Geminal Acylation with Methyl-Substituted Analogues of 1,2-Bis[(trimethylsilyl)oxy]cyclobutene

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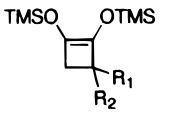
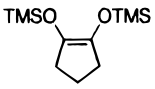
BF_3·Et_2O-catalyzed geminal acylation of ketones and acetals with 3-methyl-1,2-bis[(trimethylsilyl)oxy)]cyclobutene (**3**) provided methylcyclopentanediones in yields that ranged from 40 to 94%. The best substrates were unhindered cyclohexanones. With acetals, stereochemical preferences in the initial Mukaiyama-like aldol step giving cyclobutanones translated into the stereochemistry of the ultimate cyclopentanedione products. With ketones, equilibration of the initial cyclobutanone compounds resulted in cyclopentanedione products with a different stereochemical preference. The *gem*-dimethylcyclobutene reagent **4** reacted with ketones to give *gem*-dimethylcyclopentanediones in modest yield. The process was much more stereochemically efficient than the reaction with **3**. Rearrangement from the initial cyclobutanone compound was partially diverted toward air-sensitive 3-furanone compounds and ring-opened 1,2-diones. Only furanones (e.g., **52** and **53**) were isolated from reactions with the tetramethylcyclobutene **51**.

Introduction

The Lewis acid-catalyzed geminal acylation of an acetal with 1,2-bis[(trimethylsilyl)oxy]cyclobutene (**1**) was first reported by Kuwajima and co-workers[1] as a two-step process. An initial Mukaiyama-like aldol reaction gave a cyclobutanone derivative, which underwent acid-induced rearrangement to provide a 2-substituted 1,3-cyclopentanedione. Subsequent developments, mainly in our laboratory, led to a one-pot procedure that was more efficient for obtaining cyclopentanediones,[2,3] to analogous reactions with **2**,[4] and to reactions of **1** directly on ketones,[5] as illustrated in Scheme 1. Synthetic approaches to diverse natural products, such as trichothecanes,[6] β-bulnesene,[7] estrone,[8] khusimone,[2] pentalenene,[9] and fredericamycin A,[10] employed geminal acylation with **1** as a key step.[11] Our one-pot geminal acylation method has been cleverly incorporated into tandem processes by Curran and co-workers.[12,13]



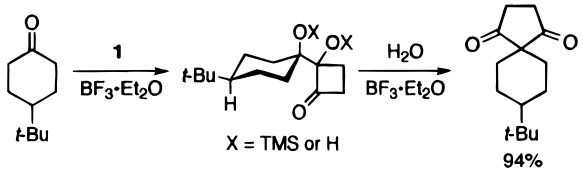
1 $R_1 = R_2 = H$
3 R_1 = Me, $R_2 = H$
4 $R_1 = R_2$ = Me



2

An important extension of the geminal acylation methodology would be to employ analogues of **1** bearing alkyl groups or a more elaborate functionality that could survive the acyloin conditions[14] by which **1** is prepared. Cyclopentane moieties bearing a single methyl group or a *gem*-dimethyl group are seen in many natural products. Therefore, we chose initially to explore reactions with the monomethylcyclobutene **3** and the *gem*-dimethylcyclobutene **4**. Even in these simple analogues, questions regarding reactivity in the initial, Mukaiyama-like step and the course of rearrangement in the second step, as well as issues of regio- and stereochemistry, could be addressed. Many alkyl-substituted 1,2-bis[(trimethylsilyl)oxy]cyclobutene compounds have been prepared, notably by Rühlmann,[15] and one example of geminal acylation with a vicinally disubstituted cyclobutene has been reported.[12]

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1997.

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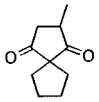
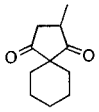
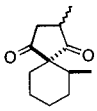
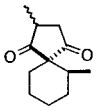
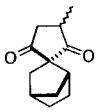
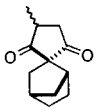
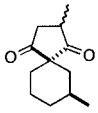
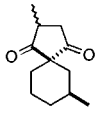
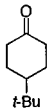
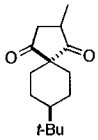
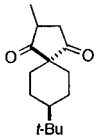
Table 1. Reactions of 3 with Ketones and Their Corresponding Acetals Derived from 1,2-Ethanediol

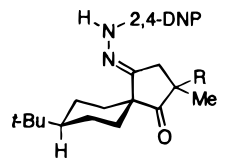
entry	substrate	product(s)	from ketone		from acetal	
			yield (%)	diastereomeric ratio (%)	yield (%)	diastereomeric ratio (%)
1		 **5a,b**	82	**a**:**b** 1:1	79	**a**:**b** 1:1
2		 **6**	49	-	40	-
3		 **7**	93	-	81	-
4		 **8a,b**  **8c,d**	75	**a**:**b**:**c**:**d** 3.8:3.0:1.4:1	57	**a**:**b**:**c**:**d** 2.9:1.7:3.1:1
5		 **9a,b**  **9c,d**	87	**a**:**b**:**c**:**d** 5.0:4.6:1.5:1	56	**a**:**b**:**c**:**d** 7.1:1.8:15:1
6		 **10a,b**  **10c,d**	91	**a**:**b**:**c**:**d** 4.2:4.1:1.1:1	91	**a**:**b**:**c**:**d** 1:1.2:1.4:1.4
7		 **11a**  **11b**	92	**a**:**b** 3.1:1	94	**a**:**b** 1:2.2 (1:7.5)[a]

[a] Ratio obtained from the dibenzyl acetal.

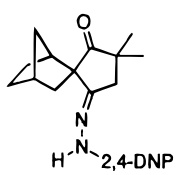
Results and Discussion

Reactions of Ketones and Acetals with Monomethylcyclobutene 3. A variety of ketones and their corresponding acetals, derived from 1,2-ethanediol, were treated with **3** and $BF_3 \cdot Et_2O$ following the procedure that we had developed for the reaction of **1** with ketones.[5] In this procedure, the initial aldol reaction was mediated by $BF_3 \cdot Et_2O$ in dichloromethane under anhydrous conditions, and then the second, rearrangement step was initiated by addition of water and a large excess of $BF_3 \cdot Et_2O$. As can be seen in Table 1, the yields of cyclopentanediones ranged from modest to excellent. Trends were similar to those seen previously in the reactions of **1** with both ketones[5] and acetals.[2,3] The ketones gave similar, or better, yields than did the acetals. Unencumbered cyclohexanones and their acetals gave the best yields (Table 1, entries 3, 6, and 7). Cyclopentanone and its acetal (Table 1, entry 2) gave more modest yields of the spirodiketone **6**. α-Substitution had a deleterious effect on the efficiency of geminal acylation, especially with the acetal (Table 1, entries 4 and 5).

Reactions with **3** introduced a stereochemical complexity that had not been present in reactions with **1**. The reaction with butanone and its acetal (Table 1, entry 1) provided **5a** and **5b** with no diastereoselectivity whatsoever. However, with 4-*tert*-butylcyclohexanone and its acetal (Table 1, entry 7) some modest selectivity was apparent. An X-ray crystal structure of a 2,4-dinitrophenylhydrazone derivative **11c** revealed that the major isomer obtained from the ketone was **11a**. Selectivity was also evident in reactions between **3** and other substituted cyclohexanones and their acetals (Table 1, entries 4−6). (Although it was not feasible to determine rigorously the stereochemistry of each component in these product mixtures, the relative stereochemistry at the spiro centers was inferred from the results presented below.) It is important to note that the selectivity was clearly different, even complementary, with ketones and their corresponding acetals.



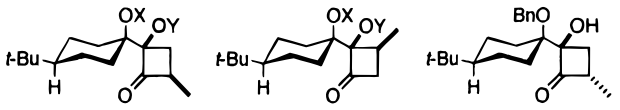
11c R = H
36b R = Me



33c

In an effort to illuminate the reason for the stereochemical difference between the ketone and the acetal

versions of the geminal acylation, we isolated the products after only the first step in the reactions of 4-*tert*-butylcyclohexanone and its acetal with **3**. The ketone provided two cyclobutanone compounds in a 3.3:1 ratio, which was very similar to the 3.1:1 ratio for the cyclopentanedione products in entry 7 (Table 1). (Minor amounts of **11a** and **11b**, in a 2.6:1 ratio, were also detected in the crude product even when no water or extra $BF_3{\cdot}Et_2O$ was added.) Comparison of the ^{13}C NMR shifts of signals arising from the cyclohexyl moiety with those of the known, equatorial product with **1**[5] indicated that both of the cyclobutanone compounds had arisen by equatorial attack on the ketone.[16] Considerable similarities between the NMR spectra of **12a** and **12b** and the spectra of **15a** and **15b** allowed unequivocal assignment of the structures of **12a** and **12b**. The isolation of intermediates from acetals was carried out in conjunction with an evaluation of the stereoselectivity of the geminal acylation with different acetals. Reaction of the acetal derived from 2,2-dimethyl-1,3-propanediol gave cyclopentanediones **11a** and **11b** in a 1:2.4 ratio, which was not significantly different from the 1:2.2 ratio for the acetal derived from 1,2-ethanediol. Cyclobutanone derivatives from the dimethyl and dibenzyl acetals were obtained by following Kuwajima's procedure.[1] The dimethyl acetal provided cyclobutanone compounds **13a** and **13b** in a 1:4.1 ratio. When this mixture was stirred in TFA, **11a** and **11b** were produced in a ratio of 1:3.6. The use of a dibenzyl acetal further improved selectivity. Cyclobutanones **14a** and **14b** were obtained in a 1:7.4 ratio. In TFA, this mixture rearranged to **11a** and **11b** in a 1:7.5 ratio. Cyclobutanones **14a** and **14b** were desilylated with tetrabutylammonium fluoride (TBAF) to keto alcohols **15a** and **15b**, and these proved to be separable by chromatography. During chromatography, a fraction of **15a** also showed a set of ^1H NMR signals attributable tentatively a very small amount of **16**. NOE measurements with both **15a** and **15b** established that the hydrogen of the methine of the cyclobutanone moiety was syn to the cyclohexane ring. Hydrogenolysis of the benzyl groups of either **15a** or **15b** over Pd on charcoal in ethanol/acetic acid provided both **12a** and **12b** in a 5.2:1 ratio, which provided evidence of acid-mediated equilibration between **12a** and **12b**. This was exactly the ratio predicted by an AM1 calculation.[17]

