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4-AMINO-6-METHYL-2H-PYRAN-2-ONE. PREPARATION AND REACTIONS WITH AROMATIC ALDEHYDES.

MARIA CERVERA, MARCIAL MORENO-MAÑAS,* and ROSER PLEIXATS.
Department of Chemistry, Universitat Autònoma de Barcelona.
08193-Bellaterra. Barcelona. Spain.

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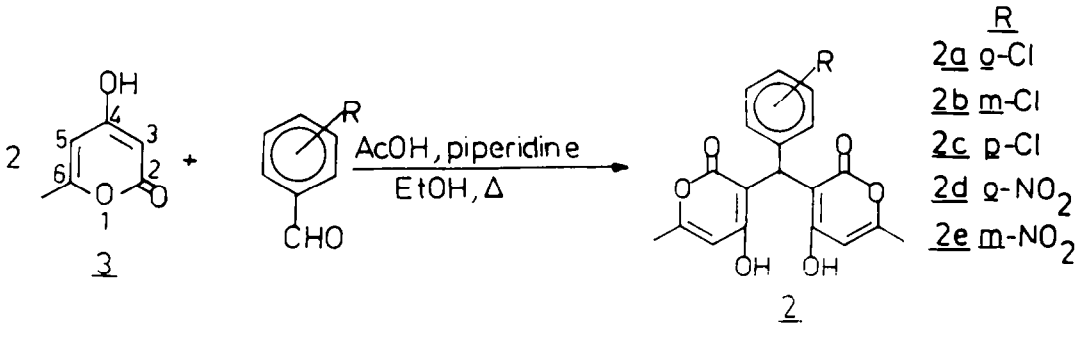
Abstract: bis(4-Amino-6-methyl-2-oxo-2H-pyran-3-yl)arylmethanes, 1, are synthesized by reaction of 4-amino-6-methyl-2H-pyran-2-one, 10, with aromatic aldehydes. The aminopyrone 10 is obtained in three steps from 4-hydroxy-6-methyl-2H-pyran-2-one (triacetic acid lactone), 3.

In the course of a synthetic project carried out at this laboratory we were interested in the preparation of bis(4-amino-6-methyl-2-oxo-2H-pyran-3-yl)arylmethanes 1 (See Scheme 4).

The synthesis of the related compounds arylbis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)methanes, 2, can be achieved[1] by reaction of triacetic acid lactone 3 with aromatic aldehydes under Knoevenagel conditions. In view of the easy access to these compounds, we considered the possibility of preparing the target molecules 1 by treatment of 2 with ammonia. However, the precedents found in the literature concerning the reactivity of related pyrones in front of amine nucleophiles pointed out that both C-2 and C-4 positions could react with them. Thus, for 5,6-dihydro-4-hydroxy-2-pyrones[2] and 4-hydroxy-2-pyridones[3] the attack of ammonia and amines takes place at the C-4 position, but for the case of 4-hydroxy-2-pyrones[4] the nucleophile reacts preferably with the lactone carbonyl group at C-2 and only at C-4 through a second attack.

Compounds 2a-e were prepared according to the published general procedure[1] (Scheme 1) and identified by spectral means and analytical data when required (Only 2c had been previously reported).

