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CONVENIENT SYNTHESIS OF FUROPYRANOPYRANDIONE DERIVATIVES BY THE CAN-MEDIATED FURAN RING FORMATION

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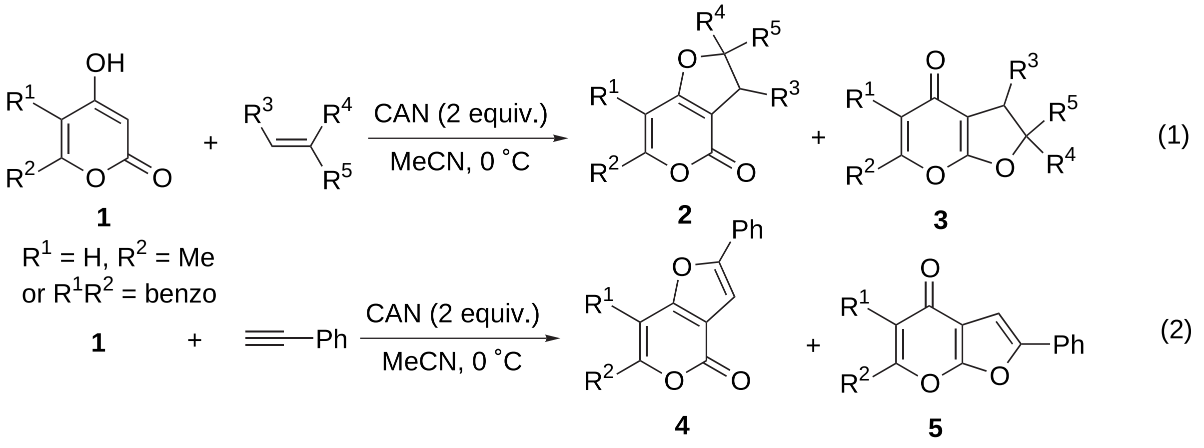
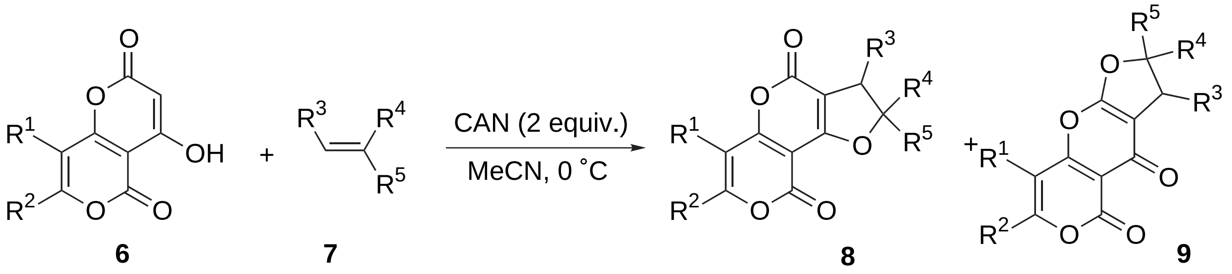
Abstract- 4*H*,9*H*-Furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (**8**) and (**10**) and 4*H*,5*H*-furo[2,3-*b*]pyrano[3,4-*e*]pyran-4,5-dione derivatives (**9**) were prepared in one step by treating 4-hydroxy-2*H*,5*H*-pyrano[4,3-*b*]pyran-2,5-diones (**6**) and alkenes (**7**) (or phenylacetylene) in acetonitrile with 2 equivalents of cerium(IV) ammonium nitrate (CAN).

We previously reported on the use of the CAN-mediated reaction for the synthesis of furopyranone derivatives (**2-5**) from 4-hydroxypyranones (**1**) and alkenes (or phenylacetylene) as shown in equations 1 and 2.[1d] During the course of our program to synthesize furan-fused aromatic[2] and heterocyclic compounds[1] we decided to examine the CAN-mediated reaction between 4-hydroxy-2*H*,5*H*-pyrano[4,3-*b*]pyran-2,5-diones (**6**) and alkenes (**7**) (or phenylacetylene) aiming at the development of a convenient method for preparing furopyranopyrandione derivatives.[3] In this paper, we wish to describe the results of our study which offer a simple and general route to furopyranopyrandione derivatives (**8–10**). To the best