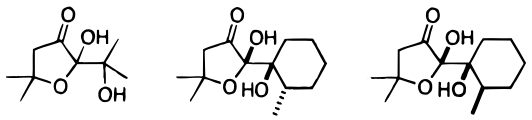


12a X = H Y = H **12b** X = H Y = H **16**
13a X = Me Y = TMS **13b** X = Me Y = TMS
14a X = Bn Y = TMS **14b** X = Bn Y = TMS
15a X = Bn Y = H **15b** X = Bn Y = H

These results lead to the following generalizations regarding reactions with **3**. The cyclobutanones obtained from acetals undergo rearrangement to cyclopentanediones by inversion at the cyclohexyl C-1, with little stereochemical scrambling. This was also true for the processes with **1** for both acetals[1b] and ketones.[5] Thus, the stereochemistry of the cyclopentanediones derived from acetals was largely determined by stereochemical preferences in the first, aldol reaction. The stereochemistry of the cyclopentanediones derived from ketones was generally opposite to that from acetals and appeared to reflect equilibration to the thermodynamically preferred cyclobutanone.

Reactions of Ketones with *gem*-Dimethylcyclobutene 4. The results of reactions of **4** with many ketones are presented in Table 2.[17] Cyclobutene **3** had shown a considerable reluctance to add to its face syn to the methyl, but with cyclobutene **4** steric hindrance between a methyl on the cyclobutene and the ketone substrate seemed unavoidable. Hence, it was not surprising that in many examples with **4** the yields of the cyclopentanediones were modest, and a very significant proportion of intractable material was generally obtained. Addition of water and extra $BF_3{\cdot}Et_2O$ was not necessary to effect rearrangement to cyclopentanediones from any of the enone substrates. The reaction with cyclohexenone (Table 2, entry 10) only gave a 32% yield of **40**, but this was still considerably better than had been seen in the reaction of cyclohexenone with **1**.[5] Both isophorone and 4,4-dimethylcyclohex-2-en-1-one (Table 2, entries 11 and 12) gave good yields of cyclopentanediones, although with the former there was some isomerization of the double bond during reaction. A comparison of the ^{13}C NMR spectrum of the predominant cyclopentanedione product from isophorone with the spectra of products from **1**[3,5] led to the assignment of structure **41**. Despite the poor yields, cyclopentanediones were produced from **4** with much higher stereoselectivity than had been seen from **3**. In two instances (Table 2, entries 7 and 9) one diastereomer of the cyclopentanedione was produced very predominantly, and the structures of their 2,4-dinitrophenylhydrazone derivatives (**33c** and **36b**) were determined by X-ray crystallography.

The yields with **4** suffered from synthetically troublesome, yet mechanistically interesting, side reactions that repeatably produced substituted furanones, 1,2-diones, and lactones. The proportion of furanone in the product mixtures did not seem to correlate in a straightforward way with the structure of the ketone substrate. A comparison of entries 7 and 8 (Table 2) illustrates this. Furanones were formed with little to no geometrical preference (Table 2, entries 2, 6, and 7), and they oxidized readily in air to dihydroxy compounds. Characterization of oxidation products **45** and **46a/b**, derived from **18** and **30a/b**, was helpful in establishing the general structure of the furanones.



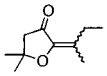
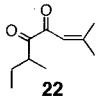
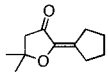
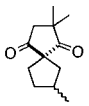
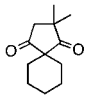
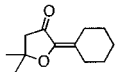
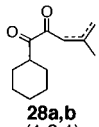
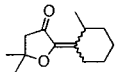
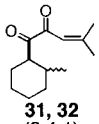
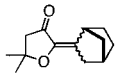
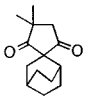
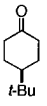
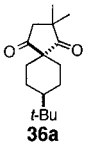
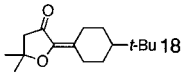
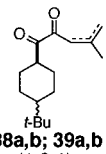
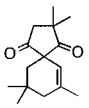
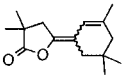
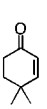
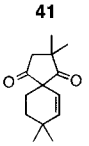
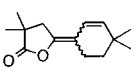
45 **46a** **46b**

1,2-Diones were isolated in lesser amounts. Careful analysis by ^1H NMR of the reactions with cyclohexanone (Table 2, entry 5) and 4-*tert*-butylcyclohexanone (Table 2, entry 9) showed that the β,γ-unsaturated compounds (**28a**, **38a**, and **39a**) were initially formed, and these rapidly isomerized in the reaction medium to conjugated, α,β-unsaturated diones (**28b**, **38b**, and **39b**). A secondary rearrangement process led to minor amounts of lactones **42a,b** and **44a,b** from enone substrates (Table 2, entries 11 and 12).

(16) With the norbornyl system, exo addition of **3** was very likely favored with both the ketone and its acetal, but, as can be seen in entry 5, this system showed the largest, yet obviously different, stereoselectivities with ketone and acetal.

(17) 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).

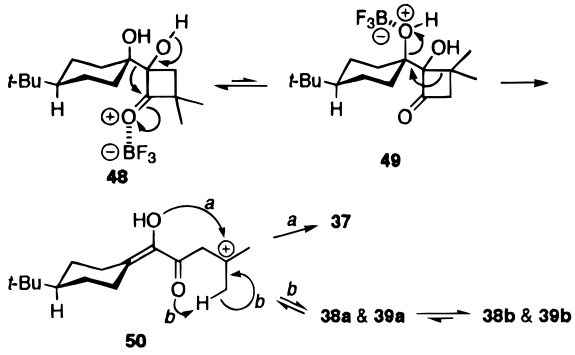
Table 2. Reactions of 4 with Ketones

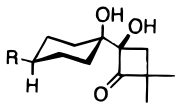
entry	substrate	products and yields (%) cyclopentanedione	furanone	1,2–dione
1		 22 **17**	 26 **18**	 <2 **19**
2		 22 **20**	 24 **21a,b** (1:1)	 <5 **22**
3		 36 **23**	 <5 **24**	
4		 30 **25a,b** (2.8:1)		
5		 40 **26**	 16 **27**	 16 **28a,b** (1.2:1)
6[a]		 12 **29a,b** (8:1)	 24 **30a,b** (1.4:1)	 16 **31, 32** (2.4:1)
7[b]		 47 **33a,b** (>100:1)	 33 **34a,b** (1.5:1)	
8		 70 **35**		
9		 40 **36a**	 18 **37**	 7 **38a,b; 39a,b** (1.2:1)
10		 32 **40**		
11		 56 **41**	 24 **42a,b** (*E*/*Z* 1.9:1)	
12		 71 **43**	 7 **44a,b** (*E*/*Z* 1:1)	

[a] Two molar equivalents of **4** were used in this reaction. [b] Chromatographic separation of **33a** and **34a,b** was incomplete. Yields reflect the isolated yields and the proportion of **33a** and **34a,b** (GC-MS) in a mixed fraction.

The dimethylcyclobutanone compounds **47** and **48** were prepared from the corresponding ketones by working up the reaction mixture without addition of extra $BF_3{\cdot}Et_2O$ and water. The structure of **48** was determined unequivocally by X-ray crystallography. This showed the reaction had resulted from equatorial addition with respect to the cyclohexanone ring and that the new C−C bond was to C-1 of cyclobutene **4**. Prolonged treatment of cyclopentanediones with $BF_3{\cdot}Et_2O$ did not provide any furanone, but when **47** was added to neat $BF_3{\cdot}Et_2O$ the result was a 3:1 mixture of **26** and **27**. On the other hand, treatment of **47** with dilute $BF_3{\cdot}Et_2O$ in dichloromethane provided only cyclopentanedione **26**. Similarly, cyclobutanone **48** in neat $BF_3{\cdot}Et_2O$ provided **36a** and **37** in an 8:1 ratio. With dilute $BF_3{\cdot}Et_2O$ in dichloromethane the ratio improved to 13:1, and $BF_3{\cdot}Et_2O$ in dichloromethane in the presence of a small amount of water provided **36a** exclusively.

Scheme 2

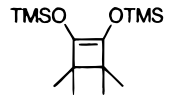




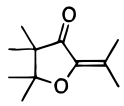
47 R = H
48 R = *t*-Bu

The formation of furanone and the 1,2-diones can be rationalized as illustrated (Scheme 2) with the reaction of 4-*tert*-butylcyclohexanone. The equilibrium between **12a** and **12b** suggests that **48** might equilibrate with cyclobutanone **49**. We were unable to observe **49**, but an AM1 calculation[17] indicated that **49** should be 6.1 kcal/mol higher in energy than **48**. Whereas both **12a** and **12b** rearranged to 1,3-diketones, an alternate pathway to the tertiary carbocation **50** presents itself with **49**. (Furanones were never observed in reactions with **1** or **3**, so the intermediacy of a carbocationic intermediate was suspected.) Cyclization of **50** gives the furanone **37**, or deprotonation of **50** with the internal assistance of an oxygen would give the terminal double bond in **38a** and **39a**. Evidence for the latter stage of this hypothesis is that treatment of a solution of the mixture of **31** and **32** in $CDCl_3$ with $BF_3{\cdot}Et_2O$ provided some **30a,b**, but treatment of furanones with acid (with or without water) under an inert atmosphere did not give any 1,2-diketone.

