led to acid **31**. Exposure of diazo ketone **32**, prepared from acid **31**, to $Rh_2(OAc)_4$ in CH_2Cl_2 at room temperature for 1 h gave crystalline keto aldehyde **33** in 70% yield whose I_2-catalyzed isomerization produced the dicarbonyl compound **34**.

Conclusion. – The above observations reveal a short, generally high-yielding route to highly functionalized ring compounds. This facile access to cyclic 1,4-diacyl-1,3-butadienes can be expected to find application in rapid synthesis of a large variety of naturally occurring substances[4]).

Experimental Part

General. The extracts of the crude reaction products were dried over anh. $MgSO_4$. Chromatography was performed on silica gel. M.p.: *Kofler* micro hot-stage; uncorrected. UV spectra: MeOH solns.; λ_{max} in nm (ε); *IBM 9400* spectrophotometer. IR spectra: $CHCl_3$ solns.; in cm^{-1}; *Perkin-Elmer-1330* spectrophotometer. ^{1}H-NMR spectra: $CDCl_3$ solns.; δ in ppm, coupling constants J in Hz, with Me_4Si as internal standard; *Varian-EM-390* spectrometer. ^{13}C-NMR spectra: $CDCl_3$ solns.; *Nicolet-QE-300* spectrometer, operating at 75.5 MHz in the *Fourier* transform mode; δ in ppm downfield from Me_4Si; $\delta(Me_4Si)=\delta(CDCl_3)+76.9$ ppm.

Ethyl 6-(2'-Furyl)-6-oxo-2,4-hexadienoate (**2**). A soln. of 0.53 ml (5.0 mmol) of ethyl diazoacetate in 4 ml of dry CH_2Cl_2 was added dropwise within 5 h into a stirred mixture of 1.20 g (89 mmol) of 2,2'-bifuryl (**1**) and 5 mg of $Rh_2(OAc)_4$ in 8 ml of dry CH_2Cl_2 under N_2. Stirring was continued for 12 h and the mixture then concentrated to 1 ml. It was placed on an alumina (act. III) column (removal of **1** and of the catalyst), the column washed with hexane/AcOEt 15:1, and the polar eluates were evaporated. A soln. of the residue and 2 mg of I_2 in 8 ml of dry CH_2Cl_2 was kept at r.t. for 18 h, washed with 10% sodium-thiosulfate soln., dried, and evaporated. Crystallization of the residue from Et_2O and sublimation gave 450 mg (40%) of crystalline **2**. M.p. 110–112°. IR: 1720*s* (C=O), 1669*s*, 1635*m* (C=C), 1607*s*, 1577*m*. ^{1}H-NMR: 1.33 (*t*, J = 7, CH_3CH_2O); 4.26 (*q*, J = 7, CH_3CH_2O); 6.29 (*d*, J = 15, H–C(2)); 6.62 (*dd*, J = 4, 1, H–C(4')); 7.12 (*d*, J = 14, H–C(5')); 7.32 (*d*, J = 4, H–C(3')); 7.42 (*dd*, J = 15, 12, H–C(3)); 7.50 (*dd*, J = 14, 12, H–C(4)); 7.67 (*d*, J = 1, H–C(5')). ^{13}C-NMR: 14.0 (CH_3); 60.7 (CH_2); 112.6 (C(3')); 117.8 (C(4')); 129.9 (C(2)); 131.1 (C(5)); 140.3 (C(3)); 146.9 (C(4), C(5')); 153.1 (C(2)); 165.7 (*C*OOEt); 177.0 (C(6)). HR-MS: 220.0742 ($C_{12}H_{12}O_4$, calc. 220.0736).

Acid Precursors of the Diazo Ketones. – *5-(2'-Furyl)pentanoic Acid* (**3c**). A soln. of 39.3 g (240 mmol) of 4-(methoxycarbonyl)butyryl chloride [12] in 120 ml of anh. $CHCl_3$ was added within 25 min to a stirred soln. of 73.4 g (1.08 mol) of freshly distilled furan in 400 ml of dry $CHCl_3$ at –50° under N_2 and stirred for another 10 min.

[4]) On completion of the present study, there appeared a communication on a similar investigation [11].

A soln. of 30.0 ml (240 mmol) of anh. $SnCl_4$ in 50 ml of dry $CHCl_3$ was added dropwise within 45 min and the resultant yellow suspension stirred at −50° for 6 h. H_2SO_4 (6N, 120 ml) was added dropwise within 45 min and the stirred suspension permitted to reach r.t. The blue precipitate was filtered and washed with a mixture of 6N H_2SO_4 (30 ml) and $CHCl_3$ (30 ml). The combined filtrate and $CHCl_3$ washings were washed with 2N $KHCO_3$ and H_2O and dried. Evaporation of $CHCl_3$, chromatography of the residue, and elution with Et_2O/hexane 4:1 yielded 17.1 g of *methyl 4-furoylbutyrate* (**7**) (*ca.* 80% purity).

A mixture of 12.5 g (51 mmol) of **7**, 10.9 g of NaOH pellets (272 mmol), and 11.4 g (228 mmol) of hydrazine hydrate in 350 ml of ethylene glycol was heated at 180° for 18 h. The cooled soln. was acidified with 4N HCl and extracted thoroughly with Et_2O. The extract was washed with sat. NaCl soln., dried, and evaporated, leading to 5.30 g (20% overall yield) of **3c** [6]. M.p. 41–42° ([6]: 42–43°). IR: 3400–3100*m* (OH), 1705*s* (C=O), 1596*w* (C=C). ^{1}H-NMR: 1.5–1.9 (*m*, CH_2(3), CH_2(4)); 2.30 (*t*, *J* = 6, CH_2(5)); 2.60 (*t*, *J* = 6, CH_2(2)); 5.90 (*d*, *J* = 2, H–C(3′)); 6.17 (*dd*, *J* = 2, 2, H–C(4′)); 7.23 (*d*, *J* = 2, H–C(5′)).

trans-*2-(2′-Furyl)cyclohexanecarboxylic Acid* (**18b**). A soln. of 5.00 g (3.6 mmol) of 3-(2-furyl)acrylic acid [4] and 3.5 g of conc. H_2SO_4 in 50 ml of abs. MeOH was refluxed for 2 h. The solvent was evaporated and an Et_2O soln. (100 ml) of the residue washed with sat. $NaHCO_3$ soln. The org. soln. was dried, evaporated, and the residue chromatographed. Elution with Et_2O/hexane 4:1 gave 5.00 g (91%) of liquid *methyl 3-(2′-furyl)acrylate* (**16**). IR: 1700*s* (C=O), 1635*s* (C=C). ^{1}H-NMR: 3.81 (*s*, CH_3O); 6.33 (*d*, *J* = 15, H–C(2)); 6.50 (*dd*, *J* = 3, 2, H–C(4′)); 6.63 (*d*, *J* = 3, H–C(3′)); 7.45 (*d*, *J* = 15, H–C(3)); 7.50 (*d*, *J* = 2, H–C(5′)).

