

## Novel Photoreductive Cyclization of 1-Aryl-2-methylpropane-1,3-diones

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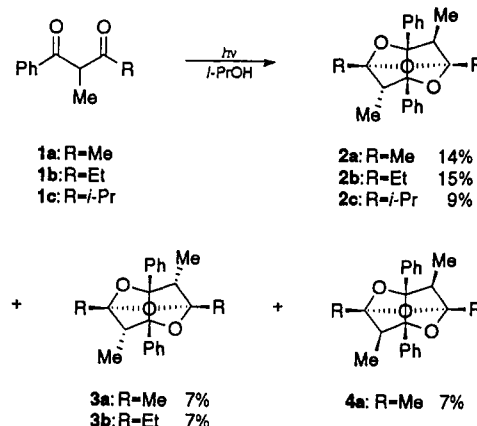
Irradiation of 2-methyl-1-phenylpropane-1,3-diones **1a-c** in 2-propanol gave trioxatricyclononanes **2a-c**, **3a,b**, and **4a**. Irradiation of 1,3-diaryl-2-methylpropane-1,3-diones **1d** and **1e** gave trioxatricyclononanes **2d** and **2e**, *dl*-pinacols **5d** and **5e**, and the bicyclic dihemiacetal **6**. The dihemiacetal **6** underwent dehydration on heating to give the trioxatricyclononane **3d**. Treatment of **2d,e**, **5d,e**, and **6** with hydrochloric acid gave dioxabicyclooctadienes **7a** and **7b**, while that of **2a-c**, **3a,b** and **4a** with hydrochloric acid gave 3-methylenecyclopentenes **8a-c** and the epoxycycloheptenone **9**.

Photoreduction of aryl ketones by hydrogen-atom-donating substrates has been extensively investigated from both synthetic<sup>2</sup> and mechanistic<sup>3</sup> points of view. A number of  $\alpha$ -substituted acetophenones form pinacols upon irradiation in 2-propanol or other suitable hydrogen-donor solvents.<sup>2</sup> Photoreduction of dicarbonyl compounds has also been investigated. Ethyl 2-benzoylalkanoates,  $\beta$ -keto esters, undergo photoreduction with 2-propanol to give 2,6-dioxabicyclo[3.3.0]octane-3,7-diones *via* the lactonization of initially formed pinacols.<sup>4</sup> Irradiation of ethyl acetoacetate in various alcohols gives 4-hydroxy-4,5-dihydrofuran-2(3*H*)-ones *via* mixed pinacols.<sup>5</sup> Acetylacetophenone, a 1,4-diketone, undergoes photoreduction with 2-propanol to give 3,8-diisopropoxy-3,8-dimethyl-1,6-diphenyl-2,7-dioxabicyclo[4.4.0]decane *via* the cyclization of an initially formed pinacol followed by the reaction with 2-propanol.<sup>6</sup> In relation to our studies on the photoreaction of aryl 1,3-diketones,<sup>7</sup> we studied the photoreduction of 1-aryl-2-methylpropane-1,3-diones **1a-e** with 2-propanol. We report here that 1,3-diketones **1a-e** undergo novel photoreductive cyclization to give 2,6,9-trioxatricyclo[3.3.1.0<sup>3,7</sup>]nonanes **2**, **3**, and **4** *via* pinacols and that compounds **2-4** are transformed to 4,8-dioxabicyclo[3.3.0]octa-2,6-dienes **7a,b**, 3-methylenecyclopentenes **8a-c**, and epoxycycloheptenone **9** by treatment with acid.