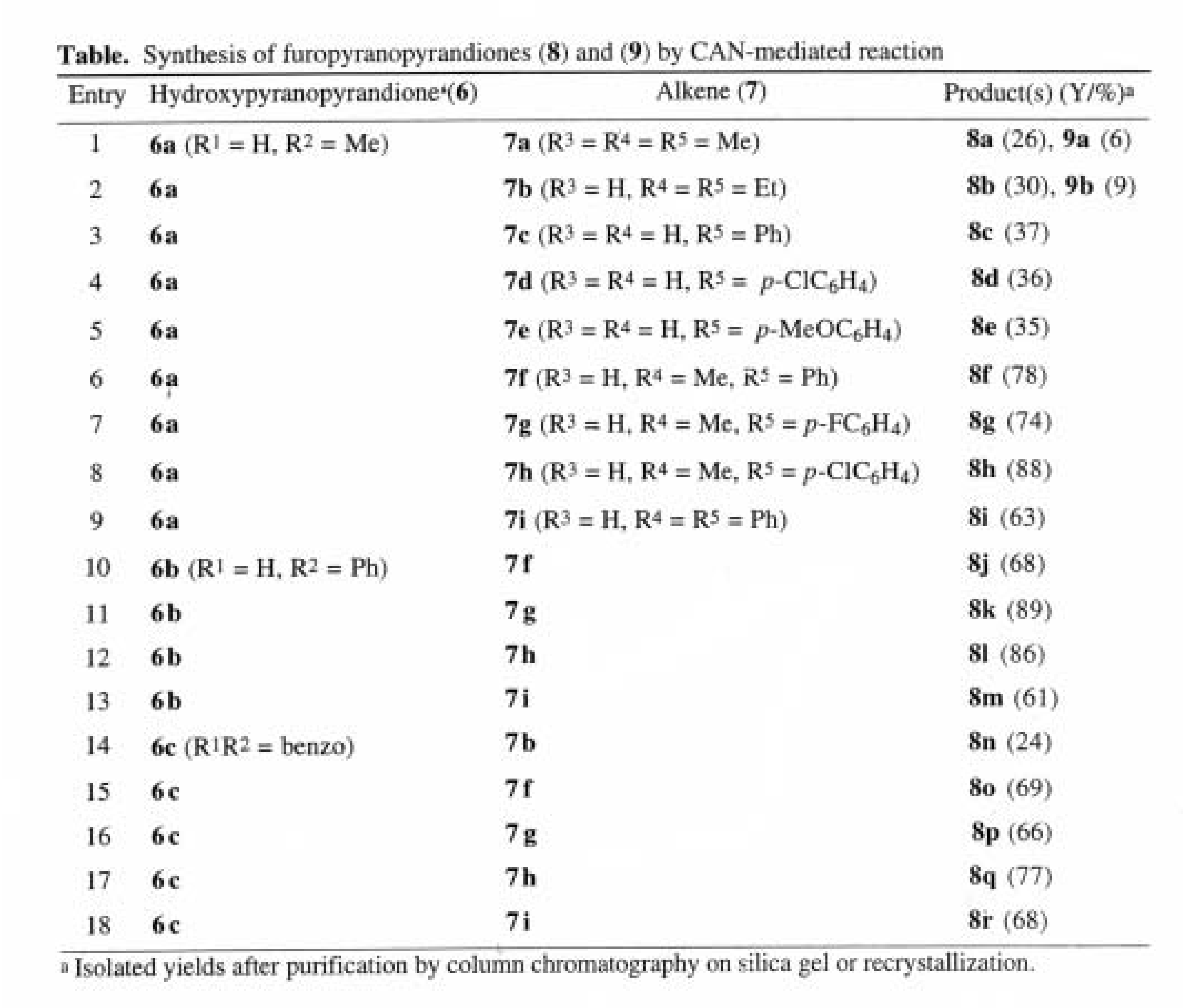
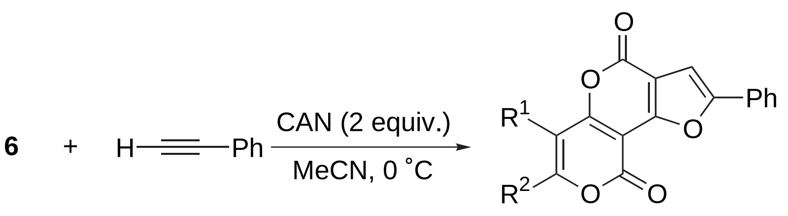