A soln. of 1.00 g (6.6 mmol) of **16** and 2.13 g (39.5 mmol) of 1,3-butadiene in 2 ml of xylenes was sealed in a 20-ml ampule at −75° and then heated at 195° for 18 h. The solvent was removed by distillation and the residue chromatographed with hexane/Et_2O 9:1 to give 960 mg (70%) of liquid *methyl* trans-*6-(2′-furyl)-3-cyclohexenecarboxylate* (**17**). IR: 1725*s* (C=O), 1650*w* (C=C), 1592*w*. ^{1}H-NMR: 2.34, 2.44 (br. *s*, H–C(2), H–C(5)); 2.6–3.0 (*m*, H–C(6)); 3.0–3.4 (*m*, H–C(1)); 3.58 (*s*, CH_3O); 5.73 (br. *s*, 2 olef. H); 6.07 (*d*, *J* = 3, H–C(3′)); 6.23 (*dd*, *J* = 3, 2, H–C(4′)); 7.30 (*d*, *J* = 2, H–C(5′)). Anal. calc. for $C_{12}H_{14}O_3$ (206.23): C 69.88, H 6.84; found: C 69.80, H 6.80.

A mixture of 3.00 g (14.5 mmol) of **17** and 300 mg of 5% Pd/C in 150 ml of abs. EtOH was stirred unter H_2 until gas uptake was complete. The mixture was filtered and the filtrate evaporated, affording 2.80 g (92%) of liquid *methyl* trans-*2-(2′-furyl)cyclohexanecarboxylate* (**18a**). IR: 1720*s* (C=O), 1590*w* (C=C). ^{1}H-NMR: 1.2–2.1 (*m*, 4 CH_2); 2.51 (*td*, *J* = 10, 3, H–C(2)); 2.88 (*td*, *J* = 10, 3, H–C(1)); 3.55 (*s*, CH_3O); 5.93 (*d*, *J* = 3, H–C(3′)); 6.22 (*dd*, *J* = 3, 2, H–C(4)); 7.25 (*d*, *J* = 2, H–C(5)). Anal. calc. for $C_{12}H_{16}O_3$ (208.25): C 69.21, H 7.74; found: C 69.15, H 7.69.

A soln. of 2.70 g (13.1 mmol) of **18a** in 50 ml of NaOH (5% soln. in H_2O/MeOH 3:1) was refluxed for 2 h. Most of the alcohol was evaporated and the residual soln. acidified with 6N HCl and extracted with Et_2O. Drying and subsequent evaporation of the extract gave 2.30 g (91%) of solid **18b**. M.p. 47–48° (pentane). IR: 3400–3100*m* (OH), 1700*s* (C=O), 1590*w* (C=C). ^{1}H-NMR: 1.2–2.1 (*m*, 4 CH_2); 2.53 (*td*, *J* = 10, 3, H–C(2)); 2.93 (*td*, *J* = 10, 3, H–C(1)); 5.96 (*d*, *J* = 3, H–C(3′)); 6.20 (*dd*, *J* = 3, 2, H–C(4′)); 7.23 (*d*, *J* = 2, H–C(5′)). Anal. calc. for $C_{11}H_{14}O_3$ (194.22): C 68.02, H 7.26; found: C 68.07, H 7.23.

3-(2′-Methyl-3′-furyl)propionic Acid (**31**). A soln. of 0.86 ml (11.9 mmol) of $SOCl_2$ and 0.90 ml (11.9 mmol) of pyridine in 15 ml of dry Et_2O was added dropwise within 0.5 h into a stirred soln. of 1.50 g (11.9 mmol) of 2-methyl-3-furoic acid (**28**) [10] in 25 ml of dry Et_2O at 0°. Stirring was continued for 3 h, while the temp. was increased slowly to 30°. The resultant suspension was filtered and the filtrate evaporated, leaving as residual oil 1.80 g (92%) of 2-methyl-3-furoyl chloride. ^{1}H-NMR: 2.57 (*s*, CH_3); 6.74 (*d*, *J* = 2, H–C(4)); 7.25 (*d*, *J* = 2, H–C(5)).

A sufficient amount (*ca.* 29 ml, *ca.* 44 mmol) of 1.6M BuLi in hexane was added slowly to a stirred soln. of 2.90 g (22 mmol) of monoethyl malonate and 2 mg of 2,2′-bipyridyl indicator, cooled in a dry ice/acetone bath, and the temp. permitted to rise to −10° until the pink indicator color persisted for 2 min [13]. A soln. of 1.77 g (11 mmol) of the above acyl chloride in 5 ml of dry THF was added dropwise within 5 min to the stirred suspension at −50° and the temp. allowed to rise to 0° within 20 min. The mixture was poured into a stirred mixture of 75 ml of Et_2O and 45 ml of cold 1N HCl. The org. phase was washed with sat. $NaHCO_3$ soln. and with H_2O, dried, and evaporated. Chromatography of the residue and elution with hexane/AcOEt 20:1 gave 2.10 g (97%) of liquid *ethyl (2′-methyl-3′-furoyl)acetate* (**29**). IR: 1735*s* (C=O), 1675*s*, 1638*m* (C=C), 1578*s*. ^{1}H-NMR: 1.27 (*t*, *J* = 7, CH_3CH_2O); 2.60 (*s*, CH_3); 3.74 (*s*, CH_2); 4.18 (*q*, *J* = 7, CH_3CH_2O); 6.57 (*d*, *J* = 2, H–C(4′)); 7.21 (*d*, *J* = 2, H–C(5′)). ^{13}C-NMR: 13.7 (CH_3); 13.9 (CH_3); 47.8 (CH_2); 60.9 (CH_2O); 109.6 (C(4′)); 120.0 (C(3′)); 140.3 (C(5′)); 159.4 (C(2′)); 166.9 (*C*OOEt); 187.9 (C=O). HR-MS: 196.0728 ($C_{10}H_{12}O_4$, calc. 196.0736).

