Thermal Addition Reaction of Aroylketenes with Cyclic Enol Ethers

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Thermal reaction of aroylketenes 2 with cyclic enol ethers such as 2,3-dihydrofuran (A), 2,3-dihydropyran (B), 1-trimethylsilyloxycyclopentene (C), 1-trimethylsilyloxycyclohexene (D), 3-trimethylsilyloxyindene (E), and 4-trimethylsilyloxy-1,2-dihydronaphalene (F) was carried out to investigate the reactivity of 2 with these olefins. The main reaction was Michael-type addition to give the 1,3-diketones 3 and 9, and the 1,3,5-triketones 13, 15, 18, and 20, depending on the olefins used. The addition of the olefins was facilitated by introduction of a nitro or chloro group into the aryl part of 2 and was profoundly retarded by steric hindrance of the olefins

Key words aroylketene; cyclic enol ether; thermal addition reaction; 4-pyrone

Acylketene is a versatile intermediate which reacts with various hetero-olefins to yield heteroaromatic compounds,[1] and also reacts with electron-rich olefins such as alkyl vinyl ether to give 4-pyrone derivatives.[2] Recently, we have reported that aroylketenes generated by pyrolysis of 5-aryl-2,3-dihydro-furan-2,3-dione reacted with acyclic enols such as 1-aryl-1-trimethylsilyloxyethylenes[3,4] to give various 1,5-diarylpentane-1,3,5-triones and 2,6-diaryl-4*H*-pyran-4-ones. In the paper, we show that introduction of electron-withdrawing substituents into the aryl part of aroylketene or introduction of electron-donating substituents into the aryl part of the aryl enol ether enhanced the reactivity and we also show, by the orbital analysis of aroylketene, that the reaction proceeds in an ionic manner.[4]

In order to examine further the reactivity of aroylketenes for thermal addition reaction with olefins we examined the reaction of various substituted aroylketenes in the aryl part with cyclic enol ethers. Reactions with cyclic olefins at the same time is expected to provide detailed mechanistic information regarding the addition of these reactants.

Results and Discussion

The aroylketenes **2** with different electronic properties [benzoyl (**2a**), *p*-nitrobenzoyl (**2b**), *o*-nitrobenzoyl (**2c**), *p*-chlorobenzoyl (**2d**), *o*-chlorobenzoyl (**2e**), *p*-methoxybenzoyl (**2f**), *o*-methoxybenzoyl (**2g**), furoyl (**2h**), and thenoyl (**2i**) derivatives] were generated *in situ* by heating a toluene solution of the 5-aryl-2,3-dihydrofuran-2,3-diones **1** and utilized for reaction with five- and six-membered cyclic enol ethers.

Thermal Addition Reaction of Aroylketenes to Dihydrofuran and Dihydropyran The reactions of the aroylketenes (**2**) with 2,3-dihydrofuran (**A**) and 2,3-dihydropyran (**B**) were carried out by heating a toluene solution of a 5-arylfuran-2,3-dione **1a**—**1i** (1 eq) and the enol ether (2 eq) at 100 °C for 1 h in a sealed Pyrex tube. The reaction with **A** gave three adducts, the diketone **3**, and two stereoisomers, *trans*-fused **4** and *cis*-fused dihydropyrone **5** (Chart 1). The reactions with **B** similarly gave three adducts, the diketone **9**, the *trans*-fused **10** and *cis*-fused dihydropyrone **11** (Chart 1). In a few cases, the aroylketene dimers **6** and acetophenones **7** were formed as by-products. The diketones **3** and **9** were obtained as major products though there is one exception: the *o*-methoxybenzoylketene **2g** gave the *trans*-dihydropyrone **4g** as a sole product. In most cases, the *trans*-**4** and **10** and/or *cis*-dihydropyrones **5** and **11** were formed as the second major products. The results are summarized in Table 1.

The structures of the products were readily characterized by elementary analyses and spectral data (IR, UV, ^{1}H- and ^{13}C-NMR) (see Experimental). The diketones **3** and **9** are completely enolized, as shown by their ^{1}H-NMR spectra, which lack the signals due to active methylene protons. The stereochemistry of the fused ring in the dihydropyrones was deduced from the coupling constants between the angular protons. The furan derivatives **4** showing a larger value (11 Hz for **4h**) were assigned as *trans* and those **5** showing a smaller one (4 Hz for **5h**) as *cis*. Similarly, the stereochemistry of the angular protons in the pyran derivatives **10** and **11** was assigned as *trans* and *cis*, respectively, on the basis of their H–H coupling constants (11 Hz for **10h** and 4 Hz for **11h**).

This stereochemical assignment was supported by the following facts. The furan-diketone **3h**, on treatment with sulfuric acid, underwent intramolecular cyclization to give the *cis*-isomer **5h**, exclusively. The pyran-diketone **9h**, on similar acidic treatment, also gave the *cis*-isomer **11h** as a sole product. Interestingly, the diketone **3d** on similar acidic treatment gave the pyran-4-one **8d** (17%) together with the *cis*-isomer **5d** (64%). Similarly, on acidic treatment the diketone **9d** gave the pyran-4-one **12d** (66%) and the *cis*-isomer **11d** (32%). This exclusive formation of the *cis*-isomer suggests that this isomer should be thermodynamically more stable than the corresponding *trans*-isomer. In accordance with this conclusion, the *cis*-isomers have smaller steric energies (28.79 kcal/mol for **5h** and 27.08 kcal/mol for **11h**) than those of *trans* isomers (32.33 kcal/mol for **4h** and 27.84 kcal/mol for **10h**).[5]

The results shown in Table 1 demonstrate that introduction of nitro and chloro groups into the aroylketene, as expected, considerably enhanced the reactivity, while that of a methoxy group decreased the reactivity. It is noteworthy that the aroylketenes **2h** and **2i** possessing a furan and a thiophene ring, respectively showed good reactivity for this addition reaction, since these aromatic rings are known to be electron-rich and should decrease the reactivity of the aroylketene. This enhancement in reactivity of **2h** and **2i** compared with that of the benzoyl-

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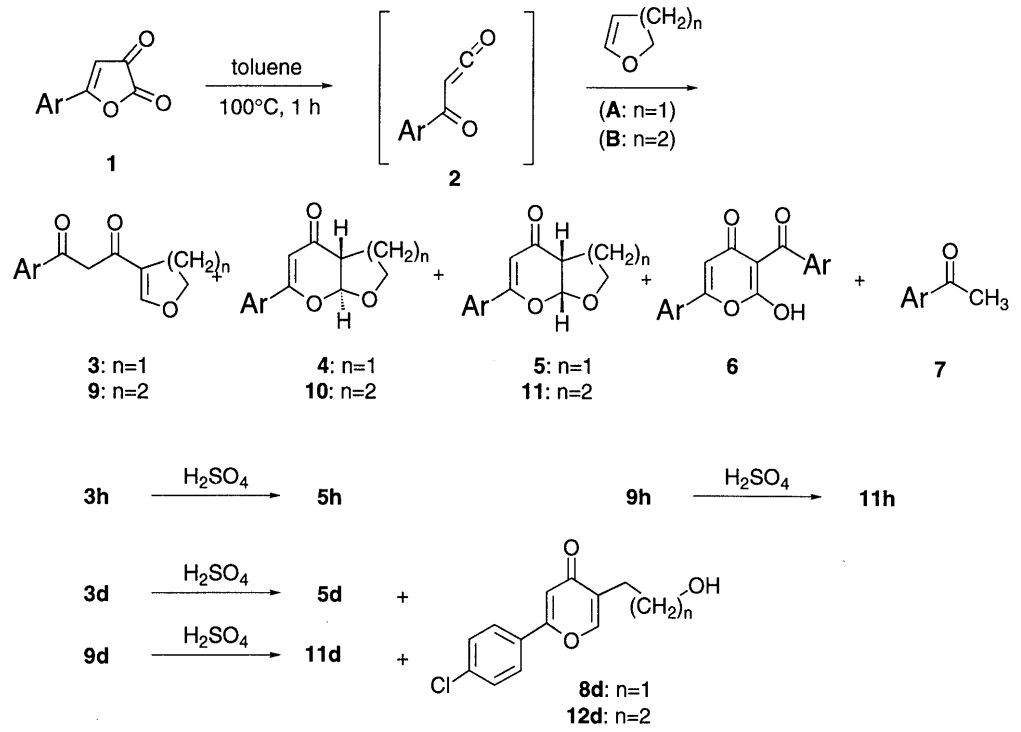

For all compounds

a : Ar =phenyl, **b**: Ar = *p*-NO_2-phenyl, **c**: Ar=*o*-NO_2-phenyl, **d**: Ar=*p*-Cl-phenyl, **e**: Ar = *o*-Cl-phenyl, **f**: Ar = *p*-OMe-phenyl, **g** : Ar = *o*-OMe-phenyl, **h** : Ar =2- furyl, **i** : Ar =2- thienyl

Chart 1

Table 1. Thermal Addition Reaction of Aroylketenes **2** with Dihydrofuran (**A**) and Dihydropyran (**B**)

