

CAN-MEDIATED FORMATION OF FUROPYRANONES AND FUROQUINOLINONES

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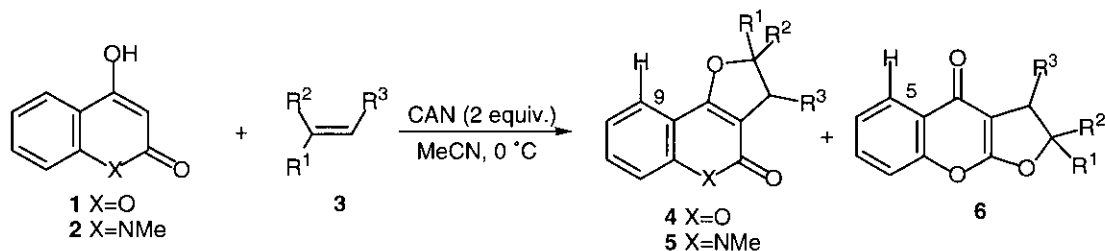
Abstract- The reaction of 4-hydroxy-2*H*-pyran-2-one derivatives (**1**), (**11**), and (**17**) with a range of alkenes or phenylacetylene in acetonitrile containing cerium(IV) ammonium nitrate (CAN) afforded the corresponding furo[3,2-*c*]pyranone (**4**, **8**, **13**, **15**, and **18**) and/or furo[2,3-*b*]pyranone derivatives (**6**, **10**, **14**, **16**, and **19**). Similar treatment of 4-hydroxy-1-methylquinolin-2(1*H*)-one (**2**) with alkenes or phenylacetylene in the presence of CAN gave furo[3,2-*c*]quinolin-4(5*H*)-one derivatives (**5**) and (**9**).

As part of a program aimed at developing new methods for the preparation of furan-fused aromatic¹ and heterocyclic compounds,² we recently reported^{1a} on a one-step construction of benzofurandione and naphthofurandione derivatives by a [3+2] type cycloaddition of 2-hydroxy-1,4-benzoquinones and 2-hydroxy-1,4-naphthoquinones with alkenes (or phenylacetylene) mediated by cerium(IV) ammonium nitrate (CAN).³ We were interested in investigating the possibility of extending this CAN-mediated cycloaddition to enolizable heterocyclic β -dicarbonyl compounds.⁴ We first examined the reactions using 4-hydroxy-2*H*-benzo-1-pyran-2-one (4-hydroxycoumarin) (**1**)⁵ and 4-hydroxy-1-methylquinolin-2(1*H*)-one (**2**).^{5,6} We found that the reaction of **1** with alkenes (**3**) or phenylacetylene (**7**) in the presence of CAN afforded the corresponding 4*H*-furo[3,2-*c*]benzo[1]pyran-4-one (**4** or **8**) and/or 4*H*-furo[2,3-*b*]benzo[1]pyran-4-one derivatives (**6** or **10**) and that the reaction of **2** with **3** or **7** gave furo[3,2-*c*]quinolin-4(5*H*)-one derivatives (**5**) or (**9**).⁷ In further investigation we found that 4-hydroxy-6-methyl-2*H*-pyran-2-one (**11**)⁵ or 1-hydroxy-3*H*-naphtho[2,1-*b*]pyran-3-one (**17**) gave 4*H*-furo[3,2-*c*]pyran-4-one (**13** and **15**) and(or) 4*H*-furo[2,3-*b*]pyran-4-one derivatives (**14** and **16**), or 4*H*-naphtho[2,1-*b*]furo[2,3-*d*]pyran-4-one (**18**) and 1*H*-naphtho[2,1-*b*]furo[3,2-*e*]pyran-1*H*-one derivatives (**19**), respectively.^{8,9} A number of efficient procedures for achieving the construction of above-mentioned furopyranone¹⁰ and furoquinolinone¹¹

derivatives have been reported. Most of them, however, are somewhat cumbersome or of limited substrate scope. The synthesis of 2,3-dihydro-4*H*-furo[3,2-*c*]benzo[1]pyran-4-one and 2,3-dihydro-4*H*-furo[2,3-*b*]benzo[1]pyran-4-one derivatives *via* a [2+2] photocycloaddition- β -scission sequence starting from 4-hydroxy-2*H*-benzo[1]pyran-2-one and alkenes has been reported.^{2a} Similar preparation of 2,3-dihydrofuro[3,2-*c*]quinolin-4(5*H*)-one derivatives along with 2,3-dihydrofuro[2,3-*b*]quinolin-4(5*H*)-one derivatives starting from 4-hydroxyquinolin-2(1*H*)-one^{2b} and a one-pot preparation of 2,3-dihydrofuro[3,2-*c*]quinolin-4(5*H*)-one derivatives by the photoinduced cycloaddition between methoxylated 4-hydroxyquinolin-2(1*H*)-ones and alkenes^{2c} have also been recorded. However, availability of a more convenient methods for their general preparation would seem to be attractive¹² because of their importance in medicinal and natural products chemistry.¹³

