JOC*Note*

Reactions of 1,2-Bis(trimethylsilyloxy)cycloalkenes with the Diethyl Acetals of Aldehydes

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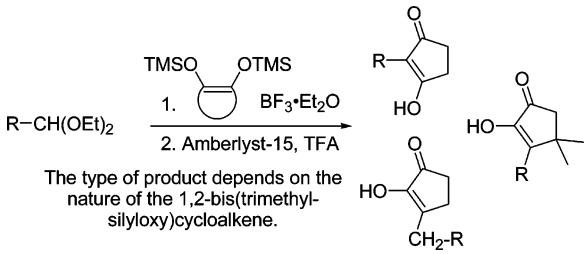
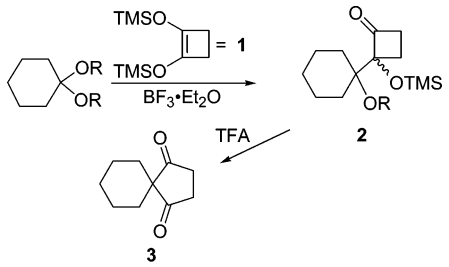


Lewis acid-mediated reactions of 1,2-bis(trimethylsilyloxy)-cyclobutene with acetals derived from a variety of aldehydes, followed by treatment with Amberlyst 15 resin in TFA, yielded 1,3-cyclopentanedione products, but reactions with 3,3-dimethyl-1,2-bis(trimethylsilyloxy)cyclobutene led to 1,2-cyclopentanediones. Reactions of 1,2-bis(trimethylsilyloxy)-cyclopentene gave intermediates that did not undergo skeletal rearrangement with Amberlyst 15 resin in TFA.

The geminal acylation of ketones and their acetals, illustrated in Scheme 1, has been studied in some detail.[1−7] The first step is a Lewis acid-mediated addition of 1,2-bis(trimethylsilyloxy)-

SCHEME 1



cyclobutene (**1**[8]) that leads to a cyclobutanone product **2**. The second rearrangement step gives a 2,2-disubstituted cyclopentane-1,3-dione **3**. The acid of choice for this second step has been TFA,[1] but both steps can be carried out in one pot when a large excess of BF_3·Et_2O is used.[2−4] Aldehydes and their acetals have received surprisingly little attention.[1b,9] Kuwajima and co-workers[1b] reported the isolation of cyclobutanones following treatment of the acetals of aldehydes with **1** in the presence of BF_3 etherate. Li and Zhang[9] showed that MgI_2 etherate is a very effective catalyst, also. However, Kuwajima and co-workers did not have much success in rearranging these cyclobutanones to cyclopentane-1,3-diones. They stated that the rearrangement was extremely slow compared to rearrangement of cyclobutanones derived from ketone acetals. A remedy for this lack of reactivity was suggested by Rao et al.,[10] who added some strongly acidic Nafion-H film to the TFA. On the other hand, Mariano and co-workers[11] started with aryl aldehydes and, following the Kuwajima procedure, obtained the 2-aryl-1,3-cyclopentanediones.

The present study began with treatment of 2-methyl-1,3-dioxolane with **1** and BF_3·Et_2O under Kuwajima's conditions.[1b] The result was a very complex mixture. However, cyclobutanone **5a**, a mixture of diastereomers in a ratio very close to 1:1, was produced efficiently from the diethyl acetal of acetaldehyde **4a**. (One might presume that silyl groups were lost during aqueous workup.) Maintaining a solution of this cyclobutanone mixture **5a** in TFA at reflux for 14 h gave just a small amount of the expected 1,3-diketone **6a**. Rao et al.[10] reported a yield of 63% for **6a** when this step was carried out in the presence of some Nafion-H membrane. In our hands, it was necessary to use vacuum-dried Nafion to realize an acceptable yield of **6a**.

