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# A FACILE ROUTE TO 5-ALKYL-2(3H)-FURANONES BY PHOTOISOMERISATION OF ENEDICARBONYL COMPOUNDS

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**Abstract**—A new and useful synthesis of a title compounds is reported. They can be obtained easily by photocyclization of enedicarbonyl compounds **3** and **4**. A different behaviour, ascribed to the geometry of a double bond, is observed; **3** are converted only to butenolides **5**, while *trans*-isomers **4** are converted into alkyl–furyl-ketones **5** and **6**. A possible mechanism is described.

Our recent interest in the chemistry of enedicarbonyl compounds,[1] particularly their utility in the synthesis of natural products, prompts this report on a new and original application photocyclization directly to 5-alkyl-2(3H)-furanones.

The photochemistry of ketones has been extensively investigated recently;[2] moreover, the photochemical behaviour of enones and dienones has been carefully studied in many systems[3] (retinal is the most important compound in vision[4]). On the contrary, very few data are reported on the photochemistry of enedicarbonyl compounds.[5]

Unsaturated $\gamma$-butyrolactones are important natural products and show several biological activities;[6] this has given rise to a considerable interest and efforts to develop synthetic routes to these molecules.[7] Lactonization of $\gamma$-keto acids is a general route to unsaturated $\gamma$-butyrolactones and related compounds. Numerous other methods, sometimes complicated, for the synthesis of these intermediates are available. Furthermore, $\gamma$-butyrolactones are useful in organic synthesis: $\alpha$-angelica lactone, 5-methyl-2(3H)-furanone, has been used in cyclopentenone preparation.[8] Recently, 5-aryl-2(3H)-furanones were used in a photochemical synthesis of chromones.[9] Therefore, the availability of a new general method for their synthesis is important. The mildness and effectiveness of our procedure, with the easy availability of the starting materials, make this new method very interesting in this field.

The starting materials, the *cis* and *trans* isomers **3** and **4**, were prepared by standard methods (Scheme 1). **3** were synthesized by this route: 2-alkyl-2,5-dihydro-2,5-dimethoxy-furan **2** (from **1** by the method of Floyd)[10] were hydrolysed with Amberlite IR-120 in THF-water solution at room temperature for 2 h.[11] Generally, **3** did not show a great stability. **4** were obtained by our previously described procedure,[1] through an oxidative ring fission of **1** with an excess of PCC (pyridinium chlorochromate) in methylene chloride at 50°.

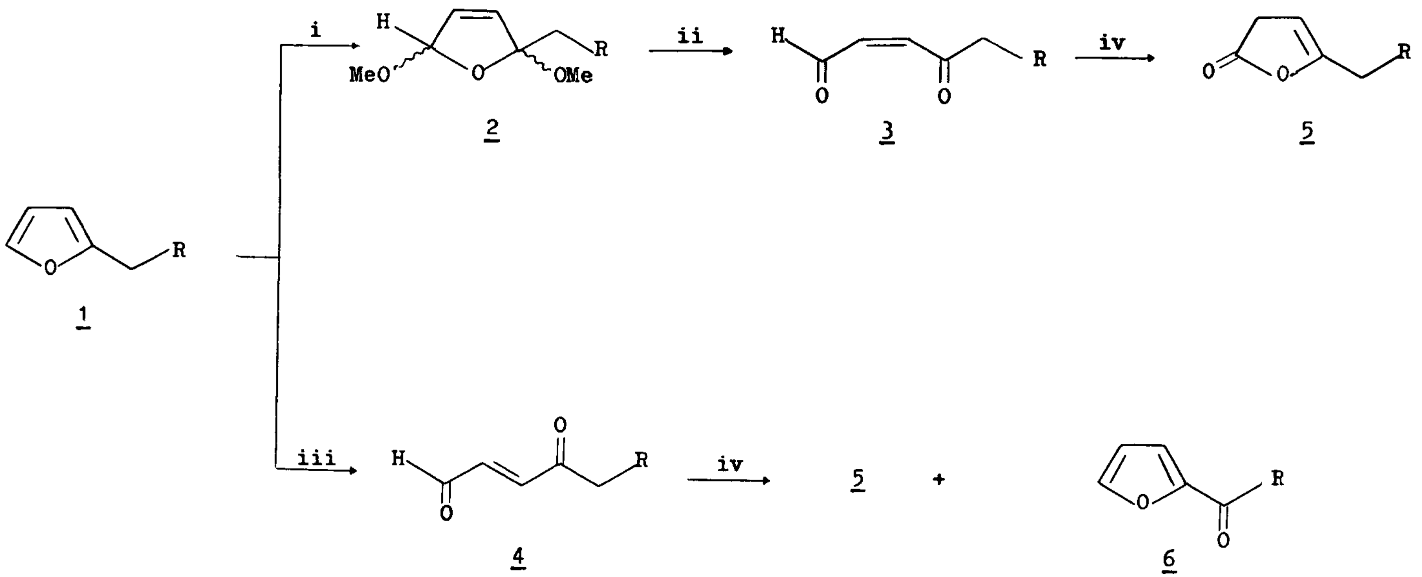
**3**, irradiated with a Hanovia 100 Watt medium pressure mercury arc for 4 h in benzene, underwent a photochemical isomerisation, giving directly only the butenolides **5** in high yields (Table 1). Analytical and spectroscopic data were in agreement with the proposed formula.[12] On the contrary, irradiation of **4** with an Ilesa 125 Watt medium pressure mercury lamp for 4 h in benzene solution, gave a complex mixture of products; we have been able to isolate only two compounds, 5-alkyl-2(3H)-furanone **5** and alkyl 2-furyl-ketone **6**; they were obtained in overall yields of 40–50% (Table 2). The use of other solvents, i.e. acetone or p-dioxane, gave always a complex mixture of unidentified products.

