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Photochemistry of Acetophenone and Acetaldehyde in Ether Solvent —Formation of Diastereoisomeric Alcohols

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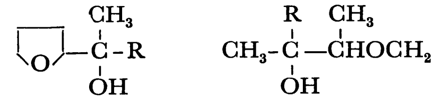
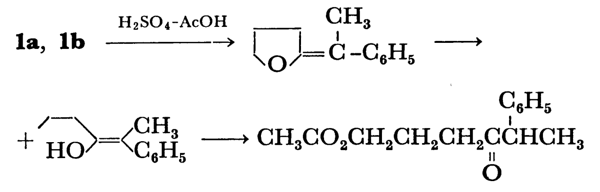
Synopsis. Irradiation of acetophenone and acetaldehyde in tetrahydrofuran or diethyl ether gave the following diastereoisomeric alcohols, 1-phenyl-1-(2-tetrahydrofuryl)-ethanol, 1-(2-tetrahydrofuryl)ethanol, 2-phenyl-3-ethoxy-2-butanol and 3-ethoxy-2-butanol.

Reports have been given on the steric effect in the addition reaction of the radical to the carbon-carbon double bond.[1,2] In order to investigate similar steric effects on the coupling reaction of unlike radicals, we isolated the diastereoisomeric alcohols obtained by the photochemical reaction of unsymmetric carbonyl compounds in ether solvent. Unsymmetric carbonyl compounds should provide a pair of radicals having asymmetrical radical centers when α hydrogen atom of diethyl ether or tetrahydrofuran (THF) is abstracted. A cross-coupling of these radicals should produce diastereoisomeric alcohols.

Irradiation of acetophenone in an excess of THF with 500 W high pressure mercury vapor lamp at room temperature for 8 hr gave diastereoisomeric alcohols **1a** (26%)[3] and **1b** (19%), *p*-(2-tetrahydrofuryl)acetophenone (4%), 2,2′-bitetrahydrofuryl and acetophenone pinacol in a 65% conversion. Diastereoisomeric alcohols could be separated by a preparative glpc and their structures were confirmed by spectral data and by means of dehydration. When each of these diastereoisomers was dehydrated with sulfuric acid–acetic acid solution,[4] both isomers (**1a**, **1b**) were found to give an identical product (**5**) as in the following.



1a, 1b, ($R=C_6H_5$) **3a, 3b** ($R=C_6H_5$)
2a, 2b, ($R=H$) **4a, 4b** ($R=H$)



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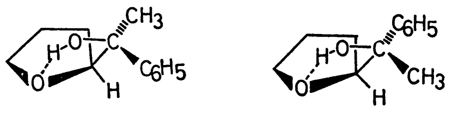
(1)

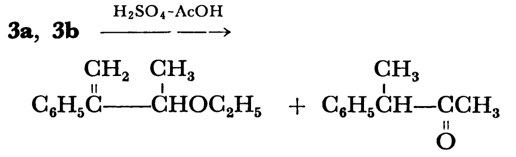
Methyl protons of **1a** and **1b** resonate at τ 8.61 and 8.42, respectively. An absorption of β-ring methylene of **1a** at τ 8.21 is shifted to a broad band at τ 8.0—9.0 in **1b**, indicating that some of the β-ring protons in **1b** lie over the plane of the aromatic ring. Accordingly, **1b** should correspond to conformation B and **1a** to A. Hydrogen bonded structures are suggested from the IR spectra of **1a** and **1b** and the NMR spectrum of 2-(2-tetrahydrofuryl)-2-propanol, which exhibits two methyl protons at different chemical shifts, *i.e.* τ 8.85 and 8.97.[5]



A B

Irradiation of acetaldehyde in THF gave diastereoisomeric alcohols **2a** (23%) and **2b** (18%), and 2,2′-bitetrahydrofuryl. Diastereoisomers were separated by a preparative glpc, both isomers showing similar spectra in NMR.