Aroylketene (Ar)		Olefin	Yield (%) of product			
			Diketone	Dihydropyrone		Others
				trans-Fused	*cis*-Fused	
2a	(Phenyl)	**A**	22 (**3a**)	18 (**4a**)	—	—
2b	(*p*-NO_2-Phenyl)	**A**	56 (**3b**)	—	6 (**5b**)	4 (**7b**)
2c	(*o*-NO_2-Phenyl)	**A**	59 (**3c**)	—	10 (**5c**)	—
2d	(*p*-Cl-Phenyl)	**A**	39 (**3d**)	12 (**4c**)	—	—
2e	(*o*-Cl-Phenyl)	**A**	36 (**3e**)	24 (**4e**)	3 (**5e**)	—
2f	(*p*-OMe-Phenyl)	**A**	15 (**3f**)	1 (**4f**)	—	—
2g	(*o*-OMe-Phenyl)	**A**	—	25 (**4g**)	—	—
2h	(2-Furyl)	**A**	48 (**3h**)	11 (**4h**)	9 (**5h**)	—
2i	(2-Thienyl)	**A**	30 (**3i**)	11 (**4i**)	2 (**5i**)	—
2a	(Phenyl)	**B**	24 (**9a**)	1 (**10a**)	4 (**11a**)	7 (**7a**)
2b	(*p*-NO_2-Phenyl)	**B**	53 (**9b**)	4 (**10b**)	10 (**11b**)	—
2c	(*o*-NO_2-Phenyl)	**B**	45 (**9c**)	20 (**10c**)	18 (**11c**)	—
2d	(*p*-Cl-Phenyl)	**B**	29 (**9d**)	—	—	1 (**7d**)
2e	(*o*-Cl-Phenyl)	**B**	44 (**9e**)	10 (**10e**)	8 (**11e**)	—
2f	(*p*-OMe-Phenyl)	**B**	5 (**9f**)	—	—	(**6f**), 2 (**7f**)
2g	(*o*-OMe-Phenyl)	**B**	15 (**9g**)	1 (**10g**)	3 (**11g**)	6 (**6g**)
2h	(2-Furyl)	**B**	39 (**9h**)	5 (**10h**)	11 (**11h**)	—
2i	(2-Thienyl)	**B**	44 (**9i**)	10 (**10i**)	8 (**11i**)	—

ketene **2a** may be attributed to the relatively low energies of the LUMO+1 which possesses a large orbital to the ketene moiety responsible for the addition reaction (−0.250 eV for **2h**, −0.214 eV for **2i**, and −0.1076 eV for **2a**).[4)]

The formation of *trans* dihydropyrones together with the *cis*-isomers observed in this addition reaction is interesting from a mechanistic point of view, since, as suggested in the reaction of 1-aryl-1-trimethylsilyloxyethylenes,[4)] it clearly demonstrates that the reaction proceeds in a stepwise manner (probably in an ionic manner), not in a concerted [4+2] manner.

Thermal Addition Reaction of Aroylketenes to Cyclic Trimethylsilyloxyethylenes For evaluation of steric fac-

tors of the olefins, 1-trimethylsilyloxy-1-cyclopentene (TMSO-cyclopentene, **C**), 1-trimethylsilyloxycyclohexene (TMSO-cyclohexene, **D**), 3-trimethylsilyloxyindene (TMSO-indene, **E**), and 4-trimethylsilyloxy-1,2-dihydronaphthalene (TMSO-dihydronaphthalene, **F**) were reacted with benzoyl-(**2a**), *o*-nitrobenzoyl-(**2c**), and *o*-chlorobenzoylketene (**2e**). The reactions proceeded under similar conditions to those described above. Triketones **13**, **15**, **18**, and **20**, dihydropyrones **16**, and pyran-4-ones **14**, **17**, **21** were obtained as products. However, the yields and distribution of products greately depended on the olefins and the aroylketenes, as shown in Table 2. The triketones **13e**, **18e**, and **20e**, on treatment with sulfuric acid, readily cyclized to give the pyran-4-ones **14e** (80%), **19e** (96%), and **21e** (85%), respectively.

Table 2. Thermal Addition Reaction of Aroylketenes **2** with Trimethylsilyloxy-cycloolefins

Aroylketene (Ar)	Olefin[a]	Yield (%) of product			
		Triketone	Dihydropyrone	Pyrone	Dimer
2a (Phenyl)	**C**	—	—	11 (**14a**)	20 (**6a**)
2c (*o*-NO_2-Phenyl)	**C**	22 (**13c**)	—	26 (**14c**)	—
2e (*o*-Cl-Phenyl)	**C**	22 (**13e**)	—	4 (**14e**)	—
2a (Phenyl)	**D**	—	7 (**16a**)	—	3 (**6a**)
2c (*o*-NO_2-Phenyl)	**D**	—	—	7 (**17c**)	—
2e (*o*-Cl-Phenyl)	**D**	<1 (**15e**)	—	—	—
2a (Phenyl)	**E**	36 (**18a**)	—	—	—
2c (*o*-NO_2-Phenyl)	**E**	62 (**18c**)	—	—	—
2e (*o*-Cl-Phenyl)	**E**	64 (**18e**)	—	—	—
2a (Phenyl)	**F**	—	—	3 (**21a**)	—
2c (*o*-NO_2-Phenyl)	**F**	30 (**20c**)	—	34 (**21c**)	—
2e (*o*-Cl-Phenyl)	**F**	44 (**20e**)	—	12 (**21e**)	—

a) **C**, 1-trimethylsilyloxycyclopentene; **D**, 1-trimethylsilyloxycyclohexene; **E**, 3-trimethylsilyloxy-1*H*-indene; **F**, 4-trimethylsilyloxy-1,2-dihydronaphthalene.

In this reaction the *o*-nitrobenzoyl-(**2c**) and *o*-chlorobenzoylketene (**2e**) also showed better reactivity than the non-substituted compound **2a**. For example, the aroylketenes **2a** and **2c** on reaction with **E** gave the triketones (36% for **18a** and 62% for **18c**) and on reaction with **F** gave the triketones (0% for **20a** and 30% for **20c**) and the pyran-4-ones (3% for **21a** and 34% for **21c**). *o*-Chlorobenzoylketene (**2e**) was proved to have a similar reactivity to **2c** for these olefins. The reaction of aroylketenes with **D** gave very poor results when compared with that of **C**. For example, the *o*-nitrobenzoylketene (**2c**) on reaction with the olefin **C** gave the triketone **13c** in 22% yield and the pyran-4-one **14c** in 26% yield, while on reaction with **D** the aroylketene **2c** gave the pyran-4-one **17c** in only 7% yield. Thus, **D** is unreactive with aroylketenes in a practical sense.

The reactivity enhancement of TMSO-indene (**E**) and TMSO-dihydronaphthalene (**F**), when compared with TMSO-cyclopentene (**C**) and TMSO-cyclohexene (**D**), should be attributable to the electron-releasing effect of the fused benzene ring and also to increased planarity of the ring system which decreases the steric hindrance effect. The greatly decreased reactivity observed in the reactions of TMSO-cyclohexene (**D**) should be attributable to the steric hindrance effect which originates from the non-planar cyclohexene ring. It is clear that this addition

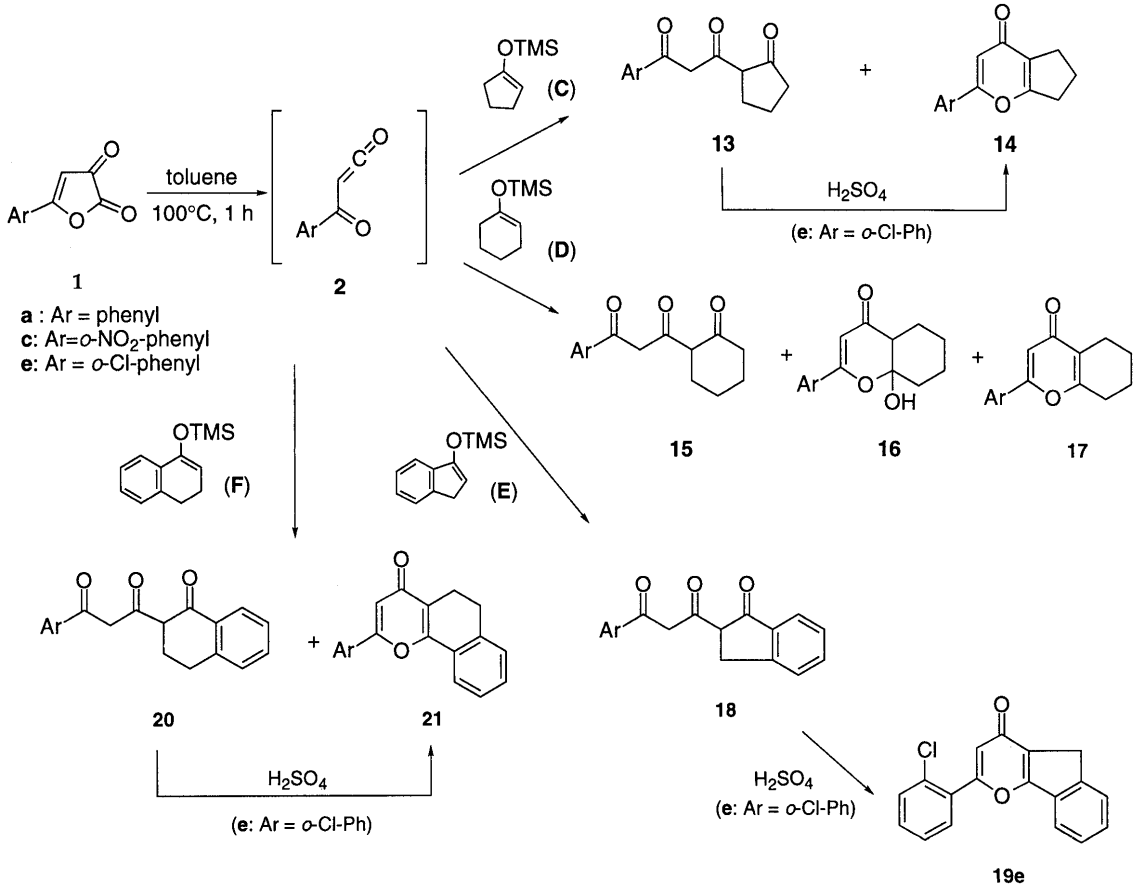

Chart 2

reaction is greately affected by steric factors.