Table. Synthesis of furopyranopyrandiones (**8**) and (**9**) by CAN-mediated reaction

Entry	Hydroxypyranopyrandione[a] (**6**)	Alkene (**7**)	Product(s) (Y/%)[a]
1	**6a** (R^1 = H, R^2 = Me)	**7a** ($R^3 = R^4 = R^5$ = Me)	**8a** (26), **9a** (6)
2	**6a**	**7b** (R^3 = H, $R^4 = R^5$ = Et)	**8b** (30), **9b** (9)
3	**6a**	**7c** ($R^3 = R^4$ = H, R^5 = Ph)	**8c** (37)
4	**6a**	**7d** ($R^3 = R^4$ = H, R^5 = p-ClC_6H_4)	**8d** (36)
5	**6a**	**7e** ($R^3 = R^4$ = H, R^5 = p-$MeOC_6H_4$)	**8e** (35)
6	**6a**	**7f** (R^3 = H, R^4 = Me, R^5 = Ph)	**8f** (78)
7	**6a**	**7g** (R^3 = H, R^4 = Me, R^5 = p-FC_6H_4)	**8g** (74)
8	**6a**	**7h** (R^3 = H, R^4 = Me, R^5 = p-ClC_6H_4)	**8h** (88)
9	**6a**	**7i** (R^3 = H, $R^4 = R^5$ = Ph)	**8i** (63)
10	**6b** (R^1 = H, R^2 = Ph)	**7f**	**8j** (68)
11	**6b**	**7g**	**8k** (89)
12	**6b**	**7h**	**8l** (86)
13	**6b**	**7i**	**8m** (61)
14	**6c** (R^1R^2 = benzo)	**7b**	**8n** (24)
15	**6c**	**7f**	**8o** (69)
16	**6c**	**7g**	**8p** (66)
17	**6c**	**7h**	**8q** (77)
18	**6c**	**7i**	**8r** (68)

[a] Isolated yields after purification by column chromatography on silica gel or recrystallization.



10a R^1 = H, R^2 = Me 62%
10b R^1 = H, R^2 = Ph 55%
10c R^1R^2 = benzo 59%

Scheme 2.

of our knowledge, these skeletons are unknown in literature.

The general procedure for the preparation of furopyranopyrandione derivatives (**8–10**) involves addition of CAN (2 equiv.) to a stirred solution of the hydroxypyranopyrandiones (**6**) (1 equiv.) and alkenes (**7**) (3–10 equiv.) or phenylacetylene (1.2 equiv.) in acetonitrile at 0 ˚C (Schemes 1 and 2). After 0.5–1 h stirring the resulting mixture was worked up usually. After purification by chromatography on silica gel or recrystallization furopyranopyrandione derivatives (**8–10**) were obtained in the yields shown in the Table and Scheme 2.

As shown in the Table, 2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-diones (**8a** and **8b**) were produced along with the corresponding 2,3-dihydro-4*H*,5*H*-furo[2,3-*b*]pyrano[3,4-*e*]pyran-4,5-diones (**9a** and **9b**) only when 2-methyl-2-butene (**7a**) and 2-ethyl-1-butene (**7b**) were used (Entries 1 and 2), though the reaction of **6c** with **7b** gave only **8n** in low yield (Entry 14). These derivatives (**8**) and (**9**) could be easily separated by chromatography on silica gel, and their structure could clearly be distinguished by comparing their IR spectra and chromatographic behaviors. Thus, each of the IR spectra of **8a** and **8b** revealed absorption bands assignable to the two lactone carbonyls at around 1750 and 1730 cm^{-1}, while those of **9a** and **9b** each revealed an absorption band assignable to the lactone carbonyl at around 1760 cm^{-1} and that assignable to the ketone carbonyl at around 1670 cm^{-1}. Compounds (**8**) were much more mobile on silica gel (R_f = *ca.* 0.8, AcOEt) than compounds (**9**) (R_f = *ca.* 0.3, AcOEt). Similar chromatographic behaviors were observed between compounds (**2**) and (**3**) previously.[1d] In general higher yields are obtained by using α-methylstyrene and its derivative and diphenylethylene (Entries 6–13 and 15-18). This may be attributable to the higher stability of the radical intermediates arising from the attack of the first generated diketoalkyl radicals to these alkenes.

