The BF_3·Et_2O-Catalyzed Reaction of 1,2-Bis[(trimethylsilyl)oxy]cyclobutene and Analogues with Aromatic Ketones

Sheldon N. Crane and D. Jean Burnell*

Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland A1B 3X7, Canada

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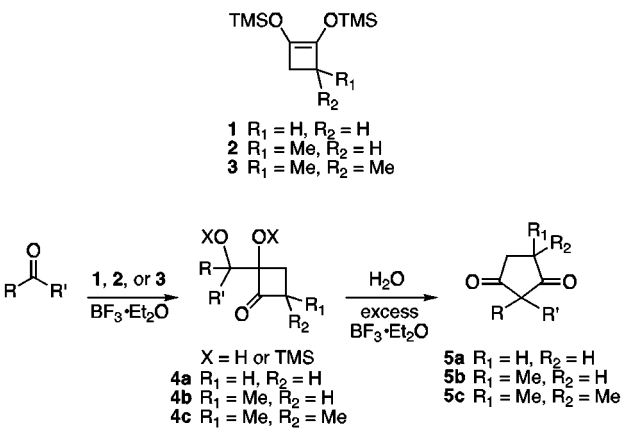
Ketones[1] and their acetals[2−5] in the presence of a Lewis acid, usually BF_3·Et_2O, were shown to react with 1,2-bis((trimethylsilyl)oxy)cyclobutene (**1**) and its methylated analogues **2** and **3**[6] to give cyclobutanone derivatives **4a**−**c**, and these could be rearranged to give geminally acylated compounds **5a**−**c** (Scheme 1). Geminal acylations with **1** have been employed in a number of synthetic endeavors.[3,7,8] In the particular case of the reactions with ketones, cyclobutanone intermediates **4a**−**c** were rearranged in the same pot to give **5a**−**c** by addition of water and excess BF_3·Et_2O. The one-pot procedure with **1** and **2** provided good to excellent yields of **5a** and **5b** when the substrates were unhindered,[1,3−6] whereas yields of **5c** using **3** were usually modest, even with unhindered ketones.[6] Reactions of some α,β-unsaturated ketones with **3** provided **5c** with yields around 80%, but, unlike the reactions of their saturated counterparts, enone substrates afforded **5c** directly, without the addition of water and excess BF_3·Et_2O. This might be attributed to allylic stabilization of a positive charge in the transition state of the rearrangement. We reasoned that a similar benzylic stabilization could arise with aromatic ketones, which might lead to an improvement in the procedure for the reaction of these substrates with **1** and an opportunity to carry out geminal acylation of aromatic ketones with both **2** and **3**.

Five aromatic substrates were subjected to very similar reaction conditions. For **1** and **2**, the ketone and 1.5 equiv of freshly distilled BF_3·Et_2O were dissolved in dry CH_2Cl_2, and 2−3 equiv of the bis((trimethylsilyl)oxy)-cyclobutene were added while maintaining anhydrous conditions. For **3**, the only difference was that up to 3 equiv of BF_3·Et_2O were employed. The reaction mixture was stirred at room temperature for approximately 24 h. Straightforward aqueous workup followed by flash chromatography provided the geminally acylated product, a 1,3-diketone. The results are summarized in Table 1.

Scheme 1



The yields of **6**, **7**, **8**, and **10** (from **1** with acetophenone, 1-indanone, 1-tetralone, and 4-chromanone) were similar to the yields by the earlier procedure that involved adding H_2O to the reaction mixture,[1] which in turn were generally better than the reactions with acetals derived from aromatic ketones.[4,5] The acetal of benzophenone was reported by Ayyangar[5] to react with **1** to give only a trace of **12**, whereas the conversion of benzophenone to **12** was 75% under these anhydrous conditions. The reactions with 1-tetralone, 4-chromanone, and benzophenone also gave minor amounts of lactones **9**, **11a,b**, and **13**, respectively. Similar lactones had been observed in the reactions of enones with **3**,[6] and Pandey reported the photochemical conversion of **7** and **8** to the corresponding lactones.[8] In our case, we postulate the formation of these lactones by the process shown in Scheme 2. Acid-promoted elimination of the benzylic oxygen function in **4a** could lead not only to 1,2-acyl shift (and thence to **5a**) but also to rupture of the four-membered ring to produce the acylium ion in **27**. Attack of the conjugated enol moiety onto the acylium ion would give the lactone.