In order to collect information about the mechanism of the above transformations, some reactions were carried with suitably deuterated substrates. The *trans*-enedicarbonyl compound **8** was obtained by oxidation with PCC of 2-ethyl-5-d-furan; this compound was prepared from 2-ethyl-furan, achieved by Wolf–Kishner reduction[13] of methyl-2-furyl-ketone, through metalation with n-BuLi in $Et_2O$ and subsequent treatment with $D_2O$. On the other hand, the *cis*-enedicarbonyl compound **7** was obtained by hydrolysis of 2-n-decyl-5-d-2,5-dimethoxy-2,5

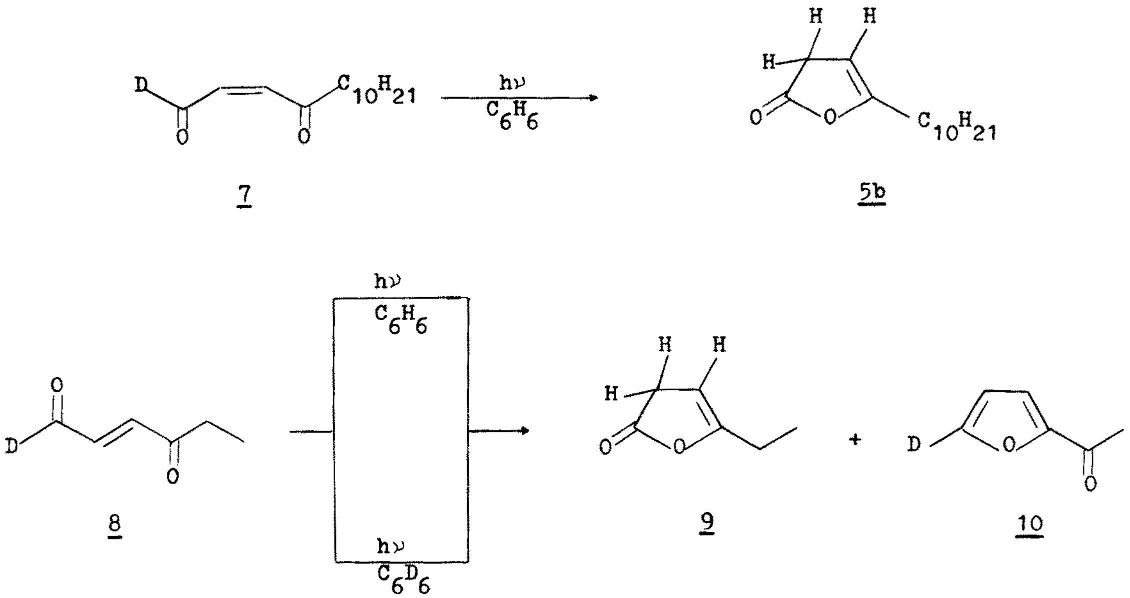
Table 1.

| Substrate | R | Product | yield (%)* |
|---|---|---|---|
| 3a | $C_7H_{15}$ | 5a | 70 |
| 3b | $C_9H_{19}$ | 5b | 72 |
| 3c | $C_{11}H_{23}$ | 5c | 65 |

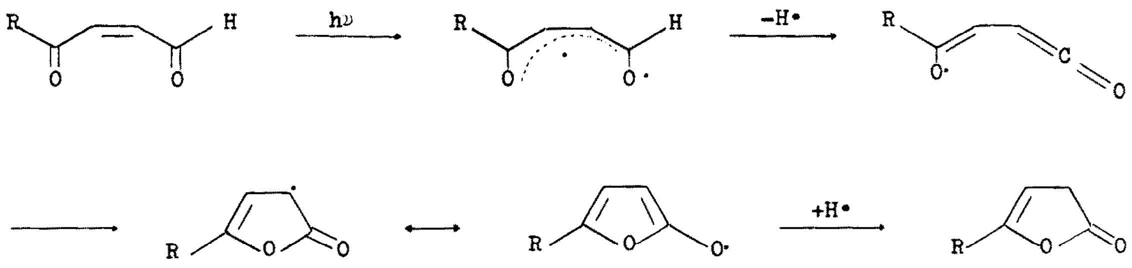
(*) - All yields refer to isolated chromatographically pure products.