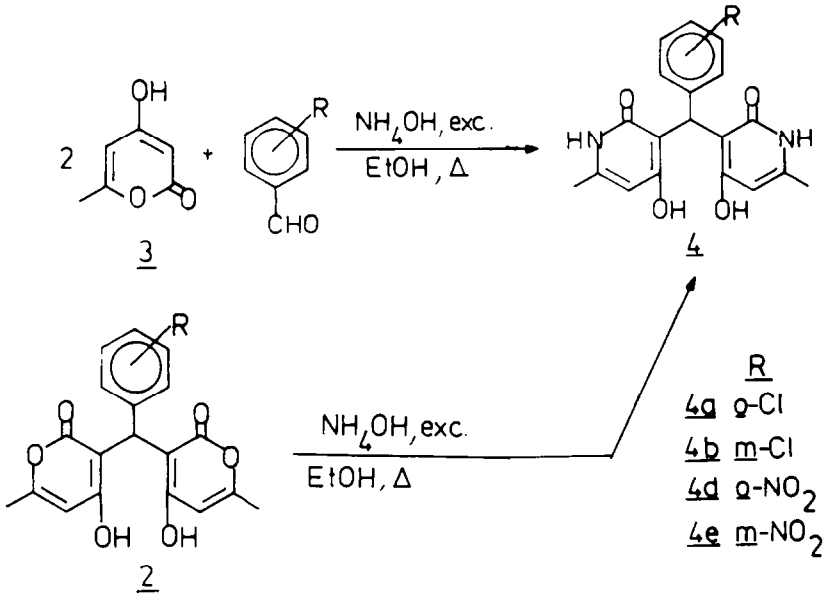
Scheme 1



3 2

The treatment of 2 with excess aqueous ammonia in ethanol in a sealed tube at 100-110ºC did not lead to 1. Instead, the corresponding arylbis(4-hydroxy-6-methyl-2-oxo-2H-pyrid-3-yl)methanes 4a (20%), 4b (23%) and 4e (86%) were isolated (Scheme 2). These products precipitated from the reaction medium, avoiding the reaction to proceed further at the C-4 position. Compounds 4a (45%), 4b (14%), 4d (44%) and 4e (11%) were also directly synthesized by heating a mixture of two equivalents of triacetic acid lactone 3, one equivalent of the corresponding aldehyde and excess aqueous ammonia in ethanol in a sealed tube at 100-110ºC (Scheme 2).

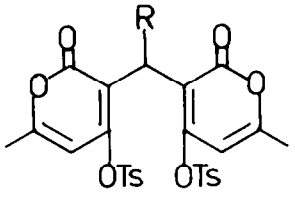
Scheme 2



Compounds 4a-e were identified by their spectroscopic and analytical data (See table 1). Broad absorptions at 3500-2600 cm^{-1} in the ir spectra indicate the presence of enol OH groups besides NH and intense peaks at 1630 cm^{-1} are attributed to the carbonyl group of the unsaturated lactame moiety. This frequency is sensibly inferior to that obtained for the lactonic carbonyl group (1679 cm^{-1}) in compounds 2 (See Table 1).

Next, we reasoned that the introduction of a good leaving group at C-4 would help to prepare the needed compounds. Some examples can be found in the literature on the substitution of chloro, methoxy, methylthio and tosyloxy groups at the C-4 position of a 2-pyrone rings by secondary amines and thiolates[5]. Since 3,6-Dioxa-9-thianthracenes 6 had been obtained from arylbis(6-methyl-2-oxo-4-tosyloxy-2H-pyran-3-yl)methane 5 by using anhydrous sodium hydrogen sulphide as nucleophile[6], we prepared 5c[6]. Nevertheless, treatment of 5c with excess gaseous ammonia in anhydrous dioxane[6] gave rise to 10-(4-chlorophenyl)-2,7-dimethyl-4,5-dioxo-3,6,9-trioxa-3,4,5,6,9,10-hexahydroanthracene 7.

Other leaving groups such as chloride or methoxy were not considered because several preliminary reactions between 4-chloro-6-methyl-2H-pyran-2-one 8 and ammonia and between 4-methoxy-6-methyl-2H-pyran-2-one 9 and primary amines were unsuccessful.



