

Photoreduction of 2-Benzoylalkanoates

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2-Benzoylalkanoates **1** undergo photoreduction with 2-propanol. The photoreduction products are classified into three types according to their origin: the homo-pinacol-type products **2**, **5**, **7**, and **8**, the mixed-pinacol-type product **3**, and the β -hydroxy ester **6**. The product distribution is affected by α -methyl substitution. The α -methyl substitution decreases the percentage of the homo-pinacol-type products and increases the percentage of the β -hydroxy ester.

Synthetic¹⁾ and mechanistic²⁾ aspects of the photoreduction of aryl alkyl ketones have been extensively investigated, and work has also been done on the photoreduction of α -dicarbonyl compounds.³⁾ A number of α -substituted acetophenones form pinacols upon irradiation in 2-propanol or other suitable hydrogen-donating solvents.⁴⁾ However, little attention has been given to the photoreduction of β -dicarbonyl compounds. Singh and Kagan reported⁵⁾ that ethyl acetoacetate undergoes photoreduction with alcohols to give 4,5-dihydro-4-hydroxy-2(3*H*)-furanones *via* mixed pinacols. We report here that 2-benzoylalkanoates **1** undergo photoreduction with 2-propanol to give the homo- and the mixed-pinacol-type products, and the β -hydroxy ester, and that the course of the photoreduction is affected by α -methyl substituents.

Results and Discussion

Irradiation of ethyl benzoylacetate (**1a**) in 2-propanol with a high-pressure mercury lamp under nitrogen yielded *meso*- and *dl*-diethyl-3,4-dihydroxy-3,4-diphenyladipates (*meso*-**2a** and *dl*-**2a**) and 4,5-dihydro-4-hydroxy-5,5-dimethyl-4-phenyl-2(3*H*)-furanone (**3a**) in 34, 32, and 6% yields, respectively. The diastereomeric pinacols *meso*-**2a** and *dl*-**2a** could be isolated by silica-gel chromatography. These compounds *meso*-**2a**, *dl*-**2a**⁶⁾ and **3a**⁷⁾ were identified by comparison with authentic samples. The dihydro-2(3*H*)-furanone **3a** can best be explained as the *secondary* product derived from an initially formed mixed pinacol **4a**. No formation of the mixed pinacol is observed in acetophenone