Scheme 1. $Br_2$, MeOH; (ii) Amberlite IR-120; (iii) PCC, $CH_2Cl_2$; (iv) hν, $C_6H_6$.



Scheme 2.



Scheme 3.

- dihydro - furan, prepared as previously described from 2-n-decyl-5-d-furan; the latter compound was achieved by metalation with n-BuLi in THF of 2-n-decyl-furan followed by quenching with $D_2O$.[14] These photoreactions are summarized in Scheme 2.

This agrees with the following mechanism for the formation of butenolides from *cis*-isomers (Scheme 3).

The α-cleavage of H· at the carbonyl group could be the key step of the process, leading to a ketene which immediately cyclized by attack of the residual radical. The photoreaction is clearly an intermolecular process; the experimental data do not allow to define exactly the nature of the other molecule (solvent or some unstable species), accepting a hydrogen radical during the lactonization.

The *trans*-isomer **8** was converted into **9** and **10**; while **10** contained deuterium in the expected position, the lactone **9** underwent an exchange reaction and completely lost deuterium.

The exchange process could occur between the sub-

Table 2.

| Substrate | R | Products (yields, %)* | |
|---|---|---|---|
| 4a | $C_7H_{15}$ | 5a (30) | 6a (15) |
| 4b | $C_9H_{19}$ | 5b (35) | 6b (15) |
| 4c | $C_{11}H_{23}$ | 5c (28) | 6c (13) |

(*) – All yields refer to isolated chromatographically pure products.

strate and the solvent, or through a different way (perhaps between **8** and a possible unstable intermediate). In this case, the reaction always showed the formation of a mixture of unidentified products (~ 50%), which decomposed despite several attempts of isolation. Using as solvent $d_6$-benzene, the first hypothesis was refuted, because deuterated compound **9** was not recovered.

About the mechanism, probably the *trans*-compounds, by irradiation, are isomerised in parts to *cis*-derivatives. It is well known that similar compounds, like $\beta$-acyl acrylic acids, can undergo a photochemical *trans–cis* isomerisation.[15] These then give the butenolides by the mechanism described in Scheme 3. The formation of alkyl-2-furyl-ketones can not be rationalized on the basis of the experimental results; they could be formed directly from the *trans*-isomer by an unknown pathway. Both butenolides and alkyl-furyl-ketones were stable under the experimental conditions of their formation.

## EXPERIMENTAL

M.ps were obtained with a Kofler block and are uncorrected. Nuclear magnetic resonance spectra were recorded with a Perkin–Elmer R 32 and with a Jeol 50 HL spectrometers, using $CCl_4$ as solvent with tetramethylsilane as internal standard. IR spectra were obtained on a Perkin–Elmer 257 and 457 spectrometers. Mass spectra were obtained on a AEI MS-12 instrument at 70 eV, by using direct insertion at source temperature 150°. Commercial Merck silica gel and alumina were used for column chromatography. Carlo Erba precoated silica gel plates were used in tlc. Gas-chromatographic analyses (glc) were carried out on a Hewlett-Packard 5880A instrument, using flame-ionization detection and a 20 in. stainless-steel column, 2% OV 101 on 100/120 Chromosorb W-HP.

2-*n*-*Octyl-furan* **1a**. 1.32 N BuLi (26 ml) was added to furan (2.24 g), diluted with 200 ml of anhyd THF, at −25° under $N_2$. The mixture was stirred for 4 hr at −15°, then, again at −25°, $C_8H_{17}Br$ (6.4 g), dissolved in 30 ml of anhyd THF, was added, and the mixture was stirred at −15° for 1 h, then at room temperature for 16 h. Then, 50 ml of a cold soln, satd with $NH_4Cl$, was added and vigorous stirring maintained for 1 h. The organic layer was separated and the aqueous phase was extracted 3 times with $Et_2O$. The neutral extracts were dried over $Na_2SO_4$ and the removal of the solvent yielded a crude product which was chromatographed on $SiO_2$. Elution with n-hexane gave 4.7 g (80%) of pure **1a** as oil. Found: C, 76.88; H, 12.95. Calc. for $C_{12}H_{20}O$: C, 76.86; H, 12.90%. $n_D^{21}$ = 1.3165. IR (film, $\nu_{max}$ cm$^{-1}$): 1598, 1558, 1470, 1380. $^1$H-NMR ($CCl_4$, $\delta$): 7.16 (m, 1H), 6.14 (m, 1H), 5.86 (m, 1H), 2.57 (t, 2H), 1.28 (m, 12H), 0.90 (t, 3H). MS (*m*/*e*): 180 ($M^+$).