A higher-yielding and simpler alternative was found. The medium for rearrangement was TFA to which a strongly acidic ion-exchange resin, Amberlyst 15, was added. Thus, following a two-step protocol of first producing the cyclobutanone mixture **5a** and then of subjecting the crude mixture to the Amberlyst 15-mediated rearrangement, the yield of **6a** was 79%.[12] Under the same conditions, acetals **4b**−**f** led to other 2-substituted cyclopentane-1,3-diones **6b**−**f** (Scheme 2) in similar yields,

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(10) Martinez, R. A.; Rao, P. N.; Kim, H. K. *Synth. Commun.* **1989**, *19*, 373−377.

(11) Lin, X.; Kavash, R. W.; Mariano, P. S. *J. Org. Chem.* **1996**, *61*, 7335−7347.

(12) It is not known whether the considerable improvement with the Amberlyst 15 stems merely from the acidity of the resin or if the polymeric structure of the resin plays an important role.

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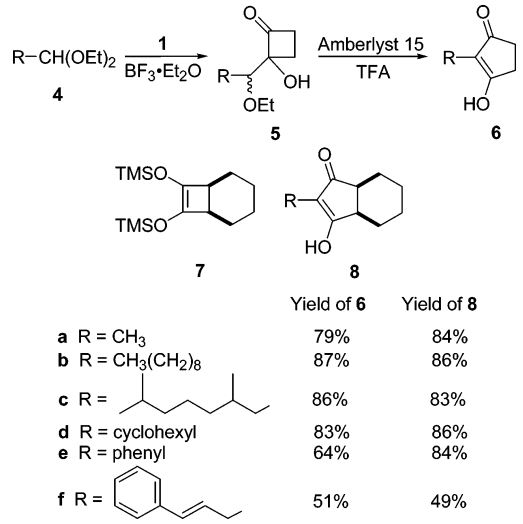
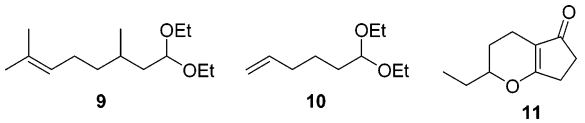
SCHEME 2



generally. The cyclobutanone **5e** was not observed. Under the acidic conditions of the initial reaction, it continued to react to provide directly the diketone **6e**. This was consistent with Mariano's observations.[11] The sparing solubility of these 1,3-diketones in common solvents made their purification by flash chromatography problematic, and this lack of solubility necessitated the NMR analyses of the diketones in TFA solution, in which they were rapidly equilibrating enol forms.[13]

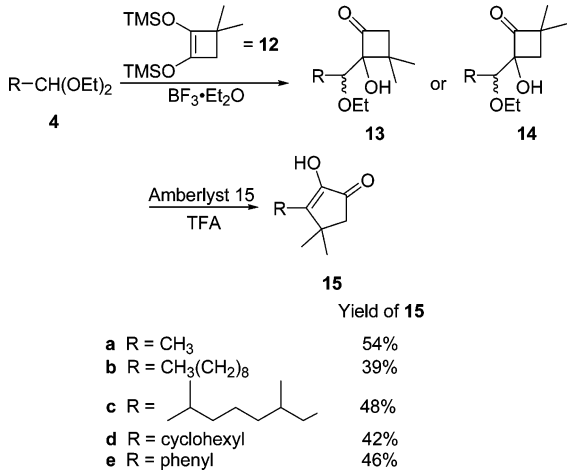
Methyl-substituted analogues of **1** reacted with ketones and their acetals to give geminal acylation products.[6] In the same way, geminal acylations using the analogue **7** were carried out with six aldehyde acetals. The yields of the 1,3-diketones, which by NMR were largely in enolized forms **8a**−**f**, were similar to those of **6a**−**f** (Scheme 2). Epimerization to a trans ring system was not seen.

The 1,3-diketones derived from *trans*-cinnamaldehyde **6f** and **8f** were obtained in a lower yield, but an earlier study[1b] using **1** had failed to produce any **6f**. However, with **1** two other olefinic substrates yielded none of the expected 1,3-diketones. Acetal **9** was not stable under the conditions of the first step. Acetal **10** did produce a cyclobutanone mixture smoothly, but its exposure to Amberlyst 15 resin in TFA gave **11** as the only isolated product in only 35% yield. Compound **11** was the product of double-bond migration and cyclization onto the enolized carbonyl of the 1,3-diketone.