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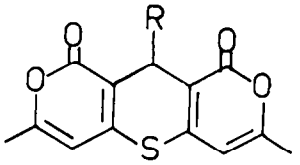

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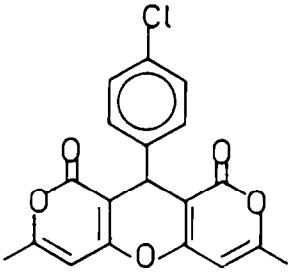
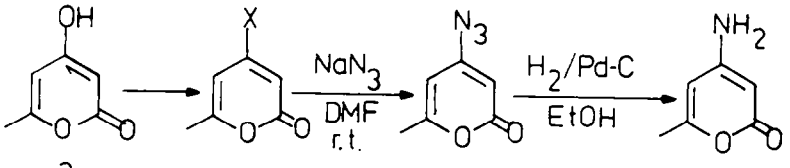


7c

5c R=4-ClC$_6$H$_4$

At this point we considered that the more feasible alternative method to synthesize compounds 1 could involve the use of the unknown 4-amino-6-methyl-2H-pyran-2-one 10 as starting material. We followed the synthetic route of Scheme 3. An analogous methodology had been applied to 4-hydroxycoumarines and 4-hydroxyquinolines[7].

Scheme 3



3 X=Cl 8 X=Br 11 X=OTs 12 13 10

A synthesis of the chloro derivative 8 had been published[8]. Nevertheless, the low yields and the tediousness of the method when scaled up moved us to begin the search for a better one. Although some different reagents were tested (PCl_3/DMF, $POCl_3$/DMF, PPh_3/CCl_4, PPh_3/CCl_4/imidazole) the yield could not be sensibly improved. Contrarily, the new compound 4-bromo-6-methyl-2H-pyran-2-one, 11, was efficiently prepared in 81% yield by treatment of 3 with a Vilsmeier reagent (phosphorus tribromide/dimethylformamide).

The reactions of both 8 and 11 with sodium azide gave rise to 4-azido-6-methyl-2H--pyran-2-one, 13, in 88 and 83% yield respectively. An analogous reaction with the tosyloxy derivative 12[5a] did not work due to the fact that nucleophilic attack took place at the sulfur atom giving tosylazide as final product.

The aminopyrone was obtained in quantitative yield by hydrogenation of 13.

In one experiment aimed to the synthesis of 8, in which a mixture of triphenylphosphine (2 equivalents), carbon tetrachloride (10 equivalents) and imidazole (4 equivalents) was refluxed in toluene, a new product was isolated (42% yield) and identified as 1-(6-methyl-2-oxo-2H-pyran-4-yl)imidazole 14.

Condensations of two equivalents of 4-amino-6-methyl-2H-pyran-2-one, 10, with the corresponding aldehydes under catalysis by p-toluenesulphonic acid in toluene, afforded bis(4-amino-6-methyl-2-oxo-2H-pyran-3-yl)arylmethanes 1c-e (Scheme 4), very insoluble compounds which precipitated from the reaction medium and were characterized by spectral and analytical data (see table 1).

Two narrow absorptions in the infrared spectra at about 3200 and 3350 cm^{-1} indicated the presence of NH_2 groups, broad absorptions due to hydroxyl groups being absent; the lactonic carbonyl absorbs at 1682-1683 cm^{-1}. Some spectral data of compounds 2, 4 and 1 are gathered in table 1.

4-Amino-6-methyl-2H-pyran-2-one, 10, is a useful synthon in heterocyclic chemistry. More information on its reactivity in front of β-diketones will be published.

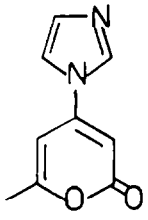


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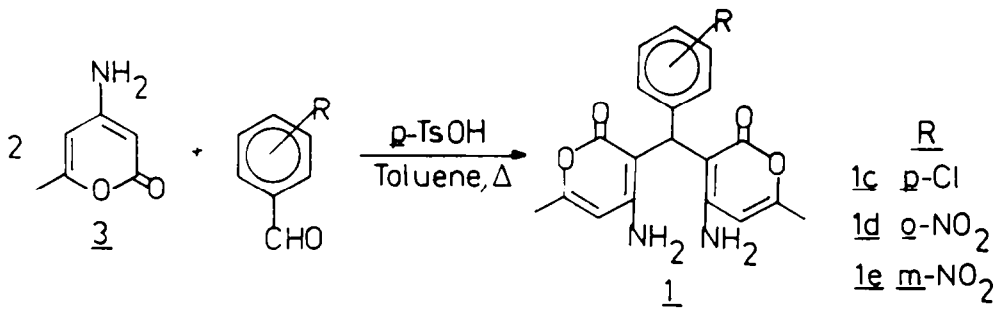
Table 1. Ir and ^{1}H-nmr data for compounds 2, 4 and 1.