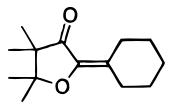
Reactions with Tetramethylcyclobutene 51. Two ketones were reacted with the tetramethylcyclobutene **51**[15] using the conditions employed with **4**. No cyclopentanedione was produced in these reactions. Instead, furanone **52** was the only isolated product from the reaction with acetone, and **53** was the only isolated product from cyclohexanone.



51



52



53

Experimental Section

General Procedures. Compounds **3**, **4**, and **51** were obtained using the method for the preparation of **1** of Bloomfield and Nelke.[14] The CH_2Cl_2 used in the geminal acylation reactions was distilled from CaH_2. All reactions were performed under N_2. Workup usually consisted of addition of the reaction mixture to H_2O, extraction of the aqueous layer with CH_2Cl_2, washing with brine, drying of the combined organic solutions over anhydrous $MgSO_4$, and evaporation of the solvent under vacuum. IR spectra were recorded as thin films unless otherwise noted. ^{1}H NMR spectra were obtained at 300 MHz in $CDCl_3$ unless specified otherwise, and shifts are relative to internal TMS. For spectral data obtained from mixtures, only clearly distinguished signals are reported. Most product ratios were determined by careful integration of ^{1}H NMR spectra. NOE measurements were made from difference spectra and are reported as follows: saturated signal (observed signal, enhancement). ^{13}C NMR spectra were recorded at 75 MHz; chemical shifts are relative to solvent; each ^{13}C chemical shift is followed in parentheses by the number of attached protons as determined by APT and heteronuclear correlation spectra. Overlap may have prevented the reporting of all resonances when the spectral data of minor components were obtained from spectra of mixtures.

3-Methyl-1,2-bis[(trimethylsilyl)oxy]cyclobutene (3): colorless liquid; $bp_{5\ mm}$ 69−72 °C; ^{1}H NMR δ 2.45 (1H, m), 2.36 (1H, dd, J = 4.3, 10.0 Hz), 1.65 (1H, dd, J = 1.2, 10.0 Hz), 1.10 (3H, d, J = 6.6 Hz), 0.21 (9H, s), 0.20 (9H, s); ^{13}C NMR δ 125.4 (0), 119.6 (0), 34.9 (2), 33.3 (1), 17.8 (3), 0.35 (6C, 3).

3,3-Dimethyl-1,2-bis[(trimethylsilyl)oxy]cyclobutene (4): colorless liquid; $bp_{3\ mm}$ 60−61 °C; ^{1}H NMR δ 1.97 (2H, s), 1.12 (6H, s), 0.21 (9H, s), 0.18 (9H, s); ^{13}C NMR δ 128.6 (0), 118.3 (0), 42.7 (2), 38.6 (0), 24.2 (2C, 3), 0.35 (6C, 3).

General Procedure for the Reactions of 3 with Ketones or Acetals. On the basis of the procedure of Jenkins and Burnell,[5] to a solution of ketone or acetal (2.0 mmol) in CH_2Cl_2 (10.0 mL) were successively added $BF_3{\cdot}Et_2O$ (0.30 mL, 2.4 mmol) and **3** (0.73 g, 3.0 mmol). The mixture was stirred at rt for 24 h before H_2O (0.30 mL) was introduced, followed 10 min later by $BF_3{\cdot}Et_2O$ (3.7 mL, 30 mmol). The resulting black solution was stirred for 24 h. Workup and decolorization of a CH_2Cl_2 solution by activated charcoal and filtration through Florisil gave the cyclopentanedione product(s). For yields and product ratios see Table 1.

2-Ethyl-2,4-dimethylcyclopentane-1,3-dione (5a,b). From spectra of the mixture: ^{1}H NMR δ 3.10−2.96 (1H from each, two overlapping dd), 2.96−2.77 (1H from each, m), 2.37 (1H, dd, J = 8.7, 18.3 Hz), 2.29 (1H, dd, J = 9.3, 18.0 Hz), 1.80−1.55 (2H from each, m), 1.29 (3H from each, d, J = 6.9 Hz), 1.12 (3H, s), 1.09 (3H, s), 0.81 (3H, t, J = 7.5 Hz), 0.76 (3H, t, J = 7.5 Hz); ^{13}C NMR δ 219.0 (0), 218.6 (0), 216.3 (0), 216.1 (0), 57.2 (0), 57.0 (0), 44.5 (2), 43.7 (2), 41.7 (1), 40.9 (1), 29.4 (2), 28.2 (2), 20.2 (3), 17.9 (3), 15.7 (3), 15.1 (3), 9.4 (3), 8.9 (3).

2-Methylspiro[4.4]nonane-1,4-dione (6): tan-colored oil; ^{1}H NMR δ 3.02 (1H, dd, J = 10.3, 17.7 Hz), 2.88 (1H, m), 2.35 (1H, dd, J = 8.2, 17.7 Hz), 1.90−1.70 (8H, m), 1.29 (3H, d, J = 7.0 Hz); ^{13}C NMR δ 220.4 (0), 217.6 (0), 61.9 (0), 42.3 (2), 39.7 (1), 35.4 (2), 32.4 (2), 25.1 (2), 25.3 (2), 13.7 (3).

2-Methylspiro[4.5]decane-1,4-dione (7): yellow oil; ^{1}H NMR δ 3.00 (1H, dd, J = 10.4, 17.6 Hz), 2.90 (1H, m), 2.34 (1H, dd, J = 8.2, 17.6 Hz), 1.90−1.42 (10H, m), 1.27 (3H, d, J = 6.9 Hz); ^{13}C NMR δ 218.0 (0), 215.3 (0), 55.5 (0), 43.1 (2), 40.3 (1), 30.5 (2), 28.6 (2), 24.9 (2), 20.5 (2), 20.3 (2), 15.6 (3).

2,6-Dimethylspiro[4.5]decane-1,4-dione (8a−d). From spectra of the mixture: for **8a**: ^{1}H NMR δ 3.03 (1H, dd, J = 10.6, 18.2 Hz), 2.12 (1H, dd, J = 9.0, 18.2 Hz), 1.25 (3H, d, J = 6.9 Hz), 0.705 (3H, d, J = 6.6 Hz); ^{13}C NMR δ 219.6 (0), 215.6 (0), 60.4 (0), 45.1 (2), 40.0 (1), 34.9 (1), 32.8 (2), 28.9 (2), 25.3 (2), 20.1 (2), 18.5 (3), 14.8 (3). For **8b**: ^{1}H NMR δ 2.70 (1H, overlapped dd), 2.41 (1H, overlapped dd), 1.31 (3H, d, J = 7.0 Hz), 0.74 (3H, d, J = 6.9 Hz); ^{13}C NMR δ 219.8 (0), 217.2 (0), 60.0 (0), 44.1 (2), 43.1 (1), 36.3 (1), 32.2 (2), 29.1 (2), 25.3 (2), 20.2 (2), 18.1 (3), 16.5 (3). For **8c**: ^{1}H NMR δ 3.08 (1H, dd, J = 10.5, 18.8 Hz), 2.18 (3H, dd, J = 6.9 Hz), 0.715 (3H, d, J = 6.4 Hz); ^{13}C NMR δ 218.3 (0), 216.5 (0), 60.7 (0), 44.6 (2), 39.9 (1), 35.2 (1), 32.9 (2), 28.9 (2), 25.4 (2), 20.2 (2), 18.3 (3), 14.8 (3). For **8d**: ^{1}H NMR δ 2.42 (1H, overlapped dd), 1.32 (3H, d, J = 7.0 Hz), 0.75 (3H, d, J = 6.3 Hz); ^{13}C NMR δ 218.6 (0), 216.2 (0), 59.6 (0), 43.6 (2), 35.7 (1), 32.0 (2), 19.9 (2), 16.3 (3).

4′-Methylspiro(bicyclo[2.2.1]heptane-2,2′-cyclopentane)-1′,3′-dione (9a−d). From spectra of the mixture: for **9a**: ^{1}H NMR δ 1.20 (3H, d, J = 6.9 Hz); ^{13}C NMR δ 215.5 (0), 213.1 (0), 66.4 (0), 49.2 (1), 44.0 (2), 39.5 (1), 37.3 (2), 36.9 (1), 33.0 (2), 28.0 (2), 24.1 (2), 15.4 (3). For **9b**: ^{1}H NMR δ 2.82 (1H, dd, J = 9.0, 16.5 Hz), 2.55 (1H, br m), 2.46 (1H, dd, J = 9.8, 16.5 Hz), 2.46 (1H, m), 2.36 (1H, m), 1.44 (3H, d, J = 7.2 Hz); ^{13}C NMR δ 216.1 (0), 213.2 (0), 65.4 (0), 48.6 (1), 43.9 (2), 42.1 (1), 37.1 (2), 36.7 (1), 33.9 (2), 27.7 (2), 24.5 (2), 17.6 (3). For **9c**: ^{1}H NMR δ 3.23 (1H, dd, J = 11.4, 19.0 Hz), 2.94 (1H, br m), 2.48 (1H, m), 2.36 (1H, m), 2.15 (1H, dd, J = 8.7, 19.0 Hz), 1.22 (3H, d, J = 6.9 Hz); ^{13}C NMR δ 215.2 (0), 212.4 (0), 66.5 (0), 49.1 (1), 43.2 (2), 40.5 (1), 37.0 (2), 36.8 (1), 32.8 (2), 27.8 (2), 24.5 (2), 14.3 (3). For **9d**: ^{13}C NMR δ 216.5 (0), 213.4 (0), 42.8 (2), 41.8 (1), 37.6 (2), 34.1 (2), 27.7 (2), 17.6 (3).

