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IODINE (III) MEDIATED ACETOXY-LACTONIZATION OF UNSATURATED NITRILES

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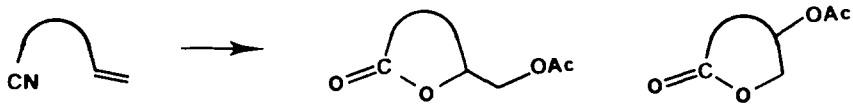
4-Pentenenitriles reacted with $PhI(OAc)_2$ in acetic acid, in the presence of 48% HBF_4, at 70 °C, to afford the dihydro-5-acetoxymethyl-2(3H)-furanones in good yields. Similarly, 3-butenenitriles gave the dihydro-4-acetoxy-2(3H)-furanones, although in lower yields. Parallel experiments showed that, under the same conditions, 4-pentenoic and 3-pentenoic acids reacted much more easily and gave the same acetoxy-lactonization process at room temperature.

The lactonization of unsaturated acids, promoted by several electrophilic reagents,[1-7] is a familiar process in organic synthesis. We have recently reported some examples of phenylseleno-lactonization[8] of unsaturated acids using a phenylselenium electrophilic reagent generated by the oxidation of diphenyl diselenide with ammonium peroxydisulphate.[9] This reagent presents several advantage over the more commonly used phenylselenenyl chloride. We have also reported that similar lactonization processes can be effected starting from unsaturated nitriles also.[10,11] In order to effect the phenylseleno-lactonization of these nitriles the oxidation of diphenyl diselenide with ammonium peroxydisulphate was carried out in the presence of a strong acid and water.[10]

We now report that unsaturated nitriles can easily give similar ring closure reactions using iodine (III) reagents. These reactions were carried out with $PhI(OAc)_2$ in acetic acid, in the presence of a strong acid and water, and gave the acetoxy lactones indicated below:

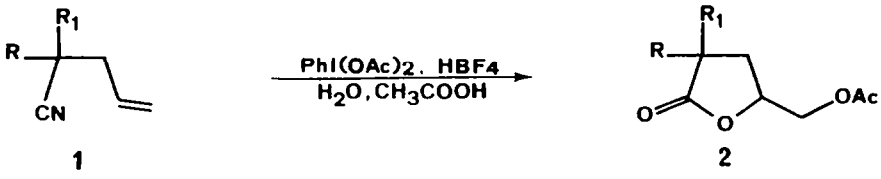


Under the same experimental conditions unsaturated carboxylic acids reacted more easily and gave the same acetoxy-lactonization process. The lactonization of alkenoic acids promoted by iodine (III) compounds has already been observed. Thus, tosyloxy lactones and phosphoryloxy lactones were obtained from the reactions of alkenoic acids with PhI(OH)OTos[7] and $PhI(OH)OPO(OPh)_2$,[12] respectively.

RESULTS AND DISCUSSION

The reactions of $PhI(OAc)_2$ with olefinic nitriles were carried out in acetic acid, at 70 °C for 2 - 15 h, in the presence of 48% HBF_4. The first substrates investigated were the 4-pentenenitriles 1a - 1f indicated in Scheme 1. The products of these reactions were identified as the 5-acetoxymethyl- γ-lactones 2. Reaction yields of isolated products, after column chromatography, are reported in Scheme 1; reaction times are indicated in parentheses. The progress of the reactions was monitored by tlc, glc-Ms, and in some cases by nmr analysis of small aliquots of the reaction mixtures.