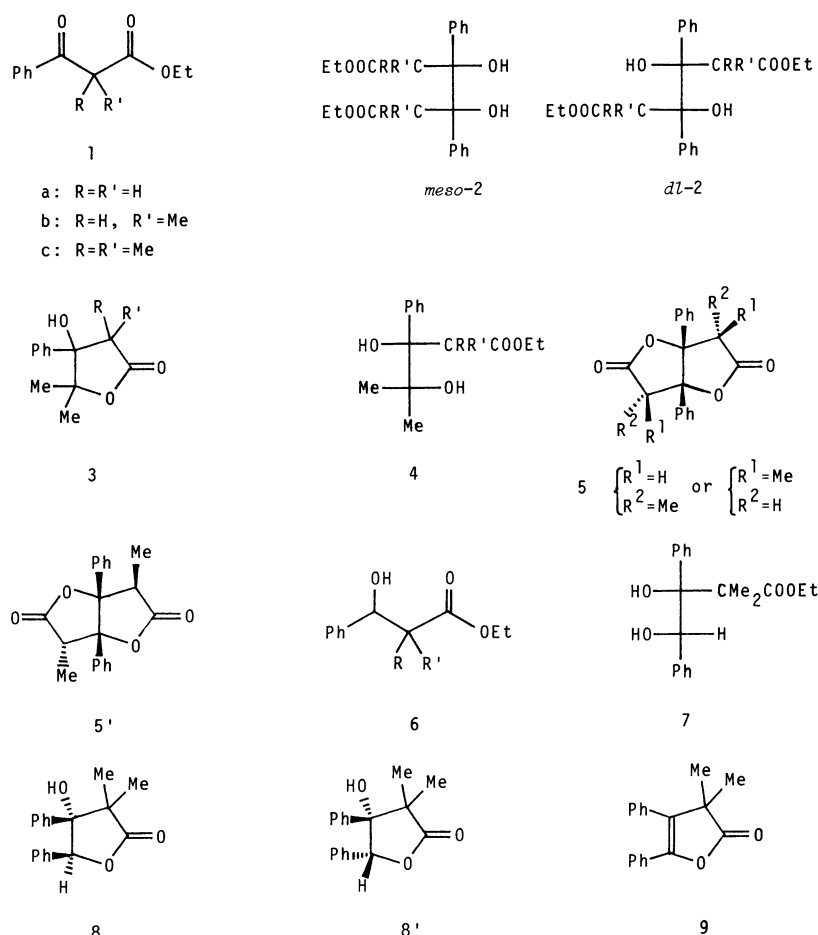


Fig. 1.

TABLE 1. YIELDS OF THE PRODUCTS IN PHOTOLYSIS OF **1a**, **1b**, AND **1c**

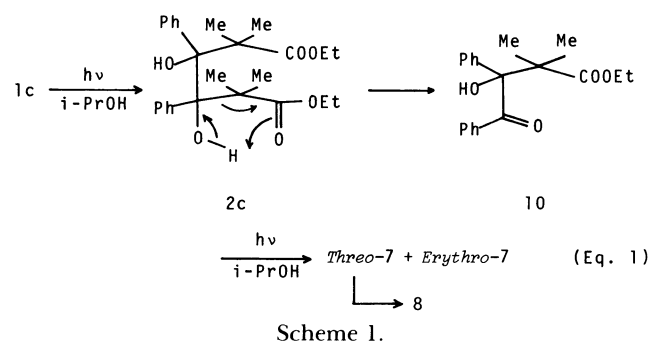
Starting compound	Homo-pinacol-type product (Yield/%)								Mixed-pinacol-type product (Yield/%)	β -Hydroxy ester (Yield/%)
	<i>meso</i> -2	<i>dl</i> -2	5	5'	7	8	8'	Total	3	6
1a	34	32	—	—	—	—	—	66	6	—
1b	5	—	12	10	—	—	—	27	—	7
1c	—	—	—	—	7	11	1	19	14	27

photoreduction by 2-propanol.² Both the adipates and the dihydro-2(3*H*)-furanone formations were efficiently quenched by 1,3-pentadiene, and ethyl 2-naphthoylacetate, which is expected to have the lowest triplet with π, π^* configuration, gave no photoreduction products under the same conditions. Therefore, both the adipates and the dihydro-2(3*H*)-furanone arise from the n, π^* triplet state of the benzoylacetate **1a**.

Irradiation of ethyl 2-benzoylpropionate (**1b**) under the same conditions gave *meso*-diethyl-3,4-dihydroxy-2,5-dimethyl-3,4-diphenyladipate (**2b**), 4,8-dimethyl-1,5-diphenyl-2,6-dioxo-bicyclo[3.3.0]octane-3,7-diones (**5** and **5'**), and ethyl 3-hydroxy-2-methyl-3-phenylpropanoate (**6b**) in 5, 22 (**5**: 12, **5'**: 10), and 7% yields, respectively. The structure of **2b** was deduced from its spectroscopic and analytical data. The *meso*- and/or *dl*-isomers seem to be produced from photoreduction of the ester **1b**. However, the isolated photoproduct **2b** is deduced to be one of the isomers because the compound has a sharp melting point (184–185°C) and shows a simple NMR spectrum. The pinacol **2b** is elucidated to have the *meso*-configuration because no dilactones were formed when the pinacol **2b** was heated at 240°C for 30 min. The *dl*-**2a** lactonizes easily by heating, while *meso*-**2a** does not.⁶ The *dl*-**2b** seems to cyclize to give dilactones **5** and **5'** under the experimental conditions. The geometry of the dilactones from *dl*-**2b** must be *cis* with respect to two phenyl groups. The stereoisomeric dilactones **5** and **5'** could be isolated by silica-gel chromatography. The IR spectra of **5** and **5'** showed the characteristic absorptions of a five-membered lactone at 1800 and 1790 cm^{-1} , respectively. The ^1H NMR signals of the two methyl groups in **5** appeared at δ 1.24 while those signals in **5'** were observed at δ 1.18 and 1.20. The methyl groups in **5** are equivalent and are either *cis* or *trans* to the neighboring phenyl group. On the other hand, one methyl group in **5'** might be *cis* to the neighboring phenyl group and the other might be *trans*. The ^{13}C NMR spectra also support the assignment of **5** and **5'**. The β -hydroxy ester **6b** was identified by direct comparison with an authentic sample.⁹ This type of the product is found in acetophenone photoreduction with 2-propanol.² No products derived from a mixed pinacol were isolated; however, the possibility of their presence in small amounts cannot be eliminated.