$NaBH_4$ (620 mg, 16.0 mmol) was added in portions within 20 min to a stirred soln. of 4.30 g (21.9 mmol) of **29a** in 50 ml of abs. EtOH at 5° and stirring continued for 20 min at 5°. The soln. was brought to pH 7 by careful addition of cold 1N HCl and concentrated to 15 ml under vacuum. H_2O (60 ml) was added, the mixture extracted

with Et_2O, the extract dried and evaporated, and the residue chromatographed with hexane/AcOEt 20:1 to give 3.90 g (90%) of liquid *ethyl 3-hydroxy-3-(2'-methyl-3'-furyl)propionate* (**29b**). IR: 3480*m* (br., OH), 1720*s* (C=O), 1628*m* (C=C). ^{1}H-NMR: 1.24 (*t*, *J* = 7, CH_3CH_2O); 2.28 (*s*, CH_3); 2.68 (*AB* of *ABX*, *J* = 16, 8, 5, CH_2(2)); 4.15 (*q*, *J* = 7, CH_3CH_2O); 5.02 (*X* of *ABX*, *J* = 8, 5, H–C(3)); 6.33 (*d*, *J* = 2, H–C(4')); 7.22 (*d*, *J* = 2, H–C(5')). ^{13}C-NMR: 11.3 (CH_3); 13.7 (CH_3CH_2O); 42.0 (C(2)); 60.5 (CH_3CH_2O); 62.6 (C(3)); 108.3 (C(4')); 120.4 (C(3')); 140.1 (C(5')); 147.8 (C(2')); 171.7 (C=O). HR-MS: 198.0890 ($C_{10}H_{14}O_4$, calc. 198.0892).

A soln. of 3.90 g (19.7 mmol) of **29b** and 15 ml of Ac_2O in 10 ml of pyridine was kept at r.t. for 18 h and then evaporated. Chromatography of the residue with hexane/AcOEt 20:1 gave 3.55 g (75%) of liquid *ethyl 3-acetoxy-3-(2'-methyl-3'-furyl)propionate* (**29c**). IR: 1735*s* (C=O), 1725*s*, 1631*m* (C=C). ^{1}H-NMR: 1.22 (*t*, *J* = 7, CH_3CH_2O); 1.98 (*s*, CH_3); 2.24 (*s*, CH_3CO); 2.83 (*AB* of *ABX*, *J* = 16, 8, 6, CH_2(2)); 4.09 (*q*, *J* = 7, CH_3CH_2O); 6.10 (*X* of *ABX*, *J* = 8, 6, H–C(3)); 6.29 (*d*, *J* = 2, H–C(4)); 7.20 (*d*, *J* = 2, H–C(5)). ^{13}C-NMR: 11.6 (CH_3); 13.9 (CH_3CH_2O); 20.8 (CH_3CO); 40.0 (C(2)); 60.5 (CH_3CH_2O); 64.7 (C(3)); 108.5 (C(4')); 117.2 (C(3')); 140.6 (C(5')); 150.0 (C(2')); 169.5 (C=O); 169.6 (C=O). HR-MS: 240.0999 ($C_{12}H_{16}O_5$, calc. 240.0997).

A mixture of 3.47 g (17.5 mmol) of **29c**, 2 g of anh. K_2CO_3, and 5 g of alumina was heated at 180° for 0.5 h and then filtered. The solid was washed repeatedly with Et_2O and the combined filtrate and washings evaporated, leaving 3.00 g (95%) of liquid *ethyl 3-(2'-methyl-3'-furyl)acrylate* (**30**). IR: 1700*s* (C=O), 1638*s* (C=C), 1592*w*. ^{1}H-NMR: 1.22 (*t*, *J* = 7, CH_3CH_2O); 2.32 (*s*, CH_3); 4.16 (*q*, *J* = 7, CH_3CH_2O); 5.98 (*d*, *J* = 16, H–C(2)); 6.41 (*d*, *J* = 2, H–C(4')); 7.20 (*d*, *J* = 2, H–C(5')); 7.47 (*d*, *J* = 16, H–C(3)). ^{13}C-NMR: 11.8 (CH_3); 14.2 (CH_3CH_2O); 60.1 (CH_3CH_2O); 107.7 (C(4')); 116.0 (C(2)); 117.2 (C(3')); 135.0 (C(3)); 141.5 (C(5')); 154.4 (C(2')); 167.2 (C=O). HR-MS: 180.0771 ($C_{10}H_{12}O_3$, calc. 180.0784).

A mixture of 3.00 g (16.7 mmol) of **30** and 0.5 g of 5% Pd/C in 50 ml of MeOH was hydrogenated under 4 atm at r.t. for 1 h, then filtered, and the filtrate evaporated. Chromatography of the residual oil with hexane/AcOEt 50:1 led to 2.50 g (82%) of liquid *ethyl 3-(2'-methyl-3'-furyl)propionate* (**29d**). IR: 1728*s* (C=O), 1639*m* (C=C). ^{1}H-NMR: 1.22 (*t*, *J* = 7, CH_3CH_2O); 2.20 (*s*, CH_3); 2.48 (*t*, *J* = 8, CH_2(3)); 2.65 (*t*, *J* = 8, CH_2(2)); 4.10 (*q*, *J* = 7, CH_3CH_2O); 6.16 (*d*, *J* = 1, H–C(4')); 7.18 (*d*, *J* = 1, H–C(5')). ^{13}C-NMR: 10.9 (CH_3); 13.8 (CH_3CH_2O); 19.9 (C(3)); 34.6 (C(2)); 59.9 (CH_3CH_2O); 110.7 (C(4')); 116.9 (C(3')); 139.6 (C(5')); 147.2 (C(2')); 172.5 (C=O). HR-MS: 182.0940 ($C_{10}H_{14}O_3$, calc. 182.0942).