We began our study by examining reactions of commercially available 4-hydroxycoumarin (**1**) with alkenes (**3**) at 0 °C in acetonitrile containing two molar amounts of CAN. In general, **1** reacted smoothly with **3** to give 2,3-dihydro-4*H*-furo[3,2-*c*][1]benzopyran-4-ones (**4**) and/or 2,3-dihydro-4*H*-furo[2,3-*b*]benzo[1]pyran-4-ones (**6**) (Scheme 1). The results using series of alkenes were summarized in Table 1. It should be noted that the reactions of **1** with vinyl benzoate (**3e**) and α -methylstyrene (**3f**) produced exclusively the furo[3,2-*c*]benzopyranone derivatives (**4e**) and (**4f**), respectively, as the sole isolated product; no more than a trace amount of the corresponding furo[2,3-*b*]benzopyranone derivatives was obtained in each of these reactions (Entries 5 and 6), while formation of both the furopyranone derivatives (**4**) and (**6**) was observed using other alkenes (**3a-d**) (Entries 1-4). These derivatives could be easily separated from each other by preparative TLC on silica gel, and their structures could clearly be distinguished by comparing their ¹H NMR and IR spectra.¹⁴ Thus, each of the ¹H NMR spectra of **4** exhibited the 9-H as a doublet (or doublet of doublet) at around δ 7.7. In contrast, those of **6** each showed a signal (d or dd) at around δ 8.25 assignable to the 5-H. This downfield shifts can be explained by the deshielding by the carbonyl group. Moreover, each of the IR spectra of **4** revealed a strong absorption band assignable to the lactone carbonyl at around 1720 cm⁻¹, while those of **6** each revealed that assignable to the ketone carbonyl at around 1635 cm⁻¹. The structure of **4b** was confirmed by comparing its ¹H NMR spectrum with that of the authentic sample previously prepared by us, which was determined by an X-Ray crystallographic analysis.^{2a} The *cis*-junction between the cyclopentane and furan rings of **6b** was determined on the basis of an NOE study; irradiation of the signal due to 9b-H (δ 3.99) resulted in an enhancement (11%) of the signal due to 3a-H (δ 5.45). Vinyl carboxylates (**3d** and **3e**) proved to be less effective; the yields of the corresponding adducts were rather lower than those of the other products (Entries 4 and 5). The reaction of **1** with a terminal alkene (such as 1-hexene) or a vinyl ether (such as 2-methoxypropene) resulted only in the intractable mixtures of products and failed to give any product having the furopyranone structure.

Reactions of 4-hydroxy-1-methylquinolin-2(1*H*)-one (**2**), a nitrogen analogue of **1**, with alkenes mediated



Scheme 1.

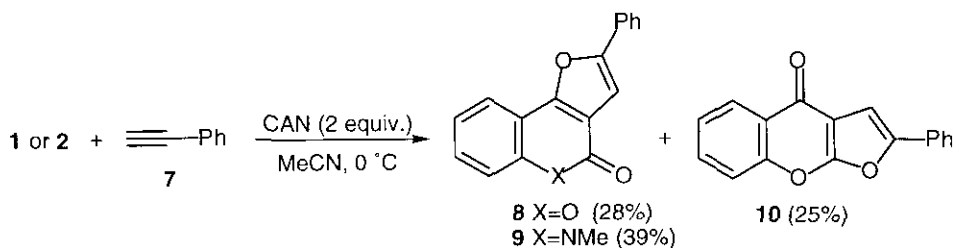
Table 1. Formation of furobenzopyranones (4) and (6), and furoquinolinones (5)

Entry	1 or 2	Alkene (3)	Product (Yield/%) ^a
1	1	3a (R ¹ = R ² = R ³ = Me)	4a (25), 6a (45)
2	1	3b [R ¹ = H, R ² R ³ = (CH ₂) ₃]	4b (31), 6b (31)
3	1	3c (R ¹ = CH ₂ OAc, R ² = Me, R ³ = H)	4c (33), 6c (30)
4	1	3d (R ¹ = OAc, R ² = R ³ = H)	4d (17), 6d (8)
5	1	3e (R ¹ = OBz, R ² = R ³ = H)	4e (15)
6	1	3f (R ¹ = Ph, R ² = Me, R ³ = H)	4f (62)
7	2	3a	5a (37)
8	2	3c	5c (24)
9	2	3g (R ¹ = OAc, R ² = Me, R ³ = H)	5g (21)