When the reaction were conducted using phenylacetylene in stead of alkenes (**7**), 2-phenyl-4*H*,9*H* -furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-diones (**10**) were obtained in fair yields, as shown in Scheme 3. In each case, the corresponding linear-type furopyraopyrandione could not be detected.

In conclusion, the procedure reported here provides a convenient and mild preparation of furopyranopyrandione derivatives. This is the first example of the construction of these novel heterocyclic skeletons. The present method may find some value in heterocycle synthesis, because the reaction procedure is simple and the starting materials are readily available.

EXPERIMENTAL

All melting points were obtained on a Laboratory Devices MEL-TEMP II melting apparatus and are uncorrected. IR spectra were determined with a Perkin-Elmer 1600 Series FT IR spectrophotometer as KBr disk. The ^{1}H NMR spectra were determined in CDCl$_3$ using TMS as an internal reference with a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz. *J* values are given in Hz. The ^{13}C NMR spectrum was determined in CDCl$_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low-resolution MS analyses were performed on a JEOL AUTOMASS 20 spectrometer (Center for Joint Research and Development, this University). TLC was carried out on a Merck Kieselgel 60 PF_{254}. All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

Starting Materials. 4-Hydroxy-7-methyl-2*H*,5*H*-pyrano[4,3-*b*]pyran-2,5-dione (**6a**) was prepared according to the literature procedure.[4] 4-Hydroxy-7-phenyl-2*H*,5*H*-pyrano[4,3-*b*]pyran-2,5-dione (**6b**) and 4-hydroxy-2*H*,5*H*-pyrano[3,2-*c*]benzo[1]pyran-2,5-dione (**6c**)[5] were prepared from 4-hydroxy-6-methyl-2*H*-pyran-2-one[6] and 4-hydroxy-2*H*-benzo[1]pyran-2-one, respectively, according to the procedure for the preparation of **6a**.[4] **6b:** mp 241–244 °C (decomp) (hexane–$CHCl_3$) ; $\square_{max}$/cm^{-1} 3450, 1737, 1689, 1637; $\square_H$ 5.64 (1H. s), 6.90 (1H, s), 7.5–8.0 (m, 5H), 10.51 (1H, s). Anal. Calcd for $C_{14}H_8O_5$: C, 65.63; H, 3.15. Found: C, 65.80; H, 3.12. **6c:** mp 242–244 °C (decomp) ($CHCl_3$) [lit.,[5] 241–243 °C (decomp)]; $\square_{max}$/cm^{-1} 3250, 1741, 1700; $\square_H$ 5.73 (1H, s), 7.45–7.55 (2H, m), 7.79 (1H, td, *J* 7.9, 1.6), 8.17 (1H, dd, *J* 7.9, 1.6), 10.89 (1H, s). All other chemicals used in this study were commercially available.

General Procedure for the CAN-Mediated Reaction of Hydroxypyranopyrandiones (6a–c) with Alkenes (7a–i) or Phenylacetylene. To a stirred solution of **6** (1 mmol) and the alkenes (**7**) or phenylacetylene [10 mmol for **7a** and **7b**, 3 mmol for **7c-h** and phenylacetylene, and 1.2 mmol for **7i**] in acetonitrile (40 mL) at 0 °C was added CAN (1.1 g, 2.0 mmol) in portions. The cerium(IV) compound dissolved gradually in the solvent (*ca*. 30 min). Stirring was continued until TLC analysis on silica gel showed complete consumption of the starting materials (0.5–1 h), after which saturated aqueous NH_4Cl (30 mL) was added. Most of the organic solvent was evaporated, and the mixture was extracted with CH_2Cl_2 three times (20 mL each). The combined extracts were washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was subjected to column chromatography on SiO_2 (EtOAc–hexane) or recrystallization to give the cycloaddition product(s) as pale yellow solids.