Yields in the reactions of (racemic) **2** with the five substrates mirrored those with **1**: 1-tetralone and 4-chromanone gave lower yields, near 50%. Unlike the products derived from **1** and **3**, those from **2** were complicated by diastereoisomerism, except in the case of **18**. Very modest stereochemical preferences were noted, with acetophenone showing the largest stereoselectivity, albeit only 2.6:1. When acetals were prepared from acetophenone, 1-indanone, and 1-tetralone, and these were reacted with **2**, geminal acylation products were obtained in slightly lower yields and again with modest diastereoselectivities. Production of the isomer that had been more abundant from the ketone reactions was reduced in the reactions with acetals. In the cases of 1-indanone and 1-tetralone, the diastereoselectivities were opposite to the reactions of their corresponding acetals. AM1 calculations[9] gave no difference in the energies of **14a** and **14b**, so any stereoselectivity was likely to be the

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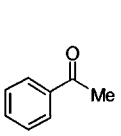
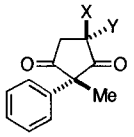
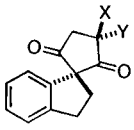
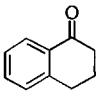
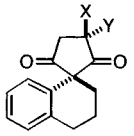
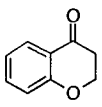
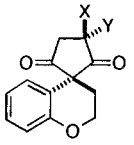
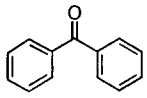
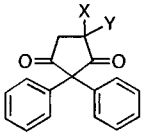
Table 1. Products and Yields in the Reactions of Five Aromatic Ketones with Cyclobutenes 1−3

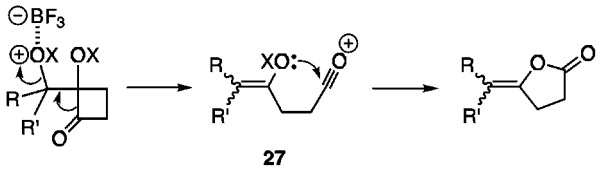
substrate	1,3-diketone product	with **1**	with **2**	with **3**
		**6** X = Y = H, 70%	**14a** X = Me, Y = H **14b** X = H, Y = Me **a/b** 1:2.6, 77% (from acetal: **a/b** 1:1.2, 63%)	**19** X = Y = Me, 76%[a]
		**7** X = Y = H, 75%	**15a** X = Me, Y = H **15b** X = H, Y = Me **a/b** 1.8:1, 62% (from acetal: **a/b** 1:1.5, 55%)	**20** X = Y = Me, 69%
		**8** X = Y = H, 42% (+ **9**, 2%)	**16a** X = Me, Y = H **16b** X = H, Y = Me **a/b** 1.5:1, 52% (from acetal: **a/b** 1:2.3, 48%)	**21** X = Y = Me, 65% (+ **22a, 22b** 2.6:1, 15%)
		**10** X = Y = H, 45% (+ **11a, 11b** 1.5:1, 11%)	**17a** X = Me, Y = H **17b** X = H, Y = Me **a/b** 1.2:1, 49%	**23** X = Y = Me, 54% (+ **24a, 24b** 2.6:1, 27%)[b]
		**12** X = Y = H, 75% (+ **13**, 12%)[c]	**18** X = Me, Y = H, 71%	**25** X = Y = Me, 68% (+ **26** 16%)

[a] An 85% yield of a 9:1 mixture of **19** and two isomeric compounds.

[b] Sum of isolated yields plus proportion of a fraction containing a mixture of **23** and **24a,b**.

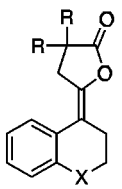
[c] An 87% yield of a 6.3:1 mixture of **12** and **13**.

Scheme 2

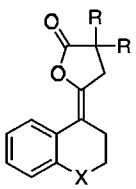


27

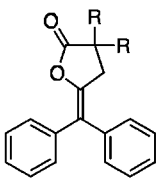
consequence of a kinetically controlled process. We suggest that the stereoselectivity was a result of facial selectivity in the initial aldol process since a regiochemical preference in the initial aldol step (to produce **4b** or its positional isomer) would have no remaining manifestation in a racemic product. It was curious that lactone products were not isolated from the reactions with **2**, although small amounts of carbonyl-containing secondary products were detected.



