

The Photochemistry of 3,3-Dialkoxy-1-phenylpropan-1-ones

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(Received March 6, 1974)

Synopsis. The irradiation of 3,3-dialkoxy-1-phenylpropan-1-ones (Ia-b) in a benzene solution afforded β -ketoesters (IIa-b), phenyl β -alkoxyvinyl ketones (IIIa-b), and tetrahydrofuranols (IVa-b).

The photoreaction of aliphatic ketones to give smaller ketones, olefins, and cyclobutanols has been widely studied.¹⁾ It is well established that the reaction proceeds *via* γ -hydrogen abstraction to give 1,4-diradicals which can either cleave to olefins, ring closure to cyclobutanols, or return to starting materials. Recently, the ultraviolet irradiation of β -alkoxy ketones has been reported to give the tetrahydrofuranols as the major product.²⁻⁴⁾ They have been considered to arise *via* δ -hydrogen abstraction by excited carbonyl oxygen. We will report here on the photochemistry of 3,3-dialkoxy-1-phenylpropan-1-ones (Ia-b), which includes a new photooxidation (IIa-b) as well as photoelimination (IIIa-b) and δ -hydrogen abstraction (IVa-b).

The irradiation of 3,3-dimethoxy-1-phenylpropan-1-one (Ia) in a benzene solution with a high-pressure mercury lamp through a Pyrex filter under nitrogen for 20 hr gave methyl benzoylacetate (IIa) (35%), phenyl β -methoxyvinyl ketone (IIIa) (6.5%), and 3-phenyl-3-hydroxy-5-methoxy-tetrahydrofuran (IVa) (5%). Compounds IIa and IIIa did not show any H-abstraction under further irradiation and were recovered almost quantitatively. The structures of IIa⁵⁾ and IIIa⁶⁾ were confirmed by a direct comparison with their authentic samples. The structure of IVa was elucidated using its physical data and by elemental analysis. The NMR spectrum showed two doublets of a doublet at δ 2.23 ($J=13.5$, $J=1.8$ Hz, 1H at C-4) and δ 2.49 ($J=13.5$, $J=3.5$ Hz, 1H at C-4), two doublets at δ 4.06 and 4.26 ($J=10$ Hz, 2H at C-2), a doublet of a doublet at δ 5.19 ($J=1.8$, $J=3.5$ Hz, 1H at C-5), a singlet at δ 3.40 (3H, $-\text{OCH}_3$), a broad singlet at δ 3.90 (1H, $-\text{OH}$, exchangeable with D_2O), and the multiplet at δ 7.15—7.65 (5H) due to the aromatic protons. The IR spectrum exhibited bands

at 3500 cm^{-1} due to the hydroxy group and at 1100 cm^{-1} attributable to the ether group. The mass spectrum displayed prominent peaks at m/e 176 ($\text{M}^+ - \text{H}_2\text{O}$), 164 ($\text{M}^+ - \text{CH}_2=\text{O}$), 144 ($\text{M}^+ - (\text{H}_2\text{O} + \text{MeOH})$), and 115 ($\text{M}^+ - (\text{H}_2\text{O} + \text{MeOH} + \text{CHO})$).

Similarly, ethyl benzoyl acetate (IIb), phenyl β -ethoxyvinyl ketone (IIIb), and 2-methyl-3-phenyl-3-hydroxy-5-ethoxy-tetrahydrofuran (IVb) were obtained in 15, 15, and 6% yield respectively by the irradiation of 3,3-diethoxy-1-phenylpropan-1-one (Ib). The structures of IIb⁵⁾ and IIIb⁷⁾ were confirmed by a direct comparison with their authentic samples, while that of IVb was elucidated by means of its spectral data and by elemental analysis.

The formation of IIa-b is presumed to proceed through the oxidation of Ia-b by light. The formation of IIIa-b can be explained by the elimination of the alcohol.⁸⁾ On the other hand, the formation of IVa-b is considered to arise *via* δ -hydrogen abstraction by an excited carbonyl through a seven-membered ring transition state.

Experimental

All the boiling points are uncorrected.

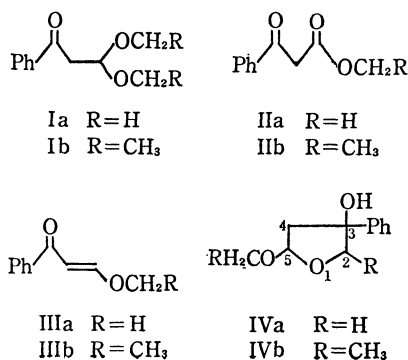
The 3,3-dimethoxy-1-phenylpropan-1-one (Ia, bp $175-178^\circ\text{C}/20\text{ mmHg}$ (lit.⁹⁾ $111-111.5^\circ\text{C}/2\text{ mmHg}$) and 3,3-diethoxy-1-phenylpropan-1-one (Ib, bp $165-170^\circ\text{C}/20\text{ mmHg}$ (lit.¹⁰⁾ $111-112^\circ\text{C}/1\text{ mmHg}$) were prepared according to the methods of previous reports.