In conclusion, the reaction of aroylketenes possessing an electron-withdrawing group with cyclic enol ethers provides a simple synthetic method for ring-fused pyran-4-one derivatives since acidic treatment of the diketones and triketones as described above can be afford the corresponding pyran-4-one derivatives.[6)]

Experimental

Melting points (mp) were determined with a Yanaco MP-S1 melting point apparatus and are uncorrected. IR spectra were measured with JASCO FT/IR-5000 Fourier-transform IR spectrometer using KBr, and are given as cm^{-1}. UV spectra were recorded on a Hitachi U-3200 spectrophotometer, and are given as nm (ε). ^{1}H- and ^{13}C-NMR spectra were obtained with a JEOL JNM-EX90 (^{1}H; 90 MHz, ^{13}C; 22.5 MHz) in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. High-resolution mass (HR-MS) and low-resolution mass (LR-MS) spectra were obtained on JEOL JMS-D300 or JMS-HX110A spectrometer at 30 eV by the direct inlet system. The 5-arylfuran-2,3-dione **5**, **12**, and **17** were prepared by the known procedure.[4)] The trimethylsilyloxyethylenes **C**, **D**, **E** and **F** were prepared by silylation of the corresponding ketones.[7)]

Reaction of 1 with 2,3-Dihydrofuran (A) and 2,3-Dihydropyran (B) (General Procedure) A solution of a 5-arylfuran-2,3-dione **1** (500 mg) and a dihydrofuran or dihydropyran (2 molar eq) in toluene (10 ml) was heated at 100 °C in a sealed Pyrex tube. The reaction mixture was concentrated *in vacuo*, and the products were purified by column chromatography over SiO_2, followed by medium-pressure (MP) LC, preparative (P) TLC and/or recrystallizations. The products and yields are given in Table 1. Aroylketene dimer **6f**, 4′-nitro-(**7b**) and 4′-chloro-(**7d**) and 4′-methoxyacetophenone (**7f**) were identified on the basis of spectral data.

Reaction of 1a with A 1-(4,5-Dihydrofur-3-yl)-3-phenyl-propane-1,3-dione (**3a**): Pale yellow prisms from CH_2Cl_2–ether, mp 122—124 °C. IR: 1607, 1574. UV: 353 (21200). ^{1}H-NMR: 2.98 (2H, dt, J=1, 9 Hz), 4.63 (2H, t, J=9 Hz), 6.11, 7.41 (each 1H, s), 7.4—7.9 (5H, m). LR-MS m/z: 216 (M^+).

(3a*R**,7a*S**)-6-Phenyl-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-4-one (**4a**): Colorless needles from CH_2Cl_2–ether, mp 132—135 °C. IR: 1680, 1591, 1564. UV: 291 (17800). ^{1}H-NMR: 2.1—2.3 (2H, m), 2.98 (1H, ddd, J=7, 11, 12 Hz), 4.27 (2H, t, J=4 Hz), 5.36 (1H, d, J=11 Hz), 6.04 (1H, s), 7.4—7.8 (5H, m). LR-MS m/z: 216 (M^+).

Reaction of 1b with A 1-(4,5-Dihydrofur-3-yl)-3-(4-nitrophenyl)propane-1,3-dione (**3b**): Pale yellow needles from benzene, mp 177—178 °C. IR: 1611, 1545. UV: 370 (20200). ^{1}H-NMR: 2.96 (2H, dt, J=2, 10 Hz), 4.68 (2H, t, J=10 Hz), 6.12 (1H, s), 7.48 (1H, t, J=2 Hz), 8.01, 8.30 (each 2H, dt, J=9, 2 Hz). LR-MS m/z: 261 (M^+).

(3a*R**,7a*R**)-2-(4-Nitrophenyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]-pyran-4-one (**5b**): Pale yellow needles from CH_2Cl_2–ether, mp 196—197 °C. IR: 1653, 1584, 1522. UV: 319 (14600). ^{1}H-NMR: 2.0—2.7 (2H, m), 3.04 (1H, ddd, J=5, 8, 11 Hz), 4.0—4.4 (2H, m), 6.05 (1H, s), 6.10 (1H, t, J=5 Hz), 7.95, 8.23 (each 2H, dt, J=9, 2 Hz). LR-MS m/z: 261 (M^+).

Reaction of 1c with A 1-(4,5-Dihydrofur-3-yl)-3-(2-nitrophenyl)propane-1,3-dione (**3c**): Eluent for column chromatography: CH_2Cl_2. Yellow prisms from CH_2Cl_2–ether, mp 97—99 °C. IR: 1626, 1603, 1535. UV: 348 (16000), 262 (9100). HR-MS m/z (M^+): Calcd for $C_{13}H_{11}NO_5$: 261.0637. Found: 261.0667.

(3a*R**,7a*R**)-6-(2-Nitrophenyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]-pyran-4-one (**5c**): Eluent for column chromatography: CH_2Cl_2, then AcOEt : hexane = 1 : 1. Pale brown gum. IR: 1669, 1620, 1599, 1562, 1524, 1510. UV: 212 (15100), 263 (11700). ^{1}H-NMR: 2.22 (1H, tt, J=9, 12 Hz), 2.4—2.5 (1H, m), 2.98 (1H, ddd, J=4, 9, 12 Hz), 4.09 (1H, dd, J=9, 16 Hz), 4.30 (1H, ddd, J=9.4, 8.8, 3.3 Hz), 5.71 (1H, d, J=1 Hz), 5.96 (1H, d, J=4 Hz), 7.55 (1H, dd, J=1, 8 Hz), 7.64 (1H, dt, J=8, 1 Hz), 7.69 (1H, dt, J=8, 1 Hz), 8.01 (1H, dd, J=1, 8 Hz). ^{13}C-NMR: 27.3 (t), 50.1 (d), 69.3 (t), 103.6 (d), 107.2 (d), 124.9 (d), 129.4 (s), 130.4 (d), 131.6 (d), 133.3 (d), 148.3 (s), 167.0 (s), 193.2 (s). CI-MS m/z: 262 (MH^+).

Reaction of 1d with A 3-(4-Chlorophenyl)-1-(4,5-dihydrofur-3-yl)propane-1,3-dione (**3d**): Yellow prisms from benzene, mp 138—140 °C. IR: 1605, 1562. UV: 259 (9500), 357 (23500). HR-MS m/z (M^+): Calcd for $C_{13}H_{11}ClO_3$: 250.0373. Found: 250.0393.

(3a*R**,7a*S**)-2-(4-Chlorophenyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-4-one (**4d**): Eluent for column chromatography: benzene : hexane = 1 : 1 and for MPLC: benzene. Colorless needles from CH_2Cl_2–ether, mp 154—157 °C. IR: 1678, 1597, 1584, 1562. UV: 224 (9400), 297 (20000). ^{1}H-NMR: 1.9—2.4 (2H, m), 2.97 (1H, ddd, J=7, 11, 12 Hz), 4.27 (1H, dd, J=4, 5 Hz), 4.37 (1H, d, J=2 Hz), 5.34 (1H, d, J=11 Hz), 6.00 (1H, s), 7.3—7.5, 7.6—7.9 (each 2H, m). ^{13}C-NMR: 21.8 (t), 50.5 (t), 69.1 (t), 103.8 (d), 106.6 (d), 127.9 (d × 2), 129.0 (d × 2), 130.3 (s), 137.9 (s), 166.5 (s), 192.7 (s). HR-MS m/z (M^+): Calcd for $C_{13}H_{11}ClO_3$: 250.0421. Found: 250.0398.

Reaction of 1e with A 3-(2-Chlorophenyl)-1-(4,5-dihydrofur-3-yl)propane-1,3-dione (**3e**): Eluent for column chromatography: benzene : hexane = 1 : 1. Yellow oil. IR: 1705, 1651, 1599, 1578, 1562. UV: 296 (7900). HR-MS m/z (M^+): Calcd for $C_{13}H_{11}ClO_3$: 250.0402. Found: 250.0397.

(3a*R**,7a*S**)-2-(2-Chlorophenyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-4-one (**4e**): Eluent for column chromatography: benzene. Pale yellow gum. IR: 1678, 1597, 1584, 1562. UV: 215 (14000), 274 (9800). ^{1}H-NMR: 1.9—2.4 (2H, m), 3.04 (1H, ddd, J=7, 11, 12 Hz), 4.26 (1H, d, J=9 Hz), 4.31 (1H, dd, J=1, 9 Hz), 5.39 (1H, d, J=11 Hz), 5.84 (1H, s), 7.2—7.6 (4H, m). ^{13}C-NMR: 21.8 (t), 50.6 (d), 69.1 (t), 106.7 (d), 109.4 (d), 126.8 (d), 130.4 (d), 130.7 (d), 131.7 (d), 132.2 (s), 132.9 (s), 166.9 (s), 192.9 (s). HR-MS m/z (M^+): Calcd for $C_{13}H_{11}ClO_3$: 250.0407. Found: 250.0397.