2,7-Dimethylspiro[4.5]decane-1,4-dione (10a−d). From spectra of the mixture: (^{1}H NMR for each isomer contains δ 3.03 (1H, m), 2.88 (1H, m), 2.33 (1H, m), 1.27 (3H, d, J = 6.9 Hz), 0.857 (±0.007) (3H, d, J = 6.3 Hz) 0.86 (3H, d, J = 6.6 Hz), 0.85 (3H, d, J = 6.6 Hz)). For **10a**/**b**: ^{13}C NMR δ 217.9/217.9 (0), 215.64/215.59 (0), 56.5 (0), 43.3 (2), 40.9 (1), 38.1/36.8 (2), 33.76 (2), 33.4 (2), 28.9 (2), 26.53/26.46 (1), 22.5/22.4 (3), 20.96/20.90 (2), 15.9 (3). For **10c**/**d**: ^{13}C NMR δ 218.2/218.1 (0), 215.0 (0), 56.6/56.5 (0), 43.4/43.3 (2), 40.3/40.2 (1), 38.6/36.5 (2), 33.80 (2), 30.9 (2), 28.5 (2), 26.7/26.3 (1), 22.6/22.3 (3), 21.02/20.8 (2), 15.7/15.6 (3).

***t*-8-*tert*-Butyl-2-methyl-*r*-1-spiro[4.5]decane-1,4-dione (11a) and *c*-8-*tert*-Butyl-2-methyl-*r*-1-spiro[4.5]decane-1,4-dione (11b).** For the mixture: for **11a**: ^{1}H NMR δ 2.96 (1H, dd, J = 10.4, 17.5 Hz), 2.33 (1H, dd, J = 7.7, 17.2 Hz), 1.26 (3H, d, J = 7.0 Hz); ^{13}C NMR δ 218.2 (0), 215.4 (0), 55.3 (0), 46.8 (1), 43.2 (2), 40.8 (1), 32.3 (0), 31.2 (2), 29.7 (2), 27.3 (3C, 3), 21.68 (2), 21.62 (2), 15.7 (3). For **11b**: ^{1}H NMR δ 3.02 (1H, dd J = 10.4, 18.0 Hz), 2.33 (1H, dd, J = 8.9, 18.0 Hz), 1.27 (3H, d, J = 6.9 Hz); ^{13}C NMR δ 218.1 (0), 215.3 (0), 55.4 (0), 46.8 (1), 43.3 (2), 40.1 (1), 32.3 (0), 31.7 (2), 29.3 (2), 27.3 (3C, 3), 21.7 (2), 21.5 (2), 15.4 (3). For the 4-(2,4-dinitrophenylhydrazone) derivative **11c** (derived from **11a**, purified by recrystallization): orange solid; mp 194.5−197.5 °C; ^{1}H NMR δ 11.11 (1H, br s), 9.12 (1H, d, J = 2.6 Hz), 8.31 (1H, dd, J = 2.5, 9.6 Hz), 7.92 (1H, d, J = 9.6 Hz), 3.27 (1H, dd, J = 10.4, 17.6 Hz), 2.83 (1H, br m), 2.43 (1H, dd, J = 8.7, 17.6 Hz), 1.85−1.60 (8H, m), 1.31 (3H, d, J = 2.9 Hz), 1.14 (1H, br m), 0.95 (9H, s); ^{13}C NMR δ 218.3 (0), 164.5 (0), 145.0 (0), 138.0 (0), 130.0 (1), 129.3 (0), 123.4 (1), 116.3 (1), 52.7 (0), 46.9 (1), 40.4 (1), 33.4 (2), 32.6 (2), 31.4 (2), 31.3 (2), 27.4 (3C, 3), 21.5 (2), 15.7 (3). The structure of **11c** was determined by X-ray crystallography.[19]

(2*R*/*S*,4*R*/*S*)-2-(*c*-4-*tert*-butyl-*r*-1-hydroxycyclohexyl)-2-hydroxy-4-methylcyclobutanone (12a) and (2*R*/*S*,3*S*/*R*)-2-(*c*-4-*tert*-Butyl-*r*-1-hydroxycyclohexyl)-2-hydroxy-3-methylcyclobutanone (12b). Compound **3** (0.34 g, 1.4

(18) Reaction of the 1,3-dioxolane derived from 4-*tert*-butylcyclohexanone with **4**, under the one-pot conditions developed for acetals with **1**,[3] gave a 1.2:1 mixture of **36a** and its epimer **36c** in a total yield of 36%. As this process showed essentially no stereoselectivity, reactions of acetals with **4** were not pursued further.

(19) Atomic coordinates for the X-ray structures of **11c**, **33c**, **36b**, **46a**, and **48** have been deposited with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

mmol) was added to a solution of 4-*tert*-butylcyclohexanone (219 mg, 1.42 mmol) and BF_3·Et_2O (0.17 mL) in CH_2Cl_2 (7.0 mL). The mixture was stirred at rt for 4.5 h. Workup gave an oily, tan solid (304 mg). ^{1}H NMR analysis revealed this to be a mixture of **12a** and **12b** in a 3.3:1 ratio, and **11a** and **11b** in a 2.6:1 ratio, with the ratio of cyclobutanone compounds to cyclopentanediones being 6:1. Highly enriched samples of **12a** and **12b** were obtained by careful hydrogenolysis of **15a** and **15b**. For **12a**: ^{1}H NMR δ 3.30 (1H, br s), 3.05 (1H, br m), 2.58 (1H, apparent t, J = 11.8 Hz), 1.86 (1H, m), 1.81−1.45 (4H, m), 1.45−1.27 (3H, m), 1.24 (3H, d, J = 7.3 Hz), 0.96 (1H, m), 0.87 (9H, s); ^{13}C NMR δ 215.7 (0), 94.5 (0), 72.7 (0), 49.6 (1), 47.7 (1), 32.6 (2), 32.4 (0), 32.3 (2), 30.9 (2), 27.5 (3C, 3), 21.9 (2), 21.8 (2), 14.4 (3). For **12b**: ^{1}H NMR δ 2.48 (1H, dd, J = 6.0, 17.8 Hz), 1.18 (3H, d, J = 6.9 Hz); ^{13}C NMR δ 213.6 (0), 95.2 (0), 73.3 (0), 50.6 (1), 47.6 (1), 32.5 (0), 32.4 (2), 32.1 (2), 30.6 (2), 27.5 (3C, 3), 21.8 (2), 21.7 (2), 14.4 (3).

(2*R*/*S*,4*R*/*S*)-2-(*c*-4-*tert*-Butyl-*r*-1-methoxycyclohexyl)-4-methyl-2-[(trimethylsilyl)oxy]cyclobutanone (13a) and (2*R*/*S*,3*S*/*R*)-2-(*c*-4-*tert*-Butyl-*r*-1-methoxycyclohexyl)-3-methyl-2-[(trimethylsilyl)oxy]cyclobutanone (13b). Based on the procedure of Kuwajima,[1] compound **3** (0.53 g, 2.1 mmol) was added dropwise over 2−3 min to a solution at −78 °C of 4-*tert*-butylcyclohexanone dimethyl acetal (0.39 g, 2.0 mmol) and BF_3·Et_2O (0.24 mL) in CH_2Cl_2 (3.0 mL). After being stirred at this temperature for 6 h, the reaction mixture was poured into aqueous $NaHCO_3$ solution (10 mL) and extracted with Et_2O (2 × 40 mL). The combined organic layers were washed with H_2O (40 mL) and brine (40 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent under vacuum left a viscous, colorless oil (0.66 g, 99%) as a 1:4.1 mixture of **13a** and **13b**. From spectra of the mixture: for **13a**: ^{1}H NMR δ 3.29 (3H, s), 0.14 (9H, s); ^{13}C NMR δ 214.2 (0), 97.1 (0), 22.5 (2), 22.3 (2), 14.5 (3), 1.7 (3C, 3). For **13b**: ^{1}H NMR δ 3.28 (3H, s), 2.94 (dd, J = 10.7, 18.0 Hz), 2.83−2.68 (m), 2.33 (dd, J = 6.3, 18.1 Hz), 2.19−2.05 (2H, m), 1.84−1.70 (m), 1.67−1.44 (2H, m), 1.40−1.00 (3H, m), 1.12 (3H, d, J = 7.1 Hz), 1.00−0.87 (m), 0.84 (9H, s), 0.16 (9H, s); ^{13}C NMR δ 212.2 (0), 99.3 (0), 75.9 (0), 51.7 (3), 50.1 (2), 47.3 (1), 32.2 (2), 27.5 (3C, 3 and 1C, 2), 27.1 (1), 22.2 (2), 22.1 (2), 15.2 (3), 1.8 (3C, 3).

This mixture of **13a** and **13b** (114 mg, 0.335 mmol) was stirred in TFA (1.0 mL) at rt for 20 h. Workup afforded 82.6 mg of a pale brown oil consisting largely of **11a** and **11b** in a 1:3.6 ratio.

(2*R*/*S*,4*R*/*S*)-2-[*r*-1-(Benzyloxy)-*c*-4-*tert*-butylcyclohexyl]-4-methyl-2-[(trimethylsilyl)oxy]cyclobutanone (14a) and (2*R*/*S*,3*S*/*R*)-2-[*r*-1-(Benzyloxy)-*c*-4-*tert*-butylcyclohexyl]-3-methyl-2-[(trimethylsilyl)oxy]cyclobutanone (14b). On the basis of the procedure of Kuwajima,[1] compound **3** (0.54 g, 2.2 mmol) was added over 2−3 min to a CH_2Cl_2 (3.0 mL) solution of 4-*tert*-butylcyclohexanone dibenzyl acetal (0.70 g, 2.0 mmol) and BF_3·Et_2O (0.25 mL) at −78 °C. After being stirred at this temperature for 9.5 h, workup and chromatography of the solution gave 0.79 g (96%) of a white solid, consisting of a 1:7.4 mixture of **14a** and **14b**. From spectra of the mixture: for **14a**: ^{1}H NMR δ 4.68 (1H, d, J = 9.7 Hz), 4.61 (1H, d, J = 10.2 Hz), 0.16 (9H, s); ^{13}C NMR δ 213.8 (0), 97.5 (0), 75.9 (0), 65.3 (2), 48.4 (1), 33.7 (2), 28.0 (2), 22.4 (2), 14.6 (3), 1.7 (3C, 3). For **14b**: ^{1}H NMR δ 7.50−7.18 (5H, m), 4.58 (1H, d, J = 11.6 Hz), 4.49 (1H, d, J = 11.8 Hz), 2.92 (1H, dd, J = 10.7, 28.9 Hz), 2.86 (1H, br m), 2.40−2.26 (2H, overlapping m), 1.89 (1H, ddd, J = 3.3, 6.6, 12.9 Hz), 1.68−1.50 (2H, m), 1.42 (1H, remnants of dddd), 1.33−1.24 (2H, m), 1.20 (1H, apparent dd, J = 4.7, 12.2 Hz), 1.13 (3H, d, J = 7.0 Hz), 0.98 (1H, br m), 0.85 (9H, s), 0.19 (9H, s); ^{13}C NMR δ 212.0 (0), 140.0 (0), 128.2 (1), 127.1 (1), 127.0 (1), 99.5 (0), 76.1 (0), 65.4 (2), 50.2 (2), 47.1 (1), 33.0 (2), 32.4 (0), 27.8 (2), 27.5 (3C, 3), 27.1 (1), 22.2 (2), 22.1 (2), 15.3 (3), 1.8 (3C, 3).