### Results and Discussion

Irradiation of a 2-propanol solution of 2-methyl-1-phenylbutane-1,3-dione (**1a**) with a high-pressure mercury lamp through a Pyrex filter (Scheme I) gave three isomeric trioxatricyclononanes **2a**, **3a**, and **4a**.<sup>8</sup> The structures of

Scheme I



these products were elucidated on the basis of analytical and spectral data. The IR spectra showed neither carbonyl nor hydroxy absorptions. The 400-MHz <sup>1</sup>H NMR spectrum of **2a** showed peaks due to two CHCH<sub>3</sub> groups as two doublets ( $\delta$  0.90 and 0.94) and two quartets ( $\delta$  2.12 and 2.35), whereas those of **3a** and **4a** showed a doublet (**3a**,  $\delta$  0.99; **4a**,  $\delta$  0.86) and a quartet (**3a**,  $\delta$  2.24; **4a**,  $\delta$  2.45). The <sup>13</sup>C NMR spectrum of **2a** showed four peaks due to quaternary carbons attached to an oxygen atom at  $\delta$  93.8, 94.3, 106.3, and 108.3, whereas those of **3a** and **4a** showed two peaks (**3a**,  $\delta$  93.6 and 106.7; **4a**,  $\delta$  94.5 and 108.2). These data indicate that **3a** and **4a** are symmetrical molecules. However, their configurations could not be assigned on the basis of these data. The configuration of **3a** was determined by X-ray crystallographic analysis,<sup>9</sup> which showed that the methyl group on the secondary carbon was *trans* to the phenyl group. Therefore, the configuration of **4a** should be *cis* with respect to the phenyl and methyl groups.

Irradiation of 2-methyl-1-phenylpentane-1,3-dione (**1b**) under the same conditions gave trioxatricyclononanes **2b**

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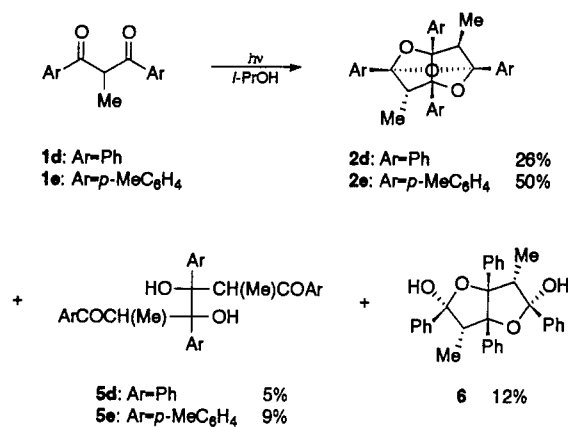
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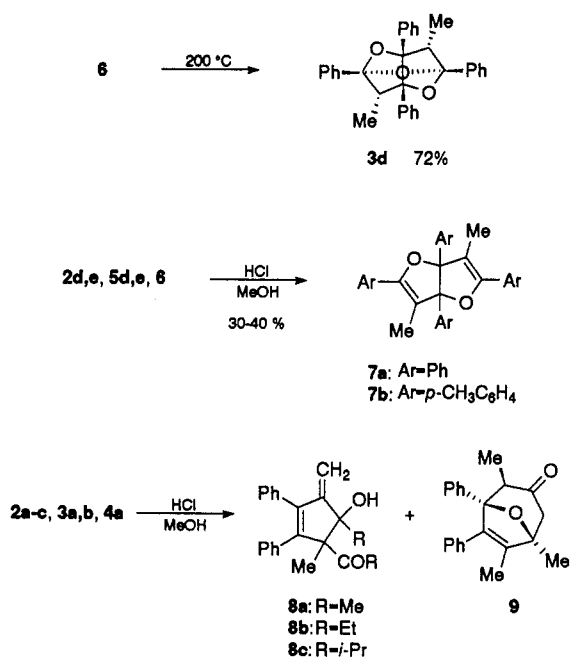
(8) When 1-phenylbutane-1,3-dione was irradiated in 2-propanol, no products were detected. Photostability of this compound may be ascribed to an internal filter effect by the enol form. Hasegawa, T.; Ohkanda, J.; Kobayashi, M.; Yoshioka, M. *J. Photochem. Photobiol. A: Chem.* 1992, 64, 299.