The yields of 1,3-diketones from the gem-dimethyl cyclobutene **12** with ketones and their acetals had been observed to be significantly lower than that with **1** due to competition with alternative rearrangement pathways.[6,7] In the present case with aldehyde acetals, the cyclobutanones (**13** or **14**) were produced easily, but their treatment with Amberlyst 15 resin in TFA did not yield 1,3-diketones, of which some would have been known compounds.[13,14] Instead, the products were enols of 1,2-diketones **15** (Scheme 3). These products could be

SCHEME 3



rationalized by rearrangement of cyclobutanones **13** (i.e., migration of the bond to the dimethylcarbon competed favorably with migration of the bond to the carbonyl). However, it is not known if these were the initial products from the reaction of **12** with the acetals or if **14** was produced first, and there was an equilibrium between **14** and a small proportion of **13** under the acidic conditions of the reaction. Previous work with ketones suggests that **14** should have been the predominant, initially formed cyclobutanone.[6]

These results indicate that the migratory aptitude of alkyl groups relative to an acyl group is tertiary alkyl > acyl > secondary alkyl. This order is derived from the observation that the reactions with **7** gave 1,3-diketones, whereas the products of **12** were 1,2-diketones.

The acetals of ketones react with the cyclopentene derivative **16** to give 2,2-disubstituted 1,3-cyclohexanediones.[3] The acetals **4a**−**e** reacted with **16** to give the expected cyclopentanone aldol products **17**, but treatment of these without purification with Amberlyst 15 resin in TFA gave compounds that were the enols of 1,2-cyclopentanediones **18a**−**e** (Scheme 4). The structure of **18e** was confirmed by X-ray crystallography. It is postulated that these surprising products might have arisen via an enol form **19** of each cyclopentanone **17**. 1,3-Hydroxyl transposition would give **20**, and then protonation of the ethoxy group (**21**) and its loss could lead to an extended, enolic molecule, which should tautomerize to **18**.

In an additional experiment with **16** (Scheme 5), the process was carried out using the acetal **22** derived from β-naphthaldehyde. In contrast with all of the other reactions with **16**, the immediate product of the aldol step was not isolable. It rearranged spontaneously in the presence of the BF_3•Et_2O, and the product (88% yield) was the 1,3-cyclohexanedione, in an enolized form **23**. It is not clear why this reaction differed significantly from that of acetal **4e**. Further experiments to probe these divergent reaction paths are planned.

In summary, the reactions of the diethyl acetals of aldehydes vary considerably depending on the nature of the 1,2-bis-(trimethylsilyloxy)cycloalkene. Using the two-step protocol described above, unsubstituted cyclobutene **1** and a vicinally disubstituted cyclobutene **7** provided the expected cyclopentane-

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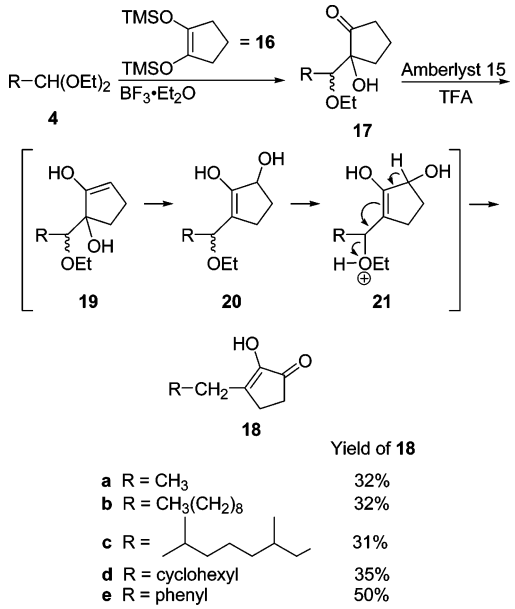
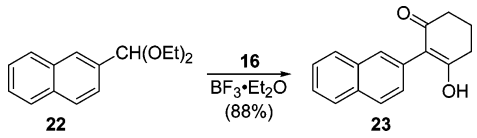
SCHEME 4



SCHEME 5



1,3-diones, which NMR revealed are largely enolized, in very good yields. The geminally disubstituted cyclobutene **12** and the cyclopentene **16** followed different reaction pathways to give cyclopentane-1,2-diones, also mainly enolized, in modest yields.