SCHEME 1



1 2

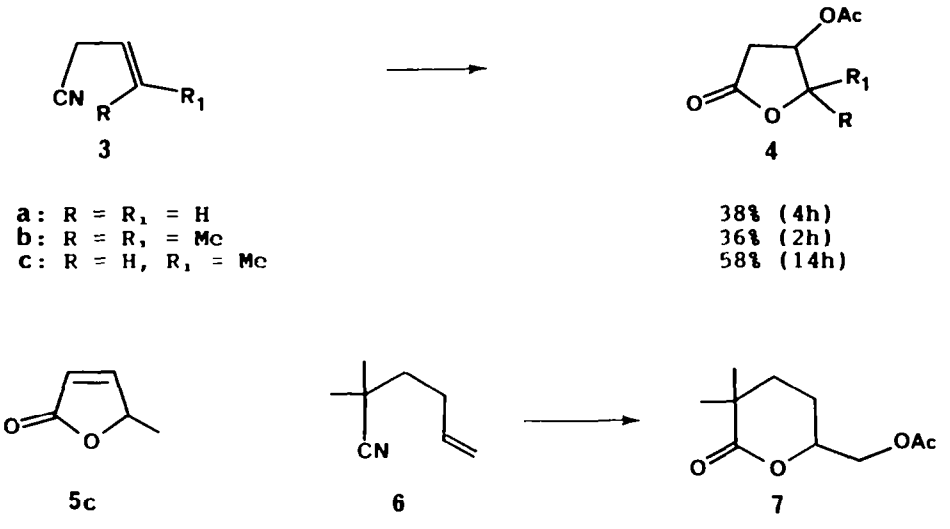
a: R = R_1 = H		83% (6h)
b: R = R_1 = Me		62% (4h)
c: R = R_1 = Ph		67% (15h)
d: R = H, R_1 = Me		63% (5h)
e: R = H, R_1 = Et		67% (5h)
f: R = H, R_1 = Ph		64% (15h)

As indicated by glc and nmr spectra, compounds 2d, 2e, and 2f were obtained as a 1:1 mixture of cis and trans isomers which could not be separated by column chromatography.

The same reaction carried out on the 3-butenenitrile 3a, 4-methyl-3-pentenenitrile 3b, and 3-pentenenitrile 3c afforded the 4-acetoxy-γ-lactones 4a - 4c (Scheme 2). Reaction yields were considerably lower in the cases of 3a and 3b. From the reaction of 3c small amounts of the

unsaturated lactone 5c (6%) were also obtained. As it will be shown below, the lactone 5c is the major reaction product when the reaction is carried out starting from the corresponding unsaturated acid. Similar results were obtained in the case of the tosyloxy-lactonization of alkenoic acids.[7] Compound 4c was a 1:1 mixture of two diastereoisomers which could be separated by column chromatography.

SCHEME 2

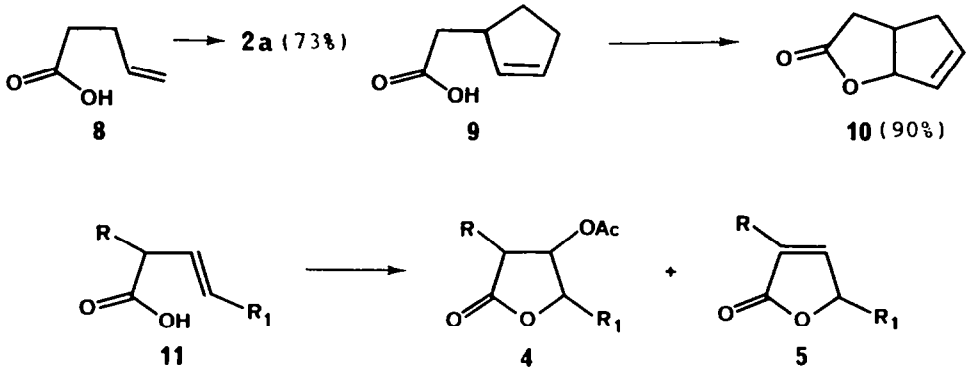


Finally the reaction of the 2,2-dimethyl-5-hexenenitrile 6 was also investigated. This compound when treated with acid in water gave the 5-ethyl-γ-lactone,[11] whereas with electrophilic phenylselenium reagents it afforded the (phenylseleno)methyl-δ-lactone.[10] In the present case also the reaction product was a δ-lactone, 7, which was obtained in good yield.

Some experiments were also carried out starting from unsaturated acids. These reactions took place much more easily than those with the corresponding nitriles. After few minutes at room temperature the starting acids were in fact completely consumed. 4-Pentenoic acid 8 afforded the lactone 2a in 73% yield, whereas 2-cyclopenteneacetic acid 9 gave exclusively the unsaturated lactone 10 in 90% yield (Scheme 3). These results are similar to those observed from the reactions of PhI(OH)OTs with the same acids.[7] The results obtained from 3-butenoic acids 11 are also reported in Scheme 3. The 4-acetoxy-γ-lactones were obtained in every case, but with the 3-pentenoic acid 11c and the 3-hexenoic acid 11d the

major reaction products were the unsaturated lactones **5c** and **5d**, respectively. This latter was obtained as the sole product (80%) from a reaction of **11d** carried out in acetonitrile. As demonstrated by glc and nmr spectra the lactones **4c** and **4d** were obtained as a single diastereoisomer. The lactone **4e** was instead a mixture (1:2) of two isomers which were separated by column chromatography.