2-*n*-*Octyl*-2,5-*dimethoxy*-2,5-*dihydro*-*furan* **2a**. Compound **1a** (3 g), dissolved in MeOH (45 ml), was added to $Na_2CO_3$ (3.3 g) at −25°. Then, bromine (1 ml), dissolved in MeOH (15 ml), was added during 2 h at −25°. The mixture was stirred for 1.5 h at room temp. The mixture was filtered and the filtrate partitioned with brine and ether. The ether extract was washed with brine and dried over $Na_2SO_4$. The removal of the solvent yielded the crude product which was chromatographed on neutral $Al_2O_3$ B III. Elution with benzene gave 2.9 g (70%) of pure **2a** as oil. Found: C, 69.35; H, 10.84. Calc. for $C_{14}H_{26}O_3$: C, 69.38; H, 10.81%. IR (film, $\nu_{max}$ cm$^{-1}$): 1630, 1470, 1373, 1340, 1195, 1170, 1120, 1102, 1040, 980, 820. $^1$H-NMR ($CCl_4$, $\delta$): 5.90 (d, 1 H, J = 6 Hz), 5.73 (dd, 1 H, $J_1$ = 6 Hz, $J_2$ = 1.5 Hz), 5.58 (m, 0.5 H), 5.32 (m, 0.5 H), 3.40 (s, 1.5 H), 3.35 (s, 1.5 H), 3.05 (s, 1.5 H), 3.00 (s, 1.5 H), 1.28 (m, 14 H), 0.90 (t, 3 H). MS (*m*/*e*): 242 ($M^+$).

cis-2-*Dodecen*-1-*al*-4-*one* **3a**. Compound **2a** (0.5 g), dissolved in 80% acqueous THF (14 ml), was treated with Amberlite IR-120 (14 g) at room temperature. The mixture was stirred for 1 h, then was filtered; the filtrate was washed with brine and dried over $Na_2SO_4$. The removal of the solvent yielded **3a** (42%, glc). $^1$H-NMR ($CCl_4$, $\delta$): 10.14 (d, 1 H, J = 8 Hz), 6.82 (d, 1 H, J = 12 Hz), 6.04 (dd, 1 H, $J_1$ = 12 Hz, $J_2$ = 8 Hz), 2.53 (t, 2 H), 1.29 (m, 12 H), 0.89 (t, 3 H).

trans-2-*Dodecen*-1-*al*-4-*one* **4a**. PCC (11.8 g) was added to 2 g of **1a**, dissolved in 150 ml of dry $CH_2Cl_2$. The mixture was refluxed for 9 h. The usual isolation procedure[16] gave a crude product which was chromatographed on $SiO_2$. Elution with benzene-$Et_2O$ (9 : 1) gave 1.2 g (56%) of pure **4a**. Found: C, 73.42; H, 10.27. Calc. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%. IR (1%, $CCl_4$, $\nu_{max}$ cm$^{-1}$): 2718, 1690, 1622, 980. $^1$H-NMR ($CCl_4$, $\delta$): 9.80 (dd, 1 H, $J_1$ = 7 Hz, $J_2$ = 3 Hz), 6.80 (m, 2 H), 2.67 (t, 2 H). MS (*m*/*e*): 196 ($M^+$).

5-*n*-*Octyl*-2(3 H)-*furanone* **5a**. The crude product of hydrolysis of **2a**, dissolved in benzene Uvasol (9 ml) was irradiated with a 100 Watt Hanovia medium pressure mercury lamp, for 4 h. The removal of the solvent yielded the crude product, which was chromatographed on $SiO_2$. Elution with benzene gave 120 mg (70%) of pure **5a**. Found: C, 73.46; H, 10.26. Calc. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27%. IR (1%, $CCl_4$, $\nu_{max}$ cm$^{-1}$): 1810, 1680, 1470, 1102, 937. $^1$H-NMR ($CCl_4$, $\delta$): 5.00 (m, 1 H), 3.05 (m, 2 H), 2.26 (m, 2 H), 1.30 (m, 12 H), 0.91 (t, 3 H). MS (*m*/*e*): 196 (*M*$^+$).

5-*n*-*Octyl*-2(3 H)-*furanone* **5a** *and n*-*Heptyl*-2-*furyl*-*ketone* **6a**. Compound **4a** (500 mg), dissolved in 20 ml of benzene (Uvasol), was irradiated with a 125 W Ilesa medium pressure mercury lamp for 4 h. Then, the removal of the solvent yielded a crude product which was chromatographed on $SiO_2$. Elution with benzene gave 150 mg (30%) of **5a**, and 74 mg (15%) of **6a**. For analytical and spectroscopic data of **5a** see above. **6a**: Found: C, 74.22; H, 9.36. Calc. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34%; IR (1%, $CCl_4$, $\nu_{max}$ cm$^{-1}$): 1690, 1572, 1477, 1163, 1090, 1018, 990; $^1$H-NMR ($CCl_4$, $\delta$): 7.45 (m, 1 H), 7.04 (m, 1 H), 6.45 (m, 1 H), 2.73 (t, 2 H), 1.28 (m, 10 H), 0.90 (t, 3 H); MS (*m*/*e*): 194 ($M^+$).