Irradiation of Ia. A solution of 1g of Ia in 150 ml of benzene was irradiated with a high-pressure mercury lamp through a Pyrex filter under nitrogen for 20 hr at room temperature. After irradiation, the benzene was evaporated *in vacuo*, and the residue was chromatographed on a silica gel column with benzene-ethyl acetate (50:1) to give 350 mg of methyl benzoyl acetate (IIa; bp $155-158^\circ\text{C}/20\text{ mmHg}$ (lit.⁵⁾ $152^\circ\text{C}/15\text{ mmHg}$), 65 mg of phenyl β -methoxyvinyl ketone (IIIa; bp $114-117^\circ\text{C}/2\text{ mmHg}$ (lit.⁶⁾ $135^\circ\text{C}/5-6\text{ mmHg}$), 50 mg of 3-phenyl-3-hydroxy-5-methoxy-tetrahydrofuran (IVa), and 50 mg of the recovered ketone.

3-Phenyl-3-hydroxy-5-methoxy-tetrahydrofuran (IVa): Bp $80^\circ\text{C}/2\text{ mmHg}$. IR: $\nu_{\text{max}}^{\text{film}}\text{ cm}^{-1}$, 3500, 3050, 2830, 1600, 1492, 1100, 750, 690. Found: C, 67.77; H, 7.18%. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_3$: C, 68.02; H, 7.27%.

Irradiation of Ib. A solution of 1 g of Ib in 150 ml of benzene was irradiated under the same conditions as have been described above for 20 hr. After the removal of the solvent, the residue was chromatographed on a silica gel column with benzene-ethyl acetate (30:1) to give 150 mg of ethyl benzoylacetate (IIb; bp $152-158^\circ\text{C}/18\text{ mmHg}$ (lit.⁵⁾ $147^\circ\text{C}/11\text{ mmHg}$), 150 mg of phenyl β -ethoxyvinyl ketone (IIIb; bp $150-152^\circ\text{C}/20\text{ mmHg}$ (lit.⁷⁾ $156-158^\circ\text{C}/28\text{ mmHg}$), 60 mg of 2-methyl-3-phenyl-3-hydroxy-5-ethoxy-tetrahydrofuran (IVb), and 100 mg of the recovered ketone.

2-Methyl-3-phenyl-3-hydroxy-5-ethoxy-tetrahydrofuran (IVb): bp $93^\circ\text{C}/2\text{ mmHg}$. IR: $\nu_{\text{max}}^{\text{film}}\text{ cm}^{-1}$, 3500, 3050, 1603, 1492,



1100, 750, 690. NMR: (δ in CDCl_3) 1.25 (t, 3H, $J=9$ Hz, methyl), 1.20 (d, 3H, $J=6.5$ Hz, methyl), 2.25 (d, 1H, $J=13.5$ Hz, methylene at C-4) and 2.63 (dd, 1H, $J=13.5$, $J=5$ Hz, methylene at C-4), 3.2–4.1 (m, 2H, methylene), 4.23 (q, 1H, $J=6.5$ Hz, methine at C-2), 5.23 (d, 1H, $J=5$ Hz, methine at C-5), 7.2–7.65 (m, 5H, aromatic protons). When the signal of the methyl protons at δ 1.25 was irradiated, the signal of the methylene protons of the ethoxy group appeared as two doublets at δ 3.49 and 3.91 with the same coupling constant of 9 Hz. This phenomenon is considered to arise from the restriction of free rotation by the weak interaction of hydroxy and ethoxy groups. Mass spectrum: m/e 204 ($\text{M}^+ - \text{H}_2\text{O}$), 178 ($\text{M}^+ - \text{CH}_3\text{CH}=\text{O}$), 158 ($\text{M}^+ - \text{H}_2\text{O} + \text{EtOH}$), 115 ($\text{M}^+ - (\text{H}_2\text{O} + \text{EtOH} + \text{CH}_3\text{C}=\text{O})$). Found: C, 70.16; H, 8.09%. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_3$: C, 70.24; H, 8.16%.

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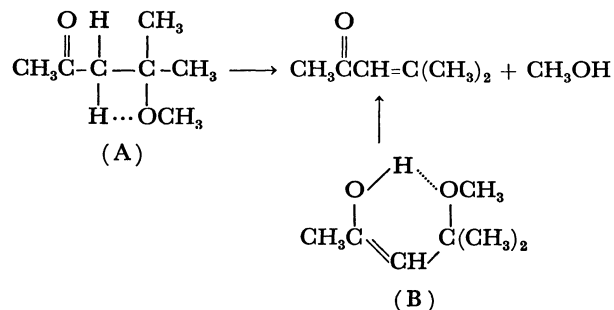
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