SUPPORTING INFORMATION

Ketone-Catalyzed Decomposition of Peroxynitrite via Dioxirane Intermediates

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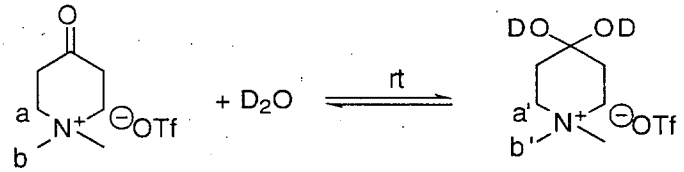
Supporting Information

Typical Procedure for Determination of the Hydrate to Ketone Ratios.



ketone **4** hydrate **4h**

Ketone **4** (3.3 mg, 12 μmol) was mixed with KH_2PO_4 (13.6 mg) and K_2HPO_4 (26.1 mg) (giving a buffer concentration of 0.25 M and pH ≈ 7.4). They were dissolved in a mixture of CD_3CN (0.1 mL) and D_2O (0.9 mL). The solution was transferred to an NMR tube. After equilibrating the sample solution at rt for 10 min, the ^1H NMR spectrum (300 MHz) was taken. From the spectrum, a triplet at δ 3.85 (J = 6.7 Hz) and a singlet at δ 3.38 were assigned to protons H_a and protons H_b of ketone **4** respectively, and a triplet at δ 3.52 (J = 5.8 Hz) and a singlet at δ 3.20 were assigned to protons $H_{a'}$ and protons $H_{b'}$ of hydrate **4h** respectively. The integration ratios $H_{a'}$:H_a and $H_{b'}$:H_b are 12.2:1 and 11.1:1 respectively, averaging to give the mole ratio of **4**:**4h** as 11.7:1. The spectrum taken at 20 min after mixing gave similar ratios. Selected spectral data for the ketones **1**–**7** and their corresponding hydrates are listed in Table 1.

Table 1. Selected Spectral Data of Ketones **1–7** and their Corresponding Hydrates.

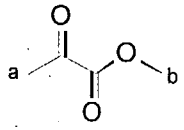
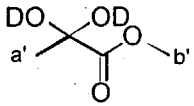
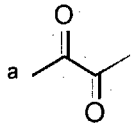
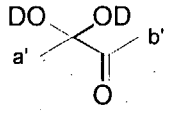
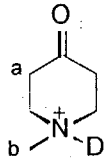
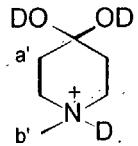
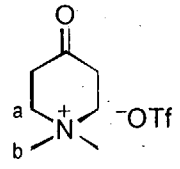
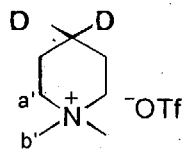
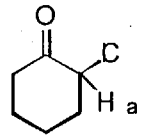
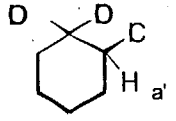
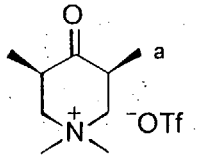
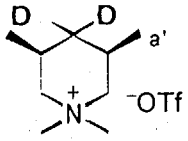
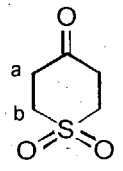
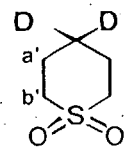
entry	ketone	hydrate	^{1}H NMR (CD_3CN/D_2O)	integration ratio	hydrate/ketone	*K*
1	 **1**	 **1h**	H_a δ 2.50 (s, 3H) H_b δ 3.89 (s, 3H) $H_{a'}$ δ 1.59 (s, 3H) $H_{b'}$ δ 3.82 (s, 3H)	$H_{a'} : H_a$ = 3.4:1 $H_{b'} : H_b$ = 3.6:1	3.5:1	3.9
2	 **2**	 **2h**	H_a δ 2.31 (s, 6H) $H_{a'}$ δ 1.48 (s, 3H) $H_{b'}$ δ 2.30 (s, 3H)	$H_{a'} : H_a + H_{b'}$ = 1:1.61	3.3:1	3.7
3	 **3**	 **3h**	H_a δ 2.73 (t, *J* = 6.3 Hz, 4H) H_b δ 2.78 (s, 3H) $H_{a'}$ δ 2.06 (t, *J* = 5.6 Hz, 4H) $H_{b'}$ δ 2.85 (s, 3H)	$H_{a'} : H_a$ = 6.9:1 $H_{b'} : H_b$ = 7.2:1	7.0:1	7.8
4	 **4**	 **4h**	H_a δ 3.85 (t, *J* = 6.7 Hz, 4H) H_b δ 3.38 (s, 6H) $H_{a'}$ δ 3.52 (t, *J* = 5.8 Hz, 4H) $H_{b'}$ δ 3.20 (s, 6H)	$H_{a'} : H_a$ = 12.2:1 $H_{b'} : H_b$ = 11.1:1	11.7:1	13.0

Table 1. Continued.

entry	ketone	hydrate	^{1}H NMR (CD_3CN/D_2O)	integration ratio	hydrate/ketone	*K*
5	 **5**	 **5h**	H_a δ 4.75 (dd, *J* = 11.3, 5.9 Hz, 1H) $H_{a'}$ δ 4.00 (dd, *J* = 10.7, 4.3 Hz, 1H)	$H_{a'}$: H_a = 0.63:1	0.63:1	0.7
6	 **6**	 **6h**	H_a δ 0.96 (d, *J* = 6.4 Hz, 6H) $H_{a'}$ δ 0.91 (d, *J* = 6.7 Hz, 6H)	$H_{a'}$: H_a = 0.47:1	0.47:1	0.52
7	 **7**	 **7h**	H_a δ 2.95 (t, *J* = 6.6 Hz, 4H) H_b δ 3.57 (t, *J* = 6.5 Hz, 4H) $H_{a'}$ δ 2.23 (t, *J* = 5.9 Hz, 4H) $H_{b'}$ δ 3.23 (t, *J* = 5.9 Hz, 4H)	$H_{a'}$: H_a = 13.0:1 $H_{b'}$: H_b = 12.6:1	12.8:1	14.2