(2*R*/*S*,4*R*/*S*)-2-[*r*-1-(Benzyloxy)-*c*-4-*tert*-butylcyclohexyl]-2-hydroxy-4-methylcyclobutanone (15a) and (2*R*/*S*,3*S*/*R*)-2-[*r*-1-(Benzyloxy)-*c*-4-*tert*-butylcyclohexyl]-2-hydroxy-3-methylcyclobutanone (15b). Treatment of the above mixture of **14a,b** (0.20 g, 0.48 mmol) with TBAF (0.60 mL, 1.0 M in THF) in Et_2O (4.0 mL) followed by chromatography afforded **15a** and **15b** (total 0.142 g, 84%). ^{1}H NMR signals for a very minor third isomer, tentatively ascribed structure **16**, were noted in some fractions that were mainly **15a**. For **15a**: ^{1}H NMR δ 7.60−7.21 (5H, m), 4.71 (1H, d, J = 11.1 Hz), 4.40 (1H, d, J = 11.0 Hz), 3.45 (1H, s), 3.00 (1H, m), 2.59 (1H, apparent t, J = 12.1 Hz), 2.04 (1H, ddd, J = 3.0, 6.0, 13.4 Hz), 1.96 (1H, ddd, J = 3.1, 6.1, 13.1 Hz), 1.72 (1H, dd, J = 9.2, 12.4 Hz), 1.71−1.58 (2H, m), 1.55−1.27 (4H, m), 1.24 (3H, d, J = 7.2 Hz), 1.01 (1H, unresolved dddd), 0.87 (9H, s); NOE data 3.00 (2.59, 2%; 2.04−1.96, 1.6%; 1.24, 6%), 2.59 (3.00, 3%; 1.72, 22%; 1.48−1.39, 9%), 2.04−1.96 (4.71, 1.2%; 3.00, 1%; 4.40, 3%; 1.48−1.39, 31%), 1.72 (2.59, 9%; 1.24, 2%); ^{13}C NMR δ 214.8 (0), 138.7 (0), 128.4 (2C, 1), 127.5 (2C, 1), 95.6 (0), 76.9 (0), 64.4 (2), 49.0 (1), 47.4 (1), 32.8 (2), 32.4 (0), 31.2 (2), 28.3 (2), 27.5 (3C, 3), 22.0 (2C, 2), 14.4 (3). For **15b**: ^{1}H NMR δ 7.54−7.20 (5H, m), 4.73 (1H, d, J = 11.2 Hz), 4.42 (1H, d, J = 11.2 Hz), 3.35 (1H, s), 2.99 (1H, dd, J = 10.4, 17.7 Hz), 2.62 (1H, br m), 2.48 (1H, dd, J = 6.4, 17.7 Hz), 2.08 (1H, ddd, J = 3.2, 6.2, 13.7 Hz), 1.93 (1H, ddd, J = 3.1, 6.0, 12.9 Hz), 1.64 (2H, m), 1.55−1.26 (4H, m), 1.20 (3H, d, J = 7.0 Hz), 1.02 (1H, unresolved dddd), 0.87 (9H, s); NOE data 4.73 (2.08, 3%), 2.99 (2.62, 4.5%; 2.48, 13%), 2.62 (2.99, 4%); 1.49−1.36, 6.5%; 1.20, 4%), 2.48 (2.99, 8%; 1.20, 1.6%), 2.08 (4.42, 3%; 1.49−1.36, 13%), 1.93 (1.36, 16%), 1.20 (2.62, 4%; 2.48, 4%); ^{13}C NMR δ 212.2 (0), 138.8 (0), 128.4 (2C, 1), 127.5 (2C, 1), 95.9 (0), 77.5 (0), 64.6 (2), 50.1 (2), 47.4 (1), 32.4 (0), 30.8 (2), 28.3 (1), 27.8 (2), 27.4 (3C, 3), 22.0 (2C, 2), 14.1 (3). For tentative **16** (from mixture): ^{1}H NMR δ 4.75 (1H, overlapped d), 4.49 (1H, d, J = 11.3 Hz), 2.29 (1H, dd, J = 11.4, 12.9 Hz), 1.84 (1H, dd, J = 9.9, 12.9 Hz), 1.17 (3H, d, J = 6.5 Hz).

A mixture of **15a,b** (105 mg, 0.251 mmol) was stirred in TFA (1.0 mL) at rt for 4 h. Workup afforded 76 mg of an oily, yellow solid consisting largely of **11a** and **11b** in a ratio of 1:7.5.

Hydrogenolysis of 15a and 15b. A mixture of **15a** and **15b** (4.3:1; 64 mg, 187 mmol) in EtOH (3.5 mL) and AcOH (0.5 mL) with 10% Pd on charcoal (15 mg) under H_2 (1 atm) for 18 h gave 42 mg (96%) of **12a** and **12b** (5.1:1).

Homogeneous **15b** (58 mg, 169 mmol) in EtOH (3.5 mL) and AcOH (0.5 mL) with 10% Pd on charcoal (13 mg) under H_2 (1 atm) for 48 h gave 42 mg (100%) of **12a** and **12b** (5.2:1).

General Procedure for the Reactions of 4 with Ketones. BF_3·Et_2O (0.30 mL, 2.4 mmol) and **4** (0.84 g 3.2 mmol) were added in succession to a solution of the ketone (2.0 mmol) in CH_2Cl_2 (10.0 mL). The mixture was stirred at rt for 24 h. H_2O (0.30 mL) was introduced followed 10 min later by BF_3·Et_2O (3.7 mL, 30 mmol). The resulting black solution was stirred for 1−3 h, except for 2-methylcyclohexanone, which required 24 h. Workup gave the crude product, consisting of cyclopentanedione(s), furanone(s), and 1,2-dione(s). Flash chromatography (hexane with an increasing proportion of EtOAc) could usually effectively separate the three types of product, but cyclopentanedione, furanone, and 1,2-dione isomers were generally not separable in this way. Furanones were susceptible to oxidation in air. Yields and product ratios for the individual reactions are given in Table 2.

2,2,4,4-Tetramethyl-1,3-cyclopentanedione (17): light yellow oil, which solidified below 4 °C; ^{1}H NMR δ 2.66 (2H, s), 1.25 (6H, s), 1.17 (6H, s); ^{13}C NMR δ 220.8 (0), 216.4 (0), 51.6 (0), 50.1 (2), 46.6 (0), 25.5 (2C, 3), 21.4 (2C, 3).

4,5-Dihydro-2-isopropylidene-5,5-dimethyl-3(2*H*)-furanone (18): yellow oil; ^{1}H NMR δ 2.48 (2H, s), 2.07 (3H, s), 1.79 (3H, s), 1.39 (6H, s); ^{13}C NMR δ 199.7 (0), 143.3 (0), 120.1 (0), 77.9 (0), 50.5 (2), 28.1 (2C, 3), 19.5 (3), 16.8 (3).

2,6-Dimethylhept-5-ene-3,4-dione (19): yellow oil; ^{1}H NMR δ 6.71 (1H, m), 3.47 (1H, septet, J = 6.9 Hz), 2.26 (3H, d, J = 1.2 Hz), 2.02 (3H, d, J = 1.2 Hz), 1.10 (6H, d, J = 6.9 Hz).

2-Ethyl-2,4,4-trimethylcyclopentane-1,3-dione (20): yellow oil; ^{1}H NMR δ 2.67 (1H, d, J = 18.2 Hz), 2.57 (1H, d, J = 18.2 Hz), 1.75−1.60 (2H, m), 1.25 (3H, s), 1.24 (3H, s), 1.15 (3H, s), 0.80 (3H, t, J = 7.5 Hz); ^{13}C NMR δ 221.2 (0), 216.5 (0), 56.7 (0), 51.1 (2), 46.2 (0), 29.0 (2), 26.5 (3), 24.5 (3), 20.3 (3), 9.3 (3).

4,5-Dihydro-2-isobutylidene-5,5-dimethyl-3(2*H*)-furanone (21a,b). From spectra of the mixture: ^{1}H NMR δ 2.58 (2H, q, J = 7.5 Hz), 2.16 (2H, q, J = 7.5 Hz), 2.482 (2H, s), 2.475 (2H, s), 2.06 (3H, s), 1.78 (3H, s), 1.39 (6H, s), 1.38 (6H, s), 1.02 (3H, t, J = 7.5 Hz), 1.00 (3H, t, J = 7.5 Hz); ^{13}C NMR

δ 200.5 (0), 199.6 (0), 143.3 (0), 142.9 (0), 126.6 (0), 126.0 (0), 78.1 (0), 78.0 (0), 50.7 (2), 50.6 (2), 28.21 (3), 28.16 (3), 26.4 (2), 23.4 (2), 16.9 (3), 14.5 (3), 12.9 (3), 11.4 (3).

