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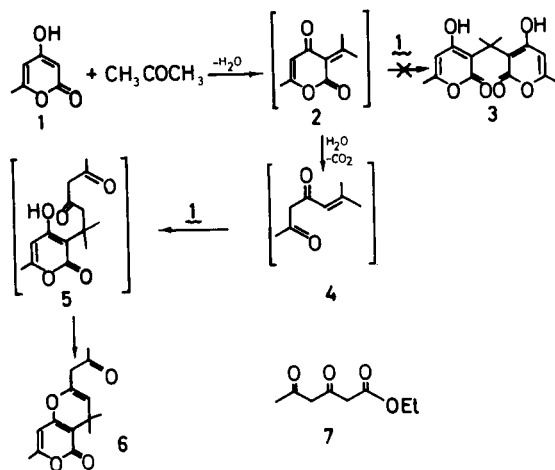
4-Hydroxy-6-methyl-2-pyrone (triacetic acid lactone) reacts at C-3 with acetone, mesityl oxide and pentane-2,4-dione. The structures of the final products have been elucidated.

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The reactions of 4-hydroxy-6-methyl-2-pyrone (triacetic acid lactone), **1**, with several saturated and unsaturated aldehydes have been described [1,2,3]. Moreover, the reactions of the related lactone 4-hydroxy-2-chromenone with  $\alpha,\beta$ -unsaturated ketones have also been studied [4,5,6,7]. However, to the best of our knowledge, the reactions of the lactone **1** with saturated ketones,  $\alpha,\beta$ -unsaturated ketones and  $\beta$ -diketones have not been described. Due to our interest on the chemistry of dehydroacetic acid and triacetic acid lactone, we decided to study the behaviour of **1** towards simple model ketones.

When the Knoevenagel experimental conditions were adopted in the reaction of **1** with acetone, the bispyrone **3**, expected to be formed in analogy with the aldehydes behaviour, was not isolated. Instead, 2-acetyl-4,4,7-trimethyl-4*H*,5*H*-pyrano[3,2-*c*]pyran-5-one, **6**, could be isolated in 44% yield (Scheme 1) together with ethyl 3,5-dioxohexanoate, **7**, formed by opening of **1** by the ethanol used as solvent. Most probably **6** arises from the intermediate **2** by opening and decarboxylation to generate the  $\beta$ -diketone **4**, which reacts with more triacetic acid lactone yielding the pyrone **5**, that gives **6** by dehydration of the internal hemiketal.

Scheme 1

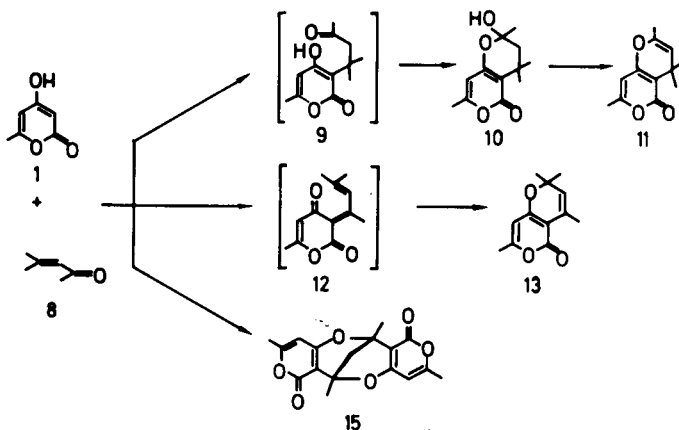


Since the involved mechanistic steps are similar to those operating in the Doebner reaction, we next studied the re-

action between **1** and acetone in pyridine as solvent with no catalyst added. In these conditions the bicyclic product **6** could be isolated in 58% yield.