(9) The X-ray data for compound **9** has 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.

Scheme II



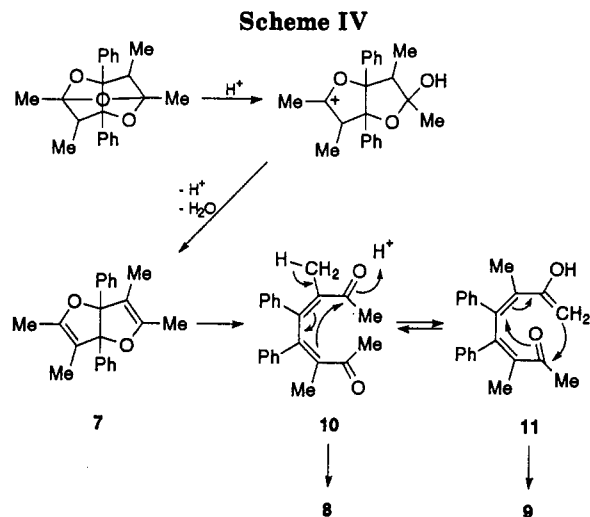
Scheme III



and 3b, and that of 2,4-dimethyl-1-phenylpentane-1,3-dione (1c) gave 2c. Only one symmetrical trioxatricyclononane and no symmetrical trioxatricyclononanes were obtained from 1b and 1c, respectively, owing probably to steric compression. The configuration of 3b was assigned by comparison of its <sup>1</sup>H NMR spectrum with those of 2a, 3a, and 4a. The <sup>1</sup>H NMR spectrum of 3a showed a doublet due to the C<sub>4</sub>- and C<sub>8</sub>-methyl groups at lower field than those of 2a and 4a. A quartet due to the C<sub>4</sub>- and C<sub>8</sub>-methine protons of 3a appeared at higher field than that of 4a and between two quartets of 2a (*vide supra*). The <sup>1</sup>H NMR spectrum of 3b showed a doublet (δ 0.94) due to the C<sub>4</sub>- and C<sub>8</sub>-methyl groups at lower field than two doublets (δ 0.88 and 0.89) of 2b and a quartet (δ 2.15 and 2.35) of 2b.

Irradiation of 2-methyl-1,3-diphenylpropane-1,3-dione (1d) under the same conditions (Scheme II) gave the trioxatricyclononane 2d, the *dl*-pinacol 5d, and the bicyclic dihemiacetal 6, and that of 2-methyl-1,3-bis(*p*-methylphenyl)propane-1,3-dione (1e) gave the trioxatricyclononane 2e and the *dl*-pinacol 5e. The configuration of 6 was elucidated on the basis of dehydration on heating at 200 °C to give the trioxatricyclononane 3d, the configuration of which was assigned by comparison of its <sup>1</sup>H NMR spectrum with those of 2a-d, 3a, b, and 4a (Scheme III). The pinacols 5d, e underwent dehydration to give dioxabicyclooctadienes 7a, b by treatment with hydrochloric acid, probably *via* the bicyclic dihemiacetal. The treatment of 6 with the acid also gave 7a. The trioxatricyclononanes 2d, e were also converted to 7a, b by the acid.