Experimental Section

General Procedure: 2-Methylcyclopentane-1,3-dione (6a). A solution of acetaldehyde diethyl acetal **4a** (0.118 g, 1.00 mmol) in dry CH_2Cl_2 (20 mL) was cooled in a dry ice/acetone bath under N_2. Freshly distilled BF_3 etherate (0.25 mL, 2.0 mmol) was added, followed by a solution of **1** (0.34 g, 1.5 mmol) in dry CH_2Cl_2 (5.0 mL) over 10 min. The mixture was stirred overnight by which time the mixture had attained rt. Saturated aqueous $NaHCO_3$ was added, and the aqueous layer was re-extracted with ether. The combined organic solutions were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give **5a** as an oily residue. For the crude **5a**: ^{13}C NMR ($CDCl_3$): δ 212.2, 210.1, 93.52, 93.47, 76.1, 76.0, 65.3, 65.0, 41.6, 40.9, 24.1, 23.7, 15.5 (2C), 14.1 (2C). The mixture **5a**, without further purification, was dissolved in TFA (2.0 mL), and Amberlyst 15 (0.1 g) was added. The solution was heated under reflux for 10 h. After cooling, the solution was diluted with Et_2O (20 mL). Activated charcoal was added, and the suspension was stirred for 30 min at reflux temperature. The suspension was filtered through Celite and evaporated under reduced pressure to provide **6a** (0.088 g, 79%) as a colorless solid; mp: 213-215 °C (from EtOH), lit.[10] 210−211 °C; ^{1}H NMR (TFA): δ 2.57 (4H, s), 1.37 (3H, s); ^{13}C NMR (TFA): δ 209.5, 119.3, 31.8, 5.4.

2-Nonylcyclopentane-1,3-dione (6b): Colorless solid. mp: 132−133 °C (from EtOAc); IR (Nujol): 1711 cm^{-1}; ^{1}H NMR (TFA): δ 2.94 (4H, s), 2.26 (2H, t, J = 7.5 Hz), 1.40 (2H, m), 1.22−1.16 (12H, m), 0.74 (3H, t, J = 6.5 Hz); ^{13}C NMR (TFA): δ 210.0, 124.4, 33.7, 32.1, 31.2, 31.1, 31.0, 30.9, 28.8, 24.3, 22.1, 14.6.

2-(2,6-Dimethylheptyl)cyclopentane-1,3-dione (6c): Pale yellow solid. mp: 123−124 °C (from EtOAc); ^{1}H NMR (TFA): δ 2.95 (4H, s), 2.25 (1H, dd, J = 14.0, 6.1 Hz), 2.08 (1H, dd, J = 14.0, 8.0 Hz), 1.64 (1H, m), 1.39 (1H, apparent septet, J = 6.5 Hz), 1.29 (1H, m), 1.17 (2H, m), 1.04 (3H, m), 0.75 (3H, d, J = 6.5 Hz), 0.72 (6H, d, J = 6.5 Hz); ^{13}C NMR (TFA): δ 210.0, 123.6, 40.9, 38.8, 33.8, 32.0, 29.7, 29.5, 26.3, 23.2, 23.1, 19.9.

2-Cyclohexylcyclopentane-1,3-dione (6d): Solid. mp: 216−218 °C (from EtOAc); ^{1}H NMR (TFA): δ 2.94 (4H, s), 2.53 (1H, m), 1.74−1.50 (6H, m), 1.22 (4H, m); ^{13}C NMR (TFA): δ 209.7, 128.2, 35.3, 32.1, 30.9, 27.9, 27.1.

