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# 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.

Synthetic[1] and mechanistic[2] 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 reported[5] 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-benzoyl-alkanoates **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

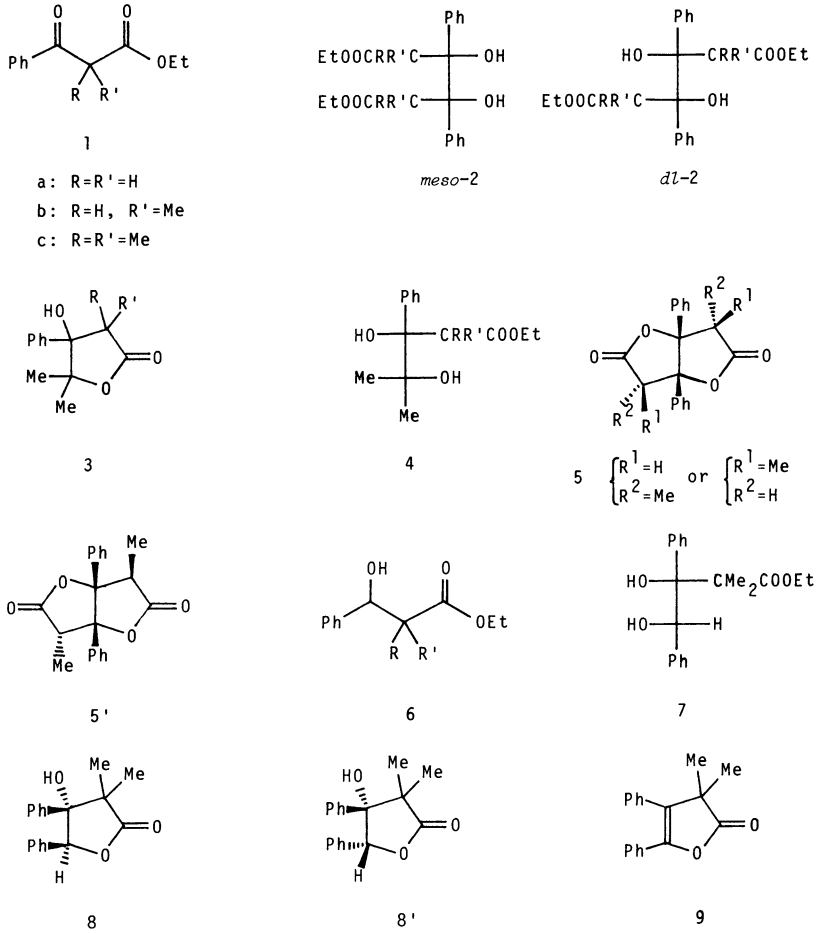



Fig. 1.

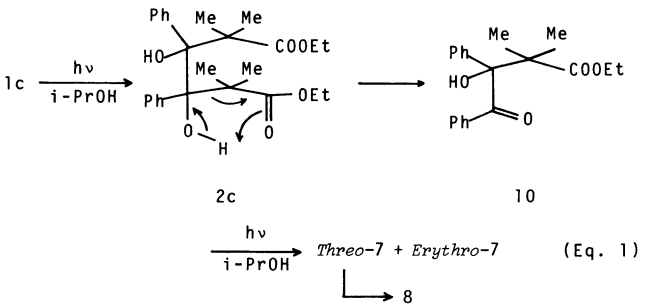
Table 1. Yields of the products in photolysis of **1a**, **1b**, and **1c**

| Starting compound | Homo-pinacol-type product (Yield/%) | | | | | | | | Mixed-pinacol-type product (Yield/%) | β-Hydroxy ester (Yield/%) |
|---|---|---|---|---|---|---|---|---|---|---|
| | *meso*-**2** | *dl*-**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 $\pi,\pi^*$ configuration, gave no photoreduction products under the same conditions. Therefore, both the adipates and the dihydro-2(3*H*)-furanone arise from the $n,\pi^*$ 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-dioxa-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 $\delta$ 1.24 while those signals in **5′** were observed at $\delta$ 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.[8] 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 $\delta$ 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-




Scheme 1.

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 $C_4$-phenyl and the $C_3$-hydroxyl group. The $C_4$-phenyl group must be eclipse to the $C_3$-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 $^{13}C$ 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-naphthoylacetate[11] were pepared according to the reported methods.