	ir(KBr) (cm^{-1})		^{1}H-nmr (δ, ppm)			
Product	OH and/or NH_2	C=O st.	CH_3	-CH-	-CH=	Solvent
2a	3600-2400 (OH)	1679	2.29	5.93	6.00	$CDCl_3$
2b	3300-2550 (OH)	1679	2.33	5.70	6.09	$CDCl_3$
2d	3350-2500 (OH)	1679	2.16	6.04	5.96	d_6-DMSO
2e	3400-2400 (OH)	1679	2.33	5.76	6.10	$CDCl_3$
4a	3650-2600 (OH,NH)	1630	2.14	6.14	5.77	d_6-DMSO
4b	3350-2600 (OH,NH)	1632	2.18	5.92	5.92	d_6-DMSO
4d	3600-3200 (OH,NH) 3100-2850	1632	2.14	6.45	5.83	d_6-DMSO
4e	3300-2500 (OH,NH)	1630	2.17	6.09	5.90	d_6-DMSO
1c	3336, 3168 (NH_2)	1683	2.12	5.37	5.93	d_6-DMSO
1d	3351, 3207 (NH_2)	1684	2.12	5.96	5.87	d_6-DMSO
1e	3369, 3210 (NH_2)	1683	2.15	5.50	6.00	d_6-DMSO

Scheme 4



Experimental section

General. All melting points are uncorrected. ^{1}H-nmr and ^{13}C-nmr spectra were recorded at 80 and 20 MHz respectively using TMS as internal standard and mass spectra were run at 70 eV; only peaks with intensity higher than 20% are given unless they are significant. Compounds 2a-2e were prepared according to the reported general method[1].

2-Chlorophenylbis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)methane, 2a: (14% yield) mp 155-156°C (dichloromethane/hexane); ir (ν, cm^{-1}) (KBr) 3600-2400, 1679, 1623, 1574, 1447, 1412, 1300; ^{1}H-nmr (δ, ppm) ($CDCl_3$) 2.29 (s, 6H), 5.93 (s, 1H), 6.00 (s, 2H), 7.09-7.47 (m, 4H), 10.50-11.00 (broad band, 2H); ^{13}C-nmr (δ, ppm) (d_6-DMSO) 19.02, 34.74, 100.48, 100.75, 126.08, 127.19, 128.65, 129.97, 132.68, 138.99, 160.42, 164.47, 166.46; ms (m/z, relative intensity) 376 (M+2, 7), 375 (M+1, 4), 374 (M, 19), 227 (22), 213 (84), 85 (43), 69 (36), 43 (100). Anal. Calcd for $C_{19}H_{15}ClO_6$: C, 60.89; H, 4.01. Found: C, 60.72; H, 4.02.

3-Chlorophenylbis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)methane, 2b: (54% yield) mp 188-190°C (dichloromethane/diethyl ether); ir (ν, cm^{-1}) (KBr) 3300-2550, 1679, 1630, 1574, 1447, 1412, 1342, 1293; ^{1}H-nmr (δ, ppm) ($CDCl_3$) 2.33 (s, 6H), 5.70 (s, 1H), 6.09 (s, 2H), 7.05-7.35 (m, 4H), 11.00 (s, 2H); ^{13}C-nmr (δ, ppm) ($CDCl_3$) 19.55, 34.51, 103.11, 124.64, 126.57, 126.81, 129.57, 134.44, 137.96, 161.78, 164.67, 169.50; ms (m/z, relative intensity) 374 (M, 2), 85 (24), 43 (100). Anal. Calcd for $C_{19}H_{15}ClO_6$: C, 60.89; H, 4.01. Found: C, 60.70; H, 4.17.

