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Aldehydes react with 4-hydroxy-6-methyl-2-pyrone, **2**, under Knoevenagel conditions to afford very electrophilic intermediates, which can be trapped by more **2** or thiols to give dilactones **3** or monolactones **4**.

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In the course of a synthetic project carried out at this laboratory we needed products of the general constitution **1** or equivalent synthons.

The chemistry of 4-hydroxy-6-methyl-2-pyrone (triacetic acid lactone), **2**, at the C-3 position is well known. However reactions with aldehydes have been only exceptionally described (1,2,3).

We have found that **2** reacts with several aldehydes under typical Knoevenagel conditions to afford arylbis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)methanes **3a-e**. We can reasonably assume the intermediacy of products **1**, which are very electrophilic and react with an additional equivalent of **2** to afford **3**. All attempts to stop the reactions at the products **1** were unsuccessful. Then we reasoned that the presence of thiols in the reactions media could give rise to products of general structure **4**, which can be considered as synthetic equivalents to **1**, since the organic chemistry armamentarium includes well known methods to prepare double bonds from sulfur based functions. Indeed when mixtures of **2**, an aldehyde and a thiol (molar ratio 1:1:3) were treated under the mentioned conditions, products **4a-e** were formed in very good yields.

## EXPERIMENTAL

Phenylbis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)methane (**3a**).

The lactone **2** (1.26 g, 0.01 mole), benzaldehyde (0.53 g, 0.005 mole), acetic acid (0.5 ml) and piperidine (0.5 ml) were left in ethanol (30 ml).

The precipitate appeared in 2 hours and was filtered off, dissolved in chloroform and the organic solution was washed with diluted hydrochloric acid, dried over sodium sulphate and evaporated to afford 3.3 g (98%) of **3a**, mp 214-215° (from ethanol, lit (1), mp 215°); ir (potassium bromide): 3100 (broad, OH), 1680 (C=O), 1630 (C=C), 1570 cm<sup>-1</sup> (C=C); nmr (d<sub>6</sub>-dimethyl sulfoxide): δ 2.06 (s, CH<sub>3</sub>, 6H), 5.9 (s, CH, 1H), 6.0 (s, CH, 2H), 6.85-7.25 (m, aromatic, 5H); ms: 340 (M<sup>+</sup>, 0.7), 84 (70), 43 (84), 28 (100).

The following compounds were prepared in a similar manner.

4-Chlorophenylbis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)methane (**3b**).

This compound was obtained in a yield of 89% by heating at 70° for 20 hours, mp 202-205° dec from methylene chloride; ir (potassium bromide): 3100 (broad, OH), 1680 (C=O), 1610 (C=C), 1570 cm<sup>-1</sup> (C=C); nmr (deuteriochloroform): δ 2.25 (s, CH<sub>3</sub>, 6H), 5.7 (s, CH, 1H), 6.05 (s, CH, 2H), 6.95, 7.08, 7.14, 7.27 (AA'BB' system, aromatic, 4H); ms: 374 (M<sup>+</sup>, 4), 85 (71), 69 (53), 43 (100).

Anal. Calcd. for C<sub>19</sub>H<sub>15</sub>ClO<sub>6</sub>: C, 60.86; H, 4.03; Cl, 9.45. Found: C, 60.81; H, 3.93; Cl, 9.85.

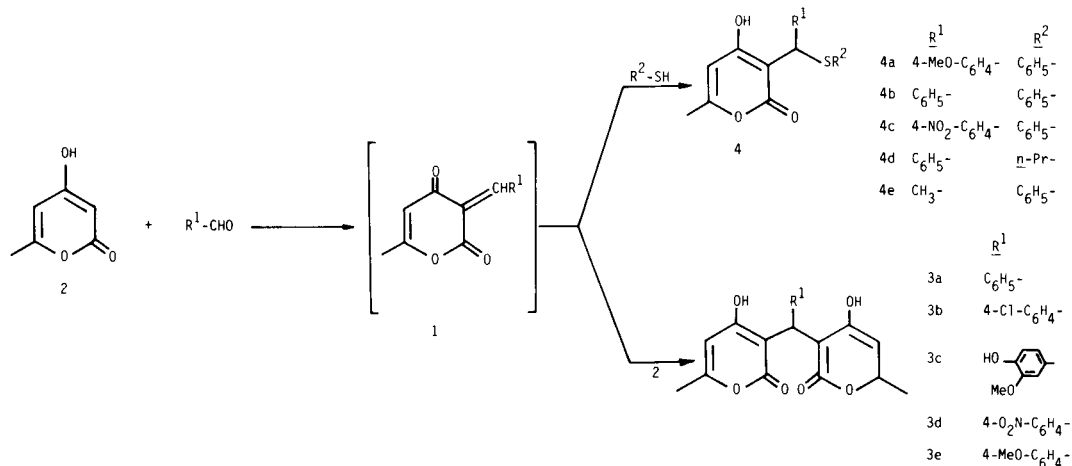
(4-Hydroxy-3-methoxyphenyl)bis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)methane (**3c**).