2-Phenylcyclopentane-1,3-dione (6e): Colorless solid. mp: 233−234 °C (dec) (from EtOAc), lit.[1b] 231−232 °C; ^{1}H NMR (TFA): δ 7.28 (5H, m), 2.98 (4H, s); ^{13}C NMR (TFA): δ 207.5, 131.4, 130.8, 130.6, 127.4, 122.7, 31.8.

2-(2-Phenyl-1-ethenyl)cyclopentane-1,3-dione (6f): Colorless solid. mp: 209−210 °C (from EtOH); ^{1}H NMR (TFA): δ 7.34−7.15 (6H), 6.64 (1H, d, J = 16.7 Hz), 2.99 (4H, s); ^{13}C NMR (TFA): δ 208.0, 138.4, 138.2, 131.0, 130.9, 128.6, 120.1, 112.4, 32.2.

(*cis*)-8-Methylbicyclo[4.3.0]nonane-7,9-dione (8a): Colorless solid. mp: 151−151.5 °C (from EtOAc), lit.[15] 149−151 °C; IR (Nujol): 1699 cm^{-1}; ^{1}H NMR (TFA): δ 3.06 (2H, m), 2.04 (2H, m), 1.75 (3H, s), 1.66−1.28 (6H, m); ^{13}C NMR (TFA): δ 212.5, 118.3, 44.5, 25.0, 20.4, 5.5; MS *m*/*z*: 166 (M$^+$).

(*cis*)-8-Nonylbicyclo[4.3.0]nonane-7,9-dione (8b): Colorless liquid. IR (film): 1709 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.81 (2H, broad m), 2.60−0.85 (m); ^{13}C NMR ($CDCl_3$): δ 202.7, 117.8, 41.9, 32.1, 29.8, 29.7, 29.5, 29.5, 28.3, 23.4, 22.8, 22.8, 19.6, 14.2; MS *m*/*z*: 278 (M$^+$).

(*cis*)-8-(2,6-Dimethylheptyl)bicyclo[4.3.0]nonane-7,9-dione (8c): Colorless solid. mp: 111−112 °C (from hexane); IR (Nujol): 1708 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.73 (2H, m), 2.15 (1H, dd, J = 6.8, 3.0 Hz), 2.01 (1H, dd, J = 6.8, 4.0 Hz), 1.88 (2H, m), 1.70 (3H, m), 1.48 (1H, m), 1.45 (4H, narrow m), 1.36−1.19 (3H, m), 1.15−1.05 (3H, m), 0.85 (6H, d, J = 7.0 Hz), 0.82 (3H, d, J = 6.5 Hz); ^{13}C NMR ($CDCl_3$): δ 200.4, 116.2, 41.9, 39.6, 37.4, 32.5, 28.8, 28.2, 25.1, 23.8, 23.0, 22.8, 20.2, 19.7.

(*cis*)-8-Cyclohexylbicyclo[4.3.0]nonane-7,9-dione (8d): Colorless solid. mp: 210−212 °C (from EtOAc); IR (Nujol): 1704 cm^{-1}; ^{1}H NMR (TFA): δ 3.08 (2H, m), 2.48 (1H, m), 2.01−1.86 (2H, m), 1.73−1.08 (16H); ^{13}C NMR (TFA): δ 212.3, 127.3, 44.5, 35.1, 31.1, 27.9, 27.1, 25.0, 20.0.

(*cis*)-8-Phenylbicyclo[4.3.0]nonane-7,9-dione (8e): Colorless solid. mp: 227−228 °C (from EtOAc), lit.[16] 229−230 °C; ^{1}H NMR (TFA): δ 7.30 (3H, m), 7.15 (2H, m), 3.18 (2H, m), 2.00 (2H, m), 1.75 (2H, m), 1.54 (4H, m); ^{13}C NMR (TFA): δ 210.6, 132.2, 131.4, 131.2, 127.0, 122.2, 44.4, 25.2, 20.7.