2,6-Dimethyloct-2-ene-4,5-dione (22): yellow oil; ^{1}H NMR δ 6.72 (1H, m), 3.36 (1H, q, J = 6.7 Hz), 2.06 (3H, s), 2.02 (3H, s), 1.69 (1H, m), 1.38 (1H, m), 1.07 (3H, d, J = 7.0 Hz), 0.88 (3H, t, J = 7.4 Hz); ^{13}C NMR δ 205.2 (0, 188.2 (0), 163.4 (0), 117.5 (1), 40.0 (1), 28.5 (3), 25.3 (2), 21.6 (3), 15.0 (3), 11.5 (3).

2,2-Dimethylspiro[4.4]nonane-1,4-dione (23): very pale yellow oil; ^{1}H NMR δ 2.62 (2H, m), 1.93−1.75 (8H, m), 1.24 (6H, s); ^{13}C NMR δ 221.6 (0), 216.4 (0), 61.6 (0), 50.9 (2), 46.4 (0), 36.5 (2C, 2), 27.2 (2C, 2), 25.2 (2C, 3).

2-Cyclopentylidene-4,5-dihydro-5,5-dimethyl-3(2*H*)-furanone (24): ^{1}H NMR (impure sample) δ 2.78 (2H, m), 2.48 (2H, s), 1.42 (6H, s).

2,2,7-Trimethylspiro[4.4]nonane-1,4-dione (25a,b). From spectra of the mixture: for the major isomer: ^{1}H NMR δ 2.64 (1H, d, J = 17.8 Hz), 2.56 (1H, d, J = 17.8 Hz), 2.25 (1H, br m), 2.05−1.68 (4H, m), 1.55−1.30 (2H, m), 1.22 (6H, s), 1.04 (1H, d, J = 6.6 Hz); ^{13}C NMR δ 221.5 (0), 216.0 (0), 61.9 (0), 50.9 (2), 46.2 (0), 44.3 (2), 36.2 (2), 35.9 (1), 35.3 (2), 25.3 (3), 25.1 (3), 18.6 (3). For the minor isomer: ^{1}H NMR δ 1.23 (6H, s); ^{13}C NMR δ 221.3 (0), 216.2 (0), 62.0 (0), 50.7 (2), 46.3 (0), 43.8 (2), 35.8 (1), 35.6 (2), 35.2 (2), 25.2 (3), 25.0 (3), 19.5 (3).

2,2-Dimethylspiro[4.5]decane-1,4-dione (26): white solid; mp 41.5−43 °C; ^{1}H NMR δ 2.61 (2H, m), 1.75−1.40 (10H, m), 1.22 (6H, s); ^{13}C NMR δ 220.3 (0), 216.3 (0), 54.9 (0), 50.3 (2), 46.2 (0), 30.5 (2), 25.7 (2C, 3), 25.0 (2C, 2), 20.6 (2C, 2).

2-Cyclohexylidene-4,5-dihydro-5,5-dimethyl-3(2*H*)-furanone (27): yellow oil; ^{1}H NMR δ 2.74 (2H, m), 2.48 (2H, s), 2.25 (2H, apparent triplet, J = 5.4 Hz), 1.65−1.40 (6H, m), 1.38 (6H, s); ^{13}C NMR δ 200.8 (0), 140.8 (0), 128.7 (0), 77.8 (0), 50.9 (2), 28.6 (2), 28.1 (2C, 3), 27.9 (2), 27.3 (2), 26.3 (2), 25.9 (2).

1-Cyclohexyl-5-methylpent-4-ene-1,2-dione (28a) and 1-Cyclohexyl-5-methylpent-3-ene-1,2-dione (28b). An attempt to separate a 1.2:1 mixture by preparative TLC led predominantly to isomerization of **28a** to **28b**. For **28a** (from the mixture): ^{1}H NMR δ 4.97 (1H, m), 4.79 (1H, m), 3.13 (1H, m), 3.44 (2H, s), 1.77 (3H, s). For **28b**: yellow oil; ^{1}H NMR δ 6.69 (1H, m), 3.24 (1H, m), 2.26 (3H, s), 2.01 (3H, s), 1.79 (3H, m), 1.70 (1H, m), 1.30 (4H, m); ^{13}C NMR δ 204.5 (0), 188.3 (0), 163.3 (0), 117.6 (1), 43.1 (1), 28.5 (3), 27.8 (2C, 2), 25.8 (2), 25.4 (2C, 2), 21.6 (3).

2,2,6-Trimethylspiro[4.5]decane-1,4-dione (29a,b). From spectra of the mixture: major isomer: ^{1}H NMR δ 2.69 (1H, d, J = 18.3 Hz), 2.39 (1H, d, J = 18.3 Hz), 1.26 (3H, s), 1.20 (3H, s), 0.74 (3H, d, J = 6.5 Hz); ^{13}C NMR δ 222.0 (0), 216.2 (0), 60.4 (0), 51.9 (2), 45.6 (0), 35.7 (1), 33.8 (2), 29.0 (2), 26.8 (3), 25.4 (2), 24.6 (3), 20.4 (2), 18.7 (3). Minor isomer: ^{1}H NMR δ 2.74 (1H, d, J = 18.6 Hz), 2.46 (1H, d, J = 18.6 Hz), 1.29 (3H, s), 1.16 (3H, s), 0.73 (3H, d, J = 6.2 Hz).

4,5-Dihydro-5,5-dimethyl-2-(2-methylcyclohexylidene)-3(2*H*)-furanone (30a,b). From spectra of the mixture: ^{1}H NMR δ 4.02 (1H, m), 3.64 (1H, br d, J = 14.6 Hz), 2.98 (1H, m), 2.60 (1H, m), 2.48 (4H, narrow m), 1.40 (3H, s), 1.384 (3H, s), 1.376 (3H, s), 1.36 (3H, s), 1.11 (6H, d, J = 7.2 Hz); ^{13}C NMR δ 201.1 (0), 200.4 (0), 140.8 (0), 140.6 (0), 133.0 (0), 132.6 (0), 77.9 (0), 77.8 (0), 51.0 (2), 33.1 (2), 32.7 (2), 29.7 (1), 26.7 (1), 28.1 (3), 27.5 (2), 27.1 (2), 23.7 (2), 21.3 (2), 20.6 (2), 20.4 (2), 19.0 (3), 17.7 (3).

***trans*- (31) and *cis*-4-Methyl-1-(2-methylcyclohexyl)-pent-3-ene-1,2-dione (32).** From spectra of a 2.4:1 mixture: for **31**: ^{1}H NMR δ 6.74 (1H, m), 3.06 (1H, m), 2.26 (3H, s), 2.02 (3H, s), 0.79 (3H, d, J = 6.2 Hz); ^{13}C NMR δ 204.9 (0), 187.9 (0), 163.5 (0), 117.1 (1), 49.4 (1), 20.6 (3). For **32**: ^{1}H NMR δ 6.67 (1H, m), 3.46 (1H, m), 2.26 (3H, s), 2.02 (3H, s), 0.81 (3H, d, J = 6.4 Hz); ^{13}C NMR δ 204.8 (0), 188.5 (0), 163.2 (0), 117.4 (1), 45.7 (1), 14.9 (3).

(1*R*/*S*,2*S*/*R*,4*S*/*R*)-4′,4′-Dimethylspiro(bicyclo[2.2.1]-heptane-2,2′-cyclopentane)-1′,3′-dione (33a): yellow oil; ^{1}H NMR δ 2.72 (1H, d, J = 16.9 Hz), 2.43 (1H, d, J = 16.9 Hz), 2.49 (1H, m), 2.36 (1H, m), 2.05 (1H, apparent d of pentets, J = 1.9, 9.9 Hz), 1.69 (1H, ddd, J = 2.9, 4.0, 12.2 Hz), 1.53 (1H, br m), 1.43 (3H, s), 1.42−1.28 (4H, m), 1.23 (1H, apparent d of pentets, J = 1.5, 9.9 Hz), 1.04 (3H, s); ^{13}C NMR δ 218.5 (0), 213.6 (0), 64.8 (0), 51.2 (2), 49.1 (1), 46.1 (0), 37.4 (2), 36.7 (1), 34.5 (2), 27.7 (2), 26.5 (3), 25.6 (3), 24.6 (2). For the 1′-(2,4-dinitrophenylhydrazone) derivative **33c** (purified by recrystallization): red-orange solid; mp 199.5−201 °C; ^{1}H NMR δ 11.2 (1H, br s), 9.15 (1H, d, J = 2.6 Hz), 8.36 (1H, dd, J = 2.5, 9.6 Hz), 7.99 (1H, d, J = 9.6 Hz), 2.81 (1H, d, J = 16.6 Hz), 2.49 (1H, d, J = 16.6 Hz), 2.41 (2H, apparent t, J = 4.2 Hz), 2.15 (1H, apparent d of pentets, J = 2.6, 10.2 Hz), 1.96 (1H, ddd, J = 2.7, 3.9, 12.0 Hz), 1.73 (1H, dd, J = 2.8, 12.1 Hz), 1.69−1.55 (2H, m), 1.49 (1H, br m), 1.40−1.28 (2H, m); ^{13}C NMR δ 218.9 (0), 162.1 (0), 145.1 (0), 138.0 (0), 130.2 (1), 129.2 (0), 123.4 (1), 116.1 (1), 61.1 (0), 48.6 (1), 45.7 (0), 39.4 (2), 37.6 (2), 37.3 (2), 36.8 (1), 28.1 (2), 26.6 (3), 26.2 (3), 24.4 (2). The structure of **33c** was determined by X-ray crystallography.[19]

(1*R*/*S*,2*R*/*S*,4*S*/*R*)-4′,4′-Dimethylspiro(bicyclo[2.2.1]-heptane-2,2′-cyclopentane)-1′,3′-dione (33b). One chromatographic fraction contained a minor amount of the isomer **33b** along with **33a**. Signals for **33b** in the mixture: ^{1}H NMR δ 2.88 (1H, d, J = 18.1 Hz), 1.33 (3H, s), 1.13 (3H, s).