SCHEME 3



a: R = R_1 = H	65%	---
c: R = H, R_1 = Me	25%	41%
d: R = H, R_1 = Et	20%	48%
e: R = Me, R_1 = H	51%	---

It has been reported that $PhI(OAc)_2$ in chloroform reacts with HBF_4 and water to give the iodosobenzene tetrafluoborate, $PhI^{+}\text{-}O\text{-}I^{+}Ph\ 2BF_4^-$, which can be obtained as a yellow solid.[11] This can be formed under the conditions employed in the present work also. However, it can also be suggested that in acetic acid the reactive species is the acetoxy phenyliodonium tetrafluoborate generated according to the following simple reaction:

$$PhI(OAc)_2 + HBF_4 \longrightarrow Ph\text{-}I^{+}\text{-}OAc\ BF_4^- + CH_3COOH$$

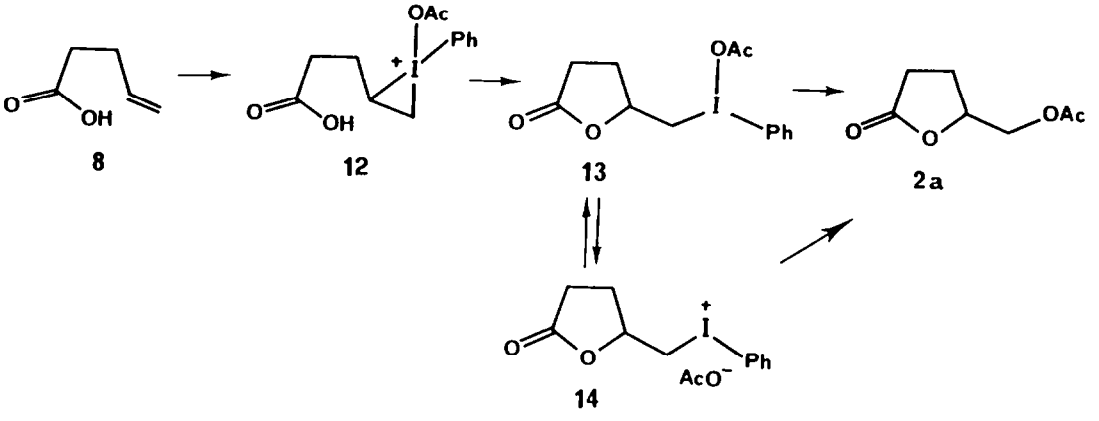
For the sake of simplicity, in the following discussion we will consider that this is the iodine (III) reactive species.

The formation of the acetoxy lactones from unsaturated acids can be explained in a way similar to that proposed for the tosyloxy-lactonization reaction.[7] As indicated in Scheme 4 for compound **8**, it can be suggested

that the iodine reagent effects the electrophilic addition to the carbon-carbon double bond to give the intermediate 12 which suffers intramolecular capture by the carboxy group to form 13 which can be in equilibrium with the iodonium ion 14. Reductive elimination of PhI from 13 or nucleophilic substitution in 14 would eventually afford the observed acetoxy lactone 2a.

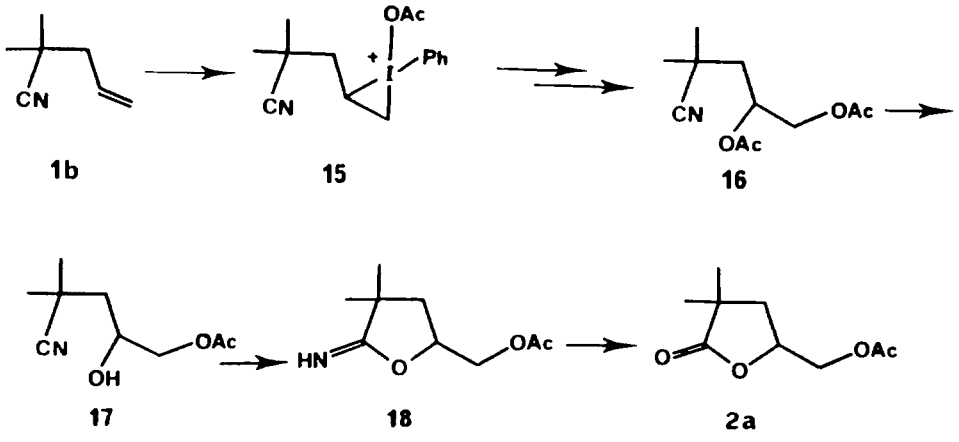
As far as the acetoxy-lactonization of unsaturated nitriles is concerned, it could be suggested that these are first hydrolyzed to the corresponding