11a R = H, X = O
22a R = Me, X = CH_2
24a R = Me, X = O

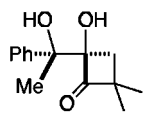


9 R = H, X = CH_2
11b R = H, X = O
22b R = Me, X = CH_2
24b R = Me, X = O



13 R = H
26 R = Me

Geminal acylation using **3** with the five substrates gave 1,3-diketones in moderate yield. With acetophenone, **19** was the dominant component of the product, which also contained small amounts of isomeric compounds that were inseparable by flash chromatography. The reactions of **3** with 1-tetralone and 4-chromanone provided minor, but significant, amounts of the lactone pairs **22a,b** and **24a,b** (2.6:1 ratio in each case), and NOE measurements indicated that the *E*-isomer was the more abundant isomer.[10] A lactone **26** was also a byproduct of the reaction with benzophenone. Solutions of diketone **23** in CH_2Cl_2 were stirred for 24 h at room temperature with 4 equiv of $BF_3{\cdot}Et_2O$ under anhydrous conditions, and with 15 equiv of $BF_3{\cdot}Et_2O$ and 6 equiv of water. In neither case were lactones **24a,b** observed. Furthermore, when the reaction of **3** with acetophenone was conducted at −20 °C it was possible to intercept two diastereomeric cyclobutanone intermediates **28** and **29**, in a 5.7:1 ratio.[11]



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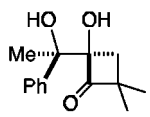

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(The relative stereochemistry of the minor product was determined by X-ray crystallography.[12]) Thus, the regioselectivity of the initial aldol step was very high, and facial selectivity was responsible for the production of **28**

(9) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909 using SPARTAN, Version 4.1 (Wavefunction, Inc., Irvine, CA).

(10) The ^{1}H NMR spectra of the (minor) *Z*-lactones **22b** and **24b** showed one aromatic resonance just downfield of δ 8. This feature was used to assign the *Z*-lactone structures to **9** and **11b**.

(11) Similar attempts to obtain cyclobutanone intermediates from 1-indanone and 1-tetralone at −20 °C gave only the 1,3-diketone and lactone products.

over **29**. The process shown in Scheme 2 would also account for the formation **22a,b**, **24a,b**, and **26** from **4c**.

In summary, geminal acylation of aromatic ketones with **1** and its methylated analogues **2** and **3** can take place in fair to good yield. In contrast with the process for the geminal acylation of saturated ketones, both steps in the geminal acylation of aromatic and α,β-unsaturated ketones occur readily under anhydrous conditions.

Experimental Section

General Section. Compounds **1**−**3** were obtained by using the method for the preparation of **1** of Bloomfield and Nelke.[13] ^{1}H NMR spectra were obtained at 300 MHz in $CDCl_3$ unless specified otherwise, and shifts are relative to internal TMS. NOE measurements were made from difference spectra and are reported as the saturated signal (observed signal, enhancement). ^{13}C NMR spectra were recorded at 75 MHz. Chemical shifts are relative to solvent, and each ^{13}C chemical shift is followed in parentheses by the number of attached protons as determined by APT and heteronuclear correlation spectra.

General Procedure. 2-Methyl-2-phenylcyclopentane-1,3-dione (6). A solution of acetophenone (241 mg, 2.01 mmol), **1** (0.73 g, 3.2 mmol), and freshly distilled $BF_3{\cdot}Et_2O$ (0.30 mL, 2.4 mmol) in CH_2Cl_2 (10 mL, distilled from CaH_2) was stirred at rt under N_2 for 25.5 h. Aqueous workup provided a viscous tan-colored oil (406 mg). Flash chromatography (MeOH−CH_2Cl_2 1:200) afforded **6** as a very pale yellow oil (267 mg, 70%). Spectra were the same as previously reported.[4] Spectra for **7** and **8** also were reported in previous work.[1]

3,4-Dihydro-5-(1-naphthylidene)-2-furanone (9). Beige solid; ^{1}H NMR δ 8.04 (1H, d, J = 7.7 Hz), 7.24−7.06 (3H, m), 3.01 (2H, apparent t, J = 8.6 Hz), 2.85−2.66 (4H, m), 2.37 (2H, apparent t, J = 6.2 Hz), 1.86 (2H, apparent t, J = 6.3 Hz).