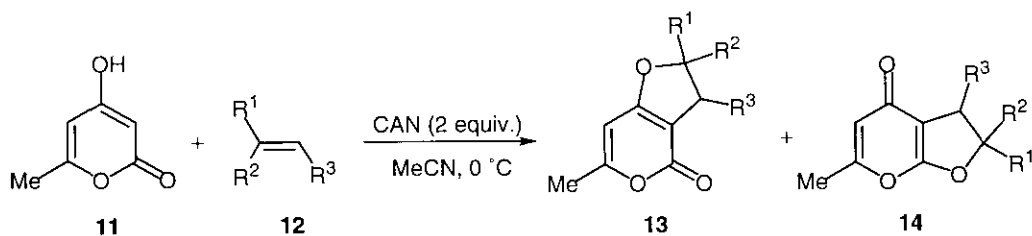
^a Yields are based on **1** or **2** and isolated products after preparative TLC on silica gel.

by CAN under the same conditions as described above gave complicated mixtures of products, purification of which by preparative TLC on silica gel afforded the corresponding cycloaddition products, 2,3-dihydrofuro[3,2-*c*]quinolin-4(5*H*)-ones (**5**), in low to moderate yields. These results are also listed in Table 1 (Entries 7–9). In contrast to the reactions of **1**, the formation of the corresponding linear-type products, 2,3-dihydrofuro[2,3-*b*]quinolin-4(9*H*)-ones, were not observed in the reactions using **2**. The structures of these products were distinguishable from the corresponding linear-type products in a manner similar to that described for furopyranones (**4**) and (**6**) (see EXPERIMENTAL).

In further experiments, we found that, in addition to alkenes, phenylacetylene (**7**) was successfully employed in the present cycloaddition procedure. Thus, as shown in Scheme 2, similar treatment of the hydroxybenzopyranone (**1**) with **7** in the presence of CAN gave the corresponding 2-phenyl-4*H*-furo[3,2-*c*]benzo[1]pyran-4-one (**8**) and 2-phenyl-4*H*-furo[2,3-*b*]benzo[1]pyran-4-one (**10**) in good combined yield. Replacement of **1** with the hydroxyquinolinone (**2**) in the reaction with **7** resulted in the formation of 2-phenylfuro[3,2-*c*]quinolin-4(5*H*)-one (**9**); no formation of the corresponding furo[2,3-*b*]quinolinone derivative was observed. The structures of these products were also determined by means of IR, ¹H NMR,



Scheme 2.



Scheme 3.

and MS spectrum analyses (see EXPERIMENTAL).

Next, the CAN-mediated reactions of 4-hydroxy-6-methyl-2H-pyran-2-one (**11**) with a range of alkenes were attempted (Scheme 3). The results were summarized in Table 2. Styrene (**12c**) and its derivatives (**12d-f**) afforded satisfactory yields of the corresponding 2-aryl-2,3-dihydro-4H-furo[3,2-c]pyran-4-ones (**13c-f**), and no more than a trace amount of the corresponding furo[2,3-b]pyranone derivative (**14**) was obtained in each of the reactions. The alkenes (**12a**) and (**12b**), however, produced both types of furopyranones. These two types of furopyranones could be clearly distinguished by IR spectroscopy; compounds (**13**) and (**14**) revealed their carbonyl absorption bands at around 1720 cm^{-1} and at around 1665 cm^{-1} , respectively.

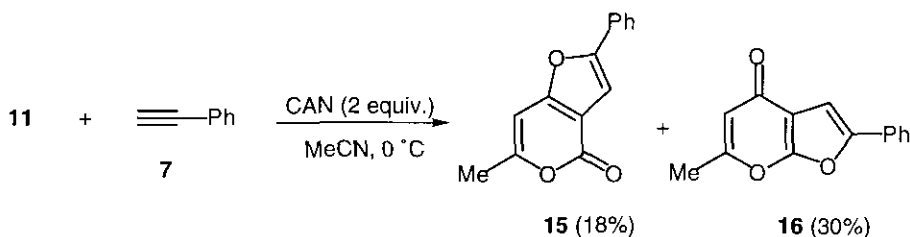
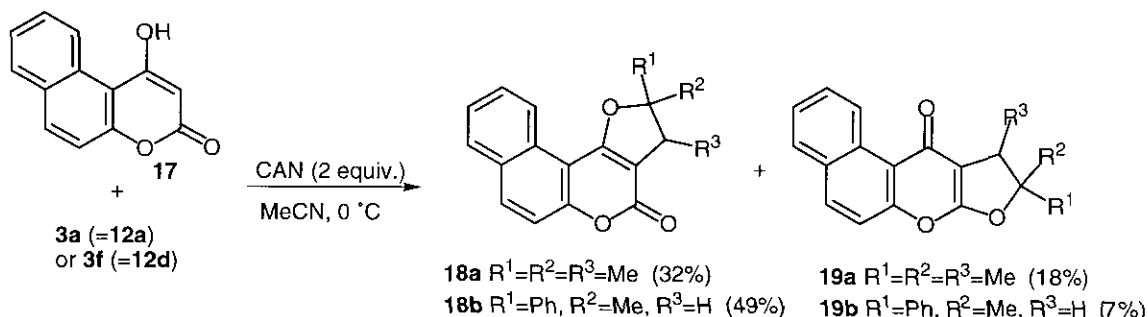
When the reaction of **11** with phenylacetylene (**7**) in the presence of CAN was conducted under similar conditions as described above, 6-methyl-2-phenyl-4H-furo[3,2-c]pyran-4-one (**15**) and 6-methyl-2-phenyl-4H-furo[2,3-b]pyran-4-one (**16**) were obtained (Scheme 4). These were also quite distinguishable by chromatography and IR spectroscopy (see EXPERIMENTAL). All attempts to prepare furopyridone derivatives by reacting 4-hydroxy-2-pyridones with alkenes in acetonitrile containing CAN under similar conditions were ineffective and resulted in the formation of complicated mixture of products.