This compound was obtained in a yield of 58% by heating at 60° for 48 hours, mp 205-207° dec from methylene chloride; ir (potassium bromide): 3200 (broad, OH), 1690 (C=O), 1635 (C=C), 1575 cm<sup>-1</sup> (C=C); nmr (d<sub>6</sub>-dimethyl sulfoxide): δ 2.1 (s, CH<sub>3</sub>, 6H), 3.6 (s, OCH<sub>3</sub>, 3H), 5.95 (s, CH, 1H), 6.05 (s, CH, 2H), 6.3-6.8 (m, aromatic, 3H); ms: 386 (M<sup>+</sup>, 0.6), 43 (100).

Anal. Calcd. for C<sub>20</sub>H<sub>18</sub>O<sub>8</sub>: C, 62.18; H, 4.70. Found: C, 61.81; H, 4.74.

Bis(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-4-nitrophenylmethane (**3d**).

This compound was obtained in a yield of 74% by heating at 60° for 2 hours, mp 214-217° from chloroform; ir (potassium bromide): 3100 (broad, OH), 1680 (C=O), 1620 (C=C), 1560 (C=C), 1520 (NO<sub>2</sub>), 1350 cm<sup>-1</sup> (NO<sub>2</sub>); nmr (d<sub>6</sub>-dimethyl sulfoxide): δ 2.05 (s, CH<sub>3</sub>, 6H), 5.7 (s, CH, 1H),



5.85 (s, CH, 2H), 7.03, 7.18, 7.82, 7.97 (AA'BB' system, aromatic, 4H); ms: 385 (M<sup>+</sup>, 3), 85 (38), 69 (31), 43 (100).

*Anal.* Calcd. for C<sub>15</sub>H<sub>15</sub>NO<sub>6</sub>: C, 59.22; H, 3.92; N, 3.63. Found: C, 59.27; H, 3.87; N, 3.98.

Bis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-4-methoxyphenylmethane (3e).

This compound was obtained in a yield of 95% by heating at 60° for 2.5 hours, mp 174-176° from carbon tetrachloride-methylene chloride; ir (potassium bromide): 3100 (broad, OH), 1680 (C=O), 1620 (C=C), 1560 cm<sup>-1</sup> (C=C); nmr (deuteriochloroform): δ 2.25 (s, CH<sub>3</sub>, 6H), 3.7 (s, OCH<sub>3</sub>, 3H), 5.7 (s, CH, 1H), 5.95 (s, CH, 2H), 6.65, 6.82, 6.94, 7.11 (AA'BB' system, aromatic, 4H); ms: 370 (M<sup>+</sup>, 4), 85 (52), 69 (89), 43 (100). This product never gave a satisfactory combustion analysis.

(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)(4-methoxyphenyl)phenylthioethane (4a).

Lactone **2** (3.15 g, 0.025 mole) in ethanol (50 ml) was slowly added into a stirred solution of 4-methoxybenzaldehyde (3.40 g, 0.025 mole), thiophenol (8.25 g, 0.075 mole), acetic acid (0.6 ml) and piperidine (0.6 ml) in ethanol (20 ml) at 55°. The solution was allowed to stand for 48 hours and then evaporated. The residue was chromatographed through silica gel. Thiophenol was eluted with hexane-ethyl acetate (95:5) and **4a** with hexane-ethyl acetate (1:1). The lactone **4a** (83%) could not be crystallized; ir (carbon tetrachloride): 3200 (broad, OH), 1700 (C=O), 1660 (C=C), 1580 cm<sup>-1</sup> (C=C); nmr (deuteriochloroform): δ 2.15 (s, CH<sub>3</sub>, 3H), 3.85 (s, OCH<sub>3</sub>, 3H), 5.95 (s, CH, 1H), 6.05 (s, CH, 1H), 6.85, 7.03 (part BB' of the AA'BB' system, aromatic, 2H), 7.27-7.70 (m, aromatic, 7H), 10.05 (s, OH, 1H); ms: 244 (M-110, 1), 110 (93), 65 (100).