2,2,3,7-Tetramethyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8a): mp 190–192 °C (hexane–Et_2O); $\square_{max}$/cm^{-1} 1749, 1727, 1640; $\square_H$ 1.25 (3H, d, *J* 6.9), 1.50 (3H, s), 1.54 (3H, s), 2.33 (3H, br s), 3.10 (1H, q, *J* 6.9), 6.18 (1H, d, *J* 1.0); MS *m/z* 262 (M^+, 48), 247 (100). Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 63.96; H, 5.25.

2,2,3,7-Tetramethyl-2,3-dihydro-4*H*,5*H*-furo[2,3-*b*]pyrano[3,4-*e*]pyran-4,5-dione (9a): mp 131–134 °C (hexane–Et_2O–CH_2Cl_2); $\square_{max}$/cm^{-1} 1758, 1669, 1621; $\square_H$ 1.25 (3H, d, *J* 6.9), 1.46 (3H, s), 1.53 (3H, s), 2.33 (3H, s), 3.25 (1H, q, *J* 6.9), 6.12 (1H, s); MS *m/z* 262 (M^+, 59), 136 (100). Anal. Calcd for $C_{14}H_{14}O_5$: C, 64.12; H, 5.38. Found: C, 64.12; H, 5.29.

2,2-Diethyl-7-methyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8b): mp 170–171 °C (hexane–Et_2O); $\square_{max}$/cm^{-1} 1756, 1734, 1639, 1602; $\square_H$ 0.97 (6H, t, *J* 7.3), 1.85 (4H, q, *J*

7.3), 2.34 (3H, s), 2.83 (2H, s), 6.18 (1H, s); □$_{C}$ 7.58, 20.57, 31.72, 33.36, 94.74, 99.18, 99.78, 100.29, 156.85, 158.43, 166.02, 166.84, 167.91; MS *m/z* 276 (M^{+}, 41), 207 (100). Anal. Calcd for $C_{15}H_{16}O_{5}$: C, 65.21; H, 5.84. Found: C, 65.46; H, 5.84.

2,2-Diethyl-7-methyl-2,3-dihydro-4*H*,5*H*-furo[2,3-*b*]pyrano[3,4-*e*]pyran-4,5-dione (9b): mp 176–179 °C (hexane–Et$_{2}$O); □$_{max}$/cm^{-1} 1759, 1666, 1623; □H 0.97 (6H, t, *J* 7.3), 1.82 (4H, q, *J* 7.3), 2.32 (3H, s), 2.91 (2H, s), 6.11 (1H, s); □C 7.33, 20.47, 31.33, 33.49, 98.04, 98.45, 105.20, 157.86, 165.16, 165.86, 165.95, 172.24; MS *m/z* 276 (M^{+}, 41), 207 (100). Anal. Calcd for $C_{15}H_{16}O_{5}$: C, 65.21; H, 5.84. Found: C, 65.36; H, 5.76.

7-Methyl-2-phenyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8c): mp 243–244 °C (CHCl$_{3}$-hexane); □$_{max}$/cm^{-1} 1750, 1728, 1644, 1604; □$_{H}$ 2.36 (3H, s), 3.12 (1H, dd, *J* 15.5, 7.9), 3.54 (1H, dd, *J* 15.5, 10.6), 6.11 (1H, dd, *J* 10.6, 7.9), 6.23 (1H, s), 7.3–7.45 (5H, m); MS *m/z* 296 (M^{+}, 100). Anal. Calcd for $C_{17}H_{12}O_{5}$: C, 68.92; H, 4.08. Found: C, 68.73; H, 4.09.