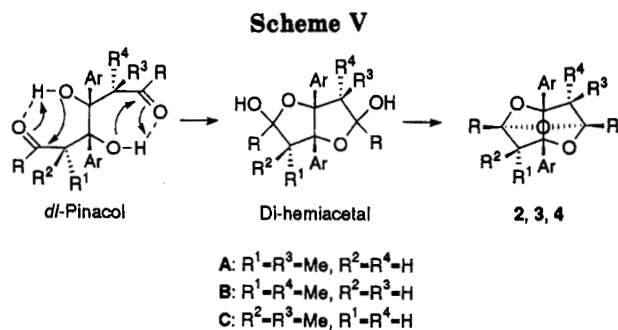
In contrast to 2d and 2e, when 2a was treated with hydrochloric acid, the 3-methylenecyclopentene 8a and the epoxyheptenone 9 were formed in 45 and 9% yields, respectively. The treatment of 3a and 4a with the acid gave the similar results. The compounds 2b and 2c were also converted to 8b and 8c in 37 and 9% yields, respectively. The <sup>1</sup>H NMR spectra of compounds 8 showed two singlets due to exomethylene protons between δ 5.0 and 5.2. The <sup>1</sup>H NMR spectrum of 9 showed an AB quartet due to two methylene protons at δ 2.48 and 2.77. The structure of 9 was finally determined by X-ray crystallographic analysis.<sup>9</sup> The formation of 8 and 9 can be explained by the initial formation of the dioxabicyclooctadiene 7 which opens the ring to the 3,5-octadiene-2,7-dione 10 (Scheme IV). The dione 10 contains a small amount of the isomeric trienone 11. Acid-catalyzed



cyclization of 10 gives 8 and intramolecular [4 + 2] cycloaddition of 11 gives 9.

Photoreduction of aryl 1,3-diketone 1 gives both *dl*- and *meso*-pinacols.<sup>10</sup> The formation of trioxatricyclononanes 2-4 can best be rationalized in terms of cyclization of the *dl*-pinacol to give the bicyclic dihemiacetal and subsequent dehydration, while *meso*-pinacols or products arising from them could not be isolated. The *dl*-pinacols from 1 have a conformation where the hydroxy groups are located close enough to the carbonyl groups owing to hydrogen bonding so that they cyclize even at room temperature to give bicyclic dihemiacetals which under dehydration to give trioxatricyclononanes 2, 3, and 4 (Scheme V). Three isomers A, B, and C are possible for *dl*-pinacols from 1. The trioxatricyclononanes 2, 3, and 4 may be formed from A, B, and C, respectively, though these pinacols, except 5d and 5e, could not be isolated. The pinacols 5d and 5e were stable at room temperature. However, when 5d was heated at 180 °C, it underwent quantitative retro-aldol cleavage to give propiophenone and benzil in 2:1 ratio.

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Since two of three possible *dl*-pinacols from **1d** were transformed to trioxatricyclononanes **2d** and **3d**, the pinacol **5d** has configuration C. Cyclization of **5d** to the bicyclic dihemiacetal results in significant crowding. Therefore, the pinacol **5d** undergoes retro-aldol cleavage in preference to cyclization to the dihemiacetal.

### Experimental Section

Melting points were uncorrected.  $^1\text{H}$  NMR spectra were recorded at 400 MHz using tetramethylsilane as an internal standard with  $\text{CDCl}_3$  as solvent.  $^{13}\text{C}$  NMR spectra were recorded at 100 MHz with  $\text{CDCl}_3$  as solvent. IR spectra were recorded for solutions in  $\text{CCl}_4$  unless otherwise stated. A 100-W high-pressure mercury lamp was used as an irradiation source. Compounds **1a** and **1d** were prepared by the methylation of benzoylacetone and dibenzoylmethane with methyl iodide. Compounds **1b,c,e** were prepared by the condensation of the aryl ethyl ketone with the aldehyde according to previously described methods.<sup>7</sup>

**General Procedure for Photoreduction.** A solution of 1 g of **1** in 120 mL of 2-propanol was irradiated with a high-pressure mercury lamp through a Pyrex filter for 3–10 h. The photo-products were isolated by silica gel column chromatography using hexane/ethyl acetate (6:1) as eluant. IR spectra of compounds **2**, **3**, and **4** have neither carbonyl nor hydroxy absorptions.