(*cis*)-8-(2-Phenyl-1-ethenyl)bicyclo[4.3.0]nonane-7,9-dione (8f): Colorless solid. mp: 207−209 °C (from EtOAc); ^{1}H NMR (TFA): δ 7.36−7.16 (6H), 6.63 (1H, d, J = 16.8 Hz), 3.12 (2H, m), 2.11−1.95 (2H, m), 1.76−1.52 (6H); ^{13}C NMR (TFA): δ 210.0, 138.7, 138.3, 131.0, 130.8, 130.8, 128.6, 112.3, 44.5, 25.3, 20.6.

2-Ethyl-3,4,6,7-tetrahydro-2*H*-cyclopenta[*b*]pyran-5-one (11): Colorless liquid. IR (film): 1732, 1694 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.07 (1H, m), 2.54 (2H, m), 2. 43 (2H, m), 2.28 (1H, m), 2.14 (1H, m), 1.94 (1H, m), 1.78 (1H, m), 1.68 (1H, m), 1.56 (1H, m), 1.04 (3H, t, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$): δ 205.0, 185.9, 114.8, 81.7, 33.1, 27.6, 26.8, 25.5, 16.2, 9.7; MS *m*/*z*: 166 (M$^+$).

3,4,4-Trimethylcyclopentane-1,2-dione (15a): Colorless solid. mp: 79−80 °C (from EtOAc); IR (Nujol): 1702, 1656 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.51 (1H, broad s), 2.31 (2H, s), 1.92 (3H, s), 1.19 (6H, s); ^{13}C NMR ($CDCl_3$): δ 202.0, 152.8, 147.5, 48.5, 37.6, 27.1, 9.3; MS *m*/*z*: 140 (M$^+$).

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4,4-Dimethyl-3-nonylcyclopentane-1,2-dione (15b): Colorless liquid. IR (film): 1708, 1639 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.01 (1H, s), 2.29 (2H, m), 1.63 (2H, quintet, $J = 7.5$ Hz), 1.37−1.25 (14H), 1.20 (6H, s), 0.88 (3H, t, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$): δ 201.9, 155.3, 147.6, 48.5, 38.1, 32.0, 30.3, 29.6, 29.5, 29.4, 27.6 (2C), 27.5, 25.6, 22.8, 14.2.

3-(2,6-Dimethylheptyl)-4,4-dimethylcyclopentane-1,2-dione (15c): Colorless solid. mp: 43−44 °C (from EtOAc); IR (film): 1709 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.11 (1H, s), 2.30 (2H, narrow m), 2.11 (2H, m), 1.53 (1H, septet, $J = 6.6$ Hz), 1.40−1.12 (13H, including a 6H singlet at 1.20), 0.91 (3H, d, $J = 6.0$ Hz), 0.87 (6H, d, $J = 6.6$ Hz); ^{13}C NMR ($CDCl_3$): δ 201.9, 154.0, 147.9, 48.6, 39.3, 38.2, 38.0, 33.5, 31.3, 28.0, 27.9, 27.8, 24.9, 22.8, 22.7, 20.2.

3-Cyclohexyl-4,4-dimethylcyclopentane-1,2-dione (15d): Colorless solid. mp: 174−175 °C (from EtOAc); IR (Nujol): 1693, 1644 cm^{-1}; ^1H NMR ($CDCl_3$): δ 6.04 (1H, s, OH), 2.27 (2H, s), 2.14 (1H, tt, $J = 12.0$, 3.4 Hz), 1.91−1.86 (2H, m), 1.81 (2H. m), 1.71 (1H, m), 1.59 (2H, d, $J = 3.7$ Hz), 1.32−1.27 (3H, m), 1.20 (6H, s); ^{13}C NMR ($CDCl_3$): δ 202.4, 158.8, 147.0, 48.0, 38.1, 37.1, 29.6, 27.2, 26.6, 25.8.