1′,2′,3′,4′-Tetrahydro-4′-oxaspiro[cyclopentane-1,1′-naphthalene]-2,5-dione (10). Pale yellow solid, mp 110−111.5 °C; ^{1}H NMR δ 7.19 (1H, apparent dt, J = 1.3, 7.7 Hz), 6.91 (1H, d, J = 7.3 Hz), 6.85 (1H, apparent t, J = 7.5 Hz), 6.58 (1H, dd, J = 1.6, 7.7 Hz), 4.33 (2H, apparent t, J = 5.2 Hz), 3.02 (4H, symmetric m), 2.08 (2H, apparent t, J = 5.1 Hz); ^{13}C NMR δ 213.6 (2C, 0), 155.2 (0), 129.2 (1), 128.0 (1), 120.9 (1), 117.7 (1), 117.6 (0), 60.7 (2), 60.0 (0), 35.2 (2C, 2), 28.9 (2).

3,4-Dihydro-5-(1-(1′,2′,3′,4′-tetrahydro-4-oxanaphthylidene))-2-furanone (11a,b). Gummy, yellow solid (1.5:1 mixture of geometric isomers). Major isomer: ^{1}H NMR (discernible signals) δ 7.19 (1H, br d, J = 7.8 Hz), 2.53 (2H, br t). Minor isomer: ^{1}H NMR (discernible signals) δ 8.10 (1H, dd, J = 1.6, 8.0 Hz), 3.25 (2H, br t). ^{13}C NMR (signals for both isomers) δ 174.9/174.0 (0), 154.6/153.7 (0), 143.5/142.5 (0), 108.3/104.7 (0), 65.9/65.5 (2).

2,2-Diphenylcyclopentane-1,3-dione (12). Pale yellow solid, mp 158−160 °C; ^{1}H NMR δ 7.40−7.28 (6H, m), 7.12−7.04 (4H, m), 2.96 (4H, s); ^{13}C NMR δ 211.3 (2C, 0), 136.5 (2C, 0), 128.9 (1), 128.1 (1), 72.2 (0), 36.0 (2C, 2).

3,4-Dihydro-5-(diphenylmethylene)-2-furanone (13). Yellow solid, mp 103.5−106.5 °C; ^{1}H NMR δ 7.44−7.16 (10H, m), 2.92 (2H, dd, J = 9.1, 11.1 Hz), 2.70 (2H, dd, J = 9.0, 10.9 Hz); ^{13}C NMR δ 174.7 (0), 146.2 (0), 138.7 (0), 137.5 (0), 129.9 (2C, 1), 129.2 (2C, 1), 128.6 (2C, 1), 127.9 (2C, 1), 127.3 (1), 126.8 (1), 118.5 (0), 27.5 (2), 25.9 (2).

(2*R,4*R**)-2,4-Dimethyl-2-phenyl-1,3-cyclopentanedione (14a).** Colorless oil; ^{1}H NMR δ 7.39−7.25 (3H, m), 7.25−7.17 (2H, m), 3.13 (1H, dd, J = 11.7, 18.2 Hz), 3.01 (1H, m), 2.34 (1H, dd, J = 8.0, 18.2 Hz), 1.43 (3H, s), 1.28 (3H, d, J = 6.9 Hz); ^{13}C NMR δ 215.0 (0), 212.6 (0), 137.4 (0), 129.3 (2C, 1), 127.8 (1), 126.2 (2C, 1), 62.1 (0), 43.9 (2), 40.8 (1), 20.1 (3), 14.7 (3).

(2*R,4*S**)-2,4-Dimethyl-2-phenyl-1,3-cyclopentanedione (14b).** Pale yellow oil; ^{1}H NMR δ 7.40−7.25 (3H, m), 7.25−7.19 (2H, m), 2.98 (1H, dd, J = 9.6, 16.7 Hz), 2.86 (1H, m), 2.53 (1H, dd, J = 8.6, 16.7 Hz), 1.47 (3H, s), 1.29 (3H, d, J = 7.1 Hz); NOE data 2.53 (2.98, 6%; 2.86, 4%), 1.43 (7.22, 8%; 2.86, 2%); ^{13}C NMR δ 216.2 (0), 212.7 (0), 137.0 (0), 129.0 (2C, 1), 127.7 (1), 126.4 (2C, 1), 61.0 (0), 43.7 (2), 42.0 (1), 20.8 (3), 16.9 (3).