(3a*R**,7a*R**)-2-(2-Chlorophenyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-4-one (**5e**): Eluent for column chromatography: benzene. Pale yellow oil. IR: 1665,1609,1586. UV: 212 (14300), 278 (11200). ^{13}C-NMR: 27.7 (t), 49.8 (d), 69.1 (t), 104.9 (d), 106.0 (d), 126.9 (d), 130.6 (d), 131.1 (d), 131.6 (d), 132.7 (s), 132.9 (s), 167.3 (s), 193.4 (s). HR-MS m/z (M^+): Calcd for $C_{13}H_{11}ClO_3$: 250.0395. Found: 250.0395.

Reaction of 1f with A (3a*R**,7a*S**)-2-(4-Methoxyphenyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-4-one (**4f**): Eluent for column chromatography: CH_2Cl_2. Pale yellow prisms from CH_2Cl_2–ether, mp 134—136 °C. IR: 1673, 1607, 1589, 1562, 1512. UV: 226 (8700), 309 (20200). ^{1}H-NMR: 2.1—2.2 (1H, m), 2.3 (1H, m), 2.96 (1H, ddd, J=7, 11, 11 Hz), 3.86 (3H, s), 4.3 (2H, m), 5.33 (1H, d, J=11 Hz), 5.96 (1H, s), 6.94 (2H, d, J=9 Hz), 7.7—7.8 (4H, m). ^{13}C-NMR: 21.9 (t), 50.5 (d), 55.5 (q), 69.1 (t), 102.2 (d), 106.5 (d), 114.2 (d × 2), 124.1 (s), 128.6 (d × 2), 162.6 (s), 167.9 (s), 193.0 (s). HR-MS m/z (M^+): Calcd for $C_{14}H_{14}O_4$: 246.0890. Found: 246.0929.

(3a*R**,7a*R**)-2-(4-Methoxyphenyl)-2,3,3a,7a-tetrahydro-4*H*-furo-[2,3-*b*]pyran-4-one (**5f**): Eluent for column chromatography: CH_2Cl_2 and for MPLC: benzene : acetone = 20 : 1. Pale yellow prisms from CH_2Cl_2–ether, mp 129—131 °C. IR: 1655, 1607, 1593, 1570, 1512. UV: 228 (7400), 265 (4400), 313 (16900). ^{1}H-NMR: 2.1—2.2 (1H, m), 2.4—2.5 (1H, m), 2.95 (1H, ddd, J=5, 9, 14 Hz), 4.09 (1H, q, J=8 Hz), 4.29 (1H, dt, J=8, 4 Hz), 5.92 (1H, s), 6.01 (1H, d, J=5 Hz), 6.9—7.0 (2H, m), 7.7—7.8 (2H, m). ^{13}C-NMR: 27.9 (t), 49.5 (d), 55.5 (q), 69.0 (t), 98.2 (d), 105.5 (d), 114.1 (d × 2), 124.6 (s), 128.7 (d × 2), 162.7 (s), 167.2 (s), 193.2 (s). HR-MS m/z (M^+): Calcd for $C_{14}H_{14}O_4$: 246.0890. Found: 246.0874.

Reaction of 1g with A (3a*R**,7a*S**)-2-(2-Methoxyphenyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-4-one (**4g**): Eluent for column chromatography: AcOEt : hexane = 2 : 5. Pale yellow needles from CH_2Cl_2–ether, mp 123—125 °C. IR: 1680, 1599, 1557. UV: 282 (13800), 303 (9100), 316 (10400). ^{1}H-NMR: 1.9—2.4 (2H, m), 2.8—3.1 (1H, m), 3.89 (3H, s), 4.2—4.4 (2H, m), 5.31 (1H, d, J=13 Hz), 6.41 (1H, s), 6.9—7.5 (3H, m), 7.8—7.9 (1H, m). ^{13}C-NMR: 21.9 (t), 50.4 (d), 55.6 (q), 68.9 (t), 106.2 (d), 108.8 (d), 111.5 (d), 120.6 (d), 120.9 (s), 129.6 (d), 132.5 (d), 158.2 (s), 164.7 (s), 194.2 (s). HR-MS m/z (M^+): Calcd for $C_{14}H_{14}O_4$: 246.0892. Found: 246.0893.

Reaction of 1h with A 1-(2-Furyl)-3-(4,5-dihydrofur-3-yl)propane-1,3-dione (**3h**): Eluent for column chromatography: benzene : acetone = 15 : 1. Brown oil. UV: 213 (4000), 275 (7500), 344 (10300), 358 (10300). ^{1}H-NMR: 2.8—3.0 (2H, m), 4.61 (2H, dt, J=4, 10 Hz), 5.99 (1H, s), 6.54 (1H, dd, J=2, 4 Hz), 7.12 (1H, dd, J=1, 4 Hz), 7.37 (1H, t, J=2 Hz), 7.55 (1H, dd, J=1, 2 Hz). LR-MS m/z: 206 (M^+).

(3a*R**,7a*S**)-2-(2-Furyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-4-one (**4h**): Eluent for column chromatography: benzene : acetone = 15 : 1. Pale yellow prisms from CH_2Cl_2–ether, mp 150—151 °C. IR: 1671, 1611, 1539. UV: 307 (24000). ^{1}H-NMR: 2.0—2.3 (2H, m), 2.97 (1H, ddd, J=7, 11, 12 Hz), 4.2—4.4 (2H, m), 5.31 (1H, d, J=11 Hz), 5.98 (1H, s), 6.54 (1H, dd, J=2, 4 Hz), 7.01 (1H, d, J=4 Hz), 7.55

(1H, dd, $J=1$, 2 Hz). ^{13}C-NMR: 21.9 (t), 50.9 (d), 69.2 (t), 102.0 (d), 106.4 (d), 112.6 (d), 114.2 (d), 145.8 (d), 146.8 (s), 158.7 (s), 192.6 (s). HR-MS m/z (M^+): Calcd for $C_{11}H_{10}O_4$: 206.0579. Found: 206.0582.

(3a*R**,7a*R**)-2-(2-Furyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-4-one (**5h**): Eluent for column chromatography: benzene : acetone = 15 : 1. Yellow prisms from CH_2Cl_2–ether, mp 140—142 °C. IR: 1657, 1620, 1547. UV: 312 (14300). ^{1}H-NMR: 2.2—2.5 (2H, m), 2.8—3.0 (1H, m), 3.95—4.38 (2H, m), 5.93 (1H, s), 5.96 (1H, d, $J=6$ Hz), 6.54 (1H, dd, $J=2$, 4 Hz), 7.02 (1H, dd, $J=1$, 4 Hz), 7.56 (1H, dd, $J=1$, 2 Hz). ^{13}C-NMR: 27.8 (t), 50.0 (d), 69.1 (t), 97.9 (d), 105.5 (d), 112.5 (d), 114.5 (d), 146.0 (d), 147.2 (s), 158.2 (s), 192.6 (s). HR-MS m/z (M^+): Calcd for $C_{11}H_{10}O_4$: 206.0576. Found: 206.0558.

Reaction of 1i with A 1-(4,5-Dihydrofur-3-yl)-3-(2-thienyl)propane-1,3-dione (**3i**): Eluent for column chromatography: benzene : acetone = 70 : 1. Yellow prisms from CH_2Cl_2–ether, mp 86—89 °C. IR: 1632. UV: 212 (4500), 267 (11000), 367 (23100). ^{1}H-NMR: 2.9 (2H, dt, $J=2$, 10 Hz), 4.63 (2H, t, $J=10$ Hz), 5.89 (1H, s), 7.12 (1H, dd, $J=4$, 5 Hz), 7.36 (1H, t, $J=2$ Hz), 7.57 (1H, dd, $J=1$, 5 Hz), 7.67 (1H, dd, $J=1$, 4 Hz). LR-MS m/z: 222 (M^+).

(3a*R**,7a*S**)-6-(2-Thienyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-4-one (**4i**): Eluent for column chromatography: benzene : acetone = 70 : 1. Brown prisms from CH_2Cl_2–ether, mp 99—100 °C. IR: 1725, 1667, 1574. UV: 265 (7400), 317 (9600). ^{1}H-NMR: 2.0—2.3 (2H, m), 2.98 (1H, ddd, $J=7$, 11, 12 Hz), 3.9—4.4 (2H, m), 5.35 (1H, d, $J=11$ Hz), 5.94 (1H, s), 7.12 (1H, dd, $J=4$, 5 Hz), 7.53 (1H, dd, $J=1$, 5 Hz), 7.60 (1H, dd, $J=1$, 4 Hz). ^{13}C-NMR: 21.9 (t), 50.7 (d), 69.2 (t), 102.5 (d), 106.5 (d), 128.4 (d), 129.2 (d), 130.7 (d), 135.6 (s), 162.9 (s), 192.5 (s). HR-MS m/z (M^+): Calcd for $C_{11}H_{10}O_3S$: 222.0349. Found: 222.0334.