4,4-Dimethyl-3-phenylcyclopentane-1,2-dione (15e): Colorless solid. mp: 164−165 °C (from EtOAc); IR (Nujol): 1694, 1651 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.61 (2H, d, $J = 7.6$ Hz), 7.43 (2H, t, $J = 7.6$ Hz), 7.36 (1H, t, $J = 7.6$ Hz), 5.89 (1H, s, OH), 2.48 (2H, s), 1.41 (6H, s); ^{13}C NMR ($CDCl_3$): δ 201.8, 148.6, 147.2, 133.1, 128.8, 128.6, 128.5, 50.0, 39.0, 28.7; MS *m*/*z*: 202 (M^+).

3-Ethylcyclopentane-1,2-dione (18a): Liquid. ^1H NMR ($CDCl_3$): δ 2.48−2.41 (6H, m), 1.16 (3H, t, $J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$): δ 203.5, 149.4, 148.4, 31.9, 24.8, 21.9, 11.3.

3-Decylcyclopentane-1,2-dione (18b): Colorless solid. mp: 69−71 °C (from hexane); IR (Nujol): 1697 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.73 (2H, t, $J = 6.3$ Hz), 2.64 (2H, t, $J = 6.3$ Hz), 2.44 (2H, t, $J = 7.5$ Hz), 1.59 (2H, m), 1.26 (14H), 0.88 (3H, t, $J = 6.9$ Hz); ^{13}C NMR ($CDCl_3$): δ 203.2, 148.6, 148.1, 32.0, 31.9, 29.8, 29.7, 29.7, 29.5, 29.5, 28.8, 27.0, 25.3, 22.8, 14.2; MS *m*/*z*: 238 (M^+).

3-(3,7-Dimethyloctyl)cyclopentane-1,2-dione (18c): Liquid. IR (film): 1712, 1652 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.42 (6H, m), 1.60−1.10 (10H), 0.97 (3H, d, $J = 6.4$ Hz), 0.90 (6H, d, $J = 7.4$ Hz); ^{13}C NMR ($CDCl_3$): δ 203.2, 148.6, 148.5, 39.4, 37.1, 34.0, 32.9. 31.9, 28.1, 26.4, 25.3, 24.8, 22.8, 22.7, 19.5; MS *m*/*z*: 238 (M^+).

3-(Cyclohexylmethyl)cyclopentane-1,2-dione (18d): Colorless waxy solid. mp: ca. 25 °C; IR (Nujol): 1713 cm^{-1}; ^1H NMR ($CDCl_3$): δ 2.43 (4H, narrow m), 2.31 (2H, d, J 7.0 = Hz), 1.96−0.82 (10H); ^{13}C NMR ($CDCl_3$): δ 203.8, 149.6, 148.5, 36.7, 36.5, 33.6, 32.1, 26.4, 26.3, 26.1.

3-(Phenylmethyl)cyclopentane-1,2-dione (18e): Colorless solid. mp: 96−96.5 °C (from EtOAc/hexane); IR (Nujol): 1696, 1652 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.30−7.22 (5H), 3.74 (2H, s), 2.36 (4H, m); ^{13}C NMR ($CDCl_3$): δ 203.5, 148.7, 145.6, 137.8, 129.1, 128.8, 126.8, 35.0, 32.0, 24.9; MS *m*/*z*: 188 (M^+).

2-(2-Naphthyl)cyclohexane-1,3-dione (23): Colorless solid. mp: 204.5−205 °C (from EtOAc); ^1H NMR ($CDCl_3$): δ 7.90 (1H, d, $J = 8.4$ Hz), 7.82 (2H, m), 7.67 (1H, s), 7.49 (2H, m), 7.27 (1H, dd, $J = 8.4$, 1.6 Hz), 2.62 (2H, t, $J = 5.8$ Hz), 2.50 (2H, t, $J = 5.8$ Hz), 2.08 (2H, m); ^{13}C NMR ($CDCl_3$): δ 197.3, 171.4, 133.8, 133.1, 129.5, 129.1, 128.8, 128.7, 128.0, 127.9, 126.6, 126.4, 118.2, 37.0, 28.2, 20.6.

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Supporting Information Available: Spectral data and NMR spectra for all diketones and **11**, ORTEP of **18e**, and X-ray data for **18e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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