Irradiation of acetophenone in diethyl ether gave diastereoisomeric alcohols **3a** (22%) and **3b** (22%), 1-phenylethanol (4%), 2,3-diethoxybutane (40%) in a 60% conversion. In this case, diastereoisomers could not be separated by glpc under various conditions. However, the NMR spectrum of a mixture of **3a** and **3b** indicates the presence of two isomers, exhibiting two singlets at τ 8.50 and 8.61, two doublets at τ 9.24 and 8.98 and two triplets at τ 8.81 and 8.92 attributable to the corresponding methyl protons. A mixture of **3a** and **3b** was treated with sulfuric acid-acetic acid to give a dehydration product (**6**) and a rearranged ketone (**7**).



$$\mathbf{3a},\ \mathbf{3b} \xrightarrow{H_2SO_4\text{-}AcOH} C_6H_5C(=CH_2)\text{—}CH(CH_3)OC_2H_5 + C_6H_5CH(CH_3)\text{—}C(=O)CH_3 \qquad (2)$$

6 **7**

Irradiation of acetaldehyde in diethyl ether gave diastereoisomeric alcohols **4a** (20%) and **4b** (20%), 3-hydroxy-2-butanone (3%) and 2,3-diethoxybutane in a 70% conversion. The conformations of **4a** and **4b** could not be determined because of the spectral similarities of the isomers.

Most of the products obtained can be elucidated as combination products of the radicals resulting from a hydrogen abstraction by *n*-π* excited carbonyls. A cross-coupling of the two radicals provides the diastereoisomeric alcohols. The isomeric ratio of these diastereoisomers is 1.0 when diethyl ether is employed as a hydrogen donor, and 1.4 and 1.3 when THF is used. Similar diastereoisomers were obtained in a nearly equal amount when β-keto esters were photolyzed in ether solvent.[6] In the case of acetophenone in THF, **1a** having conformation A predominates over **1b**. This might be explained from the point of view that an approach of nearly planar radicals *via* a sterically less hindered pathway should yield **1a** predominantly.

p-(2-Tetrahydrofuryl)acetophenone can be produced by a substitution reaction of tetrahydrofuryl radical to acetophenone.[7] A combination of acetyl and α-hydroxyethyl radical[8] should provide 3-hydroxy-2-butanone.

Experimental

Quantitative glpc analyses were carried out with an internal standard. All mps and bps are uncorrected.

Photochemistry of Acetophenone in THF. A mixture of acetophenone (0.01 mol) and THF (0.4 mol) in a quartz tube was cooled in water and externally irradiated with a 500 W high pressure mercury vapor lamp for 8 hr. Distillation and a preparative glpc (FFAP column; col. temp., 250°) of the irradiation mixture gave **1a**, **1b**, *p*-(2-tetrahydrofuryl)acetophenon and 2,2′-bitetrahydrofuryl.

1-Phenyl-1-(2-tetrahydrofuryl)ethanol (**1a**) has n_D^{23} 1.5344; IR(CCl_4) 3540, 3450 cm^{-1}; NMR(CCl_4) τ 8.61 (s, 3H), 8.21 (m, 4H), 7.54 (s, 1H), 5.9—6.9 (m, 3H), 2.8 (m, 5H); *m/e* 192(M$^+$), 121, 71. Found: C, 74.75; H, 8.33%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

The IR and mass spectra of **1b** are similar to those of **1a**. Diastereoisomer **1b** has n_D^{23} 1.5309; NMR(CCl_4) τ 8.42 (s, 3H) 8.0—9.0 (m, 4H), 7.58 (s, 1H), 5.9—6.5 (m, 3H), 2.7 (m, 5H). Found: C, 74.64; H, 8.38%.

p-(2-Tetrahydrofuryl)acetophenone was identified from spectral data: IR (CCl_4) 1760—2000 (characteristic absorption of *p*-substituted acetophenone), 1680 cm^{-1}; NMR-(CCl_4) τ7.55 (s, 3H), 8.05 (m, 4H), 6.10 (m, 2H), 5.23 (t, 1H), 2.70 (d, 2H), 2.16 (d, 2H); *m/e* 190(M$^+$), 175, 147, 71, 43. Found: C, 75.48; H, 7.38%. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%. 2,4-Dinitrophenylhydrazone, mp 169.0—170.5 °C.

Photochemistry of Acetaldehyde in THF. A preparative glpc of the irradiation mixture gave diastereoisomeric alcohols **2a**, **2b** and 2,2′-bitetrahydrofuryl.