4-Chlorophenylbis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)methane, 2c: (68% yield) mp 202-205°C (dichloromethane/hexane) (Lit.[1] mp 202-205°C)

Bis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)(2-nitrophenyl)methane, 2d: (76% yield) mp 223-227°C(d) (acetone); ir (ν, cm^{-1}) (KBr) 3350-2650, 1679, 1609, 1567, 1525, 1473, 1450, 1412, 1370; ^{1}H-nmr (δ, ppm) (d_6-DMSO) 2.16 (s, 6H), 5.96 (s, 2H), 6.04 (s, 1H), 7.16-7.84 (m, 4H), 9.50-11.00 (broad band); ^{13}C-nmr (δ, ppm) (d_6-DMSO) 19.06, 32.83, 100.08, 123.51, 126.76, 130.02, 131.87, 135.33, 149.34, 160.60, 164.07, 166.51; ms (m/z, relative intensity) 385 (M, < 3), 283 (30), 266 (43), 213 (46), 160 (36), 89 (20), 85 (58), 69 (39), 43 (100). Anal. Calcd for $C_{19}H_{15}NO_8$: C, 59.22; H, 3.92; N, 3.63. Found: C, 59.37; H, 4.09; N, 3.18.

Bis(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)(3-nitrophenyl)methane, 2e: (67% yield) mp 193-194°C (dichloromethane/hexane); ir (ν, cm^{-1}) (KBr) 3400-2400, 1679, 1567, 1525, 1412, 1349, 1271; ^{1}H-nmr (δ, ppm) ($CDCl_3$) 2.33 (s, 6H), 5.76 (s, 1H), 6.10 (s, 2H), 7.42-7.48 (m, 2H), 7.92-8.17 (m, 2H), 10.88 (broad band); ^{13}C-nmr (δ, ppm) (d_6-DMSO) 19.56, 34.60, 102.49, 103.17, 121.60, 121.76, 129.28, 132.60, 138.37, 148.60, 162.22, 169.04, 169.81; ms (m/z, relative intensity) 386 (M+1, 4), 385 (M, 20), 85 (55), 69 (31), 43 (100). Anal. Calcd for $C_{19}H_{15}NO_8$: C, 59.22; H, 3.92; N, 3.63. Found: C, 59.10; H, 4.01; N, 3.64.

Bis(4-hydroxy-6-methyl-2-oxo-2H-pyrid-3-yl)(3-nitrophenyl)methane, 4e from 2e.
A mixture of 2e (3.850 g, 10.00 mmol), 25% NH_4OH (8 ml) and ethanol (70 ml) was heated in a sealed tube at 100-110ºC for 26 h. The formed solid was filtered, washed with 1M HCl and dried (3.297 g, 8.61 mmol, 86% yield of 4e): mp > 300ºC; ir ($\bar{\nu}$, cm^{-1}) (KBr) 3300-2500, 1630, 1532, 1461, 1391, 1349; ^{1}H-nmr (δ, ppm) (d_6-DMSO) 2.17 (s, 6H), 5.90 (s, 2H), 6.09 (s, 1H), 7.46-7.63 (m, 2H), 7.78 (d, J= 0.75 Hz, 1H), 7.98-8.07 (m, 1H), 10.16-10.99 (broad band); ^{13}C-nmr (δ, ppm) (d_6-DMSO) 18.15, 33.72, 101.83, 108.59, 120.53, 120.94, 129.26, 133.39, 142.15, 144.57, 147.72, 165.52, 166.99. Anal. Calcd for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.16; H, 4.50; N, 10.84.

Compounds 4a (20%) and 4b (23%) were prepared by the same procedure.