SCHEME 4



acids which then undergo the process described above. However, in the case of the phenylseleno-lactonization of the same nitriles, carried out under experimental conditions very similar to those employed in the present case, we observed that the first step of the reaction was the phenylseleno-hydroxylation of the carbon-carbon double bond.[10] Thus, in order to find experimental evidences that in the present case also a similar mecchanism is operating, the reaction of **1b** was carried out at room temperature. After 4 h, together with minute amounts of the lactone **2a** and most of the unreacted nitrile, a new compound was detected. This was isolated by column chromatography and identified as the 2,2-dimethyl-4,5-diacetoxypentanenitrile **16** (Scheme 5). When this compound was treated, in acetic acid at 70 °C, with 48% HBF_4, it was quantitatively transformed into the lactone **2a**. In the light of this result we propose that in the case of unsaturated nitriles the reaction takes the course indicated in Scheme 5 for compound **1b**. It is suggested that the initially formed organoiodine intermediate **15** is captured by acetic acid to give the diacetoxy nitrile **16**, as it is known to occur with other alkenes.[11]

SCHEME 5



Reaction of **16** with acid and water can give the hydroxy compound **17**. As it has been shown to occur with other hydroxy nitriles having similar structures,[10,11] the acid catalyzed hydrolysis of the cyano group can occur with intramolecular assistance by the hydroxy group to give the cyclic ether bearing an exo-imino substituent **18**. Further reaction with acid and water should eventually occur very easily to afford the observed lactone **2a**.

The results reported in this paper further emphasize the synthetic importance of the iodine (III) reagents. We have shown that starting from the commercially available $PhI(OAc)_2$ it is possible to effect the acetoxy-lactonization of unsaturated acids and nitriles in a very simple and efficient way. The procedure described in this paper can easily find further useful applications.

EXPERIMENTAL

Glc analyses and MS spectra were carried out with an HP 5890 gaschromatograph (dimethyl silicone capillary column, 12.5 m) equipped with an HP 5971 Mass Selective Detector. Proton and carbon-13 nmr spectra were recorded at 200 and 50.32 MHz, respectively, on a Bruker AC 200 instrument; $CDCl_3$ was used as solvent and TMS as standard. IR spectra were recorded on a Perkin Elmer 1320 spectrophotometer. Elemental analyses were carried out on a Carlo Erba 1106 Elemental Analyzer.
Compounds **3a**, **3c**, **8**, **9**, **11a**, and **11d** were commercial products and were used without further purifications. Compounds **1a**, **1b**, **1d**, **1e**, **1f** and **6** were prepared as previously described.[10] Compounds **1c**,[14] **3b**,[14] and **11e**[15] were prepared as described in the literature. The acid **11c** was obtained from the corresponding nitrile after hydrolysis under basic conditions. All these compounds were fully characterized by MS, proton and carbon-13 spectroscopy.

Acetoxy-Lactonization of Unsaturated Nitriles. General Procedure.
To a solution of $PhI(OAc)_2$ (10 mmol) in acetic acid (8 ml) 48% HBF_4 (1.8 ml) was added. The resulting yellow solution was stirred at 70 °C and the nitrile (5 mmol) was added. The progress of the reaction was monitored by tlc, glc and in some cases by nmr. After the time indicated in Schemes 1 and 2 the reaction mixture was poured on water and extracted with chloroform. The organic layer was washed with a solution of sodium carbonate and with water and then dried and evaporated. The reaction products were obtained in pure form after column chromatography on silica gel using mixtures of light petroleum and ether as eluant. Reaction yields are indicated in Schemes 1 and 2. Physical and spectral data are given below. All the acetoxylactones presented two carbonyl absorptions at about 1740 an 1770 cm $^{-1}$.