Irradiation of ethyl 2-benzoyl-2-methylpropanoate (**1c**) under the same conditions gave 4,5-dihydro-4-hydroxy-3,3,5,5-tetramethyl-4-phenyl-2(3*H*)-furanone (**3c**), ethyl 3-hydroxy-2,2-dimethyl-3-phenylpropanoate (**6c**), ethyl 3,4-dihydroxy-2,2-dimethyl-3,4-diphenylbutanoate (**7**), and 4,5-dihydro-4-hydroxy-3,3-dimethyl-4,5-diphenyl-2(3*H*)-furanones (**8** and **8'**) in 14, 27, 7, and 12 (**8**: 11, **8'**: 1) % yields, respectively. The hydroxy ester **6c** was identified by comparison with an

authentic sample.⁹ The structural assignment of **3c** was based on its spectroscopic and analytical data. The IR spectrum of **3c** showed a γ -lactone carbonyl band at 1760 cm^{-1} and hydroxy bands at 3600 and 3400 cm^{-1} . The ^1H NMR spectrum showed four methyl singlets at δ 1.04, 1.20, 1.45, and 1.60. The lactone **3c** seems to be the *secondary* product derived from an initially formed mixed pinacol **4c**. In the photoreduction of isobutyrophenone or pivalophenone by 2-propanol, no mixed pinacols are found.² The structures of **7**, **8**, and **8'** were deduced from their spectroscopic and analytical data and further supported by the chemical evidence. The hydroxy lactone **8'** underwent dehydration to give 3,3-dimethyl-4,5-diphenyl-2(3*H*)-furanone (**9**) by heating in dioxane in the presence of *p*-toluenesulfonic acid, while the lactone **8** was recovered under the same conditions. Therefore, the hydroxyl group should be *trans* in **8'** and *cis* in **8** to the C_5 -hydrogen atom. The dihydroxy ester **7** cyclized to give the lactone **8'** when the ester was heated at 250°C for 15 min. No isomeric lactone **8** could be detected. This fact suggests that the dihydroxy ester **7** has an *erythro*-geometry. The ester **7** seems to be produced from the homo-pinacol *meso*-**2c** and/or *dl*-**2c** via a phenyl ketone **10**, though these intermediates could not be isolated (Eq. 1). Elimination of ethyl 2-



methylpropanoate from the pinacol **2c** probably occurs easily owing to the steric compression. Photoreduction of the ketone **10** will give the *erythro*-dihydroxy ester **7** and its *threo*-isomer. The IR absorption at 1690 cm^{-1} in the *erythro*-ester **7** suggests the presence of the intramolecular hydrogen bonding between the carbonyl group and the C_3 -hydroxyl group. The hydrogen bonding is also expected in the *threo*-isomer. The rate of lactonization of these dihydroxy esters might be enhanced by the participation of the C_3 -hydroxyl group because of the decrease in electron density at the carbonyl carbon atom. The *threo*-isomer is probably reactive enough to lactonize easily to give **8**. However, the *erythro*-isomer is stable under the experimental conditions. The stability of the *erythro*-isomer may be explained in terms of the lack of the participation of the C_3 -hydroxyl group in the early stage of the transition

state, because of steric repulsive interaction between the C₄-phenyl and the C₃-hydroxyl group. The C₄-phenyl group must be eclipse to the C₃-hydroxyl group in the transition state.