The lactone **1** reacted also with mesityl oxide, **8**, in refluxing pyridine in the same way as described for 4-hydroxy-2-chromenone [4,7] (Scheme 2) the following compounds being formed: 2-hydroxy-2,4,4,7-tetramethyl-3,4-dihydro-2*H*,5*H*-pyrano[3,2-*c*]pyran-5-one, **10** (6% yield), a mixture of the isomers 2,2,4,7-tetramethyl-2*H*,5*H*-pyrano[3,2-*c*]pyran-5-one, **13**, and 2,4,4,7-tetramethyl-4*H*,5*H*-pyrano[3,2-*c*]pyran-5-one, **11** in a 1:4 ratio and 23% yield, and 3,6,9,12-tetramethyl-1*H*,6*H*,7*H*,12*H*-6,12-methanodipyrano[4,3-*b*:4,3-*f*]dioxocin-1,7-dione, **15** (7% yield).

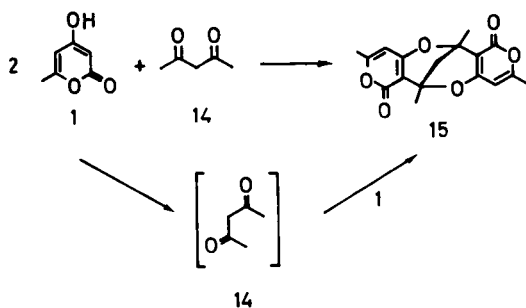
Scheme 2



The electrophilicity of **8** at two different centers accounts for the isolated products **10**, **11** and **13**. However, the presence of **15** was quite unexpected and it was assumed to arise from a partial hydrolysis and decarboxylation of **1** to pentane-2,4-dione, **14**, followed by further reaction of **1** with **14**.

To check this hypothesis, the reaction of **1** with **14** was performed both in refluxing pyridine and in an excess of refluxing pentane-2,4-dione in the presence of a small amount of pyridine. In both cases (Scheme 3), **15** could be isolated in 13% and 62% yield respectively. Further evidence to confirm our hypothesis was obtained by boiling the lactone **1** in pyridine for 7 hours; in this case compound **15** was isolated in 10% yield.

Scheme 3



## EXPERIMENTAL

The ir spectra were recorded on a Perkin-Elmer 1310 spectrophotometer. The pmr and cmr spectra were recorded on a Bruker WP80SY spectrometer. The ms were run on a Hewlett-Packard 5985-B spectrometer; only peaks with intensity higher than 20% are given.

## 2-Acetyl-4,4,7-trimethyl-4H,5H-pyrano[3,2-c]pyran-5-one (6).

The lactone **1** (1.008 g, 8 mmoles), acetone (3.5 ml) and pyridine (5 ml) were heated at 90° under magnetic stirring for 17 hours in a closed reactor. The mixture was poured into hydrochloric acid and ice and extracted with chloroform. The organic layer was washed, dried over sodium sulfate and evaporated to give 800 mg of a dark oil which was purified by passing it through a silica gel column eluted with methylene chloride. The lactone **6** (570 mg, 58%) had mp 88-90° (from ether-pentane); ir (potassium bromide): 1705, 1650, 1580 cm<sup>-1</sup>; pmr (deuteriochloroform): δ 1.44 (s, 6H), 2.19 (d, J = 1 Hz, 3H), 2.22 (s, 3H), 3.17 (s, 2H), 4.76 (s, 1H), 5.73 (broad s, 1H); cmr (deuteriochloroform): δ 19.5, 28.8, 29.1, 30.3, 47.3, 98.8, 104.5, 114.8, 140, 6, 159.8, 160.8, 162.5; ms: 248 (M<sup>+</sup>, 2), 234 (15), 233 (100), 191 (87), 43 (18).

Anal. Calcd. for C<sub>14</sub>H<sub>16</sub>O<sub>4</sub>: C, 67.73; H, 6.50. Found: C, 67.40; H, 6.56.

Reaction of **1** With Mesityl Oxide in Refluxing Pyridine.