Further versatility of this furopyranone synthesis was shown by the reaction of the 1-hydroxy-3H-naphtho[2,1-b]pyran-3-one (**17**) with alkenes. As shown in Scheme 5, compound (**17**) was uneventfully reacted with 2-methyl-2-butene (**3a**) or α -methylstyrene (**3f**) in the presence of CAN under the same reaction conditions to give the corresponding 2,3-dihydro-4H-naphtho[2,1-b]furo[2,3-d]pyran-4-ones (**18**) and 9,10-dihydro-11H-naphtho[2,1-b]furo[3,2-e]pyran-11-ones (**19**) in moderate combined yields.

Table 2. Preparation of furopyranones (**13**) and (**14**)

Entry	Alkene (12)	Product(s) (Yield/%) ^a
1	12a = 3a	13a (21), 14a (21)
2	12b (R ¹ = R ² = Et, R ³ = H)	13b (35), 14b (29)
3	12c (R ¹ = Ph, R ² = R ³ = H)	13c (69)
4	12d = 3f	13d (62)
5	12e (R ¹ = 4-MeC ₆ H ₄ , R ² = R ³ = H)	13e (55)
6	12f (R ¹ = 4-ClC ₆ H ₄ , R ² = R ³ = H)	13f (49)

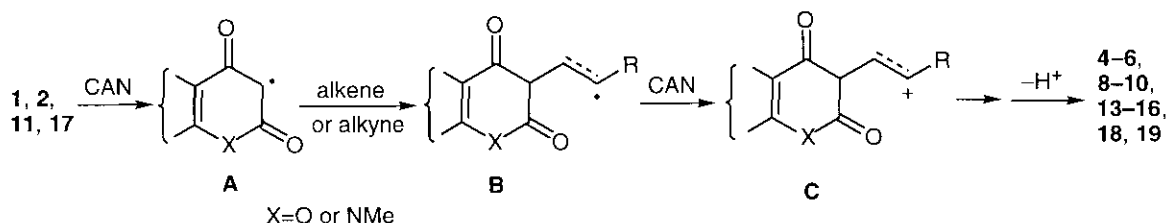
^a Yields are based on **11** and isolated products after preparative TLC on silica gel.

**Scheme 4.****Scheme 5.**

The formation of furopyranones and furoquinolinones is thought to proceed by the path outlined in Scheme 6, which is analogous to that proposed previously for the dihydrofuran formation from 1,3-dicarbonyls and alkenes.³ The initial formation of the radical intermediate (**B**) through **A** was followed by oxidation to give the carbenium ion intermediate (**C**). Intramolecular trapping of this cation with either of two carbonyl oxygens, followed by loss of a hydrogen, gives rise to the product(s). The formation of each product was completely regioselective and no trace of the corresponding regioisomer was obtained. It seems likely that many factors may be responsible for the selectivity for the formation of angular- (**4**, **5**, **8**, **9**, **13**, **15**, and

18) and linear-type products (**6**, **10**, **14**, **16**, and **19**) in the present furoheterocycle formation. The less effectiveness of **2**, compared to **1**, would be attributable to the dimerizable character of the radical generated from **2**.⁶ It can be assumed that the low yield of the product from vinyl carboxylates is due to loss of an acyl radical from the corresponding radical intermediate (**B**).

The foregoing experiments confirmed that the CAN-mediated reactions of hydroxypyranones and a hydroxyquinolinone with a variety of alkenes or phenylacetylene provide a direct entry to furopyranones and furoquinolinones.



Scheme 6.

EXPERIMENTAL

The mps were recorded with a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncorrected. The IR spectra were determined for KBr discs (unless specified otherwise) with a Perkin-Elmer 1600 Series FT IR spectrophotometer. The ¹H NMR spectra were determined in CDCl₃ using SiMe₄ as an internal reference with a JEOL JNM-GX270 FT NMR spectrometer operating at 270 MHz. *J* values are given in Hz. Mass spectra were recorded with a JEOL AUTOMASS 20 spectrometer (Center for Joint Research and Development, this University). High resolution MS analyses were performed with a JEOL JMS-AX505 HA spectrometer (Faculty of Agriculture, this University). TLC was carried out on a Merck Kieselgel 60 PF₂₅₄. 4-Hydroxy-1-methylquinolin-2(1*H*)-one (**2**) was prepared following the procedure reported by Coppola.¹⁵ 2-Methyl-2-propenyl acetate (**3c**) was prepared by treating 2-methyl-2-propen-1-ol with acetic acid.¹⁶ 1-Hydroxy-2*H*-naphtho[2,1-*b*]pyran-2-one (**17**) was prepared following the procedure reported by Kamijo *et al.*¹⁷ All other organic materials used in this study were commercially available.