*Photoreaction of 1a.* A solution of **1a** (1.018 g, 5.30 mmol) in 2-propanol (60 $cm^3$) 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.[6,7]

*Photoreaction of 1b.* A solution of **1b** (1.200 g, 5.83 mmol) in 2-propanol (120 $cm^3$) 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.[8] *meso*-**2b** mp 184—185 °C; IR ($CHCl_3$) 3500 and 1700 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ= 0.59 (6H, d, $J$=7.0 Hz, $CH_3$), 0.78 (6H, t, $J$=7.2 Hz, $CH_3$), 3.55 (2H, q, $J$=7.0 Hz, CH), 3.56 (4H, q, $J$=7.2 Hz, $CH_2$), 3.86 (1H, s, OH), *ca.* 7.10—7.30 (6H, m, aromatic), and *ca.* 7.50—7.70 (4H, m, aromatic); $^{13}C$ NMR ($CDCl_3$) 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 $C_{24}H_{30}O_6$: C, 69.54; H, 7.30%. **5** mp 191—192 °C; IR ($CHCl_3$) 1800 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ=1.24 (6H, d, $J$=7.2 Hz, $CH_3$), 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); $^{13}C$ NMR ($CDCl_3$) 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 $C_{20}H_{18}O_4$: C, 74.51; H, 5.62%. **5'** mp 167—168 °C; IR ($CHCl_3$) 1790 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ=1.18 (3H, d, $J$=8.4 Hz, $CH_3$), 1.20 (3H, d, $J$=7.2 Hz, $CH_3$), 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); $^{13}C$ NMR ($CDCl_3$) 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 $C_{20}H_{18}O_4$: C, 74.51; H, 5.62%.

*Photoreaction of 1c.* A solution of **1c** (4.000 g, 18.18 mmol) in 2-propanol (400 $cm^3$) 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 ($CHCl_3$) 3600, 3400, and 1760 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ=1.04 (3H, s, $CH_3$), 1.20 (3H, s, $CH_3$), 1.45 (3H, s, $CH_3$), 1.60 (3H, s, $CH_3$), 2.31 (1H, s, OH), and *ca.* 7.15—7.50 (5H, m, aromatic); $^{13}C$ NMR ($CDCl_3$) 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 $C_{14}H_{18}O_3$: C, 71.77; H, 7.74%. **7** mp 106—107 °C; IR ($CHCl_3$) 3600, 3450, and 1690 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ=0.94 (3H, s, $CH_3$), 1.05 (3H, t, $J$=7.0 Hz, $CH_3$), 1.32 (3H, s, $CH_3$), 2.76 (1H, d, $J$= 7.0 Hz, OH, $D_2O$ exchangeable), *ca.* 3.10—3.70 (2H, m, $CH_2$), 5.32 (1H, d, $J$=7.0 Hz, CH), 5.64 (1H, s, OH, $D_2O$ exchangeable), and *ca.* 7.20—7.80 (10H, m, aromatic); $^{13}C$ NMR ($CDCl_3$) 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 $C_{20}H_{24}O_4$: C, 73.14; H, 7.37%. **8** mp 169—170 °C; IR ($CHCl_3$) 3550 and 1775 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ=1.08 (3H, s, $CH_3$), 1.23 (3H, s, $CH_3$), 1.54 (1H, s, OH), 6.24 (1H, s, CH), and *ca.* 7.20—7.65 (10H, m, aromatic); $^{13}C$ NMR ($CDCl_3$) 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 $C_{18}H_{18}O_3$: C, 76.57; H, 6.43%. **8'** mp 207—208 °C (lit,[12] 210—212 °C); IR ($CHCl_3$) 3450 and 1775 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) δ=0.94 (3H, s, $CH_3$), 1.56 (3H, s, $CH_3$), 2.44 (1H, s, OH), 5.76 (1H, s, CH), and *ca.* 6.90—7.40 (10H, m, aromatic); $^{13}C$ NMR ($CDCl_3$) 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 $C_{18}H_{18}O_3$: 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 $cm^3$ 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(3*H*)-furanone (**9**): mp 107—108 °C; IR ($CHCl_3$) 1800 $cm^{-1}$; $^1H$-NMR ($CDCl_3$) δ=1.36 (6H, s, $CH_3$) and *ca.* 7.10—7.50 (10H, m, aromatic); $^{13}C$ NMR ($CDCl_3$) 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 $C_{18}H_{16}O_2$: 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(3*H*)-furanone **8'** in a 1:1:1:1 ratio.

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