Photochemical Cleavage and Release of Carboxylic Acids from α -Keto Amides.

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Supporting Information

FT-IR Spectra. Figure 3 shows the FT-IR spectra recorded in D₂O containing 25 mM phosphate ion buffer (pD 6) using a CaF₂ cell with a 50 μ m spacer. The spectra include the acetate derivative of α -keto amides **1c**, the trifluoroacetate salt of γ -aminobutyrate (GABA) derivative **1d**, trifluoroacetic acid at pD 6, the authentic photoproducts acetate, GABA, and diastereomeric hemiacetals **2**.

Figure 3. FT-IR spectra in 25 mM phosphate buffer (D₂O) at pD 6: A, sodium acetate; B, acetate derivative **1c**; C, GABA; D, trifluoroacetate salt of GABA derivative **1d**; E, trifluoroacetic acid; F, diastereomeric hemiacetals **2**.

NMR Spectral data for the α -Keto Amide Derivative of Benzoate 1a. ^1H NMR

(CDCl_3) 1.16 (t, $J = 7$ Hz, 3 H), 1.23 (t, $J = 7$ Hz, 3 H), 3.42 (q, $J = 7$ Hz, 4 H), 5.28 (s, CH_2), 7.46 (m, 2 H), 7.59 (m, 1 H), 8.09 (m, 2 H). ^{13}C NMR (CDCl_3) 12.30, 14.24, 39.72, 41.98, 66.94, 128.14, 128.54, 129.55, 133.20, 163.54, 165.68, 192.62.

NMR Spectral Data of α -Keto Amide Derivative of Phenylacetate 1b. ^1H NMR

(CDCl_3) 1.18 (t, $J = 7$ Hz, 3 H), 1.21 (t, $J = 7$ Hz, 3 H), 3.35 (q, $J = 7$ Hz, 2H), 3.40 (q, $J = 7$ Hz, 2H), 5.07 (s, 2 H), 7.2-7.4 (m, 5 H). ^{13}C NMR (CDCl_3) 13.24, 15.07, 40.42, 41.01, 42.62, 67.32, 126.94, 128.19, 128.98, 132.83, 163.19, 170.48, 191.88.

NMR Spectral Data of α -Keto Amide Derivative of Acetate 1c. ^1H NMR (CDCl_3)

1.16 (t, $J = 7$ Hz, 3 H), 1.20 (t, $J = 7$ Hz, 3 H), 2.15 (s, 3 H), 3.35 (q, $J = 7$ Hz, 2 H), 3.88 (q, $J = 7$ Hz, 2 H), 5.0 (s, 2 H). ^{13}C NMR (CDCl_3) 13.30, 15.17, 21.07, 40.50, 42.68, 67.11, 163.25, 169.86, 192.13.

NMR Spectral Data of α -Keto Amide Derivative of γ -Aminobutyrate 1d. ^1H NMR

(25 mM phosphate buffer, D_2O) 1.13 (t, $J = 7$ Hz, 3 H), 1.17 (t, $J = 7$ Hz, 3 H), 1.97 (tt, $J = 7, 7.5$ Hz, 2 H), 2.62 (t, $J = 7$ Hz, 2 H), 3.03 (br t, $J = 7.5$ Hz, 2 H), 3.35 (q, $J = 7$ Hz, 2 H), 3.39 (q, $J = 7$ Hz, 2 H), 5.14 (s, 2 H). ^{13}C NMR (25 mM phosphate buffer, D_2O) 15.03, 16.66, 25.26, 33.37, 41.69, 43.35, 45.99, 70.04, 166.97, 175.75, 197.49.

^1H and ^{13}C NMR Spectra of Isolated Hemiacetals **2.**

Figure 4. ^1H NMR spectrum of isolated diastereomeric hemiacetals **2** in CDCl_3 .

Figure 5. ^{13}C NMR spectrum of isolated diastereomeric hemiacetals **2** in CDCl_3 .