General Procedure for the Cycloaddition Reactions. To a stirred solution of **1**, **2**, **11**, or **17** (2 mmol) and the alkenes (**3** or **12**) or phenylacetylene (**7**) [20 mmol for **3a** (=12a), **3b**, **3d**, **3g**, and **12b**; 5.0 mmol for the others] in acetonitrile (80 mL) at 0 °C was added CAN (2.2 g, 4.0 mmol) in portions. The cerium(IV) compound dissolved gradually in the solvent (*ca.* 30 min). Stirring was continued until TLC on silica gel showed complete consumption of the starting materials (40–90 min), after which saturated aqueous NH₄Cl (30 mL) were added. Most of the organic solvent was evaporated, and the mixture was extracted with Et₂O three times (40 mL each). The combined extracts were washed with brine, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The residue was subjected to preparative

TLC on SiO₂ (EtOAc–hexane or THF–benzene) to give the cycloaddition product(s).

2,2,3-Trimethyl-2,3-dihydro-4H-furo[3,2-c][1]benzopyran-4-one (4a): this product had spectral (IR and ¹H NMR) properties identical to those of authentic samples prepared previously by one of the present authors;^{2a} mp 81–83 °C (hexane) (lit.,^{2a} 80–82 °C).

2,2,3-Trimethyl-2,3-dihydro-4H-furo[2,3-b][1]benzopyran-4-one (6a): this product had spectral (IR and ¹H NMR) properties identical to those of authentic samples prepared previously by one of the present authors;^{2a} mp 121–122 °C (hexane) (lit.,^{2a} 121.5–122.5 °C).

cis-7,8,9,9a-Tetrahydro-7bH-cyclopenta[4,5]furo[3,2-c][1]benzopyran-6-one (4b): this product had spectral (IR and ¹H NMR) properties identical to those of an authentic sample prepared previously by one of the present authors;^{2a} mp 102–104 °C (Et₂O) (lit.,^{2a} 103–104 °C).

cis-2,3,3a,9b-Tetrahydro-1H-cyclopenta[4,5]furo[2,3-b][1]benzopyran-9-one (6b): a viscous oil; *R*_f 0.18 (1:3 EtOAc–hexane); *v*_{max}/cm⁻¹ (neat) 1633; δ_H 1.7–1.9 (4H, m), 2.1–2.25 (2H, m), 3.99 (1H, br t, *J* 7.9), 5.45 (1H, br t, *J* 7.9), 7.3–7.45 (2H, m), 7.58 (1H, ddd, *J* 8.3, 7.3, 1.8), 8.22 (1H, dd, *J* 8.3, 1.8); MS *m/z* 228 (M⁺, 90), 121 (100). Anal. Calcd for C₁₄H₁₂O₃: C, 73.67; H, 5.30. Found: C, 73.49; H, 5.29.

2-Acetoxymethyl-2-methyl-2,3-dihydro-4H-furo[3,2-c][1]benzopyran-4-one (4c): mp 124–125 °C (Et₂O–EtOAc); *v*_{max}/cm⁻¹ 1744, 1722, 1650; δ_H 1.61 (3H, s), 2.06 (3H, s), 2.94 (1H, d, *J* 15.3), 3.16 (1H, d, *J* 15.3), 4.25 (1H, d, *J* 12.1), 4.30 (1H, d, *J* 12.1), 7.28 (1H, t, *J* 7.9), 7.38 (1H, d, *J* 7.9), 7.57 (1H, td, *J* 7.9, 1.6), 7.65 (1H, dd, *J* 7.9, 1.6); MS *m/z* 274 (M⁺, 10), 232 (23), 214 (56), 199 (100). Anal. Calcd for C₁₅H₁₄O₅: C, 65.69; H, 5.14. Found: C, 65.83; H, 5.18.

2-Acetoxymethyl-2-methyl-2,3-dihydro-4H-furo[2,3-b][1]benzopyran-4-one (6c): a viscous oil; *R*_f 0.47 (1:4 THF–benzene); *v*_{max}/cm⁻¹ (neat) 1745, 1631, 1613; δ_H 1.62 (3H, s), 2.09 (3H, s), 2.98 (1H, d, *J* 14.5), 3.20 (1H, d, *J* 14.5), 4.26 (2H, s), 7.35–7.45 (2H, m), 7.61 (1H, td, *J* 8.4, 2.1), 8.23 (1H, dd, *J* 8.4, 2.1); MS *m/z* 274 (M⁺, 10), 232 (22), 214 (58), 199 (100). Anal. Calcd for C₁₅H₁₄O₅: C, 65.69; H, 5.14. Found: C, 65.75; H, 5.45.