(2*R,4*R**)-2′,3′-Dihydro-4-methylspiro(cyclopentane-2,1′-[1*H*]indene)-1,3-dione (15a).** Viscous, yellow oil; ^{1}H NMR δ 7.30 (1H, d, J = 8.0 Hz), 7.23 (1H, apparent t, J = 7.4 Hz), 7.15 (1H, apparent t, J = 7.2 Hz), 6.93 (1H, d, J = 7.7 Hz), 3.32 (1H, m), 3.29−3.09 (3H, m), 2.59−2.32 (2H, m), 2.49 (1H, m), 1.37 (3H, d, J = 7.3 Hz); ^{13}C NMR δ 214.9 (0), 212.8 (0), 144.6 (0), 141.0 (0), 128.1 (1), 126.7 (1), 125.2 (1), 122.2 (1), 69.5 (0), 44.1 (2), 41.6 (1), 32.6 (2), 31.6 (2), 15.1 (3).

(2*R,4*S**)-2′,3′-Dihydro-4-methylspiro(cyclopentane-2,1′-[1*H*]indene)-1,3-dione (15b).** Viscous, pale yellow oil; ^{1}H NMR δ 7.30 (1H, d, J = 7.5 Hz), 7.24 (1H, apparent t, J = 7.2 Hz), 7.16 (1H, apparent t, J = 7.4 Hz), 6.83 (1H, d, J = 7.1 Hz), 3.26−3.09 (3H, m), 3.02 (1H, m), 2.62 (1H, dd, J = 9.6, 18.0 Hz), 2.49−2.26 (2H, m), 1.41 (3H, d, J = 6.8 Hz); NOE data 6.83 (2.62, 1%), 2.62 (6.83, 2%; 3.19 dd, 6%; 3.02, 2%; 1.41, 1%), 1.41 (6.83, 2%; 3.02, 5%; 2.62, 4%); ^{13}C NMR δ 216.3 (0), 212.7 (0), 145.3 (0), 140.8 (0), 128.1 (1), 126.8 (1), 124.9 (1), 123.2 (1), 69.1 (0), 44.5 (2), 41.9 (1), 35.6 (2), 31.5 (2), 15.1 (3).

(2*R,4*R**)-1′,2′,3′,4′-Tetrahydro-4-methylspiro[cyclopentane-2,1′-naphthalene]-1,3-dione (16a).** Yellow resin; ^{1}H NMR δ 7.23−7.12 (2H, m), 7.08 (1H, m), 6.56 (1H, d, J = 7.6 Hz), 3.11 (1H, m), 3.08−2.92 (2H, m), 2.85 (2H, m), 2.69 (1H, br dd, J = 8.5, 16.1 Hz), 2.14−1.79 (4H, m), 1.45 (3H, d, J = 7.1 Hz); ^{13}C NMR δ 217.0 (0), 214.8 (0), 138.4 (0), 132.2 (0), 129.9 (1), 127.9 (1), 127.5 (1), 126.3 (1), 61.5 (0), 43.7 (1), 43.2 (2), 31.5 (2), 28.7 (2), 18.0 (2), 16.5 (3).

(2*R,4*S**)-1′,2′,3′,4′-Tetrahydro-4-methylspiro[cyclopentane-2,1′-naphthalene]-1,3-dione (16b).** Colorless resin; ^{1}H NMR δ 7.22−7.12 (2H, m), 7.09 (1H, m), 6.48 (1H, d, J = 7.8 Hz), 3.32 (1H, dd, J = 10.4, 18.2 Hz), 3.20 (1H, m), 2.84 (2H, m), 2.48 (1H, dd, J = 8.6, 18.4 Hz), 2.11−1.81 (4H, m), 1.37 (3H, d, J = 6.6 Hz); NOE data 2.48 (6.48, 1%; 3.32, 5%; 3.20, 3%), 1.37 (6.48, 2%; 3.20, 6%; 2.48, 4%); ^{13}C NMR δ 217.2 (0), 213.9 (0), 138.5 (0), 132.0 (0), 129.6 (1), 128.7 (1), 127.5 (1), 126.2 (1), 63.0 (0), 44.6 (2), 40.0 (1), 32.1 (2), 28.7 (2), 18.0 (2), 15.4 (3).

(2*R,4*R**)-1′,2′,3′,4′-Tetrahydro-4-methyl-4-oxaspiro[cyclopentane-2,1′-naphthalene]-1,3-dione (17a).** White resin; ^{1}H NMR δ 7.17 (1H, ddd, J = 1.5, 7.2, 8.4 Hz), 6.90 (1H, dd, J = 0.9, 8.3 Hz), 6.83 (1H, ddd, J = 1.3, 7.2, 7.8 Hz), 6.60 (1H, dd, J = 1.6, 7.8 Hz), 4.43 (1H, ddd, J = 4.2, 6.8, 11.0 Hz), 4.32 (1H, ddd, J = 4.0, 7.0, 11.6 Hz), 3.25−3.05 (2H, m), 2.64 (1H, m), 2.06 (2H, m), 1.43 (3H, d, J = 7.0 Hz); ^{13}C NMR δ 215.6 (0), 213.5 (0), 155.1 (0), 129.2 (1), 127.6 (1), 120.9 (1), 118.0 (1), 117.9 (0), 61.1 (2), 56.2 (0), 43.4 (1), 43.3 (2), 28.9 (2), 16.0 (3).