(3a*R**,7a*R**)-6-(2-Thienyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-4-one (**5i**): Eluent for column chromatography: benzene : acetone = 70 : 1. Pale brown prisms from CH_2Cl_2–ether, mp 144—145 °C. IR: 1649, 1584. UV: 261 (5700), 321 (18300). ^{1}H-NMR: 2.0—2.7 (2H, m), 2.96 (1H, ddd, $J=4$, 9, 11 Hz), 4.0—4.4 (2H, m), 5.88 (1H, s), 6.00 (1H, d, $J=4$ Hz), 7.12 (1H, dd, $J=4$, 5 Hz), 7.55 (1H, dd, $J=1$, 5 Hz), 7.61 (1H, dd, $J=1$, 4 Hz). ^{13}C-NMR: 27.8 (t), 49.7 (d), 69.1 (t), 98.4 (d), 105.7 (d), 128.3 (d), 129.3 (d), 130.3 (d), 136.3 (s), 162.3 (s), 192.6 (s). CI-MS m/z: 223 (MH^+).

Reaction of 1a with B 1-(4,5-Dihydropyran-3-yl)-3-phenylpropane-1,3-dione (**9a**): Eluent for column chromatography: AcOEt : hexane = 1 : 3. Yellow oil. IR: 1738, 1624, 1562. UV: 348 (15400). ^{1}H-NMR: 1.9—2.1 (2H, m), 2.36 (2H, t, $J=5$ Hz), 6.22 (1H, s), 7.77 (1H, br s), 7.3—8.1 (5H, m). LR-MS m/z: 230 (M^+).

(4a*R**,8a*S**)-2-Phenyl-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]-pyran-4-one (**10a**): Eluent for column chromatography: CH_2Cl_2 and for PTLC: benzene : acetone = 15 : 1. Pale yellow prisms from CH_2Cl_2–ether, mp 88—98 °C. IR: 1659, 1601, 1574. UV: 294 (17700). ^{1}H-NMR: 1.5—1.9 (4H, m), 2.3—2.7 (1H, m), 3.5—4.3 (2H, m), 5.11 (1H, d, $J=11$ Hz), 6.04 (1H, s), 7.4—7.9 (5H, m).

(4a*R**,8a*R**)-2-Phenyl-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]-pyran-4-one (**11a**): Eluent for column chromatography: CH_2Cl_2 and for PTLC: benzene : acetone = 15 : 1. Pale yellow prisms from CH_2Cl_2–ether, mp 86—89 °C. IR: 1659, 1601, 1574. UV: 294 (16600). ^{1}H-NMR: 1.7—2.0 (4H, m), 2.5—2.8 (1H, m), 3.8—4.3 (2H, m), 5.70 (1H, d, $J=4$ Hz), 6.00 (1H, s), 7.4—7.9 (5H, m).

Reaction of 1b with B 1-(3,4-Dihydro-2*H*-pyran-5-yl)-3-(4-nitrophenyl)propane-1,3-dione (**9b**): Eluent for column chromatography: benzene. Yellow prisms from acetone–ether, mp 135—137 °C. IR: 1605, 1589, 1522. UV: 364 (19100). ^{1}H-NMR: 1.9—2.1 (2H, m), 2.38 (2H, t, $J=6$ Hz), 4.15 (2H, t, $J=6$ Hz), 6.26, 7.76 (each 1H, s), 8.01, 8.29 (each 2H, dt, $J=9$, 2 Hz). LR-MS: m/z: 275 (M^+).

(4a*R**,8a*S**)-2-(4-Nitrophenyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano-[2,3-*b*]pyran-4-one (**10b**): Eluent for column chromatography: CH_2Cl_2 : hexane = 1 : 1 and for MPLC: benzene : acetone = 15 : 1. Pale yellow prisms from AcOEt–hexane, mp 195—199 °C. IR: 1669, 1586, 1518. UV: 250 (9800), 316 (15300). ^{1}H-NMR: 1.3—1.9 (3H, m), 2.4—2.7 (2H, m), 3.5—3.8 (1H, m), 4.2—4.3 (1H, m), 5.15 (1H, d, $J=11$ Hz), 6.11 (1H, s), 7.9—8.0 (2H, m), 8.2—8.4 (2H, m). ^{13}C-NMR: 21.1 (t), 24.5 (t), 47.4 (d), 67.5 (t), 104.0 (d), 104.5 (d), 123.8 (d × 2), 127.4 (d × 2), 137.8 (s), 149.5 (s), 164.2 (s), 193.4 (s).

(4a*R**,8a*R**)-2-(4-Nitrophenyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano-[2,3-*b*]pyran-4-one (**11b**): Eluent for column chromatography: CH_2Cl_2 : hexane = 1 : 1 and for MPLC: benzene : acetone = 15 : 1. Pale yellow prisms from AcOEt–hexane, mp 206—211 °C. IR: 1657, 1586, 1524. UV: 319 (15200). ^{1}H-NMR: 1.6—2.0 (4H, m), 2.6—3.0 (1H, m), 3.9—4.1 (2H, m), 5.74 (1H, d, $J=4$ Hz), 6.09 (1H, s), 7.97, 8.31 (each 2H, dt, $J=9$, 2 Hz). ^{13}C-NMR: 21.1 (t), 24.5 (t), 47.4 (d), 67.5 (d), 104.0 (d), 104.5 (d), 123.8 (d × 2), 127.4 (d × 2), 137.8 (s), 149.5 (s), 164.2 (s), 193.4 (s). LR-MS m/z: 275 (M^+).

Reaction of 1c with B 1-(3,4-Dihydro-2*H*-pyran-5-yl)-3-(2-nitrophenyl)propane-1,3-dione (**9c**): Eluent for column chromatography: benzene : CH_2Cl_2 = 1 : 1. Yellow prisms from CH_2Cl_2–ether, mp 68—72 °C. IR: 1622, 1562, 1531. UV: 254 (10700), 340 (14200). HR-MS m/z (M^+): Calcd for $C_{14}H_{13}NO_5$: 275.0792. Found: 275.0786.

(4a*R**,8a*S**)-2-(2-Nitrophenyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano-[2,3-*b*]pyran-4-one (**10c**): Eluent for column chromatography: benzene : CH_2Cl_2 = 1 : 1. Colorless needles from CH_2Cl_2–ether, mp 151—153 °C. IR: 1669, 1622, 1597, 1574, 1524. UV: 257 (11900). ^{1}H-NMR: 1.4—1.5 (1H, m), 1.7—1.8 (1H, m), 2.4—2.5 (1H, m), 2.51 (1H, dt, $J=4$, 12 Hz), 3.6—3.7 (1H, m), 4.2 (1H, m), 5.11 (1H, d, $J=11$ Hz), 5.76 (1H, s), 7.57 (1H, dd, $J=2$, 7 Hz), 7.65 (1H, dt, $J=2$, 8 Hz), 7.69 (1H, dt, $J=1$, 8 Hz), 8.02 (1H, dd, $J=1$, 8 Hz). ^{13}C-NMR: 21.1 (t), 24.6 (t), 47.5 (d), 67.5 (t), 104.8 (d), 106.8 (d), 124.9 (d), 128.8 (s), 130.8 (d), 131.8 (d), 133.3 (d), 148.2 (s), 166.7 (s), 193.5 (s). CI-MS m/z: 276 (MH^+).

(4a*R**,8a*R**)-2-(2-Nitrophenyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano-[2,3-*b*]pyran-4-one (**11c**): Eluent for column chromatography: CH_2Cl_2. Pale yellow prisms from CH_2Cl_2–ether, mp 108—111 °C. IR: 1673, 1622, 1601, 1574, 1522. UV: 260 (10200). ^{1}H-NMR: 1.7—2.0 (4H, m), 2.6 (1H, m), 3.8—3.7 (1H, m), 3.92 (1H, dt, $J=4$, 11 Hz), 5.66 (1H, d, $J=3$ Hz), 5.73 (1H, d, $J=1$ Hz), 7.56 (1H, dd, $J=1$, 8 Hz), 7.64 (1H, dt, $J=2$, 8 Hz), 7.69 (1H, dt, $J=1$, 8 Hz), 7.99 (1H, dd, $J=2$, 8 Hz). ^{13}C-NMR: 21.8 (t), 23.3 (t), 46.5 (d), 62.7 (t), 101.3 (d), 105.1 (d), 124.8 (d), 129.2 (s), 130.3 (d), 131.5 (d), 133.2 (d), 148.1 (s), 168.0 (s), 196.0 (s). CI-MS m/z: 276 (MH^+).

Reaction of 1d with B 3-(4-Chlorophenyl)-1-(3,4-dihydro-2*H*-pyran-5-yl)propane-1,3-dione (**9d**): Eluent for column chromatography: benzene : hexane = 1 : 2. Yellow prisms from CH_2Cl_2–ether, mp 60—63 °C. IR: 1620, 1595, 1560, 1543, 1524, 1510. UV: 257 (11000), 352 (21900). ^{1}H-NMR: 1.9—2.4 (2H, m), 2.34 (2H, t, $J=6$ Hz), 4.12 (2H, t, $J=5$ Hz), 6.16 (1H, s), 7.3—7.5 (2H, m), 7.7—7.9 (3H, m). HR-MS m/z (M^+): Calcd for $C_{14}H_{13}ClO_3$: 264.0555. Found: 264.0553.

Reaction of 1e with B 3-(2-Chlorophenyl)-1-(3,4-dihydro-2*H*-pyran-5-yl)propane-1,3-dione (**9e**): Eluent for column chromatography: benzene : hexane = 1 : 1. Yellow oil. IR: 1721, 1609, 1562. UV: 254 (5500), 339 (14200). HR-MS m/z (M^+): Calcd for $C_{14}H_{13}ClO_3$: 264.0531. Found: 264.0551.