Photoreduction products from 2-benzoylalkanoates **1a**, **1b**, and **1c** are classified into three types according to their origin: the homo-pinacol-type products **2**, **4**, **7**, **8**, and **8'**, the mixed-pinacol-type product **3**, and the β -hydroxy ester **6**. The total yield of the homo-pinacol-type products decreases upon α -methyl substitution, while that of the hydroxy ester increases upon the substitution. These results can be explained in terms of an increment of the steric hindrance in free radical combination.

Experimental

All melting points were uncorrected. The IR spectra were recorded on a JASCO IRA-2 spectrometer. The ¹H and ¹³C NMR spectra were measured on a JEOL FX-90Q spectrometer using TMS as an internal standard. The mass spectra were obtained with a JEOL JMS-OLSG-2 spectrometer. Irradiations were carried out with an Ushio 450 W high-pressure mercury lamp or a Rikoh Kagaku 100 W high-pressure mercury lamp with a water-cooled Pyrex jacket.

Chemicals. Ethyl benzoylacetate (**1a**) from Tokyo Kasei Kogyo Co. was purified by distillation. Ethyl 2-benzoylpropanoate (**1b**),⁹ ethyl 2-benzoyl-2-methylpropanoate (**1c**),¹⁰ and ethyl 2-naphthoylacetate¹¹ were prepared according to the reported methods.

Photoreaction of 1a. A solution of **1a** (1.018 g, 5.30 mmol) in 2-propanol (60 cm³) was irradiated for 30 h under nitrogen with a 450 W high-pressure mercury lamp. After removal of the solvent, the residue was chromatographed on silica gel. Elution with benzene-ethyl acetate (10:1) gave *meso*-**2a** (348 mg, 34%), *dl*-**2a** (330 mg, 32%), and **3a** (63 mg, 6%). The spectroscopic data of *meso*-**2a**, *dl*-**2a**, and **3a** were identical with those of the authentic samples.^{9,7}