2-*n*-*Decyl*-*furan* **1b**. 1.32 N BuLi (26 ml) was added to furan (2.24 g), diluted in 200 ml of anhyd THF, at −25° under $N_2$. The mixture was stirred for 4 h at −15°, then, again at −25°, $C_{10}H_{21}Br$ (7.3 g), dissolved in 30 ml of anhyd THF, was added, and the mixture was stirred at −15° for 1 h, then at room temperature for 16 h. Then, 50 ml of a cold soln, satd with $NH_4Cl$, was added and vigorous stirring maintained for 1 h. The usual isolation procedure gave a crude product which was chromatographed on $SiO_2$. Elution with n-hexane gave 5.6 g (82%) of pure **1b**, as oil. Found: C, 80.68; H, 11.63. Calc. for $C_{14}H_{24}O$: C, 80.71; H, 11.61%. $n_D^{20}$=1.4568. IR (film, $\nu_{max}$ cm$^{-1}$): 1633, 1510, 1472, 1383, 1152, 1014. $^1$H-NMR ($CCl_4$, $\delta$): 7.13 (m, 1 H), 6.12 (m, 1 H), 5.83 (m, 1 H), 2.56 (t, 2 H), 1.28 (m, 16 H), 0.90 (t, 3 H). MS (*m*/*e*): 208 ($M^+$).

2-*n*-*Decyl*-2,5-*dimethoxy*-2,5-*dihydro*-*furan* **2b**. **1b** (4.14 g), dissolved in MeOH (64 ml), was added to $Na_2CO_3$ (4.5 g), at −25°. Then, bromine (1.12 ml), dissolved in MeOH (16 ml), was added during 2 h at −25°. The mixture was stirred for 1.5 h at room temperature. The usual isolation procedure yielded the crude product which was chromatographed on neutral $Al_2O_3$ B III. Elution with benzene gave 3.8 g (71%) of pure **2b**, as oil. Found: C, 71.05; H, 11.17. Calc. for $C_{16}H_{30}O_3$: C, 71.07; H, 11.18%. IR (film, $\nu_{max}$ cm$^{-1}$): 1635, 1470, 1375, 1340, 1195 1170, 1120, 1102, 1020, 980, 820. $^1$H-NMR ($CCl_4$, $\delta$): 5.91 (d, 1 H, J=6 Hz), 5.75 (d, 1 H, J=6 Hz), 5.60 (m, 0.5 H), 5.33 (m, 0.5 H), 3.41 (s, 1.5 H), 3.35 (s, 1.5 H), 3.07 (s, 1.5 H), 3.01 (s, 1.5 H), 1.27 (m, 18 H), 0.89 (t, 3 H). MS (m/e): 270 ($M^+$).

cis-2-*Tetradecen*-1-*al*-4-*one* **3b**. Compound **2b** (0.3 g), dissolved in 80% aq. THF (9 ml), was treated with Amberlite IR-120 (9 g) at room temperature for 1 h. The usual isolation procedure yielded **3b** (42%, glc). $^1$H-NMR ($CCl_4$, $\delta$): 10.14 (d, 1 H, J = 8 Hz), 6.84 (d, 1 H, J = 12 Hz), 6.03 (dd, 1 H, $J_1$ = 12 Hz, $J_2$ = 8 Hz), 2.53 (t, 2 H), 1.28 (m, 16 H), 0.90 (t, 3 H).

trans-2-*Tetradecen*-1-*al*-4-*one* **4b**. PCC (10.3 g) was added to 2 g of **1b**, dissolved in 150 ml of dry $CH_2Cl_2$. The mixture was refluxed for 9 h. The usual isolation procedure[16] gave a crude product which was chromatographed on $SiO_2$. Elution with benzene-$Et_2O$ 9 : 1 gave 1.14 g (53%) of pure **4b**, plates from n-hexane, m.p. 48–48.5°. Found: C, 74.92; H, 10.77. Calc. for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78%. IR (1%, $CCl_4$, $\nu_{max}$ cm$^{-1}$): 2710, 1710, 1628, 1473, 1220, 1118, 1089, 985. $^1$H-NMR ($CCl_4$, $\delta$): 9.80 (dd, 1 H, $J_1$ = 7 Hz, $J_2$ = 3 Hz), 6.80 (m, 2 H), 2.68 (t, 2 H). MS (*m*/*e*): 224 ($M^+$).