(4a*R**,8a*S**)-2-(2-Chlorophenyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]pyran-4-one (**10e**): Eluent for column chromatography: benzene. Pale yellow gum. IR: 1673, 1611, 1586, 1568. UV: 276 (8600). ^{1}H-NMR: 1.3—1.9 (3H, m), 2.3—2.7 (2H, m), 3.5—3.8 (1H, m), 4.1—4.3 (1H, m), 5.16 (1H, d, $J=11$ Hz), 5.83 (1H, s), 7.2—7.6 (4H, m). ^{13}C-NMR: 21.1 (t), 24.6 (t), 47.4 (d), 67.5 (t), 103.9 (d), 108.0 (d), 126.8 (d), 130.4 (d), 130.6 (d), 131.7 (d), 132.2 (s), 132.9 (s), 166.6 (s), 193.7 (s). HR-MS m/z (M^+): Calcd for $C_{14}H_{13}ClO_3$: 264.0556. Found: 264.0559.

(4a*R**,8a*R**)-2-(2-Chlorophenyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]pyran-4-one (**11e**): Eluent for column chromatography: benzene and for PTLC: CH_2Cl_2. Pale yellow gum. IR: 1667, 1611, 1586, 1562. UV: 275 (8400). ^{1}H-NMR: 1.7—2.6 (5H, m), 3.7—4.1 (2H, m), 5.72 (1H, d, $J=3$ Hz), 5.75 (1H, s), 7.3—7.7 (4H, m). ^{13}C-NMR: 21.9 (t), 23.3 (t), 46.3 (d), 62.9 (t), 100.3 (d), 106.3 (d), 126.8 (d), 130.1 (d), 130.6 (d), 131.5 (d), 132.7 (s), 132.8 (s), 168.3 (s), 196.0 (s). HR-MS m/z (M^+): Calcd for $C_{14}H_{13}ClO_3$: 264.0531. Found: 264.0551.

Reaction of 1f with B 1-(3,4-Dihydro-2*H*-pyran-5-yl)-3-(4-methoxyphenyl)propane-1,3-dione (**9f**): Eluent for column chromatography: AcOEt : hexane = 1 : 5. Yellow gum. IR: 1626, 1605, 1514. UV: 218 (9200), 272 (9100), 350 (22500). HR-MS m/z (M^+): Calcd for $C_{15}H_{16}O_4$: 260.1046. Found: 260.1046.

2-Hydroxy-3-(4-methoxybenzoyl)-6-(4-methoxyphenyl)-4*H*-pyran-4-one (**6f**): Eluent for column chromatography: AcOEt : hexane = 5 : 1. Yellow plates from CH_2Cl_2–ether, mp 186—188 °C. IR: 1738, 1624, 1603, 1547, 1512. UV: 3.87 (17100), 296 (7500), 379 (35900). ^{1}H-NMR: 3.87, 3.89 (each 3H, s), 6.52 (1H, s), 6.9—7.1 (4H, m), 7.6—7.9 (4H, m). HR-MS m/z (M^+): Calcd for $C_{20}H_{16}O_6$: 352.0944. Found: 352.0908.

Reaction of 1g with B 1-(3,4-Dihydro-2*H*-pyran-5-yl)-3-(2-methoxyphenyl)propane-1,3-dione (**9g**): Eluent for column chromatography: AcOEt : hexane = 1 : 5. Yellow oil. IR: 1688, 1605, 1562. UV: 247 (7700), 348 (13200). HR-MS m/z (M^+): Calcd for $C_{15}H_{16}O_4$: 260.0149. Found: 260.0150.

(4a*R**,8a*S**)-2-(2-Methoxyphenyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]pyran-4-one (**10g**): Eluent for column chromatography: AcOEt : hexane = 5 : 1 and for PTLC: benzene : acetone = 5 : 1. Colorless needles from CH_2Cl_2–ether, mp 98—100 °C. IR: 1653, 1591, 1570. UV: 282 (11700), 294 (11000), 317 (9400). ^{1}H-NMR: 1.5—1.7 (4H, m), 2.4—2.7 (1H, m), 3.5—4.3 (5H, m), 5.07 (1H, d, J = 9 Hz), 6.39 (1H, s), 6.9—7.1 (2H, m), 7.3—7.5 (1H, m), 7.8—7.9 (1H, m). ^{13}C-NMR: 21.2 (t), 24.7 (t), 47.3 (d), 55.6 (q), 67.3 (t), 103.4 (d), 107.7 (d), 111.4 (d), 120.5 (d), 120.8 (s), 129.5 (d), 132.5 (d), 158.4 (s), 164.3 (s), 194.9 (s). HR-MS m/z (M^+): Calcd for $C_{15}H_{16}O_4$: 260.1049. Found: 260.1067.

(4a*R**,8a*R**)-2-(2-Methoxyphenyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]pyran-4-one (**11g**): Eluent for column chromatography: AcOEt : hexane = 5 : 1 and for PTLC: benzene : acetone = 5 : 1. Pale yellow oil. IR: 1659, 1605, 1570. UV: 283 (11000), 295 (10800), 317 (9300). ^{1}H-NMR: 1.7—2.0 (4H, m), 2.1—2.6 (1H, m), 3.8—4.1 (5H, m), 5.65 (1H, d, J = 3 Hz), 6.34 (1H, s), 6.9—7.1 (2H, m), 7.3—7.5 (1H, m), 7.8—7.9 (1H, m). ^{13}C-NMR: 21.8 (t), 23.3 (t), 46.2 (d), 55.6 (q), 63.0 (t), 99.5 (d), 106.1 (d), 111.5 (d), 120.5 (d), 121.3 (s), 129.5 (d), 132.5 (d), 158.4 (s), 165.6 (s), 197.0 (s). HR-MS m/z (M^+): Calcd for $C_{15}H_{16}O_4$: 260.1046. Found: 264.1046.

Reaction of 1h with B 1-(3,4-Dihydro-2*H*-pyran-5-yl)-3-(2-furyl)-propane-1,3-dione (**9h**): Eluent for column chromatography: benzene : acetone = 80 : 1. Pale yellow prisms from CH_2Cl_2–ether, mp 51—53 °C. IR: 1628, 1582. UV: 211 (5400), 272 (9000), 356 (22200). ^{1}H-NMR: 1.5—1.9 (4H, m), 2.3—2.6 (1H, m), 3.5—4.3 (2H, m), 5.07 (1H, d, J = 11 Hz), 5.97 (1H, s), 6.54 (1H, dd, J = 2, 4 Hz), 7.02 (1H, dd, J = 1, 4 Hz), 7.55 (1H, dd, J = 1, 2 Hz). HR-MS m/z (M^+): Calcd for $C_{12}H_{12}O_4$: 220.0733. Found: 220.0703.

(4a*R**,8a*S**)-2-(2-Furyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]-pyran-4-one (**10h**): Eluent for column chromatography: benzene : acetone = 80 : 1. Brown prisms from CH_2Cl_2–ether, mp 105—107 °C. IR: 1657, 1622. UV: 213 (5000), 307 (19000), 378 (3000). ^{1}H-NMR: 1.5—1.9 (4H, m), 2.3—2.6 (1H, m), 3.5—4.3 (2H, m), 5.07 (1H, d, J = 11 Hz), 5.94 (1H, s), 6.54 (1H, dd, J = 2, 4 Hz), 7.02 (1H, dd, J = 1, 4 Hz), 7.55 (1H, dd, J = 1, 2 Hz). ^{13}C-NMR: 21.2 (t), 24.6 (t), 47.7 (d), 67.5 (t), 100.7 (d), 103.7 (d), 112.5 (d), 114.2 (d), 145.9 (d), 146.8 (s), 158.1 (s), 193.1 (s). HR-MS m/z (M^+): Calcd for $C_{12}H_{12}O_4$: 220.0736. Found: 220.0771.

(4a*R**,8a*R**)-2-(2-Furyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]-pyran-4-one (**11h**): Eluent for column chromatography: benzene : acetone = 80 : 1. Pale yellow prisms from CH_2Cl_2, mp 131—132 °C. IR: 1655, 1620. UV: 280 (5000), 309 (17000), 380 (2400). ^{1}H-NMR: 1.7—2.0 (4H, m), 2.5—2.6 (1H, m), 3.9—4.1 (2H, m), 5.64 (1H, d, J = 4 Hz), 5.92 (1H, s), 6.55 (1H, dd, J = 2, 4 Hz), 7.03 (1H, dd, J = 1, 4 Hz), 7.57 (1H, dd, J = 1, 2 Hz). ^{13}C-NMR: 21.9 (t), 23.2 (t), 46.5 (d), 63.2 (t), 99.3 (d), 99.9 (d), 112.5 (d), 114.2 (d), 145.9 (d), 147.1 (s), 159.3 (s), 195.4 (s). HR-MS m/z (M^+): Calcd for $C_{12}H_{12}O_4$: 220.0734. Found: 220.0719.

Reaction of 1i with B 1-(3,4-Dihydro-2*H*-pyran-5-yl)-3-(2-thienyl)-propane-1,3-dione (**9i**): Eluent for column chromatography: benzene : acetone = 80 : 1. Brown prisms from CH_2Cl_2–ether, mp 49—50 °C. IR: 1628, 1549, 1516. UV: 261 (10700), 361 (16000). ^{1}H-NMR: 1.8—2.1 (2H, m), 2.3—2.6 (2H, m), 4.1—4.2 (2H, m), 6.02 (1H, s), 7.11 (1H, dd, J = 4, 5 Hz), 7.55 (1H, dd, J = 1, 5 Hz). HR-MS m/z (M^+): Calcd for $C_{12}H_{12}O_3S$: 236.0508. Found: 236.0523.