The lactone **1** (1.28 g, 0.01 mole) and mesityl oxide (1.97 g, 0.02 mole) were refluxed in pyridine for 10 hours. The mixture was evaporated to dryness to afford a brown residue which was extracted with chloroform to separate some starting material **1**. The solvent was evaporated and the residue was chromatographed through a silica gel column eluted with ethyl acetate-hexane (3/7), the following compounds being obtained: a mixture (0.49 g, 23%) of 2,2,4,7-tetramethyl-2H,5H-pyrano[3,2-c]pyran-5-one, **13**, and 2,4,4,7-tetramethyl-4H,5H-pyrano[3,2-c]pyran-5-one, **11**, in a ratio of 1:4, 0.14 g (6%) of 2-hydroxy-2,4,4,7-tetramethyl-3,4-dihydro-2H,5H-pyrano[3,2-c]pyran-5-one, **10**, and 0.12 g (7%) of 3,6,9,12-tetramethyl-1H,6H,7H,12H-6,12-methanodipyran[4,3-b:4,3-f]dioxocin-1,7-dione, **15**. The mixture of **13** and **11** had ir (potassium bromide): 1720-1700, 1640, 1630, 1540 cm<sup>-1</sup>; pmr (deuteriochloroform): δ 1.40 (s,

6H, **13**), 1.44 (s, 6H, **11**), 2.1-2.45 (6H, **13** and **11**), 5.04-5.15 (1H, **11**), 5.82 (s, 1H, **13** and **11**), 6.30 (broad s, 1H, **13**); gc/ms (capillary column OV-1 (10 meters)): first product eluted: 206 (M<sup>+</sup>, 17), 191 (100); second product eluted (without background subtraction): 206 (M<sup>+</sup>, 71), 191 (71), 163 (38), 107 (29), 91 (31), 85 (57), 79 (55), 69 (33), 51 (33), 43 (100).

Anal. Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>: C, 69.89; H, 6.84. Found: C, 69.63; H, 6.95.

A sample of nearly pure **11** was obtained by repeated column chromatography. It gave pmr (deuteriochloroform): δ 1.44 (s, 6H), 2.1-2.3 (m, 6H), 5.04-5.15 (1H), 5.82 (s, 1H).

The lactone **10** had mp 172-174°; ir (potassium bromide): 3500-3220 (broad), 1675, 1640, 1555 cm<sup>-1</sup>; pmr (deuteriochloroform): δ 1.3 (s, 3H), 1.4 (s, 3H), 1.6 (s, 3H), 1.85 and 1.95 (internal part of an AB system, 2H), 2.1 (s, 3H), 3.2 (s, 1H), 5.7 (s, 1H); cmr (deuteriochloroform): δ 163.1, 161.7, 160.0, 106.1, 100.8, 98.8, 47.6, 29.7, 29.4, 28.4, 26.2, 19.4; ms: 224 (M<sup>+</sup>, 26), 181 (35), 167 (74), 151 (30), 139 (23), 85 (34), 83 (59), 67 (24), 43 (100).

Anal. Calcd. for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub>: C, 64.27; H, 7.19. Found: C, 63.98; H, 7.11.

The dioxocindione **15** had mp 235-237° (from ethanol); ir (potassium bromide): 1715, 1635, 1555 cm<sup>-1</sup>; pmr (deuteriochloroform): δ 2.0 (s, 6H), 2.05 (s, 2H), 2.15 (s, 6H), 5.8 (s, 2H); cmr (deuteriochloroform): δ 167.2, 163.0, 161.6, 99.9, 99.2, 73.4, 43.9, 22.8, 19.8; ms: 316 (M<sup>+</sup>, 100), 301 (72), 217 (33), 204 (20), 191 (30), 164 (91), 85 (22), 69 (22), 43 (59).

Anal. Calcd. for C<sub>17</sub>H<sub>16</sub>O<sub>6</sub>: C, 64.55; H, 5.10. Found: C, 64.48; H, 4.95.

3,6,9,12-Tetramethyl-1H,6H,7H,12H-6,12-methanodipyran[4,3-b:4,3-f]-dioxocin-1,7-dione (**15**).

The lactone **1** (0.739 g, 6 mmoles) was refluxed in pentane-2,4-dione (5 ml) in the presence of five drops of pyridine. Upon cooling the dioxocindione **15** precipitated (0.575 g, 62%) in a high degree of purity. The physical data have described above.

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