Photoreaction of 1b. A solution of **1b** (1.200 g, 5.83 mmol) in 2-propanol (120 cm³) was irradiated for 3.5 h with a 100 W high-pressure mercury lamp. The usual work-up gave the unreacted ester **1b** (300 mg), *meso*-**2b** (46 mg, 5%), **5** (110 mg, 12%), **5'** (90 mg, 10%), and *threo*/*erythro* 1:1 mixture of **6b** (65 mg, 7%). The spectroscopic data of **6b** were identical with those of the authentic sample.⁹ *meso*-**2b** mp 184–185 °C; IR (CHCl₃) 3500 and 1700 cm⁻¹; ¹H NMR (CDCl₃) δ = 0.59 (6H, d, J = 7.0 Hz, CH₃), 0.78 (6H, t, J = 7.2 Hz, CH₃), 3.55 (2H, q, J = 7.0 Hz, CH), 3.56 (4H, q, J = 7.2 Hz, CH₂), 3.86 (1H, s, OH), *ca.* 7.10–7.30 (6H, m, aromatic), and *ca.* 7.50–7.70 (4H, m, aromatic); ¹³C NMR (CDCl₃) δ = 1.36 (q, 4C), 46.8 (d, 2C), 60.2 (t, 2C), 79.7 (s, 2C), 127.1 (d, 8C), 128.3 (d, 2C), 144.8 (s, 2C), and 176.7 (s, 2C). Found: C, 69.28; H, 7.21%. Calcd for C₂₄H₃₀O₆: C, 69.54; H, 7.30%. **5** mp 191–192 °C; IR (CHCl₃) 1800 cm⁻¹; ¹H NMR (CDCl₃) δ = 1.24 (6H, d, J = 7.2 Hz, CH₃), 3.30 (2H, q, J = 7.2 Hz, CH), *ca.* 6.65–7.00 (4H, m, aromatic), and *ca.* 7.00–7.40 (6H, m, aromatic); ¹³C NMR (CDCl₃) δ = 7.6 (q, 2C), 43.4 (d, 2C), 93.4 (s, 2C), 126.0 (d, 4C), 128.5 (d, 4C), 129.1 (d, 2C), 132.4 (s, 2C), and 174.5 (s, 2C); MS m/z 322 (M⁺). Found: C, 74.35; H, 5.62%. Calcd for C₂₀H₁₈O₄: C, 74.51; H, 5.62%. **5'** mp 167–168 °C; IR (CHCl₃) 1790 cm⁻¹; ¹H NMR (CDCl₃) δ = 1.18 (3H, d, J = 8.4 Hz, CH₃), 1.20 (3H, d, J = 7.2 Hz, CH₃), 3.11 (1H, q, J = 8.4 Hz, CH), 3.17 (1H, q, J = 8.4 Hz, CH), and *ca.* 6.60–7.40 (10H, m, aromatic); ¹³C NMR (CDCl₃) δ = 7.9 (q), 14.8 (q), 44.5 (d), 47.5 (d), 92.6 (s), 94.8 (s), 126.8 (d, 2C), 127.4 (d, 2C), 127.6 (d, 2C), 128.5 (d, 2C), 129.0 (d), 129.4 (d), 131.4 (s), 133.8 (s), 173.8 (s), and 176.2 (s). Found: C, 74.38; H, 5.62%. Calcd for C₂₀H₁₈O₄: C, 74.51; H,

5.62%.