A soln. of 2.10 g (11.5 mmol) of **29d** in 20 ml of 20% aq. KOH soln. was heated at 90° for 3 h. The cooled soln. was brought to pH 4 with 6N HCl and extracted exhaustively with Et_2O. The extract was dried and evaporated, leaving 1.50 g (84%) of liquid **31**. ^{1}H-NMR: 2.21 (*s*, CH_3); 2.52 (*t*, *J* = 8, CH_2(3)); 2.66 (*t*, *J* = 8, CH_2(2)); 6.14 (*d*, *J* = 2, H–C(4')); 7.18 (*d*, *J* = 2, H–C(5')). ^{13}C-NMR: 11.1 (CH_3); 19.8 (C(3)); 34.6 (C(2)); 110.8 (C(4')); 116.7 (C(3')); 139.9 (C(5')); 147.5 (C(2')); 179.2 (C=O).

α-Diazocarbonyl Compounds. – *General Procedure for the Preparation of Diazomethyl Ketones.* A soln. of 18.2 mmol of pyridine and 17.9 mmol of $SOCl_2$ in 60 ml of dry Et_2O was poured dropwise within 0.5 h into a stirred soln. of 17.9 mmol of the appropriate carboxylic acid in 30 ml of dry Et_2O under N_2 at −10°, and the mixture was stirred for 0.5 h at −10°. Dry Et_2O (50 ml) was added and the suspension filtered rapidly. The filtrate was poured dropwise within 1 h into a soln. of 71.6 mmol of diazomethane in 250 ml of dry Et_2O at 0°, then the mixture was evaporated. Chromatography of the residue with hexane/Et_2O 1:1 gave diazo ketone, ready to be used in the next reaction.

1-Diazo-4-(2'-furyl)-2-butanone (**4a**) [3]. Liquid (72%). IR: 2100*s* (C=N_2), 1630*s* (C=O), 1595*w* (C=C). ^{1}H-NMR: 2.5–3.1 (*m*, 2 CH_2); 5.23 (*s*, CHN_2); 6.00 (*d*, *J* = 2, H–C(3')); 6.27 (*dd*, *J* = 2, 2, H–C(4')); 7.27 (*d*, *J* = 2, H–C(5')).

1-Diazo-5-(2'-furyl)-2-pentanone (**8**). Liquid (87%). IR: 2100*s* (C=N_2), 1625*s* (C=O), 1595*w* (C=C). ^{1}H-NMR: 1.8–2.1 (*m*, CH_2(4)); 2.33 (*t*, *J* = 8, CH_2(5)); 2.65 (*t*, *J* = 8, CH_2(3)); 5.20 (*s*, CHN_2); 5.95 (*d*, *J* = 2, H–C(3')); 6.23 (*dd*, *J* = 2, 2, H–C(4')); 7.25 (*d*, *J* = 2, H–C(5')).

1-Diazo-6-(2'-furyl)-2-hexanone (**11**). Liquid (81%). IR: 2110*s* (C=N_2), 1630*s* (C=O), 1597*w* (C=C). ^{1}H-NMR: 1.6–1.8 (*m*, 2 CH_2); 2.32 (*t*, *J* = 8, CH_2(6)); 2.63 (*t*, *J* = 8, CH_2(3)); 5.20 (*s*, CHN_2); 5.95 (*d*, *J* = 3, H–C(3)); 6.23 (*dd*, *J* = 3, 2, H–C(4)); 7.23 (*d*, *J* = 2, H–C(5)).

*2-Diazo-1-[*trans*-2'-(2''-furyl)cyclohexyl]ethanone* (**19**). Crystalline solid (65%). M.p. 52–53°. IR: 2100*s* (C–N_2), 1625*s* (C=O), 1595*w* (C=C). ^{1}H-NMR: 1.2–2.0 (*m*, 4 CH_2); 2.50 (*td*, *J* = 10, 3, H–C(2')); 2.96 (*td*, *J* = 10, 3, H–C(1')); 5.00 (*s*, CHN_2); 5.96 (*d*, *J* = 3, H–C(3'')); 6.22 (*dd*, *J* = 3, 2, H–C(4'')); 7.26 (*d*, *J* = 2, H–C(5'')).

1-Diazo-4-(2'-methyl-3'-furyl)-2-butanone (**32**). Liquid (65%). ^{1}H-NMR: 2.19 (*s*, CH_3); 2.4–2.8 (*m*, 2 CH_2); 5.18 (*s*, CHN_2); 6.16 (*d*, *J* = 2, H–C(4')); 7.20 (*d*, *J* = 2, H–C(5')). ^{13}C-NMR: 11.0 (CH_3); 19.9 (C(4)); 41.0 (C(3)); 54.3 (C(1)); 110.8 (C(4')); 116.9 (C(3')); 139.7 (C(5')); 147.5 (C(2')); 194.1 (C=O).

2-Diazo-5-(2'-furyl)-3-pentanone (**4b**). A soln. of 88 mg (0.55 mmol) of 3-(2'-furyl)propionyl chloride (the acyl halide used for the preparation of **4a**) in 5 ml of dry Et_2O was added dropwise within 0.5 h to 5 ml of 2.4M

diazoethane in Et_2O at −30°. The soln. was stirred at −30° for 3 h, allowed to rise to r.t., and kept stirring for another 0.5 h. It was then evaporated and the residue chromatographed on neutral alumina with hexane to give 80 mg (82%) of liquid **4b**. ^{1}H-NMR: 1.97 (*s*, CH_3); 2.6–3.1 (*m*, 2 CH_2); 5.98 (*d*, *J* = 3, H–C(3')); 6.23 (*dd*, *J* = 3, 2, H–C(4')); 7.28 (*d*, *J* = 2, H–C(5')).