Dihydro-5-acetoxymethyl-2(3H)-furanone, 2a. Oil.[16] ^{1}H NMR δ 4.75 (m, 1 H), 4.3 (dd, 1 H, J = 3.1 and 12.2 Hz), 4.15 (dd, 1 H, J = 5.5 and 12.2 Hz), 2.7 - 2.3 (m, 3 H), 2.2 - 1.95 (m, 1 H), 2.1 (s, 3 H). ^{13}C NMR δ 176.4, 170.4, 77.4, 65.3, 28.2, 24.0, 20.7. MS m/e 128 (2), 98 (15), 85 (100), 57 (7), 43 (45).

Dihydro-3,3-dimethyl-5-acetoxymethyl-2(3H)-furanone, 2b. Oil. ^{1}H NMR δ 4.68 (ddt, 1 H, J = 3.0, 6.4 and 9.8 Hz), 4.33 (dd, 1 H, J = 3.0 and 12.3 Hz), 4.1 (dd, 1 H, J = 6.4 and 12.3 Hz), 2.18 (dd, 1 H, J = 6.4 and 12.8 Hz), 2.1 (s, 3 H), 1.9 (dd, 1 H, J = 9.8 and 12.8 Hz), 1.3 (s, 3 H), 1.27

(s, 3 H). ^{13}C NMR δ 180.8, 170.2, 73.7, 64.9, 39.6, 38.7, 24.7, 24.4, 20.3. MS m/e 143 (1), 126 (9), 113 (51), 85 (57), 67 (29), 43 (100). Anal. Calcd. for $C_9H_{14}O_4$: C, 58.06; H, 7.58. Found: C, 58.16; H, 7.51.

2,2-Dimethyl-4,5-diacetoxypentanenitrile, 16. Oil. IR 2250, 1740 cm^{-1}. ^{1}H NMR δ 5.35 (dddd, 1 H, J = 2.6, 3.9, 5.7 and 10.2 Hz), 4.25 (dd, 1 H, J = 3.9 and 11.8 Hz), 4.05 (dd, 1 H, J = 5.7 and 11.8 Hz), 2.1 (s, 3 H), 2.08 (s, 3 H), 2.07 (dd, 1 H, J = 10.2 and 14.8 Hz), 1.65 (dd, 1 H, J = 2.6 and 14.8 Hz), 1.4 (s, 3 H), 1.39 (s, 3 H). ^{13}C NMR δ 170.4, 124.1, 67.6, 65.1, 41.1, 29.7, 28.0, 25.9, 20.8, 20.5. MS m/e 197 (2), 154 (16), 125 (2), 112 (14), 99 (2), 86 (2), 69 (5), 44 (46), 43 (100). Anal. Calcd. for $C_{11}H_{19}NO_4$: C, 58.14; H, 7.54; N, 6.16. Found: C, 58.07; H, 7.49; N, 6.20.

Dihydro-3,3-diphenyl-5-acetoxymethyl-2(3H)-furanone, 2c. Oil. ^{1}H NMR δ 7.5 - 7.15 (m, 10 H), 4.64 - 4.45 (m, 1 H), 4.35 (dd, 1 H, J = 2.95 and 12.3 Hz), 4.1 (dd, 1 H, J = 6.1 and 12.3 Hz), 3.0 (dd, 1 H, J = 5.3 and 13.0 Hz), 2.62 (dd, 1 H, J = 10.5 and 13.0 Hz), 2.0 (s, 3 H). ^{13}C NMR δ 176.0, 170.0, 141.5, 139.4, 128.7, 128.2, 127.6, 127.4, 127.0, 74.1, 64.2, 57.4, 39.1, 20.3. MS m/e 310 (2), 206 (100), 191 (32), 178 (20), 165 (28), 128 (17), 115 (27), 103 (27), 91 (62), 77 (11), 43 (46). Anal. Calcd. for $C_{19}H_{18}O_4$: C, 73.54; H, 5.85. Found: C, 73.61; H, 5.79.

Dihydro-3-methyl-5-acetoxymethyl-2-(3H)-furanone, 2d. Oil. 1:1 Mixture of cis and trans isomers. ^{1}H NMR δ 4.8 - 4.65 (m, 1 H), 4.65 - 4.55 (m, 1 H), 4.4 - 4.0 (m, 4 H), 2.9 - 2.6 (m, 2 H), 2.6 - 2.4 (m, 1 H), 2.4 - 2.2 (m, 1 H), 2.2 - 2.0 (m, 1 H), 2.08 (s, 6 H), 1.8 - 1.6 (m, 1 H), 1.28 (d, 6 H, J = 7.0 Hz). ^{13}C NMR δ 177.9, 169.7, 74.7, 74.3, 64.8, 64.3, 34.4, 33.1, 31.8, 31.2, 19.9, 15.3, 14.4. MS m/e 112 (15), 99 (91), 71 (34), 68 (13), 43 (100); 112 (15), 99 (85), 71 (32), 68 (16), 43 (100). Anal. Calcd. for $C_8H_{12}O_4$: C, 55.81; H, 7.03. Found: C, 55.75; H, 7.11.