2-Acetoxy-2,3-dihydro-4H-furo[3,2-c][1]benzopyran-4-one (4d): mp 166–168 °C (hexane–CH₂Cl₂); *v*_{max}/cm⁻¹ 1750, 1702, 1649; δ_H 2.16 (3H, s), 3.14 (1H, dd, *J* 16.9, 7.3), 3.46 (1H, d, *J* 16.9, 2.2), 7.05 (1H, dd, *J* 7.3, 2.2), 7.31 (1H, t, *J* 7.6), 7.40 (1H, d, *J* 8.3), 7.59 (1H, dd, *J* 8.3, 7.6), 7.70 (1H, d, *J* 7.6); MS *m/z* 246 (M⁺, 1.8), 186 (76), 176 (100). Anal. Calcd for C₁₃H₁₀O₅: C, 63.42; H, 4.09. Found: C, 63.27; H, 4.08.

2-Acetoxy-2,3-dihydro-4H-furo[2,3-b][1]benzopyran-4-one (6d): a viscous oil; *R*_f 0.07 (1:1 EtOAc–hexane); *v*_{max}/cm⁻¹ (neat) 1767, 1636, 1612; δ_H 2.16 (3H, s), 3.17 (1H, dd, *J* 16.0, 2.2), 3.43 (1H, dd, *J* 16.0, 7.3), 6.91 (1H, dd, *J* 7.3, 2.2), 7.4–7.5 (2H, m), 7.64 (1H, t, *J* 8.0), 8.25 (1H, d, *J* 8.0 Hz); MS *m/z* 246 (M⁺, 1.7), 186 (77), 176 (100). Anal. Calcd for C₁₃H₁₀O₅: C, 63.42; H, 4.09. Found:

C, 63.56; H, 4.07.

2-Benzoyloxy-2,3-dihydro-4H-furo[3,2-c][1]benzopyran-4-one (4e): mp 173–175 °C (Et₂O–hexane); $\nu_{\max}/\text{cm}^{-1}$ 1731, 1711, 1652; δ_{H} 3.33 (1H, dd, *J* 17.0, 2.5), 3.59 (1H, dd, *J* 17.0, 7.3), 7.25–7.35 (2H, m), 7.4–7.5 (3H, m), 7.55–7.65 (2H, m), 7.71 (1H, dd, *J* 7.6, 1.8), 8.07 (2H, dd, *J* 7.3, 2.2); MS *m/z* 308 (M⁺, 0.1), 186 (29), 105 (100). Anal. Calcd for C₁₈H₁₂O₅: C, 70.13; H, 3.92. Found: C, 69.87; H, 3.65.

2-Methyl-2-phenyl-2,3-dihydro-4H-furo[3,2-c][1]benzopyran-4-one (4f): this product had spectral (IR and ¹H NMR) properties identical to those reported previously;^{9a} mp 104–105 °C (Et₂O–hexane) (lit.,^{9a} mp 105 °C).

2,3-Dihydro-2,2,3,5-tetramethylfuro[3,2-c]quinolin-4(5H)-one (5a): this products had spectral (IR and ¹H NMR) properties identical to those reported previously;¹⁹ mp 87–89 °C (Et₂O–hexane) (lit.,¹⁸ mp 87–88 °C).

2-Acetoxyethyl-2,5-dimethyl-2,3-dihydrofuro[3,2-c]quinolin-4(5H)-one (5c): a viscous oil; *R_f* 0.33 (1:3 EtOAc–hexane); $\nu_{\max}/\text{cm}^{-1}$ (neat) 1743, 1659, 1634; δ_{H} 1.58 (3H, s), 2.05 (3H, s), 3.01 (1H, d, *J* 16.0), 3.21 (1H, d, *J* 16.0), 3.71 (3H, s), 4.23 (1H, d, *J* 12.8), 4.28 (1H, d, *J* 12.8), 7.23 (1H, dd, *J* 8.3, 7.6), 7.38 (1H, d, *J* 8.3), 7.58 (1H, ddd, *J* 8.3, 7.6, 1.5), 7.76 (1H, dd, *J* 8.3, 1.5); MS *m/z* 287 (M⁺, 19), 227 (54), and 214 (100). HR-MS. Calcd for C₁₆H₁₇NO₄: M, 287.1158. Found: *m/z* 287.1138.

2-Acetoxy-2,5-dimethyl-2,3-dihydrofuro[3,2-c]quinolin-4(5H)-one (5g): this product had spectral (IR and ¹H NMR) properties identical to those of an authentic sample prepared previously by one of the present authors;^{2b} mp 177–179 °C (Et₂O–CH₂Cl₂) (lit.,^{2b} mp 180 °C).