(2*R,4*S**)-1′,2′,3′,4′-Tetrahydro-4-methyl-4-oxaspiro[cyclopentane-2,1′-naphthalene]-1,3-dione (17b).** White resin; ^{1}H NMR δ 7.19 (1H, m), 6.90 (1H, m), 6.85 (1H, m), 6.50 (1H, dd, J = 1.6, 7.8 Hz), 4.30 (2H, symmetric m), 3.31 (1H, dd, J = 10.5, 18.4 Hz), 3.16 (1H, m), 2.09 (2H, symmetric m), 2.56 (1H, dd, J = 9.1, 18.4 Hz), 1.41 (3H, d, J = 7.1 Hz); NOE data 2.56 (6.50, 1%; 3.31, 7%, 3.16, 2%, 1.41, 1%), 1.37 (6.50, 2%; 3.16, 5%, 2.56, 3%); ^{13}C NMR δ 216.3 (0), 212.7 (0), 155.5 (0), 129.3 (1), 128.6 (1), 121.0 (1), 118.0 (0), 117.7 (1), 60.8 (2), 57.8 (0), 44.7 (2), 40.4 (1), 29.9 (2), 15.3 (3).

4-Methyl-2,2-diphenylcyclopentane-1,3-dione (18). Yellow solid, mp 86.5−88.5 °C; ^{1}H NMR δ 7.40−7.27 (6H, m), 7.20−7.12 (2H, m), 7.30−6.95 (2H, m), 3.20 (1H, dd, J = 10.6, 17.9 Hz), 3.07 (1H, m), 2.54 (1H, dd, J = 8.7, 17.9 Hz), 1.35 (3H, d, J = 7.0 Hz); ^{13}C NMR δ 213.6 (0), 210.7 (0), 137.3 (0), 136.4 (0), 129.8 (1), 128.9 (1), 128.5 (1), 128.4 (1), 128.0 (1), 127.9 (1), 127.6 (1), 44.3 (2), 41.8 (1), 15.6 (3).

2,4,4-Trimethyl-2-phenylcyclopentane-1,3-dione (19). Pale yellow oil; ^{1}H NMR δ 7.40−7.20 (5H, m), 2.77 (1H, d, J = 17.4 Hz), 2.58 (1H, d, J = 17.4 Hz), 1.47 (3H, s), 1.24 (3H, s), 1.23 (3H, s); ^{13}C NMR δ 218.3 (0), 213.2 (0), 137.4 (0), 129.1 (2C, 1), 127.7 (1), 126.2 (2C, 1), 60.9 (0), 50.8 (2), 46.9 (0), 26.2 (3), 25.8 (3), 22.0 (3).

2′,3′-Dihydro-4,4-dimethylspiro[cyclopentane-2,1′-[1*H*]-indene]-1,3-dione (20). Yellow solid, mp 65−66.5 °C; ^{1}H NMR δ 7.28 (1H, apparent t, J = 7.0 Hz), 7.23 (1H, apparent dt, J = 1.2, 7.4 Hz), 7.15 (1H, apparent t, J = 7.1 Hz), 6.85 (1H, d, J = 7.5 Hz), 3.18 (2H, m), 2.87 (1H, d, J = 17.7 Hz), 2.76 (1H, d, J

(12) Atomic coordinates for the X-ray structure of **29** have been deposited with the Cambridge Crystallographic Data Centre. A request for these coordinates should be addressed to the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CD2 1EZ, UK.

(13) Bloomfield, J. J.; Nelke, J. M. *Organic Syntheses*; Wiley: New York, 1988; Collect. Vol. VI, pp 167−172.

= 17.6 Hz), 2.50−2.30 (2H, m), 1.39 (3H, s), 1.30 (3H, s); ^{13}C NMR δ 218.9 (0), 213.0 (0), 145.3 (0), 141.2 (0), 128.2 (1), 126.9 (1), 125.1 (1), 123.0 (1), 68.4 (0), 51.5 (2), 46.9 (0), 36.2 (2), 31.8 (2), 25.8 (3), 24.0 (3).