Ethyl 2-Diazo-5-(2'-furyl)-3-oxopentanoate (**4c**). A mixture of 1.29 g (8.1 mmol) of 3-(2'-furyl)propionyl chloride and 2.00 g (17.5 mmol) of ethyl diazoacetate was kept with occasional shaking at r.t. for 72 h. Volatile materials were removed under high vacuum at r.t., and the residue was chromatographed with hexane/AcOEt 20:1 affording 1.60 g (83%) of liquid **4c** (solid at refrigerator temp.). ^{1}H-NMR: 1.30 (*t*, *J* = 7, CH_3CH_2O); 2.92 (*t*, *J* = 8, CH_2(5)); 3.17 (*t*, *J* = 8, CH_2(4)); 4.27 (*q*, *J* = 7, CH_2CH_2O); 6.00 (*d*, *J* = 3, H–C(3')); 6.21 (*dd*, *J* = 3, 2, H–C(4')); 7.28 (*d*, *J* = 2, H–C(5')).

2-Diazo-N-[(2'-furyl)methyl]-N-methylacetamide (**25**). A mixture of 111 mg (1.0 mmol) of *N*-[(2-furyl)methyl]-*N*-methylamine (**23**) [9] and 207 mg (1.0 mmol) of *p*-nitrophenyl diazoacetate (**24**) [8] in 5 ml of Et_2O was stirred under N_2 at r.t. for 72 h and then evaporated. Chromatography of the residue with hexane/AcOEt 50:1 furnished 142 mg (98%) of pale yellow liquid **25**. IR: 2150*s* (C=N_2), 1605*s* (C=O). ^{1}H-NMR: 3.00 (*s*, CH_3); 4.57 (*s*, CH_2N); 5.16 (*s*, CHN_2); 6.2–6.4 (*m*, H–C(3'), H–C(4')); 7.32 (*d*, *J* = 2, H–C(5')).

Cyclopentenones. – *(Z)-3-Oxo-1-cyclopentene-1-acrylaldehyde* (**5a**). A mixture of 300 mg (1.8 mmol) of **4a** and 4 mg (0.009 mmol) of $Rh_2(OAc)_4$ in 37 ml of dry CH_2Cl_2 was stirred vigorously at 0° for 10 min. The catalyst was filtered through a pad of *Celite* and the filtrate evaporated. Crystallization of the residue from pentane/Et_2O 9:1 gave 200 mg (80%) of crystalline **5a** [3]. M.p. 70–71° ([3]: 65°). UV: 267 (17200). IR: 1710*s* (CO), 1671*s* (C=O, C=C). ^{1}H-NMR: 2.4–2.6 (*m*, CH_2(5)); 2.8–3.0 (*m*, CH_2(4)); 6.15 (*dd*, *J* = 12, 8, H–C(α)); 6.30 (*s*, H–C(2)); 7.15 (*d*, *J* = 12, H–C(β)); 10.08 (*d*, *J* = 8, CHO). ^{13}C-NMR: 31.5 (C(5)); 35.5 (C(4)); 136.8 (C(2)); 139.9 (C(α)); 140.4 (C(β)); 167.7 (C(1)); 190.1 (CH=O); 207.8 (C(3)). Anal. calc. for $C_8H_8O_2$ (136.14): C 70.58, H 5.92; found: C 70.28, H 5.85.

(E)-3-Oxo-1-cyclopentene-1-acrylaldehyde (**6a**). When a 0.1M soln. of **5a** in $CHCl_3$ was kept at r.t. for 24 h, crystalline **6a** was obtained quantitatively. M.p. 125–126° (pentane/Et_2O). UV: 273 (24000). IR: 1710*s* (C=O), 1685*s*, 1668*m* (C=C). ^{1}H-NMR: 2.4–2.6 (*m*, CH_2(5)); 2.7–2.9 (*m*, CH_2(4)); 6.41 (*s*, H–C(2)); 6.50 (*dd*, *J* = 15, 8, H–C(α)); 7.52 (*d*, *J* = 15, H–C(β)); 9.70 (*d*, *J* = 8, CHO). ^{13}C-NMR: 26.9 (C(5)); 34.9 (C(4)); 133.4 (C(2)); 136.9 (C(α)); 144.2 (C(β)); 167.4 (C(1)); 192.6 (CH=O); 208.1 (C(3)). HR-MS: 136.0472 ($C_8H_8O_2$, calc. 136.0465). Anal. calc. for $C_8H_8O_2$ (136.14): C 70.58, H 5.92; found: C 70.54, H 5.92.

(Z)- and (E)-2-Methyl-3-oxo-1-cyclopentene-1-acrylaldehyde (**5b** and **6b**, resp.). A mixture of 66 mg (0.37 mmol) of **4b** and 3 mg (0.006 mmol) of $Rh_2(OAc)_4$ in 5 ml of dry CH_2Cl_2 was stirred at r.t. for 5 min. The catalyst was filtered through a silica-gel pad and the filtrate evaporated. Purification of the residue on a *Chromatotron* (silica-gel plate, 1 mm thick; hexane/AcOEt 5:1) afforded 53 mg (95%) of solid **5b**. ^{1}H-NMR: 1.84 (*t*, *J* = 2, CH_3); 2.5–3.0 (*m*, 2 CH_2); 6.18 (*dd*, *J* = 13, 8, H–C(α)); 7.26 (*d*, *J* = 13, H–C(β)); 10.05 (*d*, *J* = 8, CHO). ^{13}C-NMR: 8.70 (CH_3); 30.2 (C(5)); 33.8 (C(4)); 131.9 (C(α)); 139.9 (C(β)); 190.8 (CH=O); 208.6 (C(3)).

On remaining in $CHCl_3$ soln. for 72 h, **5b** was transformed quantitatively into crystalline **6b**. M.p. 64–65° (hexane). UV: 289 (27000). IR: 1700*s* (C=O), 1672*s*, 1650*m* (C=C), 1586*m*. ^{1}H-NMR: 1.95 (*t*, *J* = 2, CH_3); 2.4–2.8 (*m*, 2 CH_2); 6.48 (*dd*, *J* = 16, 8, H–C(α)); 7.60 (*d*, *J* = 16, H–(β)); 9.73 (*d*, *J* = 8, CHO). ^{13}C-NMR: 8.3 (CH_3); 25.2 (C(5)); 33.3 (C(4)); 132.1 (C(α)); 143.1 (C(β)); 144.0 (C(2)); 158.8 (C(1)); 192.9 (CH=O); 208.1 (C(3)). HR-MS: 150.0629 ($C_9H_{10}O_2$, calc. 150.0680).