Dihydro-3-ethyl-5-acetoxymethyl-2(3H)-furanone, 2e. Oil. 1:1 Mixture of cis and trans isomers. ^{1}H NMR δ 4.8 - 4.65 (m, 1 H), 4.65 - 4.55 (m, 1 H), 4.4 - 4.2 (m, 2 H), 4.2 - 4.05 (m, 2 H), 2.74 - 2.55 (m, 1 H), 2.55 - 2.4 (m, 1 H), 2.3 - 2.0 (m, 4 H), 2.1 (s, 6 H), 2.0 - 1.8 (m, 2 H), 1.7 - 1.45 (m, 2 H), 1.05 (t, 3 H, J = 7.0 Hz), 1.02 (t, 3 H, J = 7.0 Hz). ^{13}C NMR δ 177.7, 170.3, 75.2, 75.0, 65.4, 64.9, 41.5, 40.3, 29.9, 29.4, 24.0, 23.3, 20.5, 11.3. MS m/e 158 (2), 126 (16), 113 (100), 98 (19), 85 (18), 67 (35), 57 (18), 43 (92); 158 (3), 126 (15), 113 (92), 98 (22), 85 (17), 67

(36), 57 (17), 43 (100). Anal. Calcd. for $C_9H_{14}O_4$: C, 58.06; H, 7.58. Found: C, 57.96; H, 7.64.

Dihydro-3-phenyl-5-acetoxymethyl-2(3H)-furanone, 2f. Oil. 1:1 Mixture of cis and trans isomers. ^1H NMR δ 7.47 - 7.1 (m, 10 H), 4.9 - 4.7 (m, 1 H), 4.7 - 4.55 (m, 1 H), 4.4 - 4.2 (m, 2 H), 4.2 - 4.05 (m, 2 H), 4.0 - 3.8 (m, 2 H), 2.8 - 2.5 (m, 1 H), 2.5 - 2.4 (m, 2 H), 2.2 - 2.0 (m, 1 H), 2.08 (s, 3 H), 2.04 (s, 3 H). ^{13}C NMR δ 170.0, 136.8, 136.2, 128.5, 128.4, 128.0, 127.7, 127.3, 127.2, 75.0, 64.9, 64.2, 45.9, 44.8, 32.8, 32.3, 20.2, 20.1. MS m/e 234 (24), 192 (55), 174 (9), 161 (9), 133 (27), 130 (44), 129 (63), 117 (15), 115 (29), 105 (54), 104 (31), 103 (18), 91 (15), 77 (18), 43 (100); 234 (5), 149 (11), 130 (88), 129 (51), 117 (13), 115 (27), 105 (37), 104 (29), 91 (16), 77 (15), 43 (100). Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.73; H, 5.97.

Dihydro-4-acetoxy-2(3H)-furanone, 4a. Oil.[17] ^1H NMR δ 5.44 (ddt, 1 H, J = 1.5, 4.7 and 6.5 Hz), 4.52 (dd, 1 H, J = 4.7 and 11.0 Hz), 4.35 (dd, 1 H, J = 1.2 and 11.0 Hz), 2.9 (dd, 1 H, J = 6.5 and 18.4 Hz), 2.58 (dd, 1 H, J = 1.5 and 18.4 Hz), 2.1 (s, 3 H). ^{13}C NMR δ 174.3, 170.0, 72.8, 69.7, 34.3, 20.5. MS m/e 86 (7), 84 (37), 74 (3), 71 (5), 55 (4), 43 (100).

Dihydro-4-acetoxy-5,5-dimethyl-2(3H)-furanone, 4b. Oil. ^1H NMR δ 5.1 (dd, 1 H, J = 2.2 and 6.6 Hz), 3.0 (dd, 1 H, J = 6.6 and 18.5 Hz), 2.48 (dd, 1 H, J = 2.2 and 18.5 Hz), 2.05 (s, 3 H), 1.4 (s, 3 H), 1.35 (s, 3 H). ^{13}C NMR δ 173.1, 169.6, 85.9, 74.4, 35.6, 26.0, 21.3, 20.4. MS m/e 157 (2), 144 (3), 114 (1), 101 (30), 97 (20), 86 (8), 71 (6), 59 (15), 43 (100). Anal. Calcd. for $C_8H_{12}O_4$: C, 55.81; H, 7.03. Found: C, 55.88; H, 7.10.