(4a*R**,8a*S**)-2-(2-Thienyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]pyran-4-one (**10i**): Eluent for column chromatography: benzene : acetone = 15 : 1. Pale yellow prisms from CH_2Cl_2–ether, mp 115—118 °C. IR: 1655, 1578. UV: 263 (6300), 318 (16900). ^{1}H-NMR: 1.3—1.9 (4H, m), 2.3—2.6 (1H, m), 3.5—4.4 (2H, m), 5.11 (1H, d, J = 11 Hz), 5.93 (1H, s), 7.12 (1H, dd, J = 4, 5 Hz), 7.54 (1H, dd, J = 1, 5 Hz), 7.60 (1H, dd, J = 1, 4 Hz). ^{13}C-NMR: 21.2 (t), 24.6 (t), 47.4 (d), 67.5 (t), 101.2 (d), 103.7 (d), 128.4 (d), 129.2 (d), 130.8 (d), 135.7 (s), 162.3 (s), 193.1 (s). HR-MS m/z (M^+): Calcd for $C_{12}H_{12}O_3S$: 236.0505. Found: 236.0492.

(4a*R**,8a*R**)-2-(2-Thienyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]pyran-4-one (**11i**): Eluent for column chromatography: benzene : acetone = 15 : 1. Pale yellow prisms from CH_2Cl_2–ether, mp 94—95 °C. IR: 1657, 1578. UV: 260 (6000), 319 (19000). ^{1}H-NMR: 1.71 (4H, m), 2.5—2.7 (1H, m), 3.9—4.1 (2H, m), 5.68 (1H, s), 7.13 (1H, dd, J = 4, 5 Hz), 7.55 (1H, dd, J = 1, 5 Hz), 7.62 (1H, dd, J = 1, 4 Hz). ^{13}C-NMR: 21.9 (t), 23.2 (t), 46.2 (d), 63.2 (t), 99.8 (d), 100.0 (d), 128.3 (d), 129.1 (d), 130.8 (d), 136.2 (s), 163.4 (s), 195.4 (s). *Anal.* Calcd for $C_{12}H_{12}O_3S$: C, 60.99; H, 5.12. Found: C, 60.89; H, 5.13.

Acid-Cyclization of Diketones 3d, 3h, 9d, 9h (General Procedure) The diketones **3d**, **3h**, **9d**, **9h** were each added to concentrated H_2SO_4 at 0 °C and stirred for 1 h. The reaction mixture was poured into cold water and neutralized with Na_2CO_3, then extracted with CH_2Cl_2. The organic layer was concentrated *in vacuo* and the products were purified by column chromatography over SiO_2 and recrystallizations. The products and yields are as follows: **5d** (23 mg, 64%) and **8d** (6 mg, 17%) from 36 mg of **3d**; **5h** (39 mg, 99%) from 40 mg of **3h**; **11d** (16 mg, 32%) and **12d** (33 mg, 66%) from 50 mg of **9d**; and **11h** (139 mg, 93%) from 150 mg of **9h**.

(3a*R**,7a*R**)-6-(4-Chlorophenyl)-2,3,3a,7a-tetrahydro-4*H*-furo[2,3-*b*]pyran-4-one (**5d**): Pale yellow prisms from CH_2Cl_2–ether, mp 112—114 °C. IR: 1659, 1579. UV: 226 (10700), 246 (7400), 233 (9900), 302 (19200). ^{1}H-NMR: 2.0—2.7 (2H, m), 2.98 (1H, ddd, J = 5, 8, 11 Hz), 4.0—4.4 (2H, m), 5.95 (1H, d, J = 1 Hz), 6.03 (1H, d, J = 5 Hz), 7.2—7.5 (2H, m), 7.6—8.0 (2H, m). ^{13}C-NMR: 27.8 (t), 49.6 (t), 69.0 (t), 99.7 (d), 105.7 (d), 128.0 (d × 2), 129.0 (d × 2), 130.8 (s), 138.1 (s), 166.0 (s), 193.3 (s).

2-(4-Chrolophenyl)-5-(2-hydroxyethyl)-4*H*-pyran-4-one (**8d**): Eluent for column chromatography: benzene. Colorless gum. IR: 1657, 1599. UV: 225 (9500), 248 (6400), 299 (17100). ^{1}H-NMR: 2.93 (2H, dt, J = 2, 10 Hz), 4.5—4.8 (2H, m), 6.05 (1H, s), 7.4—7.5 (3H, m), 7.8—7.9 (2H, m). ^{13}C-NMR: 27.4 (t), 73.3 (t), 93.2 (d), 115.9 (s), 128.1 (d × 2), 128.9 (d × 2), 130.7 (s), 134.1 (s), 156.3 (s), 161.2 (s), 182.9 (s). LR-MS m/z: 250 (M^+).

(4a*R**,8a*R**)-2-(4-Chlorophenyl)-4a,6,7,8a-tetrahydro-4*H*,5*H*-pyrano[2,3-*b*]pyran-4-one (**11d**): Eluent for column chromatography: benzene. Pale yellow prisms from CH_2Cl_2–ether, mp 118—121 °C. IR: 1655, 1584, 1522. UV: 226 (10800), 232 (9700), 247 (7400), 300 (17600). ^{1}H-NMR: 1.6—2.0 (4H, m), 2.5—2.7 (1H, m), 3.8—4.2 (2H, m), 5.68 (1H, d, J = 4 Hz), 5.96 (1H, d, J = 1 Hz), 7.4—7.5 (2H, m), 7.6—7.8 (2H, m). ^{13}C-NMR: 21.8 (t), 23.2 (t), 46.1 (d), 63.2 (t), 100.1 (d), 101.1 (d), 128.0 (d × 2), 129.1 (d × 2), 130.8 (s), 138.1 (s), 167.1 (s), 195.9 (s).

2-(4-Chlorophenyl)-5-(3-hydroxypropyl)-4*H*-pyran-4-one (**12d**): Eluent for column chromatography: benzene. Pale yellow prisms, mp 72—76 °C. IR: 1618, 1590. UV: 256 (10400), 350 (22000). ^{1}H-NMR: 1.9—2.0 (2H, m), 2.31 (2H, q, J = 6 Hz), 4.12 (2H, t, J = 5 Hz), 6.16 (1H, s), 7.4—7.5 (2H, m), 7.7—7.9 (3H, m). ^{13}C-NMR: 18.8 (t), 21.2 (t), 66.9 (t), 91.0 (d), 111.6 (s), 128.1 (d), 128.8 (d), 129.0 (d), 130.5 (d), 134.4 (s), 137.8 (s), 154.4 (d), 181.5 (s), 186.8 (s). LR-MS m/z: 264 (M^+).

Reaction of 1 with Trimethylsilylethylenes Possessing Five- or Six-membered Ring (General Procedure) A solution of a 5-arylfuran-2,3-dione (**1a**, **1c**, **1e**) (500 mg) and a trimethylsilyloxyethylene C, D, E or F (3 mol eq) in toluene (10 ml) was heated at 100 °C for 1—5 h in a sealed Pyrex tube. The reaction mixture was concentrated *in vacuo*, and the products were purified by column chromotography over SiO_2, followed by MPLC, PTLC and/or recrystallizations from CH_2Cl_2–ether. The aroylketene dimer **6a** gave ^{1}H-NMR data identical with the reported values.[8]

Reaction of 1a with C 2-Phenyl-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-4-one (**14a**): Eluent for MPLC: benzene : acetone = 10 : 1. Colorless needles, mp 164—165 °C. IR: 1650, 1610, 1580, 1490. UV: 270 (21300). ^{1}H-NMR: 1.6—3.1 (5H, m), 6.75 (1H, s), 7.1—8.1 (6H, m). ^{13}C-NMR: 21.3 (t), 27.4 (t), 33.1 (t), 112.0 (d), 127.0 (s), 127.8 (d × 2), 131.0 (d × 2), 133.2 (s), 133.3 (s), 167.1 (s), 173.1 (s), 181.6 (s). HR-MS m/z (M^+): Calcd for $C_{14}H_{12}O_2$: 212.0836. Found: 212.0836.

Reaction of 1c with C 1-(2-Nitrophenyl)-3-(2-oxocyclopentyl)propane-1,3-dione (**13c**): Eluent for column chromatography: benzene. Pale yellow prisms, mp 104—105 °C. IR: 1618, 1599, 1562, 1531. UV: 214 (13500), 285 (10500). HR-MS m/z (M^+): Calcd for $C_{14}H_{13}NO_5$: 275.0820. Found: 275.0794.

2-(2-Nitrophenyl)-4,5,6,7-tetrahydrocyclopentan[*b*]pyran-4-one (**14c**): Eluent for column chromatography: AcOEt : hexane = 2 : 1. Colorless prisms, mp 165—168 °C. IR: 1661, 1630, 1526. UV: 229 (22200). ^{1}H-NMR: 2.0—2.3 (2H, m), 2.7—3.0 (4H, m), 6.47 (1H, s), 7.5—7.8 (3H, m), 8.0—8.1 (1H, m). ^{13}C-NMR: 19.2 (t), 25.6 (t), 31.1 (t), 114.9 (s), 124.8 (d), 125.6 (s), 127.2 (s), 130.9 (d), 131.4 (d), 133.3 (d), 147.6 (s), 161.6 (s), 168.9 (s), 177.4 (s). HR-MS m/z (M^+): Calcd for $C_{14}H_{11}NO_4$: 257.0668. Found: 257.0685.