Ethyl-2-[(Z)- and (E)-2'-Formylethenyl]-5-oxo-1-cyclopentene-1-carboxylate (**5c** and **6c**, resp.). A mixture of 410 mg (1.7 mmol) of **4c** and 42 mg (0.095 mmol) of $Rh_2(OAc)_4$ in 20 ml of dry CH_2Cl_2 was stirred at 35° for 0.5 h. The solvent was evaporated, the residue taken up in 15 ml of Et_2O and the resultant suspension extracted with H_2O. The aq. soln. was saturated with NaCl and washed exhaustively with Et_2O. The combined Et_2O washings were dried and evaporated, leaving 280 mg (75%) of semi-solid **5c**. ^{1}H-NMR: 1.30 (*t*, *J* = 7, CH_3); 2.5–3.0 (*m*, 2 CH_2); 4.30 (*q*, *J* = 7, CH_3CH_2O); 6.22 (*dd*, *J* = 13, 8, H–C(2')); 7.46 (*d*, *J* = 13, H–C(1')); 10.0 (*d*, *J* = 8, CHO). ^{13}C-NMR: 13.7 (CH_3CH_2O); 31.1 (C(3)); 34.8 (C(4)); 61.2 (CH_3CH_2O); 133.1 (C(2')); 136.3 (C(1)); 138.9 (C(1')); 161.9 (COOEt); 170.8 (C(2)); 190.0 (CH=O); 201.8 (C(5)).

On remaining in $CHCl_3$ soln. for 120 h, **5c** was converted quantitatively into crystalline **6c**. M.p. 80–81.5° (hexane). UV: 276 (6500). IR: 1735*s* (C=O), 1708*s*, 1682*s*, 1621*w* (C=C), 1572 *m*. ^{1}H-NMR: 1.30 (*t*, *J* = 7, CH_3); 2.5–2.9 (*m*, 2 CH_2); 4.30 (*q*, *J* = 7, CH_3CH_2O); 6.60 (*dd*, *J* = 16, 7, H–C(2')); 8.10 (*d*, *J* = 16, H–C(1')); 9.80 (*d*, *J* = 7, CHO). ^{13}C-NMR: 13.9 (CH_3); 25.8 (C(3)); 34.4 (C(4)); 61.5 (CH_3CH_2O); 135.4 (C(2')); 136.1 (C(1)); 142.3 (C(1')); 162.3 (COOEt); 169.5 (C(2)); 192.8 (CH=O); 202.2 (C(5)). HR-MS: 208.0698 ($C_{11}H_{12}O_4$, calc. 208.0735).

trans- *and* cis-*3a,4,5,6,7,7a-Hexahydro-1-oxo-1H-indene-3-acrylaldehyde* (**20** and **22**, resp.) *and* trans-*5a,6,7,8,9,9a-Hexahydronaphtho[1,2-b]furan-5(4H)-one* (**21**). A mixture of 668 mg (3.1 mmol) of **19** and 6.7 mg

(0.015 mmol) of $Rh_2(OAc)_4$ in 61 ml of dry CH_2Cl_2 was stirred vigorously at r.t. for 5 min. Filtration of the mixture through *Celite*, evaporation of the filtrate, and crystallization of the residue from hexane led to 436 mg (75%) of crystalline **20**. M.p. 64–65°. UV: 270 (7600). IR: 1700*s* (C=O), 1670*s* (C=O, C=C). ^{1}H-NMR: 1.2–2.3 (*m*, 9 H, CH, CH_2); 2.4–2.7 (*m*, H–C(7a)); 6.14 (*d*, *J* = 2, H–C(2)); 6.23 (*dd*, *J* = 11, 8 H–C(α)); 7.16 (*dd*, *J* = 11, 2, H–C(β)); 9.90 (*d*, *J* = 8, CHO). ^{13}C-NMR: 23.8 (C(5)); 25.5 (C(6)); 26.3 (C(4)); 28.2 (C(7)); 49.5 (C(3a)); 56.7 (C(7a)); 133.6 (C(α)); 133.9 (C(2)); 140.2 (C(β)); 165.2 (C(3)); 190.4 (CH=O); 205.4 (C(1)). Anal. calc. for $C_{12}H_{14}O_2$ (190.23): C 75.77, H 7.41; found: C 75.42, H 7.30.

Chromatography of the mother liquor (140 mg) and elution with hexane/Et_2O 4:1 gave 45 mg (8%) of solid **21**. M.p. 60–61° (pentane). IR: 1705*s* (C=O), 1600*w* (C=C). ^{1}H-NMR: 1.2–2.1 (*m*, 9 H, CH, CH_2); 2.3–3.6 (*m*, 3 H, H–C(5a), CH_2); 6.23 (*d*, *J* = 2, H–C(3)); 7.30 (*d*, *J* = 2, H–C(2)). ^{13}C-NMR: 24.3 (C(8)); 24.6 (C(7)); 25.0 (C(6)); 29.3 (C(9)); 37.4 (C(4)); 39.2 (C(9a)); 52.8 (C(5a)); 109.8 (C(3)); 113.0 (C(3a)); 141.6 (C(2)); 151.2 (C(9b)); 209.1 (C(5)). Anal. calc. for $C_{12}H_{14}O_2$ (190.23): C 75.77, H 7.41; found: C 75.52, H 7.26.

When the crude mixture was worked up by chromatography (instead of crystallization) with hexane/Et_2O 4:1, 8% of **21** and then 181 mg (33%) of solid **22** were obtained. M.p. 69–70° (pentane). UV: 268 (12600). IR: 1700*s* (C=O), 1675*s* (C=O, C=C). ^{1}H-NMR: 1.0–2.2 (*m*, 4 CH_2); 2.5–2.7 (*m*, H–C(3a)); 2.9–3.2 (*m*, H–C(7a)); 6.20 (*dd*, *J* = 12, 8, H–C(α)); 6.23 (*d*, *J* = 2, H–C(2)); 7.13 (*dd*, *J* = 12, 2, H–C(β)); 10.00 (*d*, *J* = 8, CHO). ^{13}C-NMR: 21.3 (C(5)); 21.7 (C(6)); 22.3 (C(4)); 28.7 (C(7)); 43.0 (C(3a)); 47.0 (C(7a)); 133.6 (C(2)); 133.8 (C(α)); 140.9 (C(β)); 171.0 (C(3)); 190.4 (CH=O); 208.9 (C(1)). Anal. calc. for $C_{12}H_{14}O_2$ (190.23): C 75.77, H 7.41; found: C 75.65, H 7.32.