**1,exo-4,5,endo-8-Tetramethyl-3,7-diphenyl-2,6,9-trioxatricyclo[3.3.1.0<sup>3,7</sup>]nonane (2a):** mp 125–126 °C (hexane);  $^1\text{H}$  NMR  $\delta$  0.90 (3 H, d,  $J = 7$  Hz), 0.94 (3 H, d,  $J = 7$  Hz), 1.54 (3 H, s), 1.60 (3 H, s), 2.12 (1 H, q,  $J = 7$  Hz), 2.35 (1 H, q,  $J = 7$  Hz), 6.8–7.2 (10 H, m);  $^{13}\text{C}$  NMR  $\delta$  9.5 (q), 13.1 (q), 19.6 (q), 20.9 (q), 50.8 (d), 54.9 (d), 93.8 (s), 94.3 (s), 106.3 (s), 108.3 (s), 125.7 (2d), 126.5 (3d), 127.0 (d), 127.3 (2d), 127.7 (2d), 136.2 (s), 138.4 (s). Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{O}_3$ : C, 78.54; H, 7.19. Found: C, 78.71; H, 7.16.

**1,exo-4,5,exo-8-Tetramethyl-3,7-diphenyl-2,6,9-trioxatricyclo[3.3.1.0<sup>3,7</sup>]nonane (3a):** mp 123 °C (methanol);  $^1\text{H}$  NMR  $\delta$  0.99 (6 H, d,  $J = 7$  Hz), 1.58 (6 H, s), 2.24 (2 H, q,  $J = 7$  Hz), 6.9–7.2 (10 H, m);  $^{13}\text{C}$  NMR  $\delta$  8.4 (2q), 20.7 (2q), 48.6 (2d), 93.6 (2s), 106.7 (2s), 125.4 (4d), 126.7 (2d), 127.5 (4d), 137.8 (2s). Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{O}_3$ : C, 78.54; H, 7.19. Found: C, 78.43; H, 7.09.

**1,endo-4,5,endo-8-Tetramethyl-3,7-diphenyl-2,6,9-trioxatricyclo[3.3.1.0<sup>3,7</sup>]nonane (4a):** mp 154–155 °C (methanol);  $^1\text{H}$  NMR  $\delta$  0.86 (6 H, d,  $J = 7$  Hz), 1.59 (6 H, s), 2.45 (2 H, q,  $J =$

7 Hz), 6.9–7.2 (10 H, m);  $^{13}\text{C}$  NMR  $\delta$  13.3 (2q), 19.9 (2q), 55.7 (2d), 94.5 (2s), 108.2 (2s), 126.6 (4d), 126.8 (2d), 127.6 (4d), 136.4 (2s). Anal. Calcd for  $\text{C}_{22}\text{H}_{24}\text{O}_3$ : C, 78.54; H, 7.19. Found: C, 78.52; H, 7.21.

**3,4-Dihydroxy-2,5-dimethyl-1,3,4,6-tetraphenylhexane-1,6-dione (5d):** mp 178–179 °C (hexane–benzene); IR (KBr) 3570, 3450 br, 1670  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.48 (6 H, d), 4.74 (2 H, s), 4.75 (2 H, q,  $J = 7$  Hz), 6.9–7.9 (20 H, m). Anal. Calcd for  $\text{C}_{32}\text{H}_{30}\text{O}_4$ : C, 80.31; H, 6.32. Found: C, 80.17; H, 6.38.

**3,7-Dihydroxy-4,8-dimethyl-1,3,5,7-tetraphenyl-2,6-dioxabicyclo[3.3.0]octane (6):** mp 191–192 °C (hexane–benzene); IR (KBr) 3300 br  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.14 (6H, d,  $J = 7$  Hz), 3.13 (2 H, q,  $J = 7$  Hz), 5.51 (2 H, s), 6.9–7.8 (20 H, m). Anal. Calcd for  $\text{C}_{32}\text{H}_{30}\text{O}_4$ : C, 80.31; H, 6.32. Found: C, 80.19; H, 6.34.