2-(2-Bicyclo[2.2.1]heptylidene)-4,5-dihydro-5,5-dimethyl-3(2*H*)-furanone (34a,b). From spectra of the mixture: for the major isomer: ^{1}H NMR δ 3.87 (1H, m), 2.47 (1H, m), 1.41 (6H, s); ^{13}C NMR δ 199.4, 140.2, 133.3, 78.9. For the minor isomer: ^{1}H NMR δ 3.05 (1H, m), 2.45 (2H, s), 1.38 (6H, s); ^{13}C NMR δ 200.3, 139.5, 132.5, 79.0.

4′,4′-Dimethylspiro(bicyclo[2.2.2]octane-2,2′-cyclopentane)-1′,3′-dione (35): tan-colored solid; mp 30−32 °C; ^{1}H NMR δ 2.88 (1H, d, J = 17.3 Hz), 2.40 (1H, d, J = 17.3 Hz), 1.82 (1H, m), 1.78−1.71 (3H, m), 1.71−1.63 (2H, m), 1.63−1.52 (2H, m), 1.52−1.41 (2H, m), 1.38 (3H, s), 1.37−1.29 (2H, m), 1.06 (3H, s); ^{13}C NMR δ 218.4 (0), 214.3 (0), 61.5 (0), 49.9 (2), 45.7 (0), 32.4 (1), 28.1 (2), 26.7 (3), 25.8 (3), 24.4 (2), 24.0 (2), 23.1 (1), 21.6 (2), 20.9 (2).

***t*-8-*tert*-Butyl-2,2-dimethyl-*r*-1-spiro[4.5]decane-1,4-dione (36a):** white solid; mp 84−86 °C; ^{1}H NMR δ 2.60 (2H, m), 1.80−1.37 (8H, m), 1.21 (6H, s), 1.06 (1H, br m), 0.87 (9H, s); ^{13}C NMR δ 220.5 (0), 216.1 (0), 55.0 (0), 50.4 (2), 46.8 (1), 46.3 (0), 32.4 (0), 31.4 (2C, 2), 27.3 (3C, 3), 25.3 (2C, 3), 21.9 (2C, 2). For the 4-(2,4-dinitrophenylhydrazone) derivative **36b** (purified by recrystallization): orange solid; mp 234−235 °C; ^{1}H NMR δ 11.12 (1H, br s), 9.13 (1H, d, J = 2.5 Hz), 8.32 (1H, dd, J = 2.5, 9.6 Hz), 7.93 (1H, d, J = 9.6 Hz), 2.78 (2H, m), 1.75−1.65 (8H, m), 1.25 (6H, s), 1.17 (1H, br m), 0.95 (9H, s); ^{13}C NMR δ 220.8 (0), 164.6 (0), 145.0 (0), 137.9 (0), 130.0 (1), 129.2 (0), 123.4 (1), 116.3 (1), 52.6 (0), 46.8 (1), 46.0 (0), 38.7 (2), 33.1 (2C, 3), 32.6 (0), 27.4 (3C, 3), 25.8 (2C, 3), 21.7 (2C, 2). The structure of **36b** was determined by X-ray crystallography.[19]

***c*-8-*tert*-Butyl-2,2-dimethyl-*r*-1-spiro[4.5]decane-1,4-dione (36c).** Only unequivocal signals, from mixture: ^{1}H NMR δ 2.59 (2H, s), 1.25 (6H, s), 0.88 (9H, s); ^{13}C NMR δ 220.6 (0), 216.4 (0), 54.1 (0), 50.1 (2), 46.8 (1), 46.3 (0), 32.4 (0), 31.3 (2C, 2), 27.4 (3C, 3), 25.9 (2C, 3), 21.3 (2C, 2).

2-(4-*tert*-Butylcyclohexylidene)-4,5-dihydro-5,5-dimethyl-3(2*H*)-furanone (37): yellow oil; ^{1}H NMR δ 3.82 (1H, unresolved ddd), 2.80 (1H, unresolved ddd), 2.51 (1H, d, J = 17.7 Hz), 2.45 (1H, d, J = 17.4 Hz), 1.89 (2H, m), 1.73 (2H, m), 1.40 (3H, s), 1.38 (3H, s), 1.14 (1H, unresolved dddd); ^{13}C NMR δ 200.8 (0), 140.5 (0), 128.4 (0), 77.9 (0), 50.9 (2), 47.8 (1), 32.5 (0), 28.7 (2), 28.5 (2), 28.2 (3), 28.1 (3), 28.0 (2), 27.5 (3C, 3), 25.9 (2).

***cis*-1-(4-*tert*-Butylcyclohexyl)-4-methylpent-4-ene-1,2-dione (38a), *cis*-1-(4-*tert*-butylcyclohexyl)-4-methylpent-4-ene-1,2-dione (38b), *trans*-1-(4-*tert*-butylcyclohexyl)-4-methylpent-3-ene-1,2-dione (39a), and *trans*-1-(4-*tert*-butylcyclohexyl)-4-methylpent-3-ene-1,2-dione (39b).** Initially obtained in a 7.7:2.5:1.1:1 ratio, respectively. Preparative TLC gave only **38b** and **39b** in a 2.6:1 ratio. From spectra of the mixtures: for **38a**: ^{1}H NMR δ 5.01 (1H, m), 4.84 (1H, m), 3.44 (2H, s), 1.79 (3H, s), 0.83 (9H, s). For **38b**: ^{1}H NMR δ 6.61 (1H, m), 3.44 (1H, m), 2.25 (3H, s), 2.00 (3H, s), 0.86 (9H, s); ^{13}C NMR δ 205.9 (0), 189.4 (0), 163.1 (0), 117.9 (1), 48.0 (1), 39.1 (3), 32.5 (0), 28.5 (2), 28.4 (2), 27.4 (3C, 3), 26.6 (2C, 2), 23.6 (3). For **39a**: ^{1}H NMR δ 4.97 (1H, m), 4.80 (1H, m), 3.04 (1H, m). For **39b**: ^{1}H NMR δ 6.70 (1H, m), 3.15

(1H, tt, J = 3.2, 11.8 Hz), 2.25 (3H, s), 2.00 (3H, s); ^{13}C NMR δ 204.6 (0), 188.2 (0), 163.3 (0), 117.6 (1), 47.4 (1), 43.3 (3), 32.4 (0), 28.6 (2), 27.5 (2C, 2), 26.5 (2C, 2), 21.6 (3).

Procedure for the Reactions of 4 with Enones. BF_3·Et_2O (0.74 mL, 6.0 mmol) and **4** (1.55 g, 6.0 mmol) were added in succession to a solution of the ketone (2.0 mmol) in CH_2Cl_2 (10 mL) at −78 °C. The mixture was stirred at rt for 24 h before workup. Chromatography provided the products. Yields and product ratios for the individual reactions are given in Table 2.

2,2-Dimethylspiro[4.5]dec-6-ene-1,4-dione (40): oily tan solid; mp 30−32 °C; ^{1}H NMR δ 6.16 (1H, ddd, J = 3.8, 3.8, 9.9 Hz), 5.22 (1H, ddd, J = 2.2, 2.2, 9.9 Hz), 2.75 (1H, d, J = 17.8 Hz), 2.63 (1H, d, J = 17.6 Hz), 2.20−2.04 (2H, m), 1.95−1.68 (4H, m), 1.31 (3H, s), 1.22 (3H, s); ^{13}C NMR δ 218.5 (0), 214.1 (0), 133.3 (1), 120.6 (1), 58.5 (0), 50.2 (2), 46.9 (0), 29.2 (2), 25.7 (3), 25.1 (3), 23.8 (2), 17.2 (2).

2,2,7,9,9-Pentamethylspiro[4.5]dec-6-ene-1,4-dione (41): yellow oil; contaminated with isomeric compound(s) (approximately 15%); ^{1}H NMR δ 5.00 (1H, d, J = 1.4 Hz), 2.70 (1H, d, J = 17.0 Hz), 2.64 (1H, d, J = 17.0 Hz), 1.86 (1H, d, J = 16.8 Hz), 1.77 (1H, overlapped d), 1.71 (3H, d, J = 1.2 Hz), 1.65 (1H, d, J = 13.8 Hz), 1.52 (1H, d, J = 13.8 Hz), 1.22 (3H, s), 1.21 (3H, s), 1.00 (3H, s), 0.95 (3H, s); ^{13}C NMR δ 218.4 (0), 213.6 (0), 139.3 (0), 113.9 (1), 61.5 (0), 50.2 (2), 47.0 (0), 43.1 (2), 39.9 (2), 30.2 (3), 30.0 (0), 28.2 (3), 25.5 (3), 25.3 (3), 24.5 (3).

(*E*)- (42a) and (*Z*)-3,4-Dihydro-3,3-dimethyl-5-(3,5,5-trimethylcyclohex-2-enylidene)-2-furanone (42b). From spectra of the mixture: for **42a**: ^{1}H NMR δ 5.74 (1H, dd, J = 1.4, 3.0 Hz), 2.76 (2H, s), 2.15 (2H, apparent t, J = 1.8 Hz), 1.85 (2H, br s), 1.77 (3H, br s), 1.29 (6H, s), 0.91 (6H, s); NOE data 5.74 (2.76, 7%; 1.77, 4%), 2.76 (5.74, 13%, 1.29, 6%); ^{13}C NMR δ 180.4 (0), 145.0 (0), 135.8 (0), 116.9 (1), 113.0 (0), 44.8 (2), 40.0 (0), 38.6 (2), 36.5 (2), 29.8 (0), 28.32 (3), 25.0 (3), 24.3 (3). For **42b**: ^{1}H NMR δ 6.26 (1H, dd, J = 1.4, 2.8 Hz), 2.69 (2H), 1.85 (4H), 1.77 (3H, br s), 1.28 (6H, s), 0.92 (6H, s); NOE data 6.26 (1.77, 2%), 2.69 (1.85, 6%, 1.28, 8%); ^{13}C NMR δ 180.3 (0), 140.6 (0), 135.1 (0), 116.6 (1), 112.0 (0), 44.8 (2), 39.9 (0), 39.0 (2), 37.8 (2), 30.3 (0), 28.38 (3), 25.0 (3), 24.0 (3).