1′,2′,3′,4′-Tetrahydro-4,4-dimethylspiro[cyclopentane-2,1′-naphthalene]-1,3-dione (21). Pale yellow solid, mp 97−98.5 °C; ^{1}H NMR δ 7.24−7.04 (3H, m), 6.55 (1H, d, J = 7.8 Hz), 2.98 (1H, d, J = 18.3 Hz), 2.85 (2H, apparent t, J = 6.0 Hz), 2.70 (1H, d, J = 18.3 Hz), 2.10−1.88 (4H, m), 1.44 (3H, s), 1.34 (3H, s); ^{13}C NMR δ 219.7 (0), 214.6 (0), 138.5 (0), 132.0 (0), 129.8 (1), 128.5 (1), 127.6 (1), 126.3 (1), 62.7 (0), 50.7 (2), 46.5 (0), 32.7 (2), 28.7 (2), 26.6 (3), 26.0 (3), 18.0 (2).

3,4-Dihydro-3,3-dimethyl-5-(1-(1,2,3,4-tetrahydronaphthylidene))-2-furanone (22a,b). Major isomer **22a**: beige solid, mp 69−71.5 °C; ^{1}H NMR δ 7.16 (4H, br s), 3.02 (2H, narrow m), 2.74 (2H, t, J = 6.3 Hz), 2.65 (2H, br t, J = 6.8 Hz), 1.80 (2H, apparent pentet, J = 6.4 Hz), 1.30 (6H, s); NOE data 7.16 (3.02, 9%; 2.74, 4%), 3.02 (7.16, 24%; 1.30, 7%), 1.30 (3.02, 10%); ^{13}C NMR δ 179.8 (0), 142.2 (0), 139.4 (0), 133.5 (0), 128.5 (1), 126.32 (1), 126.28 (1), 125.5 (1), 114.7 (0), 41.9 (2), 40.1 (0), 30.4 (2), 25.2 (2), 24.8 (2C, 3), 22.7 (2). Minor isomer **22b** (discernible signals from spectrum of mixture): ^{1}H NMR δ 8.07 (1H, br d, J = 7.5 Hz), 2.85 (2H, m), 2.79 (2H, t, J = 6.2 Hz), 2.36 (2H, br t, J = 6.4 Hz), 1.86 (2H, apparent pentet, J = 6.3 Hz), 1.36 (6H, s).

1′,2′,3′,4′-Tetrahydro-4,4-dimethyl-4-oxaspiro[cyclopentane-2,1′-naphthalene]-1,3-dione (23). Tan-colored resin; ^{1}H NMR δ 7.18 (1H, ddd, J = 1.7, 7.2, 8.3 Hz), 6.90 (1H, dd, J = 1.2, 8.4 Hz), 6.84 (1H, apparent dt, J = 1.3, 7.5 Hz), 6.55 (1H, dd, J = 1.6, 7.8 Hz), 4.34 (2H, m), 2.95 (1H, d, J = 18.1 Hz), 2.80 (1H, d, J = 18.2 Hz), 2.11 (2H, m), 1.41 (3H, s), 1.38 (3H, s); ^{13}C NMR δ 220.6 (0), 215.0 (0), 156.1 (0), 135.9 (0), 129.6 (1), 128.6 (1), 121.1 (1), 117.9 (1), 59.9 (2), 56.2 (0), 49.7 (2), 45.5 (0), 29.0 (2), 24.9 (3), 23.9 (3).

3,4-Dihydro-3,3-dimethyl-5-(1-(1,2,3,4-tetrahydro-4-oxanaphthylidene))-2-furanone (24a,b). Major isomer **24a**: white solid, mp 164−165 °C; ^{1}H NMR δ 7.14 (2H, m), 6.89 (2H, m), 4.23 (2H, t, J = 5.7 Hz), 3.08 (2H, br s), 2.80 (2H, br t, J = 5.7 Hz), 1.35 (6H, s); NOE data 3.08 (d, J = 7.3 Hz, at δ 7.15, 23%; 1.35, 7%), 1.35 (3.08, 10%); ^{13}C NMR δ 179.3 (0), 154.6 (0), 141.1 (0), 128.19 (1), 126.2 (1), 120.2 (1), 120.1 (0), 117.3 (1), 109.0 (0), 66.2 (2), 41.7 (2), 40.0 (0), 25.1 (2C, 3), 24.5 (2). Minor isomer **24b** (discernible signals from spectra of mixture): ^{1}H NMR δ 8.09 (1H, dd, J = 1.6, 8.1 Hz), 2.85 (2H, br s), 2.52 (2H, apparent t, J = 5.6 Hz), 1.37 (6H, s); ^{13}C NMR δ 153.7 (0), 140.3 (0), 129.2 (1), 128.24 (1), 120.9 (1), 116.9 (1), 65.6 (2), 40.3 (2), 26.2 (2), 25.2 (2C, 3).