2-Chlorophenylbis(4-hydroxy-6-methyl-2-oxo-2H-pyrid-3-yl)methane, 4a: mp > 300ºC; ir ($\bar{\nu}$, cm^{-1}) (KBr) 3650-2600, 1630, 1454, 1398, 1356, 1335, 1271; ^{1}H-nmr (δ, ppm) (d_6-DMSO) 2.14 (s, 6H), 5.77 (s, 2H), 6.14 (s, 1H), 7.09-7.45 (m, 4H), 11.36-12.00 (broad band, 4H); ^{13}C-nmr (δ, ppm) (d_6-DMSO) 18.02, 32.32, 100.88, 108.74, 126.04, 127.13, 129.40, 130.00, 132.38, 138.55, 143.63, 165.23, 166.38. Anal. Calcd for $C_{19}H_{17}ClN_2O_4$: C, 61.21; H, 4.59; N, 7.51. Found: C, 60.93; H, 4,64; N, 7.25.

3-Chlorophenylbis(4-hydroxy-6-methyl-2-oxo-2H-pyrid-3-yl)methane, 4b: mp > 300ºC; ir ($\bar{\nu}$, cm^{-1}) (KBr) 3350-2600, 1632, 1455, 1398, 1285, 913, 821 ; ^{1}H-nmr (δ, ppm) (d_6-DMSO) 2.18 (s, 6H), 5.92 (apparent s, 3H), 6.90-7.29 (m, 4H), 11.67 (broad s, 2H), 12.16 (broad band, 2H); ^{13}C-nmr (δ, ppm) (d_6-DMSO) 18.18, 33.67, 101.77, 108.96, 124.63, 125.78, 129.41, 132.66, 142.05, 144.37, 165.64, 166.60. Anal. Calcd for $C_{19}H_{17}ClN_2O_4$: C, 61.21; H, 4.59; N, 7.51. Found: C, 61.01; H, 4.55; N, 7.26.

Bis(4-hydroxy-6-methyl-2-oxo-2H-pyrid-3-yl)(2-nitrophenyl)methane, 4d from 3.
A mixture of 2-nitrobenzaldehyde (1.567 g, 10.38 mmol), triacetic acid lactone (2.615 g, 20.76 mmol), 25% NH_4OH (10ml) and ethanol (70 ml) was heated in a sealed tube at 100-110ºC for 26 h. The formed solid was filtered and dried (1.768 g, 4.61 mmol, 44% yield of 4d): mp > 300ºC; ir ($\bar{\nu}$, cm^{-1}) (KBr) 3600-3200, 3100-2850, 1632, 1525, 1454, 1398, 1356, 1328, 1257; ^{1}H-nmr (δ, ppm) (d_6-DMSO) 2.14 (s, 6H), 5.83 (s, 2H), 6.45 (s, 1H), 7.22-7.65 (m, 4H), 11.54 (broad s, 2H), 11.81 (broad band, 2H); ^{13}C-nmr (δ, ppm) (d_6-DMSO) 18.06, 30.92, 101.16, 108.00, 123.52, 126.81, 129.43, 131.19, 133.02, 144.30, 149.57, 165.18, 166.75. Anal. Calcd for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.62; H, 4.44; N, 10.76.

Compounds 4a (45%), 4b (14%) and 4e (11%) were also prepared by the same procedure.

4-Bromo-6-methyl-2H-pyran-2-one, 11.
A solution of phosphorus tribromide (43.67 g, 161.34 mmol) in anhydrous diethyl ether (88 ml) was added dropwise to cooled and mechanically stirred dimethylformamide (130 ml). A solution of triacetic acid lactone (5.044 g, 40.00 mmol) in dimethylformamide (88 ml) was then added and the mixture heated at 60ºC for 20 h. Water (200 ml) was poured into the cold mixture and extractions with diethyl ether (6 x 600 ml) were made. The organic phase was washed with water (3 x 300 ml) and dried with anhydrous sodium sulphate. The solvent was evaporated to afford a brown crystalline solid (6.097 g, 32.27 mmol, 81 % yield of 11), which was purified by sublimation (65ºC/1 mm Hg) yielding a white crystalline solid of mp 73-74ºC: ir ($\bar{\nu}$, cm^{-1}) (KBr) 1739, 1640, 1561, 1449, 1401, 1321, 1265, 1209, 1139, 1025, 947, 858 ; ^{1}H-nmr (δ, ppm) ($CDCl_3$) 2.27 (s, 3H), 6.18 (broad s, 1H), 6.45 (broad s, 1H); ^{13}C-nmr (δ, ppm) ($CDCl_3$) 19.44, 108.13, 114.51, 140.81, 160.21, 161.99; ms (m/z, relative intensity) 190 (5), 188 (M, 5), 43 (100). Anal. Calcd for $C_6H_5BrO_2$: C, 38.13; H, 2.66. Found: C, 38.05; H, 2.55.