2-Phenyl-4H-furo[3,2-c][1]benzopyran-4-one (8):¹⁹ this products had spectral (IR and ¹H NMR) properties identical to those reported previously;^{19b} mp 180–181 °C (hexane–EtOAc) (lit.,^{19b} mp 171–173 °C).

2-Phenyl-4H-furo[2,3-b][1]benzopyran-4-one (10):^{19a} mp 189–191 °C (hexane–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 1667, 1614; δ_{H} 7.16 (1H, s), 7.3–7.55 (4H, m), 7.59 (1H, d, *J* 7.6), 7.65–7.75 (3H, m), 8.38 (1H, dd, *J* 8.0, 1.5); MS *m/z* 262 (M⁺, 100). Anal. Calcd for C₁₇H₁₀O₃: C, 77.86; H, 3.84. Found: C, 77.61; H, 4.02.

5-Methyl-2-phenylfuro[3,2-c]quinolin-4(5H)-one (9):^{9b} mp 200–205 °C (hexane–EtOAc); $\nu_{\max}/\text{cm}^{-1}$ 1661; δ_{H} 3.82 (3H, s), 7.30 (1H, s), 7.35–7.65 (7H, m), 7.86 (1H, d, *J* 8.3), 8.12 (1H, d, *J* 8.3); MS *m/z* 275 (M⁺, 100). Anal. Calcd for C₁₈H₁₃NO₂: C, 78.53; H, 4.76; N, 5.09. Found: C, 78.42; H, 4.69; N, 5.40.

2,2,3,6-Tetramethyl-2,3-dihydro-4H-furo[3,2-c]pyran-4-one (13a): a viscous oil; *R_f* 0.45 (1:3 THF–hexane); $\nu_{\max}/\text{cm}^{-1}$ (neat) 1727, 1639; δ_{H} 1.22 (3H, d *J* 7.4), 1.38 (3H, s), 1.43 (3H, s), 2.23

(3H, s), 3.05 (1H, q, J 7.4), 5.84 (1H, s); MS m/z 194 (M^+ , 55) and 179 (100). HR-MS. Calcd for $C_{11}H_{14}O_3$: M , 194.0943. Found: m/z 194.0940.

2,2,3,6-Tetramethyl-2,3-dihydro-4H-furo[2,3-*b*]pyran-4-one (14a): a viscous oil; R_f 0.06 (1:3 THF–hexane); ν_{max}/cm^{-1} 1666, 1623; δ_H 1.25 (3H, d J 7.4), 1.43 (3H, s), 1.49 (3H, s), 2.23 (3H, s), 3.16 (1H, q, J 7.4), 5.95 (1H, s); MS m/z 194 (M^+ , 42), 179 (100). HR-MS. Calcd for $C_{11}H_{14}O_3$: M , 194.0943. Found: m/z 194.0938.

2,2-Diethyl-6-methyl-2,3-dihydro-4H-furo[3,2-*c*]pyran-4-one (13b): a viscous oil; R_f 0.67 (1:1 THF–hexane); ν_{max}/cm^{-1} (neat) 1726, 1639; δ_H 0.84 (6H, t, J 7.4), 1.67 (4H, q, J 7.4), 2.17 (3H, s), 2.70 (2H, s), 5.82 (1H, s); MS m/z 208 (M^+ , 97), 179 (100). HR-MS. Calcd for $C_{12}H_{16}O_3$: M , 208.1100. Found: m/z 208.1096.

2,2-Diethyl-6-methyl-2,3-dihydro-4H-furo[2,3-*b*]pyran-4-one (14b): a viscous oil; R_f 0.24 (1:1 THF–hexane); ν_{max}/cm^{-1} (neat) 1664, 1624; δ_H 0.96 (6H, t, J 7.4), 1.79 (4H, q, J 7.4), 2.24 (3H, s), 2.83 (2H, s), 5.95 (1H, s); MS m/z 208 (M^+ , 81), 179 (100). HR-MS. Calcd for $C_{12}H_{16}O_3$: M , 208.1100. Found: m/z 208.1104.

6-Methyl-2-phenyl-2,3-dihydro-4H-furo[3,2-*c*]pyran-4-one (13c): mp 245–246 °C (hexane–EtOAc); ν_{max}/cm^{-1} 1714, 1638; δ_H 2.29 (3H, s), 3.06 (1H, dd, J 14.8, 7.9), 3.47 (1H, dd, J 14.8, 10.6), 5.89 (1H, dd, J 10.6, 7.9), 5.99 (1H, s), 7.3–7.45 (5H, m); MS m/z 228 (M^+ , 87), 144 (100). Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.31; H, 5.31.

2,6-Dimethyl-2-phenyl-2,3-dihydro-4H-furo[3,2-*c*]pyran-4-one (13d): mp 91–92 °C (hexane– CH_2Cl_2); ν_{max}/cm^{-1} 1713, 1638; δ_H 1.71 (3H, s), 2.21 (3H, s), 3.12 (2H, s), 5.81 (1H, s), 7.05–7.4 (5H, m); MS m/z 242 (M^+ , 49), 158 (100). Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.37; H, 5.84.