2-(4-Chlorophenyl)-7-methyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8d): mp 259–261 °C (hexane-EtOAc); □$_{max}$/cm^{-1} 1731, 1654, 1642, 1605; □$_{H}$ 2.37 (3H, s), 3.07 (1H, dd, *J* 15.2, 8.9), 3.59 (1H, dd, *J* 15.2, 10.5), 6.08 (1H, dd, *J* 10.5, 8.9), 6.24 (1H, s), 7.32 (2H, d, *J* 8.6), 7.37 (2H, d, *J* 8.6); MS *m/z* 330 (M^{+}, 100). Anal. Calcd for $C_{17}H_{11}O_{5}Cl$: C, 61.74; H, 3.35. Found: C, 61.54; H, 3.33.

2-(4-Methoxyphenyl)-7-methyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9 dione (8e): mp 205–206 °C (hexane-EtOAc); □$_{max}$/cm^{-1} 1732, 1640, 1604; □$_{H}$ 2.35 (3H, d, *J* 0.7), 3.12 (1H, dd, *J* 15.2, 7.9), 3.49 (1H, dd, *J* 15.2, 10.5), 3.81 (3H, s), 6.06 (1H, dd, *J* 10.5, 7.9), 6.23 (1H, br s), 6.91 (2H, d, *J* 8.6), 7.32 (2H, d, *J* 8.6); MS *m/z* 326 (M^{+}, 100). Anal. Calcd for $C_{18}H_{14}O_{6}$: C, 66.26; H, 4.32. Found: C, 66.36; H, 4.48.

2,7-Dimethyl-2-phenyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8f): mp 216–217 °C (CHCl$_{3}$–hexane); □$_{max}$/cm^{-1} 1761, 1737, 1643, 1599; □$_{H}$ 1.90 (3H, s), 2.36 (3H, s), 3.24 (1H, d, *J* 14.9), 3.33 (1H, d, *J* 14.9), 6.21 (1H, s), 7.25–7.5 (5H, m); MS *m/z* 310 (M^{+}, 100). Anal. Calcd for $C_{18}H_{14}O_{5}$: C, 69.67; H, 4.55. Found: C, 69.91; H, 4.54.

2-(4-Fluorophenyl)-2,7-dimethyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8g): mp 176–178 °C (hexane-EtOAc); □$_{max}$/cm^{-1} 1720, 1640, 1605; □$_{H}$ 1.88 (3H, s), 2.37 (3H, s), 3.24 (1H, d, *J* 15.2), 3.27 (1H, d, *J* 15.2), 6.21 (1H, s), 7.06 (2H, dd, *J* 8.9, 8.6), 7.42 (2H, dd, *J* = 8.6, 4.9); MS *m/z* 328 (M^{+}, 100). Anal. Calcd for $C_{18}H_{13}O_{5}F$: C, 65.85; H, 3.99. Found: C, 65.64; H, 3.99.

2-(4-Chlorophenyl)-2,7-dimethyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8h): mp 220–222 °C (hexane-EtOAc); □$_{max}$/cm^{-1} 1736, 1644, 1606; □$_{H}$ 1.87 (3H, s), 2.37

(3H, s), 3.25 (1H, d, *J* 15.2), 3.28 (1H, d, *J* 15.2), 6.22 (1H, s), 7.35 (2H, d, *J* 8.9), 7.38 (2H, d, *J* 8.9); MS *m/z* 344 (M$^+$, 48), 207 (100). Anal. Calcd for $C_{18}H_{13}O_5Cl$: C, 62.71; H, 3.80. Found: C, 62.41; H, 3.64.

7-Methyl-2,2-diphenyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8i): mp 185–187 °C (hexane–EtOAc); □$_{max}$/cm^{-1} 1723, 1640, 1609; □$_H$ 2.35 (3H, s), 3.80 (2H, s), 6.20 (1H, s), 7.25–7.5 (10H, m); MS *m/z* 372 (M$^+$, 100). Amal. Calcd for $C_{23}H_{16}O_5$: C, 74.19; H, 4.33. Found: C, 74.09; H, 4.19.

2-Methyl-2,7-diphenyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8j): mp 181–182 °C (hexane–EtOAc); □$_{max}$/cm^{-1} 1722, 1627, 1600; □$_H$ 1.92 (3H, s), 3.28 (1H, d, *J* 14.8), 3.36 (1H, d, *J* 14.8), 6.83 (1H, s), 7.25–7.6 (8H, m), 7.90 (2H, dd, *J* 7.9, 2.0); MS *m/z* 372 (M$^+$, 100). Anal. Calcd for $C_{23}H_{16}O_5$: C, 74.19; H, 4.33. Found: C, 74.20; H, 4.22.