2,2,8,8-Tetramethylspiro[4.5]dec-6-ene-1,4-dione (43): white solid; mp 41−42 °C; ^{1}H NMR δ 5.87 (1H, d, J = 9.9 Hz), 5.09 (1H, d, J = 9.8 Hz), 2.74 (1H, d, J = 17.6 Hz), 2.66 (1H, d, J = 17.6 Hz), 1.84−1.50 (4H, m), 1.30 (3H, s), 1.22 (3H, s), 1.06 (3H, s), 1.04 (3H, s); ^{13}C NMR δ 218.3 (0), 213.9 (0), 143.3 (1), 118.3 (1), 58.8 (0), 50.3 (2), 46.9 (0), 31.9 (2), 31.1 (0), 29.2 (3), 29.1 (3), 26.9 (2), 25.7 (3), 25.2 (3).

(*E*)- and (*Z*)-3,4-dihydro-3,3-dimethyl-5-(4,4-dimethylcyclohex-2-enylidene)-2-furanone (44a,b): ^{1}H NMR (selected signals from mixture) δ 6.37 (1H, d, J = 10.0 Hz), 5.86 (1H, d, J = 9.9 Hz), 5.56 (1H, d, J = 9.9 Hz), 5.52 (1H, d, J = 9.9 Hz), 2.75 (2H, apparent t, J = 1.6 Hz), 2.70 (2H, br s), 1.31 (6H, s), 1.02 (6H, s).

4,5-Dihydro-2-hydroxy-2-(1-hydroxy-1-methylethyl)-5,5-dimethyl-3(2*H*)-furanone (45). Exposure of **18** to air and then chromatography provided **45** as a yellow oil: ^{1}H NMR δ 3.64 (1H, OH), 2.64 (1H, d, J = 18.0 Hz), 2.55 (1H, OH), 2.43 (1H, d, J = 18.0 Hz), 1.49 (3H, s), 1.46 (3H, s), 1.27 (3H, s), 1.26 (3H, s); ^{13}C NMR δ 213.6 (0), 100.2 (0), 78.1 (0), 73.9 (0), 49.1 (2), 29.7 (3), 29.4 (3), 23.9 (3), 22.9 (3).

(1′*R/S*,2*R/S*,2′*R/S*)- (46a) and (1′*R/S*,2*R/S*,2′*S/R*)-4,5-Dihydro-2-hydroxy-2-(1-hydroxy-2-methylcyclohexyl)-5,5-dimethyl-3(2*H*)-furanone (46b). Exposure of **30a/b** to air left a waxy yellow solid. Chromatography provided a colorless oil consisting of **46a** and **46b** in a 1.5:1 ratio. Crystallization occurred during refrigeration to provide a small, homogeneous sample of **46a**: ^{1}H NMR δ 3.69 (1H, s), 2.63 (1H, d, J = 18.7 Hz), 2.53 (1H, s), 2.42 (1H, d, J = 18.7 Hz), 2.08−1.84 (3H, m), 1.70−1.50 (3H, m), 1.49 (3H, s), 1.43 (3H, s), 1.42−1.20 (3H, m), 1.00 (3H, d, J = 7.3 Hz); ^{13}C NMR δ 213.6 (0), 100.5 (0), 77.7 (0), 77.2 (0), 48.3 (2), 34.2 (1), 30.3 (3), 29.8 (3), 29.4 (2), 26.5 (2), 21.0 (2), 19.8 (2), 16.2 (3). The structure of **46a** was determined by X-ray crystallography.[19] For **46b**: ^{1}H NMR δ 3.74 (1H, s), 2.58 (1H, d, J = 18.4 Hz), 2.49 (1H, d, J = 18.4 Hz), 2.22 (1H, s), 1.48 (3H, s), 1.47 (3H, s), 1.05 (3H, d, J = 7.4 Hz), 1.77 (2H, apparent triplet); ^{13}C NMR δ 214.0 (0), 100.4 (0), 78.6 (0), 76.8 (0), 48.5 (2), 35.4 (1), 30.0 (3), 29.6 (3), 24.8 (2), 21.1 (2), 20.8 (2), 19.7 (2), 16.6 (3).

2-Hydroxy-2-(1-hydroxycyclohexyl)-4,4-dimethylcyclobutanone (47): white solid; mp 145−148 °C; ^{1}H NMR δ 3.38 (1H, br s), 2.18 (1H, d, J = 12.8 Hz), 1.91 (1H, d, J = 12.9 Hz), 1.83 (1H, m), 1.73 (1H, br m), 1.67−1.40 (6H, m), 1.36 (3H, s), 1.27−1.16 (2H, m), 1.15 (3H, s); ^{13}C NMR δ 220.0 (0), 92.6 (0), 73.3 (0), 55.2 (0), 38.6 (2), 32.1 (2), 29.6 (2), 25.6 (2), 24.7 (3), 20.9 (3), 20.8 (2), 20.7 (2).

Compound **47** (10.1 mg, 47.5 mmol) was stirred with BF_3·Et_2O (1.1 mL) for 2 h. Workup gave a yellow oil (11.8 mg), which ^{1}H NMR revealed to be a 3.0:1 mixture of **26** and **27**.

A solution of **47** (18.3 mg, 86.2 mmol) in CH_2Cl_2 (1.7 mL) and BF_3·Et_2O (0.18 mL) was stirred for 15 h at rt. Workup gave an oily, brown solid (24.4 mg), which contained only **26** but no trace of **27**.

2-(*c*-4-*tert*-Butyl-*r*-1-hydroxycyclohexyl)-2-hydroxy-4,4-dimethylcyclobutanone (48): white solid; mp 158−159.5 °C; ^{1}H NMR δ 3.30 (1H, br s), 2.15 (1H, dd, J = 0.9, 12.9 Hz), 1.91 (1H, d, J = 12.9 Hz), 1.90 (1H, m), 1.72−1.40 (6H, m), 1.37 (3H, s), 1.31 (1H, br m), 1.16 (3H, s), 0.96 (1H, apparent tt, J = 2.9, 11.8 Hz), 0.87 (9H, s); ^{13}C NMR δ 220.0 (0), 92.6 (0), 72.9 (0), 55.2 (0), 47.7 (1), 38.7 (2), 32.6 (2), 32.4 (0), 30.2 (2), 27.5 (3C, 3), 24.7 (3), 21.8 (2), 21.6 (2), 20.9 (3). The structure of **48** was determined by X-ray crystallography.[19]

Compound **48** (60.8 mg, 0.227 mmol) was stirred with BF_3·Et_2O (1.0 mL) for 20 h. Workup gave 56.0 mg of a mixture of **36a** and **37** in a 8:1 ratio by GC−MS.

A solution of **48** (122 mg, 0.489 mmol) in CH_2Cl_2 (10 mL) and BF_3·Et_2O (0.90 mL) was stirred for 21 h at rt. Workup gave an oily, tan solid (107 mg), consisting of a 13:1 mixture of **36a** and **37** by GC−MS.

A solution of **48** (84 mg, 0.31 mmol) in CH_2Cl_2 (1.6 mL) with BF_3·Et_2O (0.58 mL) and H_2O (50 μL) was stirred for 23 h at rt. Workup gave **36a** as pale yellow solid (77 mg, 98%).

3,3,4,4-Tetramethyl-1,2-bis[(trimethylsilyl)oxy]cyclobutene (51): colorless liquid; $bp_{2.5\ mm}$ 83−87.8 °C; ^{1}H NMR δ 1.01 (12H, s), 0.20 (6H, s); ^{13}C NMR δ 128.2 (2C, 0), 43.9 (2C, 0), 21.8 (4C, 3), 0.6 (6C, 3).

2-Isopropylidene-4,5-dihydro-4,4,5,5-tetramethyl-3(2*H*)-furanone (52): yellow oil (31% yield from acetone); ^{1}H NMR δ 2.08 (3H, s), 1.79 (3H, s), 1.22 (6H, s), 1.00 (6H, s); ^{13}C NMR δ 205.2 (0), 141.8 (0), 121.1 (0), 83.1 (0), 51.0 (0), 23.5 (2C, 3), 19.5 (3C, 3), 17.1 (3).

2-Cyclohexylidene-4,5-dihydro-4,4,5,5-tetramethyl-3(2*H*)-furanone (53): tan-colored oil (35% yield from cyclohexanone); ^{1}H NMR δ 2.74 (2H, m), 2.25 (2H, distorted t), 1.75−1.40 (6H, m), 1.22 (3H, s), 1.00 (3H, s); ^{13}C NMR δ 206.0 (0), 139.0 (0), 129.4 (0), 82.9 (0), 51.2 (0), 28.6 (2), 28.1 (2), 27.2 (2), 26.4 (2), 26.2 (2), 23.4 (3), 19.6 (3).

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Supporting Information Available: Additional characterization data (UV, IR, MS, HRMS); ^{1}H and ^{13}C NMR spectra of **3**, **4**, **6**, **7**, **11c**, **12a,b**, **15a,b**, **17**, **18**, **20**, **23**, **26**, **27**, **28b**, **29a,b** (8:1), **33a,c**, **35**, **36a,b**, **37**, **40**, **43**, **45**, **46a**, **47**, **48**, **51**−**53**; X-ray crystal structures for **11c**, **33c**, **36b**, **46a**, and **48** (75 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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