Photoreaction of 1c. A solution of **1c** (4.000 g, 18.18 mmol) in 2-propanol (400 cm³) was irradiated for 12 h with a 450 W high-pressure mercury lamp. The usual work-up gave the unreacted ester **1c** (2.164 g), **3c** (260 mg, 14%), **6c** (500 mg, 27%), **7** (125 mg, 7%), **8** (195 mg, 11%), and **8'** (20 mg, 1%). The spectroscopic data of **6c** was identical with those of the authentic sample.⁹ **3c** mp 151–152 °C; IR (CHCl₃) 3600, 3400, and 1760 cm⁻¹; ¹H NMR (CDCl₃) δ = 1.04 (3H, s, CH₃), 1.20 (3H, s, CH₃), 1.45 (3H, s, CH₃), 1.60 (3H, s, CH₃), 2.31 (1H, s, OH), and *ca.* 7.15–7.50 (5H, m, aromatic); ¹³C NMR (CDCl₃) δ = 23.5 (q), 23.9 (q), 26.0 (q), 27.0 (q), 48.6 (s), 83.7 (s), 88.3 (s), 126.6 (d, 2C), 127.6 (d, 2C), 127.8 (d), 140.5 (s), and 181.0 (s). Found: C, 71.53; H, 7.69%. Calcd for C₁₄H₁₈O₃: C, 71.77; H, 7.74%. **7** mp 106–107 °C; IR (CHCl₃) 3600, 3450, and 1690 cm⁻¹; ¹H NMR (CDCl₃) δ = 0.94 (3H, s, CH₃), 1.05 (3H, t, J = 7.0 Hz, CH₃), 1.32 (3H, s, CH₃), 2.76 (1H, d, J = 7.0 Hz, OH, D₂O exchangeable), *ca.* 3.10–3.70 (2H, m, CH₂), 5.32 (1H, d, J = 7.0 Hz, CH), 5.64 (1H, s, OH, D₂O exchangeable), and *ca.* 7.20–7.80 (10H, m, aromatic); ¹³C NMR (CDCl₃) δ = 13.5 (q), 20.6 (q), 25.0 (q), 47.5 (s), 61.2 (t), 76.2 (d), 82.5 (s), 127.3 (d), 127.4 (d, 2C), 127.7 (d, 2C), 128.0 (d), 128.3 (d, 2C), 129.2 (d, 2C), 140.0 (s), 140.1 (s), and 178.2 (s). Found: C, 73.03; H, 7.25%. Calcd for C₂₀H₂₄O₄: C, 73.14; H, 7.37%. **8** mp 169–170 °C; IR (CHCl₃) 3550 and 1775 cm⁻¹; ¹H NMR (CDCl₃) δ = 1.08 (3H, s, CH₃), 1.23 (3H, s, CH₃), 1.54 (1H, s, OH), 6.24 (1H, s, CH), and *ca.* 7.20–7.65 (10H, m, aromatic); ¹³C NMR (CDCl₃) δ = 16.2 (q), 22.8 (q), 49.7 (s), 81.8 (d), 83.3 (s), 126.8 (d, 3C), 128.3 (d, 3C), 128.6 (d, 2C), 128.8 (d, 2C), 133.0 (s), 137.3 (s), and 179.7 (s); MS m/z (rel intensity) 282 (M⁺, 3), 148 (100), 133 (21), 105 (40), and 77 (19). Found: C, 76.51; H, 6.36%. Calcd for C₁₈H₁₈O₃: C, 76.57; H, 6.43%. **8'** mp 207–208 °C (lit.¹² 210–212 °C); IR (CHCl₃) 3450 and 1775 cm⁻¹; ¹H NMR (CDCl₃) δ = 0.94 (3H, s, CH₃), 1.56 (3H, s, CH₃), 2.44 (1H, s, OH), 5.76 (1H, s, CH), and *ca.* 6.90–7.40 (10H, m, aromatic); ¹³C NMR (CDCl₃) δ = 19.6 (q), 21.9 (q), 48.9 (s), 84.7 (s), 85.1 (d), 125.4 (d, 2C), 125.6 (d, 2C), 127.5 (d, 2C), 127.8 (d, 2C), 127.9 (d, 2C), 134.7 (s), 138.3 (s), and 179.9 (s); MS m/z (rel intensity) 282 (M⁺, 2), 148 (100), 134 (19), 105 (26), and 77 (10). Found: C, 76.53; H, 6.42%. Calcd for C₁₈H₁₈O₃: C, 76.57; H, 6.43%.

Dehydration of 8'. A solution of 23.0 mg of **8'** and 35 mg of *p*-toluenesulfonic acid in 11 cm³ of dioxane was heated under reflux for 50 h. The solvent was evaporated, and the residue was extracted with ether. After the usual work-up, the reaction mixture was chromatographed on silica gel to give 18.8 mg (89%) of 3,3-dimethyl-4,5-diphenyl-2(3H)-furanone (**9**): mp 107–108 °C; IR (CHCl₃) 1800 cm⁻¹; ¹H-NMR (CDCl₃) δ = 1.36 (6H, s, CH₃) and *ca.* 7.10–7.50 (10H, m, aromatic); ¹³C NMR (CDCl₃) δ = 23.4 (q, 2C), 48.1 (s), 123.9 (s), 126.9 (d, 3C), 128.2 (d, 3C), 128.8 (s), 129.0 (d, 2C), 129.7 (d, 2C), 132.6 (s), 145.4 (s), and 181.0 (s). Found: C, 81.88; H, 6.04%. Calcd for C₁₈H₁₆O₂: C, 81.79; H, 6.10%.

Thermolysis of 7. The dihydroxy ester **7** (8.8 mg) was sealed in a Pyrex tube, and heated at 250 °C for 15 min. The ¹H NMR analysis showed that the thermolysis mixture consists of ethanol, ethyl 2-methylpropanoate, benzoin, and dihydro-2(3H)-furanone **8'** in a 1:1:1:1 ratio.

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