1-(2-Tetrahydrofuryl)ethanol (**2a**) has n_D^{20} 1.4421; IR-(CCl_4) 3560, 3440 cm^{-1}; NMR(CCl_4) τ 8.86 (d, 3H), 6.97 (s, 1H), 7.9—8.4 (m, 4H), 6.0—6.7 (m, 4H); *m/e* 101, 71, 45. Found: C, 61.85; H, 10.92%. Calcd for $C_6H_{12}O_2$: C, 62.04%; H, 11.03%.

The isomer **2b** has n_D^{20} 1.4060; NMR(CCl_4) τ 8.85 (d, 3H), 7.01 (s, 1H), 7.8—8.4 (m, 4H), 6.0—6.8 (m, 4H). Found: C, 61.88; H, 10.95.

Photochemistry of Acetophenone in Diethyl Ether. A preparative glpc (PEG 20M, 220 °C) of the irradiation mixture gave a mixture of diastereoisomers (**3a** and **3b**): IR(neat) 3470, 1110 cm^{-1}; NMR(CCl_4) τ 8.50 and 8.61 (s, 3H), 9.24 and 8.98 (d, 3H), 8.81 and 8.92 (t, 3H), 7.39 (s, 1H), 6.5 (m, 3H), 2.7 (m, 5H); *m/e* 194, 121, 73. Found: C, 74.02; H, 9.28%. Calcd for $C_{12}H_{18}O_2$: C, 74.30; H, 9.28%.

Photochemistry of Acetaldehyde in Diethyl Ether. A preparative glpc (PEG 20M, 120 °C) of the irradiation mixture gave the diastereoisomeric alcohols (**4a** and **4b**) and 3-hydroxy 2-butanone.

2-Hydroxy-3-ethoxybutane (**4a**) has bp 132 °C; n_D^{20} 1.4082; IR (CCl_4) 3560, 3470, 1115 cm^{-1}; NMR(CCl_4) τ 8.95 (d, 6H), 8.81 (t, 3H), 7.10 (s, 1H), 6—7 (m, 4H); *m/e* 73, 45. Found: C, 61.15; H, 11.75%. Calcd for $C_6H_{14}O_2$: C, 60.98; H, 11.94%.

The isomer **4b** has bp 125 °C; n_D^{20} 1.4112; IR(CCl_4) 3565, 3470, 1115 cm^{-1}; NMR(CCl_4) τ 8.90 (d, 6H), 8.78 (t, 3H), 7.07 (s, 1H), 6—7(m, 4H); *m/e* 73, 45. Found: C, 60.76; H, 11.72%.

*Dehydration of **1a** and **1b**.* Treatment of **1a** or **1b** (120 mg) with 0.15 ml of warm sulfuric acid–acetic acid solution[4] gave only 6-acetoxy-2-phenyl-3-hexanone (**5**): IR (CCl_4) 1735, 1715 cm^{-1}; NMR(CCl_4) τ 8.65 (d, 3H), 8.12 (s, 3H), 8.26 (q, 2H), 7.65 (t, 2H), 6.34 (q, 1H), 6.14 (t, 2H), 2.80 (5H); *m/e* 234, 129, 105, 87, 77. Found: C, 71.66; H, 7.53%. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74%.

*Dehydration of **3a** and **3b**.* Treatment of a mixture of **3a** and **3b** as mentioned above yielded 2-phenyl-3-ethoxy-1-butene (**6**) and 3-phenyl-2-butanone (**7**).

Product **6** has n_D^{20} 1.5092; IR(CCl_4) 1620, 910 cm^{-1}; NMR(CCl_4) τ 8.80 (t, 3H), 8.82 (d, 3H), 6.51 (q, 2H), 5.86 (q, 1H), 4.82 (s, 2H), 2.6—2.9 (m, 5H); *m/e* 161, 132, 117, 77, 73. Found: C, 81.60, H, 9.11%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

The other product **7** has n_D^{20} 1.5064; IR(CCl_4) 1715 cm^{-1}; NMR (CCl_4) τ 8.70 (d, 3H), 8.07 (s, 3H), 6.42 (q, 1H), 2.85 (m, 5H); *m/e* 148, 105. Found: C, 80.69; H, 8.32%. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16%.

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