2-(4-Fluorophenyl)-2-methyl-7-phenyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8k): mp 183–184 °C (hexane-EtOAc); □$_{max}$/cm^{-1} 1724, 1628, 1603; □$_H$ 1.91 (3H, s), 3.28 (1H, d, *J* 15.2), 3.32 (1H, d, *J* 15.2), 6.83 (1H, s), 7.07 (2H, dd, *J* 8.9, 8.6), 7.45 (2H, dd, *J* 8.6, 5.3), 7.5–7.6 (3H, m), 7.90 (2H, dd, *J* 7.6, 2.0); MS *m/z* 390 (M$^+$, 100). Anal. Calcd for $C_{23}H_{15}O_5F$: C, 70.77; H, 3.87. Found: C, 70.52; H, 3.61.

2-(4-Chlorophenyl)-2-methyl-7-phenyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8l): mp 220–222 °C (hexane-EtOAc); □$_{max}$/cm^{-1} 1732, 1630, 1602; □$_H$ 1.90 (3H, s), 3.28 (1H, d, *J* 15.1), 3.30 (1H, d, *J* 15.1), 6.83 (1H, s), 7.3–7.6 (7H, m), 7.90 (2H, dd, *J* 7.6, 2.0); MS *m/z* 406 (M$^+$, 100). Anal. Calcd for $C_{23}H_{15}O_5Cl$: C, 67.90; H, 3.72. Found: C, 67.64; H, 3.70.

2,2,7-Triphenyl-2,3-dihydro-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (8m): mp 239–241 (decomp); □$_{max}$/cm^{-1} 1724, 1629, 1603; □$_H$ 3.83 (2H, s), 6.82 (1H, s), 7.25–7.4 (6H, m), 7.45–7.6 (7H, m), 7.89 (2H, dd, *J* 7.6, 2.0); MS *m/z* 434 (M$^+$, 100). Anal. Calcd for $C_{28}H_{18}O_5$: C, 77.41; H, 4.18. Found: C, 77.35; H, 4.19.

2,2-Diethyl-2,3-dihydro-4*H*,11*H*-furo[3,2-*c*]pyrano[3,4-*e*]benzo[1]pyran-4,11-dione (8n): mp 194–196 °C (hexane-EtOAc); □$_{max}$/cm^{-1} 1745, 1627; □$_H$ 1.00 (6H, t, *J* 7.3), 1.8–2.0 (4H, m), 2.90 (3H, s), 7.35–7.45 (2H, m), 7.68 (1H, t, *J* 8.2), 8.12 (1H, dd, *J* 8.2, 1.7); MS *m/z* 312 (M$^+$, 53), 243 (100). Anal. Calcd for $C_{18}H_{16}O_5$: C, 69.22; H, 5.16. Found: C, 69.44; H, 5.04.

2-Methyl-2-phenyl-2,3-dihydro-4*H*,11*H*-furo[3,2-*c*]pyrano[3,4-*e*]benzo[1]pyran-4,11-dione (8o): mp 192–194 °C (hexane-EtOAc); □$_{max}$/cm^{-1} 1737, 1627, 1609; □$_H$ 1.93 (3H, s), 3.31 (1H, d, *J* 15.0), 3.40 (1H, d, *J* 15.0), 7.25–7.55 (7H, m), 7.69 (1H, td, *J* 8.2, 1.6), 8.12 (1H, dd, *J* 8.2, 1.6); MS *m/z* 346 (M$^+$, 31), 184 (100). Anal. Calcd for $C_{21}H_{14}O_5$: C, 72.83; H, 4.07. Found: C, 72.89; H, 4.13.