**Pyrolysis of 6.** Compound **6** (40 mg) was placed in a sealed glass tube under reduced pressure (0.4 Torr) and heated at 200 °C for 4 h. The mixture was chromatographed on silica gel (hexane/ethyl acetate 6:1) to give **3d** (28 mg, 72%).

**General Procedure for the Treatment of 2–6 with Hydrochloric Acid.** A solution of 50 mg of **2–6** in 20 mL of methanol in the presence of 1 drop of concentrated hydrochloric acid was heated under reflux for 3–10 h. The solvent was evaporated and the residue was chromatographed on silica gel (hexane/ethyl acetate (4:1 to 6:1)) to give **7**, **8**, and/or **9**. IR spectra of compounds **7a** and **7b** have neither carbonyl nor hydroxy absorptions.

**2,6-Dimethyl-1,3,5,7-tetraphenyl-4,8-dioxabicyclo[3.3.0]octa-2,6-diene (7a):** mp 165–166 °C (hexane);  $^1\text{H}$  NMR  $\delta$  1.84 (6 H, s), 6.9–8.0 (20 H, m);  $^{13}\text{C}$  NMR  $\delta$  10.1 (2q), 102.8 (2s), 109.3 (2s), 126.8 (2d), 127.0 (4d), 127.4 (4d), 127.6 (4d), 128.3 (4d), 128.5 (2d), 131.7 (2s), 138.7 (2s), 150.7 (2s). Anal. Calcd for  $\text{C}_{32}\text{H}_{26}\text{O}_2$ : C, 86.85; H, 5.92. Found: C, 86.57; H, 6.05.

**5-Acetyl-4-hydroxy-4,5-dimethyl-3-methylene-1,2-diphenyl-1-cyclopentene (8a):** mp 144 °C (hexane); IR 3600, 3450 br, 1710  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.19 (3 H, s), 1.52 (3 H, s), 2.27 (1 H, s), 2.37 (3 H, s), 5.01 (1 H, s), 5.19 (1 H, s), 6.8–6.9 (2 H, m), 7.1–7.2 (5 H, m), 7.2–7.3 (3 H, m);  $^{13}\text{C}$  NMR  $\delta$  15.1 (q), 28.5 (q), 28.6 (q), 69.2 (s), 93.7 (s), 105.4 (t), 127.5 (d), 127.6 (d), 128.0 (2d), 128.3 (2d), 128.8 (2d), 129.7 (2d), 134.8 (2s), 142.1 (s), 145.9 (s), 160.5 (s), 211.0 (s). Anal. Calcd for  $\text{C}_{22}\text{H}_{22}\text{O}_2$ : C, 82.99; H, 6.96. Found: C, 83.09; H, 6.94.

**3,6-Epoxy-3,4,7-trimethyl-5,6-diphenylcyclohept-4-en-1-one (9):** mp 105 °C (hexane); IR 1705  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.03 (3 H, d), 1.56 (3 H, s), 1.63 (3 H, s), 2.48 (1 H) and 2.77 (1 H) (AB system,  $J = 15$  Hz), 2.92 (1 H, q,  $J = 7$  Hz), 6.5–6.6 (2 H, m), 7.1–7.3 (8 H, m) (ArH);  $^{13}\text{C}$  NMR  $\delta$  10.0 (q), 12.7 (q), 21.7 (q), 47.0 (t), 49.8 (d), 84.5 (s), 90.1 (s), 126.0 (2d), 127.2 (d), 127.4 (d), 127.8 (4d), 129.6 (2d), 132.9 (s), 137.9 (s), 139.2 (s), 143.2 (s), 211.1 (s). Anal. Calcd for  $\text{C}_{22}\text{H}_{22}\text{O}_2$ : C, 82.99; H, 6.96. Found: C, 82.92; H, 6.95.

**Supplementary Material Available:** Compound characterization data for **2b–e**, **3b**, **3d**, **5e**, **7b**, **8b** and **8c** and ORTEP diagrams of **3a** and **9** (5 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.