5-*n*-*Decyl*-2(3 H)-*furanone* **5b**. Compound **3b**, dissolved in benzene (Uvasol; 6 ml), was irradiated with a 100 Watt Hanovia medium pressure mercury lamp, for 3 h. The removal of the solvent yielded the crude product which was chromatographed on $SiO_2$. Elution with benzene gave 75 mg (72%) of pure **5b**. Found: C, 74.90; H, 10.75. Calc. for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78%. IR (1%, $CCl_4$, $\nu_{max}$ cm$^{-1}$): 1810, 1680, 1470, 1102, 937. $^1$H-NMR ($CCl_4$, $\delta$): 5.00 (m, 1 H), 3.04 (m, 2 H), 2.26 (m, 2 H), 1.30 (m, 16 H), 0.92 (t, 3 H). MS (*m*/*e*): 224 (M$^+$).

5-*n*-*Decyl*-2(3 H)-*furanone* **5b** *and n-Nonyl-2-furyl-ketone* **6b**. Compound **4b** (300 mg), dissolved in 10 ml of benzene (Uvasol), was irradiated with a 125 Watt Ilesa medium pressure mercury lamp for 4 h. Removal of the solvent yielded a crude product which was chromatographed on $SiO_2$. Elution with benzene gave 105 mg (35%) of **5b** and 44.6 mg (15%) of **6b**. For analytical and spectroscopic data of **5b** see above. **6b**: Found: C, 75.64; H, 9.99. Calc. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97%. IR (1%, $CCl_4$, $\nu_{max}$ cm$^{-1}$): 1690, 1572, 1477, 1163, 1090, 1018, 990. $^1$H-NMR ($CCl_4$, $\delta$): 7.43 (m, 1 H), 7.03 (m, 1 H), 6.44 (m, 1 H), 2.73 (t, 2 H), 1.28 (m, 14 H), 0.88 (t, 3 H). MS (*m*/*e*): 222 (M$^+$).

2-*n*-*Dodecyl-furan* **1c**. 1.32 N BuLi (26 ml) was added to 2.24 g of furan, diluted with 200 ml of anhyd THF, at −25° under $N_2$. The mixture was stirred for 4 h at −15°, then, again at −25°, 7.2 ml of $C_{12}H_{25}Br$, dissolved in 30 ml of anhyd THF, were added and the mixture was stirred at −15° for 1.5 h, then at room temperature for 16 h. Then, 50 ml of a cold soln, satd with $NH_4Cl$, were added and vigorous stirring maintained for 1 h. The usual isolation procedure yielded the crude product which was chromatographed on $SiO_2$. Elution with n-hexane gave 6.06 g (78%) of pure **1c**, as oil. Found: C, 81.43; H, 11.75. Calc. for $C_{16}H_{28}O$: C, 81.29; H, 11.94%. $n_D^{21} = 1.4604$. IR (film, $\nu_{max}$ cm$^{-1}$): 1595. $^1$H-NMR ($CCl_4$, $\delta$): 7.20 (m, 1 H), 6.18 (m, 1 H), 5.90 (m, 1 H), 2.53 (t, 2 H), 1.25 (m, 20 H), 0.90 (t, 3 H). MS (*m*/*e*): 236 (M$^+$).

2 - *n* - *Dodecyl* - 2,5 - *dimethoxy* - 2,5 - *dihydro-furan* **2c**. Compound **1c** (3.9 g), dissolved in MeOH (60 ml), was added to $Na_2CO_3$ (4.5 g) at −25°. Then, bromine (1.14 ml), dissolved in MeOH (30 ml), was added during 2 h at −25°. The mixture was stirred for 1.5 h at room temperature. The usual isolation procedure yielded the crude product which was chromatographed on neutral $Al_2O_3$ B III. Elution with benzene gave 3.4 g (70%) of pure **2c** as oil. Found: C, 72.40; H, 11.50. Calc. for $C_{18}H_{34}O_3$: C, 72.44; H, 11.48%. IR (film, $\nu_{max}$ cm$^{-1}$): 1625, 1460, 1370, 1190, 1165, 1113, 1098, 1015, 971, 816. $^1$H-NMR ($CCl_4$, $\delta$): 5.88 (d, 1 H, J = 6 Hz), 5.73 (d, 1 H, J = 6 Hz), 5.57 (m, 0.5 H), 5.32 (m, 0.5 H), 3.40 (s, 1.5 H), 3.34 (s, 1.5 H), 3.05 (s, 1.5 H), 2.99 (s, 1.5 H), 1.27 (m, 22 H), 0.95 (t, 3 H). MS (*m*/*e*): 298 (M$^+$).