4,4-Dimethyl-2,2-diphenylcyclopentane-1,3-dione (25). White solid, mp 67−68 °C; ^{1}H NMR δ 7.40−7.23 (6H, m), 7.15−7.03 (4H, m), 2.78 (2H, s), 1.39 (6H, s); ^{13}C NMR δ 216.4 (0), 211.2 (0), 137.4 (2C, 0), 128.7 (1), 127.8 (1), 51.3 (2), 47.3 (0), 26.1 (2C, 3).

3,4-Dihydro-3,3-dimethyl-5-(diphenylmethylene)-2-furanone (26). Pale yellow solid, mp 111−113 °C; ^{1}H NMR δ 7.40−7.17 (10H, m), 2.77 (2H, s), 1.33 (6H, s); ^{13}C NMR δ 179.9 (0), 144.1 (0), 138.8 (0), 137.5 (0), 130.0 (1), 129.4 (1), 128.5 (1), 128.0 (1), 127.2 (1), 126.9 (1), 119.3 (0), 41.6 (2), 39.8 (0), 24.7 (2C, 3).

(1′*R,2*S**)- (28) and (1′*R**,2*R**)-4,4-Dimethyl-2-hydroxy-2-(1-hydroxy-1-phenylethyl)cyclobutanone (29).** A solution of acetophenone (0.41 g, 3.4 mmol) in CH_2Cl_2 (10 mL) was cooled to −78 °C before BF_3·Et_2O (0.42 mL, 3.4 mmol) and **3** (0.97 g, 3.7 mmol) were added. The temperature was raised to −20 °C, and the mixture was stirred for 29 h. The mixture was poured into H_2O, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated under vacuum to give a yellow viscous oil (0.76 g) composed of acetophenone, **28**, **19**, and **29** in a ratio of 11:5.7:3.4:1 by ^{1}H NMR. Flash chromatography using an increasing proportion of EtOAc in hexanes provided **28** (167 mg, 21%) and **29** (29 mg, 4%). Major diastereomer **28**: white solid, mp 79.5−80.5 °C; ^{1}H NMR (CD_3OD) δ 7.45 (2H, d, J = 7.1 Hz), 7.29 (2H, apparent t, J = 7.4 Hz), 7.21 (1H, apparent t, J = 7.0 Hz), 2.35 (1H, d, J = 12.5 Hz), 1.72 (1H, d, J = 12.5 Hz), 1.64 (3H, s), 1.18 (3H, s), 0.51 (3H, s); ^{13}C NMR (CD_3OD) δ 219.7 (0), 145.8 (0), 128.8 (2C, 1), 128.4 (2C, 1), 128.0 (1), 94.6 (0), 76.1 (0), 55.2 (0), 40.5 (2), 25.5 (3), 25.0 (3), 20.8 (3). Minor diastereomer **29**: white solid, mp 150−151.5 °C; ^{1}H NMR (CD_3OD) δ 7.57 (2H, d, J = 7.2 Hz), 7.29 (2H, apparent t, J = 7.4 Hz), 7.20 (1H, apparent t, J = 7.2 Hz), 2.33 (1H, d, J = 12.5 Hz), 1.67 (3H, s), 1.47 (1H, d, J = 12.5 Hz), 1.21 (3H, s), 1.02 (3H, s); ^{13}C NMR (CD_3OD) δ 221.0 (0), 146.4 (0), 128.6 (2C, 1), 128.0 (2C, 1), 127.9 (1), 94.0 (0), 76.0 (0), 55.1 (0), 40.6 (2), 25.4 (3), 24.5 (3), 21.2 (3). The relative stereochemistry of **29** was determined by X-ray crystallography.[12]

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Supporting Information Available: Reaction conditions and additional charaterization data (UV, IR, MS, HRMS), ^{1}H and ^{13}C NMR spectra for products, and X-ray structure report for **29** (80 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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