(Z)- and (E)-2,5-Dihydro-1-methyl-5-oxo-1H-pyrrol-3-acrylaldehyde (**26** and **27**, resp.). A mixture of 100 mg (0.56 mmol) of **25** and 6 mg (0.0012 mmol) of $Rh_2(OAc)_4$ in 6 ml of dry CH_2Cl_2 was stirred vigorously at r.t. for 5 min. The catalyst was filtered through a *Celite* pad, whereupon the latter was washed with CH_2Cl_2. The combined filtrate and washings were evaporated, and the residue (110 mg) was chromatographed rapidly on 5 g of silica gel with hexane/AcOEt 2:1 to give 15.5 mg (14%) of a crystalline *ca.* 2:1 mixture of **26** and **27**. **26**: IR: 1670*s* (C=O), 1653*s*, 1650*s* (C=C). ^{1}H-NMR: 3.15 (*s*, CH_3); 3.46 (*s*, CH_2N); 4.62 (*s*, H–C(4)); 5.78 (*dd*, *J* = 12, 7, H–C(α)); 6.82 (*d*, *J* = 12, H–C(β)); 10.01 (*d*, *J* = 8, CHO).

A soln. of 15.5 mg of **26/27** in 2 ml of $CHCl_3$ was kept at r.t. for 12 h and then evaporated. Crystallization of the residue (15.2 mg, m.p. 42–44°) from hexane/Et_2O 4:1 yielded 14.7 mg (95%) of crystalline **27**. IR: 1703*m* (CO), 1653*s*, 1610*s* (C=C). ^{1}H-NMR: 3.16 (*s*, CH_3); 3.24 (*s*, CH_2N); 4.62 (*s*, H–C(4)); 5.98 (*dd*, *J* = 15, 8, H–C(α)); 7.19 (*d*, *J* = 15, H–C(β)); 9.54 (*d*, *J* = 8, CHO). HR-MS: 151.0625 ($C_8H_9NO_2$, calc. 151.0633).

Cyclohexenones. – *(Z)- and (E)-3-Oxo-1-cyclohexene-1-acrylaldehyde* (**9** and **10**, resp.). A mixture of 209 mg (1.2 mmol) of **8** and 2.6 mg (0.005 mmol) of $Rh_2(OAc)_4$ in 47 ml of dry CH_2Cl_2 was stirred vigorously at 0° for 70 min. The catalyst was filtered (*Celite* pad) and the filtrate evaporated. Fast chromatography of the residue with Et_2O /pentane 9:1 gave 115 mg (65%) of liquid **9**. IR: 1670*s* (C=O), 1655*s* (C=C). ^{1}H-NMR: 1.9–2.2 (*m*, CH_2(5)); 2.3–2.6 (*m*, CH_2(6), CH_2(4)); 6.10 (*s*, H–C(2)); 6.12 (*dd*, *J* = 12, 8, H–C(α)); 7.08 (*d*, *J* = 12, H–C(β)); 9.96 (*d*, *J* = 8, CHO). ^{13}C-NMR: 22.5 (C(5)); 29.3 (C(6)); 37.1 (C(4)); 131.3 (C(α)); 132.6 (C(2)); 146.3 (C(β)); 154.2 (C(1)); 190.6 (CH=O); 198.5 (C(3)).

Slow chromatography of **9** with pentane/Et_2O 1:1 gave crystalline **10** (54%). M.p. 54–55° (pentane). UV: 280 (28500). IR: 1665*s* (C=O), 1655*s* (C=C). ^{1}H-NMR: 2.0–2.2 (*m*, CH_2(5)); 2.3–2.6 (*m*, CH_2(6), CH_2(4)); 6.17 (*s*, H–C(2)); 6.40 (*dd*, *J* = 15, 8, H–C(α)); 7.15 (*d*, *J* = 15, H–C(β)); 9.64 (*d*, *J* = 8, CHO). ^{13}C-NMR: 21.9 (C(5)); 24.7 (C(6)); 37.5 (C(4)); 132.9 (C(2)); 133.3 (C(α)); 151.1 (C(β)); 153.2 (C(1)); 192.8 (CH=O); 199.2 (C(3)). Anal. calc. for $C_9H_{10}O_2$ (150.17): C 71.98, H 6.70; found: C 72.10, H 6.50.

(Z)-(2-Methyl-4-oxo-2-cyclohexen-1-ylidene)acetaldehyde (**33**). A mixture of 150 mg (0.77 mmol) of **32** and 10 mg (0.22 mmol) of $Rh_2(OAc)_4$ in 20 ml of dry CH_2Cl_2 was stirred at r.t. for 1 h. The catalyst was filtered (silica-gel pad) and the filtrate evaporated. Purification of the residue on a *Chromatotron* (silica-gel plate, 1 mm thick; hexane/AcOEt 10:1) gave 90 mg (70%) of crystalline **33**. M.p. 90–93° (hexane). UV: 282 (8800). IR: 1664*s* (C=O), 1610*w* (C=C), 1577*m*. ^{1}H-NMR: 2.41 (*d*, *J* = 1, CH_3); 2.61 (*t*, *J* = 7, CH_2(5)); 2.85 (*t*, *J* = 7, CH_2(6)); 6.14 (*q*, *J* = 1, H–C(3)); 6.15 (*d*, *J* = 8, C*H*CHO); 10.22 (*d*, *J* = 8, CHO). ^{13}C-NMR: 25.5 (CH_3); 35.9 (C(6)); 37.2 (C(5)); 130.0 (*C*HCHO); 132.8 (C(3)); 151.8 (C(2) or C(1)); 152.8 (C(1) or C(2)); 190.7 (CH=O); 197.4 (C(4)). HR-MS: 150.0684 ($C_9H_{10}O_2$, calc. 150.0680).