cis-2-*Hexadecen*-1-*al*-4-*one* **3c**. Compound **2c** (0.6 g), dissolved in 80% aq. THF (20 ml), was treated with Amberlite IR-120 (18 g) at room temperature for 1 h. The usual isolation procedure yielded **3c** (45%, glc). $^1$H-NMR ($CCl_4$, $\delta$): 10.06 (d, 1 H, J = 8 Hz), 6.84 (d, 1 H, J = 12 Hz), 6.02 (dd, 1 H, $J_1$ = 12 Hz, $J_2$ = 8 Hz), 2.55 (t, 2 H), 1.27 (m, 20 H), 0.89 (t, 3 H).

trans-2-*Hexadecen*-1-*al*-4-*one* **4c**. PCC (8.56 g) was added to 1.9 g of **1c**, dissolved in 150 ml of dry $CH_2Cl_2$. The mixture was refluxed for 9 h. The usual isolation procedure[16] gave a crude product which was chromatographed on $SiO_2$. Elution with benzene–$Et_2O$ (9:1) gave 1.2 g (60%) of pure **4c**, prisms from n-hexane, m.p. 58–59°. Found: C, 76.25; H, 11.30. Calc. for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18%. IR (1%, $CHCl_3$, $\nu_{max}$ cm$^{-1}$): 2720, 1690, 1620, 980. $^1$H-NMR ($CDCl_3$): 9.80 (dd, 1 H, $J_1$ = 7 Hz, $J_2$ = 2 Hz), 6.82 (m, 2 H), 2.68 (t, 2 H). MS (*m*/*e*): 252 (M$^+$).

5-*n*-*Dodecyl*-2(3 H)-*furanone* **5c**. The crude product of hydrolysis of **2c**, dissolved in benzene (Uvasol; 10 ml), was irradiated with a 100 Watt Hanovia medium pressure mercury lamp, for 4 h. The removal of the solvent yielded the crude product which was chromatographed on $SiO_2$. Elution with benzene gave 150 mg (65%) of pure **5c**. Found: C, 76.10; H, 11.22. Calc. for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18%. IR (1%, $CCl_4$, $\nu_{max}$ cm$^{-1}$): 1815, 1680, 1465, 1110, 945. $^1$H-NMR ($CCl_4$, $\delta$): 4.99 (m, 1 H), 3.02 (m, 2 H), 2.24 (m, 2 H), 1.26 (m, 20 H), 0.89 (t, 3 H). MS (*m*/*e*): 252 (M$^+$).

5-*n*-*Dodecyl*-2(3 H)-*furanone* **5c** *and* 5-*n*-*Undecyl*-2-*furyl-ketone* **6c**. Compound **4c** (300 mg), dissolved in benzene (Uvasol; 10 ml), was irradiated with a 125 Watt Ilesa medium pressure mercury lamp for 4 h. Then, the removal of the solvent yielded a crude product which was chromatographed on $SiO_2$. Elution with benzene gave 84 mg (28%) of pure **5c**, and 37 mg (12.5%) of pure **6c**. For analytical and spectroscopic data of **5c**, see above. **6c**: Found: C, 76.78; H, 10.52. Calc. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47%; IR (1%, $CCl_4$, $\nu_{max}$ cm$^{-1}$): 1680, 1565, 1468, 1158, 1085, 1010, 982. $^1$H-NMR ($CCl_4$, $\delta$): 7.43 (m, 1 H), 7.02 (m, 1 H), 6.43 (m, 1 H), 2.73 (t, 2 H), 1.27 (m, 20 H), 0.90 (t, 3 H). MS (*m*/*e*): 250 (M$^+$).

2-*n*-*Decyl*-5-*d*-*furan*. 1.32 N BuLi (7.3 ml) was added to 2-n-decylfuran **1b** (2 g), diluted in 100 ml of anhyd THF, at −20°. The mixture was stirred for 2 h at −20°, then, 1 ml of $D_2O$ was added and the mixture was stirred at room temperature for 6 h. A cold soln (50 ml), satd with $NH_4Cl$, was added and vigorous stirring maintained for 1 h. The usual work-up gave a crude product which was chromatographed on $SiO_2$. Elution with n-hexane gave 1.9 g (95%) of 2-n-decyl-5-d-furan (50% deuterated). IR (film, $\nu_{max}$ cm$^{-1}$): 1608, 1480, 1161, 1028. $^1$H-NMR ($CCl_4$, $\delta$): 7.17 (m, 0.5 H), 6.13 (m, 1 H), 5.73 (m, 1 H), 2.54 (t, 2 H), 1.27 (m, 16 H), 0.90 (t, 3 H). MS (*m*/*e*) 209 (M$^+$).