2-(4-Fluorophenyl)-2-methyl-2,3-dihydro-4*H*,11*H*-furo[3,2-*c*]pyrano[3,4-*e*]benzo[1]pyran-4,11-dione (8p): mp 200–201 °C (hexane-EtOAc); □$_{max}$/cm^{-1} 1732, 1627; □$_{H}$ 1.92 (3H, s), 3.31 (1H, d, *J* 15.2), 3.37 (1H, d, *J* 15.2), 7.08 (2H, dd, *J* 8.9, 8.6), 7.35–7.5 (4H, m), 7.70 (1H, td, *J* 8.2, 1.3), 8.13 (1H, dd, *J* 8.2, 1.3); MS *m/z* 364 (M$^+$, 100). Anal. Calcd for $C_{21}H_{13}O_5F$: C, 69.23; H, 3.60. Found: C, 69.30; H, 3.58.

2-(4-Chlorophenyl)-2-methyl-2,3-dihydro-4*H*,11*H*-furo[3,2-*c*]pyrano[3,4-*e*]benzo[1]pyran-4,11-dione (8q): mp 230–231 °C (hexane-EtOAc); □$_{max}$/cm^{-1} 1739, 1628; □$_{H}$ 1.92 (3H, s), 3.32 (1H, d, *J* 15.2), 3.35 (1H, d, *J* 15.2), 7.3–7.45 (6H, m), 7.70 (1H, td, *J* 8.2, 1.3), 8.12 (1H, dd, *J* 8.2, 1.3); MS *m/z* 380 (M$^+$, 74), 243 (100). Anal. Calcd for $C_{21}H_{13}O_5Cl$: C, 66.24; H, 3.44. Found: C, 65.98; H, 3.66.

2,2-Diphenyl-2,3-dihydro-4*H*,11*H*-furo[3,2-*c*]pyrano[3,4-*e*]benzo[1]pyran-4,11-dione (8r): mp 225–227 °C (hexane-EtOAc); □$_{max}$/cm^{-1} 1728, 1654, 1629; □$_{H}$ 3.87 (2H, s), 7.3–7.55 (12H, m), 7.69 (1H, td, *J* 7.9, 2.0), 8.11 (1H, dd, *J* 7.9, 2.0); MS *m/z* 408 (M$^+$, 88), 246 (100). Anal. Calcd for $C_{26}H_{16}O_5$: C, 76.46; H, 3.95. Found: C, 76.57; H, 4.04.

7-Methyl-2-phenyl-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (10a): mp 180 °C (decomp) (AcOEt–hexane); □$_{max}$/cm^{-1} 1772, 1732, 1634; □$_{H}$ 2.41 (3H, s), 6.33 (1H, s), 7.13 (1H, s), 7.35–7.55 (3H, m), 7.85 (2H, d, *J* 8.6); □H 20.61, 95.60, 99.26, 101.61, 111.47, 124.82, 128.37, 129.00, 129.41, 155.54, 156.17, 156.86, 157.52, 163.39, 164.38; MS *m/z* 294 (M$^+$, 100). Anal. Calcd for $C_{17}H_{10}O_5$: C, 69.39; H, 3.43. Found: C, 69.68; H, 3.70.

2,7-Diphenyl-4*H*,9*H*-furo[3,2-*c*]pyrano[3,4-*e*]pyran-4,9-dione (10b): mp 205 °C (decomp) (AcOEt-hexane); □$_{max}$/cm^{-1} 1760, 1728, 1614; □$_{H}$ 6.88 (1H, s), 7.09 (1H, s), 7.3–7.5 (6H, m), 7.75–7.9 (4H, m); MS *m/z* 356 (M$^+$, 100). Anal. Calcd for $C_{22}H_{12}O_5$: C, 74.16; H, 3.39. Found: C, 74.37; H, 3.39.

2-Phenyl-4*H*,11*H*-furo[3,2-*c*]pyrano[3,4-*e*]benzo[1]pyran-4,11-dione (10c): mp 295 °C (decomp) (AcOEt-hexane); □$_{max}$/cm^{-1} 1757, 1728, 1666, 1629, 1612; □$_{H}$ 7.19 (1H, s), 7.35–7.55 (5H, m), 7.6–7.8 (2H, m), 7.88 (1H, dd, *J* 7.9, 1.6), 7.75–7.9 (1H, m); MS *m/z* 330 (M$^+$, 100). Anal. Calcd for $C_{20}H_{10}O_5$: C, 72.73; H, 3.05. Found: C, 72.78; H, 3.15.

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