(E)-(2-Methyl-4-oxo-2-cyclohexen-1-ylidene)acetaldehyde (**34**). A soln. of 10 mg (0.067 mmol) of **33** and one crystal of I_2 in 0.5 ml of dry $CHCl_3$ was kept at r.t. for 3 h and then poured into a *Chromatotron* (silica-gel plate, 1mm thick). Elution with hexane/AcOEt 10:1 gave quantitatively crystalline **34**. M.p. 81–85°. UV: 284 (16000). IR: 1661*s* (C=O), 1603*w* (C=C), 1578*m*. ^{1}H-NMR: 2.06 (*d*, *J* = 1, CH_3); 2.56 (*t*, *J* = 7, CH_2(5)); 3.22 (*t*, *J* = 7, CH_2(6)); 6.11 (br. *s*, H–C(3)); 6.20 (*d*, *J* = 8, C*H*CHO); 10.2 (*d*, *J* = 8, CHO). ^{13}C-NMR: 20.0 (CH_3); 25.1 (C(6));

36.4 (C(5)); 127.7 (*C*HCHO); 132.5 (C(3)); 152.4 (C(1) or C(2)); 153.0 (C(2) or C(1)); 190.3 (CH=O); 197.2 (C(4)). HR-MS: 150.0686 ($C_9H_{10}O_2$, calc. 150.0690).

Cycloheptenones. – A mixture of 1.50 g (7.8 mmol) of **11** and 3.5 mg (0.0008 mmol) of $Rh_2(OAc)_4$ in 313 ml of dry CH_2Cl_2 was stirred vigorously and refluxed for 10 min. Filtration of the catalyst (*Celite* pad), evaporation of the filtrate, and chromatography of the residue with Et_2O/hexane 3:2 led firstly to 400 mg (16%) of crystalline *trans-1,12-bis(2'-furyl)-6-dodecene-5,8-dione* (**14**) [14]. M.p. 76–77° (hexane). UV: 226 (16000). IR: 1685*s* (C=O), 1660*m* (C=C). ^{1}H-NMR: 1.5–1.7 (*m*, 4 CH_2); 2.5–2.7 (*m*, CH_2(1), CH_2(12), CH_2(4), CH_2(9)); 5.93 (*d*, *J* = 2, 2 H, H–C(3')); 6.23 (*dd*, *J* = 2, 2, 2 H, H–C(4')); 6.76 (*s*, H–C(6), H–C(7)); 7.20 (*d*, *J* = 2, 2 H, H–C(5')). ^{13}C-NMR: 23.0 (C(2), C(11)); 27.4 (C(3), C(10)); 27.6 (C(1), C(12)); 41.2 (C(4), C(9)); 104.9 (C(3')); 110.0 (C(4')); 136.1 (C(6), C(7)); 140.7 (C(5')); 155.5 (C(2')); 200.1 (C(5), C(8)). Anal. calc. for $C_{20}H_{24}O_4$ (328.39): C 73.15, H 7.36; found: C 69.98, H 7.25.

The elution then gave 400 mg of oil whose rechromatography with Et_2O/hexane 3:2 afforded 200 mg (15%) of liquid, unstable *3-furfurylcyclopentanone* (**15**). IR: 1725*s* (C=O), 1586*w* (C=C). ^{1}H-NMR: 1.5–1.9 (*m*, H–C(3), CH_2(4), CH_2–C(3)); 2.3–2.7 (*m*, CH_2(2), CH_2(5)); 5.93 (*d*, *J* = 3, H–C(3')); 6.23 (*dd*, *J* = 3, 2, H–C(4')); 7.23 (*d*, *J* = 2, H–C(5')). ^{13}C-NMR: 28.9 (C(4)); 33.2 (*C*H_2–C(3)); 36.1 (C(3)); 38.2 (C(5)); 44.6 (C(2)); 106.0 (C(3')); 110.0 (C(4')); 141.4 (C(5')); 153.8 (C(2')); 218.9 (C(1)).

The final eluate yielded 300 mg of oil whose rechromatography with Et_2O/hexane 3:2 led to 250 mg (19%) of liquid *(Z)-3-oxo-1-cycloheptene-1-acrylaldehyde* (**12**). IR: 1670*s* (C=O), 1660*s*, 1665*s* (C=C). ^{1}H-NMR: 1.8–2.0 (*m*, 2 CH_2); 2.4–2.7 (*m*, CH_2(7), CH_2(4)); 5.96 (*dd*, *J* = 12, 8, H–C(α)); 6.06 (*s*, H–C(2)); 7.06 (*d*, *J* = 12, H–C(β)); 9.80 (*d*, *J* = 8, CHO). ^{13}C-NMR: 21.0 (C(5)); 25.0 (C(6)); 32.2 (C(7)); 42.2 (C(4)); 131.3 (C(α)); 134.9 (C(2)); 149.5 (C(β)); 150.8 (C(1)); 190.8 (CH=O); 202.3 (C(3)).

A soln. of 100 mg (0.6 mmol) of **12** and a crystal of I_2 in 5 ml of dry CH_2Cl_2 was kept at r.t. for 0.5 h and then evaporated. Fast chromatography of the residue and elution with Et_2O gave 95 mg (95%) of crystalline *(E)-3-oxo-1-cycloheptene-1-acrylaldehyde* (**13**). M.p. 35–36° (pentane). UV: 281 (34000). IR: 1660*s* (C=O), 1655*s* (C=C). ^{1}H-NMR: 1.8–2.0 (*m*, 2 CH_2); 2.5–2.8 (*m*, CH_2(7), CH_2(4)); 6.28 (*s*, H–C(2)); 6.41 (*dd*, *J* = 15, 8, H–C(α)); 7.14 (*d*, *J* = 15, H–C(β)); 9.67 (*d*, *J* = 8, CHO). ^{13}C-NMR: 21.0 (C(5)); 24.6 (C(6)); 27.5 (C(7)); 42.0 (C(4)); 132.0 (C(α)); 137.9 (C(2)); 149.6 (C(1)); 154.1 (C(β)); 192.9 (CH=O); 203.4 (C(3)). Anal. calc. for $C_{10}H_{12}O_2$ (164.20): C 73.15, H 7.36; found: C 73.00, H 7.20.

E. W. expresses his heartfelt thanks to Dr. *G. Ohloff* and his colleagues at *Firmenich SA* for their generous hospitality during his sabbatical quarter in Geneva in the fall 1986. *F. P.* is indebted to the *C. N. R.* (Roma) for a 1986 fellowship.

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