4-Azido-6-methyl-2H-pyran-2-one, 13.
A mixture of 11 (3.780 g, 20.00 mmol), sodium azide (1.950 g, 30.00 mmol) and dimethylformamide (75 ml) was magnetically stirred at room temperature for one hour. The mixture was poured into ice-water (200 ml), stirred for 10 min and extracted with diethyl ether (6 x 100 ml). The organic phase was washed with water (3 x 100 ml), dried with anhydrous sodium sulphate and the solvent evaporated to afford 13 (2.514 g, 16.65 mmol, 83% yield): mp 88ºC; ir ($\bar{\nu}$, cm^{-1}) (KBr) 2118, 1737, 1640, 1560, 1449, 1401, 1320, 1264,

1208, 1138, 1024, 946, 843, 718; ^{1}H-nmr (δ, ppm) ($CDCl_3$) 2.25 (s, 3H), 5.75 (s, 2H); ^{13}C-nmr (δ, ppm) ($CDCl_3$) 19.74, 96.78, 98.87, 156.13, 162.19, 163.70.
The azido derivative 13 was also obtained from 4-chloro-6-methyl-2H-pyran-2-one by a similar procedure.

4-amino-6-methyl-2H-pyran-2-one, 10.
A strongly stirred mixture of 13 (0.453 g, 3.0 mmol), 10% Pd/C (0.045 g) and ethanol (50 ml) was treated with hydrogen at atmospheric pressure and room temperature, following the evolution of the reaction by thin layer chromatography. After about one hour, the catalyst was filtered off through celite and the filtrate was evaporated to afford 10 (0.374 g, 3.0 mmol, 100% yield): mp 159-162ºC (dichloromethane); ir (ν, cm^{-1}) (KBr) 3370, 3186, 1675, 1609, 1548, 1472, 1292; ^{1}H-nmr (δ, ppm) (d_6-DMSO) 2.06 (s, 3H), 4.78 (d, J= 2 Hz, 1H), 5.75 (m, 1H), 6.78 (broad band, 2H); ^{13}C-nmr (δ, ppm) (d_6-DMSO) 19.54, 80.47, 98.68, 159.84, 161.47, 163.69; ms (m/z, relative intensity) 176 (M, 0.2), 125 (74), 110 (61), 97 (98), 68 (28), 54 (100). Anal. Calcd for $C_6H_7NO_2$: C, 57.59; H, 5.64; N, 11.19. Found: C, 57.20; H, 5.74; N, 11.03.