2 - *n* - *Decyl* - 2,5 - *dimethoxy* - 2,5 - *dihydro* - 5 - *d* - *furan*. 2-n-Decyl-5-d-furan (1.5 g), dissolved in MeOH (23 ml), was added to $Na_2CO_3$ (1.6 g), at −25°. Bromine (0.4 ml), dissolved in MeOH (6 ml), was added during 2 hr at −25°. This mixture was stirred for 1.5 h at room temperature. The usual work up yielded the crude product which was chromatographed on neutral $Al_2O_3$ B III. Elution with benzene gave 1.35 g (70%) of pure 2 - n - decyl - 2,5 - dimethoxy - 2,5 - dihydro - 5 - d - furan (50% deuterated). IR (film, $\nu_{max}$ cm$^{-1}$): 1641, 1480, 1382, 1360, 1202, 1175, 1127, 1110, 1073, 1033, 990, 958. $^1$H-NMR ($CCl_4$, $\delta$): 5.90 (d, 1 H, J = 6 Hz), 5.70 (d, 1 H, J = 6 Hz), 5.53 (m, 0.25 H), 5.27 (m, 0.25 H), 3.41 (s, 1.5 H), 3.34 (s, 1.5 H), 3.04 (s, 1.5 H), 2.98 (s, 1.5 H), 1.27 (m, 18 H), 0.90 (t, 3H). MS (*m*/*e*): 271 (M$^+$).

*Hydrolysis of* 2 - *n* - *decyl* - 2,5 - *dimethoxy* - 2,5 - *dihydro* - 5 - *d* - *furan and photochemistry of* **7**. 2 - n - Decyl - 2,5 - dimethoxy - 2,5 - dihydro - 5 - d - furan (0.6 g), dissolved in 80% aq. THF (18 ml), was treated with Amberlite IR-120 (18 g) at room temperature for 1 h. Then, the mixture was filtered; the filtrate was washed with brine and dried over $Na_2SO_4$. The removal of the solvent yielded **7**. **7**, dissolved in benzene (Uvasol; 12 ml), was irradiated with a 100 Watt Hanovia medium pressure mercury lamp, for 3 h. The removal of the solvent yielded the crude product which was chromatographed on $SiO_2$. Elution with benzene gave pure **5b**. $^1$H-NMR ($CCl_4$, $\delta$): 5.00 (m, 1 H), 3.07 (m, 2 H). MS (*M*/*e*): 224 (M$^+$).

2-*Ethyl*-5-*d*-*furan*. 1.32 N BuLi (24 ml) was added to 2-ethylfuran (3 g), diluted with 50 ml of anhyd $Et_2O$, at −20° under $N_2$. The mixture was refluxed for 4 h, then, again at −10°, 1 ml of $D_2O$ was added. After 1 h, 60 ml of a cold soln, satd with $NH_4Cl$, was added. The usual work up yielded the crude product which was distilled giving pure 2-ethyl-5-furan (b.p. 92°) (40%). IR (film, $\nu_{max}$ cm$^{-1}$): 1615, 1500, 1225. $^1$H-NMR ($CCl_4$, $\delta$): 6.16 (d, 1 H, J = 3 Hz), 5.87 (d, 1 H, J = 3 Hz), 2.62 (q, 2 H), 1.23 (t, 3 H). MS (*m*/*e*): 97 (M$^+$).

trans-2-*Hexen*-1-*d*-1-*al*-4-*one* **8**. PCC (11 g) was added to 1 g of 2-ethyl-5-d-furan, dissolved in 150 ml of dry $CH_2Cl_2$. The mixture was refluxed for 9 h. The usual isolation procedure[16] gave a crude product which was chromatographed on $SiO_2$. Elution with benzene–$Et_2O$ (9:1) gave 565 mg (50%) of pure **8**. IR (film, $\nu_{max}$ cm$^{-1}$): 1695, 1620, 1458, 1370, 988. $^1$H-NMR ($CCl_4$, $\delta$): 6.75 (m, 2 H), 2.69 (q, 2 H), 1.23 (t, 3 H). MS (*m*/*e*): 113 (M$^+$).

5-*Ethyl*-2(3 H)-*furanone* **9** *and* **5**-*d*-2-*furyl-methyl-ketone* **10**. Compound **8** (0.3 g), dissolved in 16 ml of benzene (Uvasol), was irradiated with a 125 Watt Ilesa medium pressure mercury lamp, for 4 h. The removal of the solvent yielded a crude product, separated by chromatography **10**: $^1$H-NMR ($CCl_4$, $\delta$): 6.97 (d, 1 H, J = 4 Hz), 6.28 (d, 1 H, J = 4 Hz), 2.31 (s, 3 H). **9**: $^1$H-NMR ($CCl_4$, $\delta$): 4.82 (m, 1 H), 2.90 (m, 2 H).

*Photochemistry of* **8** *in* $d_6$-*benzene*. Compound **8** (0.2 g), dissolved in 4 ml of $d_6$-benzene, was irradiated with a 125 Watt Ilesa medium pressure mercury lamp for 4 h. The removal of the solvent yielded a crude product which was shown by $^1$H NMR to be a mixture of **9** and **10**.

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