6-Methyl-2-(4-methylphenyl)-2,3-dihydro-4H-furo[3,2-*c*]pyran-4-one (13e): a viscous oil; R_f 0.43 (1:1 hexane–THF); ν_{max}/cm^{-1} (neat) 1730, 1640; δ_H 2.28 (3H, s), 2.36 (3H, s), 3.06 (1H, dd, J 14.8, 7.9), 3.44 (1H, dd, J 14.8, 10.6), 5.85 (1H, dd, J 10.6, 7.9), 5.97 (1H, s), 7.23 (4H, s); MS m/z 242 (M^+ , 100). HR-MS. Calcd for $C_{15}H_{14}O_3$: M , 242.0943. Found: m/z 242.0941.

2-(4-Chlorophenyl)-6-methyl-2,3-dihydro-4H-furo[3,2-*c*]pyran-4-one (13f): a viscous oil; R_f 0.50 (2:1 hexane–THF); ν_{max}/cm^{-1} (neat) 1723, 1641; δ_H 2.28 (3H, s), 3.00 (1H, dd, J 15.3, 7.9), 3.47 (1H, dd, J 15.3, 10.0), 5.86 (1H, dd, J 10.0, 7.9), 6.00 (1H, s), 7.27 (2H, s, J 8.4), 7.37 (2H, d, J 8.4). MS m/z 262 (M^+ , 52), 115 (82), 85 (100). HR-MS. Calcd for $C_{14}H_{11}O_3^{35}Cl$: M , 262.0397. Found: m/z 262.0389.

6-Methyl-2-phenyl-4H-furo[3,2-*c*]pyran-4-one (15): mp 152–154 °C (hexane– CH_2Cl_2); ν_{max}/cm^{-1} 1732, 1618; δ_H 2.36 (3H, s), 6.46 (1H, s), 7.04 (1H, s), 7.3–7.5 (3H, m), 7.70 (2H, d, J

8.3). MS m/z 226 (M^+ , 100). Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.11; H, 4.61.

6-Methyl-2-phenyl-4H-furo[2,3-*b*]pyran-4-one (16): mp 199–200 °C (hexane– CH_2Cl_2); ν_{max}/cm^{-1} 1651; δ_H 2.41 (3H, s), 6.15 (1H, s), 7.02 (1H, s), 7.3–7.5 (3H, m), 7.66 (2H, dd, J 7.9, 1.6); MS m/z 226 (M^+ , 81), 105 (100). Anal. Calcd for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46. Found: C, 74.24; H, 4.27.

2,2,3-Trimethyl-2,3-dihydro-4H-naphtho[2,1-*b*]furo[2,3-*d*]pyran-4-one (18a) and 9,9,10-trimethyl-9,10-dihydro-11H-naphtho[2,1-*b*]furo[3,2-*e*]pyran-11-one (19a): ca. 2 : 1; a viscous oil; R_f 0.39 (3:1 hexane–EtOAc); ν_{max}/cm^{-1} (neat) 1721, 1630; δ_H 1.35 (1.8H, d, J 7.4), 1.41 (1.2H, d, J 7.4), 1.52, 1.58, 1.60, and 1.62 (6H, 4s), 3.25 (0.6H, q, J 7.4), 3.39 (0.4H, q, J 7.4), 7.45–7.75 (3H, m), 7.85–8.05 (2H, m), 8.96 (0.4H, d, J 8.4), 10.20 (0.6H, d, J 8.9); MS m/z 280 (M^+ , 53), 265 (100). HR-MS. Calcd for $C_{18}H_{16}O_3$: M, 280.1099. Found: m/z 280.1092.

2-Methyl-2-phenyl-2,3-dihydro-4H-naphtho[2,1-*b*]furo[2,3-*d*]pyran-4-one (18b) and 9-methyl-9-phenyl-9,10-dihydro-11H-naphtho[2,1-*b*]furo[3,2-*e*]pyran-11-one (19b): ca. 7 : 1; a viscous oil; R_f 0.28 (3:1 hexane–EtOAc); ν_{max}/cm^{-1} (neat) 1722, 1633; δ_H 1.93 (0.375H, s), 2.00 (2.625H, s), 3.35–3.45 (2H, m), 7.25–7.75 (8H, m), 7.9–8.05 (2H, m), 9.09 (0.875H, d, J 8.4), 10.18 (0.125 H, d, J 8.4); MS m/z 328 (M^+ , 44), 158 (100). HR-MS. Calcd for $C_{18}H_{16}O_3$: M, 328.1100. Found: m/z 328.1117.

ACKNOWLEDGEMENTS

We wish to thank Mrs. Miyuki Tanmatsu of this department for determining the mass spectra.

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Received, 5th July, 1999