Reaction of 1e with C 1-(2-Chlorophenyl)-3-(2-oxocyclopentyl)propane-1,3-dione (**13e**): Eluent for column chromatography: benzene : hexane = 3 : 2. Pale yellow gum. IR: 1605, 1551. UV: 212 (10000), 301 (8000), 343 (7100). HR-MS m/z (M^+): Calcd for $C_{14}H_{13}ClO_3$: 264.0585. Found: 264.0554.

2-(2-Chlorophenyl)-4,5,6,7-tetrahydrocyclopenta[*b*]pyran-4-one

(**14e**): Eluent for column chromatography: benzene : acetone = 20 : 1, then AcOEt : hexane = 2 : 3. Colorless plates, mp 100—103 °C. IR: 1653, 1626. UV: 214 (23600), 256 (14600). ^{13}C-NMR: 19.4 (t), 25.9 (t), 31.6 (t), 116.7 (d), 125.5 (s), 127.0 (s), 130.6 (d), 130.7 (d), 131.5 (s, d), 132.8 (s), 162.2 (s), 169.3 (s), 178.0 (s). HR-MS *m/z* (M^+): Calcd for $C_{14}H_{11}ClO_2$: 246.0484. Found: 246.0448.

Reaction of 1a with D 8a-Hydroxy-2-phenyl-4a,5,6,7,8,8a-hexahydro-4*H*-benzo[*b*]pyran-4-one (**16a**): Eluent for MPLC :benzene, then benzene : acetone = 10 : 1. Colorless needles, mp 56 °C. IR: 1713, 1622, 1578. UV: 287 (14200). ^{1}H-NMR: 1.3—2.4 (9H, m), 5.88 (1H, s), 7.3—7.8 (5H, m), ^{13}C-NMR: 22.4 (t × 2), 24.7 (t), 33.7 (t), 91.4 (d), 107.2 (s), 126.3 (d × 2), 128.8 (d),131.2 (s), 132.0 (d × 2), 161.9 (s), 164.5 (s). HR-MS *m/z* (M^+): $C_{15}H_{16}O_3$: 244.1097. Found: 244.1086.

Reaction of 1c with D 2-(2-Nitrophenyl)-5,6,7,8,-tetrahydro-4*H*-benzo[*b*]pyran-4-one (**17c**): Eluent for column chromatography: AcOEt : hexane = 1 : 1. Pale yellow gum. IR: 1667, 1622. UV: 233 (22500). ^{1}H-NMR: 1.7—1.9 (4H, m), 2.4—2.6 (4H, m), 6.47 (1H, s), 7.5—7.8 (3H, m), 8.0—8.1 (1H, m). LR-MS *m/z*: 271 (M^+).

Reaction of 1e with D 1-(2-Chlorophenyl)-3-(2-oxocyclohexyl)propane-1,3-dione (**15e**): Eluent for column chromatography: benzene : hexane = 3 : 2. Yellow oil. IR: 1659, 1638. UV: 419 (3400).

Reaction of 1a with E 3-Phenyl-1-(1-oxo-2,3-dihydroinden-2-yl)propane-1,3-dione (**18a**): Eluent for column chromatography: benzene. Yellow needles from benzene, mp 127—128 °C. IR: 1628, 1611, 1593, 1562, 1545. UV: 389 (27600). HR-MS *m/z* (M^+): Calcd for $C_{18}H_{14}O_3$: 278.0942. Found: 278.0952.

Reaction of 1c with E 1-(2-Nitrophenyl)-3-(1-oxo-2,3-dihydroinden-2-yl)propane-1,3-dione (**18c**): Eluent for column chromatography: benzene. Yellow prisms, mp 119—122 °C. IR: 1638, 1624, 1605, 1591, 1562, 1526. UV: 247 (12500), 300 (10200), 383 (16900). HR-MS *m/z* (M^+): Calcd for $C_{18}H_{13}NO_5$: 323.0748. Found: 323.0791.

Reaction of 1e with E 1-(2-Chlorophenyl)-3-(1-oxo-2,3-dihydroinden-2-yl)propane-1,3-dione (**18e**): Eluent for column chromatography: benzene : hexane = 3 : 2. Yellow prisms, mp 128—131 °C. IR: 1615, 1589, 1555. UV: 246 (9200), 297 (8400), 381 (26400). HR-MS *m/z* (M^+): Calcd for $C_{18}H_{13}ClO_3$: 312.0549. Found: 312.0551.

Reaction of 1a with F 5,6-Dihydro-2-phenyl-4*H*-naphto[1,2-*b*]pyran-4-one (**21a**): Eluent for column chromatography: benzene and for MPLC: benzene : acetone = 5 : 2. Colorless prisms, mp 175—176 °C. IR: 1650, 1618. UV: 291 (19300). ^{1}H-NMR: 2.9 (4H, m), 6.88 (1H, s), 7.3—7.9 (9H, m). HR-MS *m/z* (M^+): Calcd for $C_{19}H_{14}O_2$: 274.0991. Found: 274.0983.

Reaction of 1c with F 1-(2-Nitrophenyl)-3-(1-oxo-1,2,3,4-tetrahydronaphtalen-2-yl)propane-1,3-dione (**20c**): Eluent for column chromatography: benzene. Yellow prisms, 108—111 °C, IR: 1603, 1586, 1547, 1531. UV: 305 (7400), 394 (15300). LR-MS *m/z*: 324 (M^+).

5,6-Dihydro-2-(2-nitrophenyl)-4*H*-naphto[1,2-*b*]pyran-4-one (**21c**): Eluent for column chromatography: CH_2Cl_2 : hexane = 1 : 1. Pale yellow prisms, mp 173—178 °C. IR: 1653, 1626, 1531. UV: 262 (17500), 289 (15800), 307 (14000). ^{1}H-NMR: 2.9 (4H, m), 6.63 (1H, s), 7.2—7.4 (3H, m), 7.4—7.6 (1H, m), 7.6—7.9 (3H, m), 8.0—8.1 (1H, m). ^{13}C-NMR: 18.6 (t), 26.7 (t), 114.4 (d), 121.0 (s), 123.0 (d), 124.8 (d), 127.1 (d), 127.4 (s × 2), 128.1 (d), 130.9 (d), 131.0 (d), 131.6 (d), 133.2 (d), 138.6 (s), 148.2 (s), 158.3 (s), 160.3 (s), 178.2 (s).

Reaction of 1e with F 3-(2-Chlorophenyl)-1-(1-oxo-1,2,3,4-tetrahydronphtalen-2-yl)propane-1,3-dione (**20e**): Eluent for column chromatography: benzene : hexane = 1 : 4. Yellow prisms, 95—98 °C. IR: 1605, 1584, 1547. UV: 243 (8900), 309 (7000), 394 (24800). HR-MS *m/z* (M^+): Calcd for $C_{19}H_{15}O_3Cl$: 326.0675. Found: 326.0707.

2-(2-Chlorophenyl)-5,6-dihydro-4*H*-naphto[1,2-*b*]pyran-4-one (**21e**): Eluent for column chromatography: AcOEt : hexane = 1 : 1. Colorless prisms, mp 118—121 °C. IR: 1655, 1622, 1611. UV: 267 (14900), 277 (15700), 289 (15400), 309 (13000). ^{1}H-NMR: 2.9 (4H, m), 6.67 (1H, s), 7.2—7.7 (7H, m), 7.8—7.9 (1H, m). ^{13}C-NMR: 18.6 (t), 26.8 (t), 115.9 (d), 120.7 (s), 123.4 (d), 127.0 (d), 127.1 (d), 128.0 (s), 128.2 (d), 130.6 (d), 130.8 (d), 130.9 (d), 131.6 (d), 132.8 (s), 138.7 (s), 158.4 (s), 161.2 (s × 2), 178.6 (s). HR-MS *m/z* (M^+): Calcd for $C_{19}H_{13}ClO_2$: 308.0615. Found: 308.0605.

Acid-Cyclization of Triketones 13e, 18e, 20e Triketones **13e**, **18e** and **20e** (each 50 mg) were each added to a concentrated H_2SO_4 at 0 °C and the solution stirred for 1 h. The reaction mixture was poured into cold water, neutralized Na_2CO_3, and then extracted with CH_2Cl_2. The organic layer was concentrated *in vacuo* and the products were purified by recrystallizations to give **14e** (37 mg, 80%), **19e** (45 mg, 96%) and **21e** (40 mg, 85%).

2-(2-Chlorophenyl)-4,5-dihydro-4*H*-indene[1,2-*b*]pyran-4-one (**19e**): Colorless prisms from CH_2Cl_2–ether, mp 184—186 °C. IR: 1651. UV: 286 (18700), 299 (17900). ^{1}H-NMR: 3.82 (2H, s), 6.72 (1H, s), 7.4—7.8 (8H, m). ^{13}C-NMR: 31.6 (t), 117.5 (d), 120.3 (d), 125.1 (s), 125.6 (d), 127.1 (d), 127.4 (d), 129.9 (d), 130.7 (d), 130.8 (d), 131.4 (s), 131.6 (d), 133.0 (s), 134.9 (s), 142.9 (s), 161.4 (s), 164.8 (s), 176.7 (s). HR-MS *m/z* (M^+): Calcd for $C_{18}H_{11}ClO_2$: 294.0433. Found: 294.0445.

References and Notes

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