*Anal.* Calcd. for C<sub>20</sub>H<sub>18</sub>O<sub>5</sub>S: C, 67.77; H, 5.11; S, 9.04. Found: C, 67.40; H, 5.24; S, 9.32.

The following products were prepared in a similar manner.

(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)phenyl-phenylthioethane (4b).

This compound was prepared in a yield of 88% by heating at 60° for 120 hours, mp 163-164° from chloroform-hexane; ir (potassium bromide): 3100 (broad, OH), 1660 (C=O), 1575 cm<sup>-1</sup> (C=C); nmr (d<sub>6</sub>-dimethyl sulfoxide): δ 2.0 (s, CH<sub>3</sub>, 3H), 5.65 (s, CH, 1H), 5.95 (s, CH, 1H), 7.0-7.6 (m, aromatic, 10H); ms: 215 (M-109, 16), 109 (100).

*Anal.* Calcd. for C<sub>17</sub>H<sub>16</sub>O<sub>5</sub>S: C, 70.34; H, 4.97; S, 9.88. Found: C, 70.43; H, 4.94; S, 10.00.

(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)(4-nitrophenyl)phenylthioethane (4c).

This compound was obtained in a yield of 86% by heating at 60° for 52 hours, mp 96-100° dec from chloroform-hexane; ir (potassium bromide): 1670 (C=O), 1640 (C=C), 1590 (C=C), 1565 (NO<sub>2</sub>), 1350 cm<sup>-1</sup> (NO<sub>2</sub>); nmr (d<sub>6</sub>-dimethyl sulfoxide): δ 2.0 (s, CH<sub>3</sub>, 3H), 5.7 (s, CH, 1H), 5.95 (s, CH, 1H), 7.15 (s, aromatic, 5H), 7.60, 7.75, 8.00, 8.15 (AA'BB' system, aromatic, 4H), 8.10 (s, OH, 1H); ms: 260 (M-109, 3), 110 (70), 43 (100).

*Anal.* Calcd. for C<sub>17</sub>H<sub>15</sub>NO<sub>5</sub>S: C, 61.77; H, 4.09; N, 3.7; S, 8.67. Found: C, 61.78; H, 4.06; N, 4.1; S, 8.62.

(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)phenyl-*n*-propylthioethane (4d).

This compound was obtained in a yield of 72% by heating at 60° for 24 hours, mp 121-124° from carbon tetrachloride-methylene chloride; ir (potassium bromide): 3150 (broad, OH), 1660 (C=O), 1580 cm<sup>-1</sup> (C=C); nmr (deuteriochloroform): δ 1.0 (t, CH<sub>3</sub>, 3H, J = 7 Hz), 1.4-2.0 (m, CH<sub>2</sub>, 2H), 2.2 (s, CH<sub>3</sub>, 3H), 2.45-2.85 (m, SCH<sub>2</sub>, 2H), 5.55 (s, CH, 1H), 5.85 (s, CH, 1H), 7.1-7.5 (m, aromatic, 5H), 9.0-9.6 (broad, OH, 1H); ms: 290 (M<sup>+</sup>, 4), 215 (M-75, 100), 102 (56).

*Anal.* Calcd. for C<sub>18</sub>H<sub>18</sub>O<sub>5</sub>S: C, 66.18; H, 6.25; S, 11.04. Found: C, 66.07; H, 6.27; S, 10.87.

1-(4-Hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-1-phenylthioethane (4e).

This compound was prepared in a yield of 96% by allowing the reaction mixture to stand at 20° for 17 hours, mp 163-166° dec from ethanol; ir (potassium bromide): 1670 (shoulder, C=O), 1620 (C=C), 1570 cm<sup>-1</sup> (C=C); nmr (d<sub>6</sub>-dimethyl sulfoxide): δ 1.4 (d, CH<sub>3</sub>, 3H, J = 8 Hz), 2.0 (s, CH<sub>3</sub>, 3H), 4.65 (q, CH, 1H, J = 8 Hz), 5.95 (s, CH, 1H), 7.1-7.5 (m, aromatic, 5H); ms: 262 (M<sup>+</sup>, 2), 152 (M-110, 44), 110 (100), 85 (43), 69 (53).

*Anal.* Calcd. for C<sub>14</sub>H<sub>14</sub>O<sub>5</sub>S: C, 64.10; H, 5.37; S, 12.22. Found: C, 64.30; H, 5.35; S, 12.16.

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