Dihydro-4-acetoxy-5-methyl-2(3H)-furanone, 4c. Proton NMR spectra[18] and n.O.e. experiments allowed to assign the structure of the two isomers.
Trans: Oil. ^1H NMR δ 5.05 (dt, 1 H, J = 2.2 and 6.9 Hz), 4.6 (dq, 1 H, J = 2.2 and 6.7 Hz), 2.98 (dd, 1 H, J = 6.9 and 18.6 Hz), 2.56 (dd, 1 H, J = 2.2 and 18.6 Hz), 2.1 (s, 3 H), 1.42 (d, 3 H, J = 6.7 Hz). ^{13}C NMR δ 173.6, 170.0, 81.3, 74.2, 33.8, 20.5, 18.4. MS m/e 130 (1), 114 (6), 98 (8), 87 (17), 86 (26), 71 (6), 55 (5), 43 (100). Anal. Calcd. for $C_7H_{10}O_4$: C, 53.17; H, 6.37. Found: C, 53.24; H, 6.43.
Cis: Oil. ^1H NMR δ 5.45 (ddd, 1 H, J = 1.2, 4.1 and 5.7 Hz), 4.74 (dq, 1 H, J = 4.1 and 6.5 Hz), 2.95 (dd, 1 H, J = 5.7 and 18.2 Hz), 2.6 (dd, 1 H, J = 1.2 and 18.2 Hz), 2.12 (s, 3 H), 1.4 (d, 3 H, J = 6.5 Hz). ^{13}C NMR δ

173.7, 169.5, 78.5, 70.9, 36.2, 20.2, 13.7. MS m/e 130 (1), 114 (6), 98 (2), 87 (18), 86 (27), 71 (6), 55 (2), 43 (100). Found: C, 53.13; H, 6.32.

5-Methyl-2(5H)-furanone, 5c. Oil.[19] ^{1}H NMR δ 7.5 (dd, 1 H, J = 1.5 and 5.7 Hz), 6.15 (dd, 1 H, J = 1.9 and 5.7 Hz), 5.15 (tq, 1 H, J = 1.7 and 6.9 Hz), 1.5 (d, 3 H, J = 6.9 Hz). MS m/e 98 (51), 83 (54), 69 (15), 55 (100), 54 (27), 43 (59).

Tetrahydro-3,3-dimethyl-6-acetoxymethyl-2H-pyran-2-one, 7. Oil. ^{1}H NMR δ 5.15 - 5.0 (m, 1 H), 4.26 (dd, 1 H, J = 3.6 and 11.9 Hz), 4.05 (dd, 1 H, J = 5.4 and 11.9 Hz), 2.1 (s, 3 H), 1.9 - 1.5 (m, 4 H), 1.35 (s, 6 H). ^{13}C NMR δ 170.3, 170.1, 124.2, 70.9, 64.5, 36.4, 31.9, 26.4, 20.7, 20.5. MS m/e 168 (11), 126 (16), 103 (2), 81 (3), 69 (2), 43 (100). Anal. Calcd. for $C_{10}H_{16}O_4$: C, 59.99; H, 8.05. Found: C, 59.92; H, 8.11.

Acetoxy-Lactonization of Unsaturated Acids. General Procedure.
To a solution of $PhI(OAc)_2$ (10 mmol) in acetic acid (8 ml) 48 % HBF_4 (1.8 ml) was added. To the resulting yellow solution the acid (5 mmol) was added. A colourless solution was obtained. The mixture was stirred at room temperature for 1 h and then poured on water. The reaction mixture was worked up as described above in the case of the nitriles. Reaction yields are indicated in Scheme 3. Compounds **2a**, **4a**, and **5c** have been described above. Physical and spectral data of all the other reaction products are given below.