1-(6-Methyl-2-oxo-2H-pyran-4-yl)imidazole, 14.
To a mixture of triacetic acid lactone (1.135 g, 9 mmol), imidazole (2.450 g, 36.0 mmol) and toluene (60 ml), a solution of triphenylphosphine (1.945 g, 18 mmol) in carbon tetrachloride (8.7 ml, ca 13.844 g, ca 90 mmol) was added. The mixture was refluxed for 20 h, two phases being formed. Ethanol (30 ml) was added and the solvents evaporated. The residue was chromatographed through silica gel, affording 14 by elution with chloroform/metanol (97:3) (0.670 g, 3.8 mmol, 42% yield): mp 183-185ºC (ethanol); ir (ν, cm^{-1}) (KBr) 3151, 3098, 1712, 1644, 1570, 1489, 1458, 1346, 1299, 1290, 1257, 1056, 1034, 875, 863, 813; ^{1}H-nmr (δ, ppm) ($CDCl_3$) 2.37 (s, 3H), 6.12 (d, J= 2 Hz, 1H), 6.25 (m, 1H), 7.30 (m, 2H), 8.00 (broad s, 1H); ^{13}C-nmr (δ, ppm) (d_6-DMSO) 19.60, 95.81, 97.72, 117.00, 131.02, 136.05, 148.62, 162.20, 164.16; ms (m/z, relative intensity) 177 (M+1, 1), 176 (M, 13), 148(17), 67(6), 43 (100). Anal. Calcd for $C_9H_8N_2O_2$: C, 61.36; H, 4.57; N, 15.90. Found: C, 61.29; H, 4.49; N, 15.60.

Bis(4-amino-6-methyl-2-oxo-2H-pyran-3-yl)(2-nitrophenyl)methane, 1d.
A mixture of 10 (1.000 g, 8 mmol), 2-nitrobenzaldehyde (0.604 g, 4 mmol), a catalytic amount of anhydrous p-toluenesulphonic acid and anhydrous toluene (60 ml) was refluxed for 16.5 h. The crystalline solid formed was filtered and identified as 1d (1.271 g, 3.32 mmol, 83% yield): mp > 300ºC (ethanol); ir (ν, cm^{-1}) (KBr) 3351, 3207, 1684, 1609, 1529, 1465, 1361; ^{1}H-nmr (δ, ppm) (d_6-DMSO) 2.12 (s, 6H), 5.87 (s, 2H), 5.96 (s, 1H), 7.00-8.00 (m, 8H); ^{13}C-nmr (δ, ppm), (d_6-DMSO) 19.08, 32.66, 99.64, 123.88, 126.95, 128.26, 131.61, 132.71, 149.55, 158.16, 159.99. Anal. Calcd for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.23; H, 4.70; N, 10.20. This compound retains ethanol strongly.
Compounds 1c and 1e were obtained by the same procedure.

Bis(4-amino-6-methyl-2-oxo-2H-pyran-3-yl)(4-chlorophenyl)methane, 1c: mp 280-284ºC(d) (ethanol); ir (ν, cm^{-1}) (KBr) 3336, 3168, 1683, 1608, 1545, 1524, 1464, 821; ^{1}H-nmr (δ, ppm) (d_6-DMSO) 2.12 (s, 6H), 5.37 (s, 1H), 5.93 (s, 2H), 6.92-7.32 (m, 8H); ^{13}C-nmr (δ, ppm) (d_6-DMSO) 19.19, 35.30, 91.83, 99.90, 127.80, 128.47, 129.84, 137.71, 158.21, 159.95, 165.38. Anal. Calcd for $C_{19}H_{17}ClN_2O_4$: C, 61.21; H, 4.59; N, 7.51. Found: C, 60.86; H, 4.76; N, 7.16.

Bis(4-amino-6-methyl-2-oxo-2H-pyran-3-yl)(3-nitrophenyl)methane, 1e: mp 252-255ºC(d); ir (ν, cm^{-1}) (KBr) 3369, 3210, 1683, 1608, 1549, 1524, 1466, 1346; ^{1}H-nmr (δ, ppm) (d_6-DMSO) 2.15 (s, 6H), 5.50 (s, 1H), 6.00 (s, 2H), 7.00-8.06 (m, 8H); ^{13}C-nmr (δ, ppm) (d_6-DMSO) 19.17, 35.62, 91.20, 99.88, 120.61, 121.03, 129.36, 133.81, 141.35, 147.84, 158.29, 160.19, 165.34. Anal. Calcd for $C_{19}H_{17}N_3O_6$: C, 59.53; H, 4.47; N, 10.96. Found: C, 59.45; H, 4.57; N, 10.57.

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