Tetrahydro-2H-cyclopenta[b]furan-2-one, 10. Oil.[20] ^{1}H NMR δ 6.15 - 6.05 (m, 1 H), 5.9 - 5.8 (m, 1 H), 5.55 - 5.45 (m, 1 H), 3.25 - 3.15 (m, 1 H), 2.95 - 2.65 (m, 2 H), 2.4 - 2.2 (m, 2 H). ^{13}C NMR δ 176.6, 136.6, 128.4, 89.1, 39.1, 35.4, 34.6. MS m/e 124 (37), 95 (20), 81 (18), 80 (94), 79 (100), 77 (19), 68 (16), 67 (23), 65 (11), 55 (12), 53 (12), 41 (21).

Dihydro-4-acetoxy-5-methyl-2(3H)-furanone, 4c. Cis isomer. Oil. ^{1}H NMR δ 5.45 (ddd, 1 H, J = 1.2, 4.1 and 5.7 Hz), 4.74 (dq, 1 H, J = 4.1 and 6.5 Hz), 2.95 (dd, 1 H, J = 5.7 and 18.2 Hz), 2.6 (dd, 1 H, J = 1.2 and 18.2 Hz), 2.12 (s, 3 H), 1.4 (d, 3 H, J = 6.5 Hz). ^{13}C NMR δ 173.7, 169.5, 78.5, 70.9, 36.2, 20.2, 13.7. MS m/e 130 (1), 114 (6), 98 (2), 87 (18), 86 (27), 71 (6), 55 (2), 43 (100).

Dihydro-4-acetoxy-5-ethyl-2(3H)-furanone, 4d. Oil.[21] ^{1}H NMR δ 5.5 (dd, 1 H, J = 5.1 and 5.9 Hz), 4.45 (ddd, 1 H, J = 4.0, 5.1 and 8.3 Hz), 2.9 (dd,

1 H, J = 5.9 and 18.2 Hz), 2.56 (d, 1 H, J = 18.2 Hz), 2.1 (s, 3 H), 2.0 - 1.6 (m, 2 H), 1.05 (t, 3 H, J = 7.5 Hz). ^{13}C NMR δ 173.9, 169.7, 84.0, 70.3, 36.7, 21.8, 20.5, 9.7. MS m/e 143 (2), 114 (5), 101 (23), 86 (21), 83 (24), 43 (100).

5-Ethyl-2(5H)-furanone, 5d. Oil.[7,16] ^{1}H NMR δ 7.45 (dd, 1 H, J = 1.4 and 5.7 Hz), 6.15 (dd, 1 H, J = 1.8 and 5.7 Hz), 5.0 (ddt, 1 H, J = 1.4, 1.8 and 6.2 Hz), 2.0 - 1.6 (m, 2 H), 1.0 (t, 3 H, J = 7.3 Hz). ^{13}C NMR δ 172.6, 156.0, 121.0, 83.9, 25.8, 8.4. MS m/e 112 (6), 84 (14), 83 (100), 57 (11), 55 (21).

Dihydro-3-methyl-4-acetoxy-2(3H)-furanone, 4e. N.O.e. experiments allowed to assign the structure of the two isomers. Trans: Oil. ^{1}H NMR δ 5.06 (dt, 1 H, J = 3.6 and 5.7 Hz), 4.6 (dd, 1 H, J = 5.7 and 10.6 Hz), 4.2 (dd, 1 H, J = 3.6 and 10.6 Hz), 2.7 (dq, 1 H, J = 4.0 and 7.6 Hz), 2.1 (s, 3 H), 1.38 (d, 3 H, J = 7.6 Hz). ^{13}C NMR δ 176.6, 169.8, 75.2, 70.0, 40.1, 20.2, 12.9. MS m/e 116 (4), 98 (21), 85 (4), 72 (10), 58 (5), 57 (7), 56 (7), 43 (100). Anal. Calcd. for $C_7H_{10}O_4$: C, 53.17; H, 6.37. Found: C, 53.22; H, 6.34.
Cis: Oil. ^{1}H NMR δ 5.5 (dd, 1 H, J = 3.6 and 5.8 Hz), 4.4 (dd, 1 H, J = 3.6 and 11.1 Hz), 4.25 (d, 1 H, J = 11.1 Hz), 2.8 (dq, 1 H, J = 5.8 and 7.2 Hz), 2.12 (s, 3 H), 1.22 (d, 3 H, J = 7.2 Hz). ^{13}C NMR δ 176.9, 169.8, 71.8, 71.2, 37.9, 20.4, 8.2. MS m/e 116 (5), 100 (3), 98 (12), 72 (15), 58 (5), 57 (8), 56 (7), 43 (100). Found: C, 53.14; H, 6.42.

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