

Supporting Information for

Formaldehyde Encapsulated in Zeolite: A Long-lived, Highly Activated One-carbon Electrophile to Carbonyl-ene Reactions

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General Experimental:

Infrared (IR) spectra were recorded on a JASCO FT/IR-550 Fourier transform infrared spectrometer. ^1H NMR spectra were recorded on a JNM-GSX 270 (270 MHz). ^{13}C NMR spectra were recorded on a JNM-GSX 270 (68 MHz). ^{13}C MAS NMR spectra were recorded at 25 °C on a CMX-300 (75 MHz). High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700V GCmate. Analytical TLC was performed on Merck DC-Platten Kieselgel 60 F254 plates. Silica gel column chromatography was carried out with Merck Kieselgel (60-mesh). NaX (UNION SHOWA Co., LTD., 13X, Si/Al=1.5) and NaY (TOSOH Co., LTD., 320NAA, Si/Al=2.7) were purchased in a powder form, and activated at 400 °C under vacuum for 4 hours. Paraformaldehyde was purchased from Tokyo Kasei Kogyo Co., LTD. Paraformaldehyde (99% ^{13}C -enriched) was purchased from Cambridge Isotopes. Commercial samples of alkenes, hexane, cyclohexane, and methanol were purchased and used as received. Styrenes were prepared from the corresponding acetophenones and methyltriphenylphosphonium bromide by the Wittig reaction.

^{13}C MAS NMR Spectra.

^{13}C NMR spectra were recorded at 25 °C using the single-pulse sequences with ^1H high power decoupling under MAS conditions at a spinning rate of 4.5 KHz.

Preparation of HCHO@NaY or NaX.

The gaseous formaldehyde was generated by the thermal depolymerization of paraformaldehyde (4.0 g) at 150 °C and induced to the flask containing NaY or NaX (30.0 g) at 0 °C. Maximum adsorption of HCHO was observed with equivalent units of HCHO one half that of sodium cations in the zeolite (about 72 mg of HCHO per g of NaX or NaY, *ca.* 2.4 mmol/g).

Typical experimental procedure for the carbonyl-ene reaction using HCHO@NaY.

To a solution of 3',4'-dichloro- α -methylstyrene (1.0 mmol) in cyclohexane (4 ml) was added HCHO@NaY (3.0 mmol as HCHO) at 20 °C. After the mixture was stirred at 20 °C for 1 h, MeOH (5 ml) was added. The mixture was stirred for 10 min, and then the NaY was filtered out, washed with methanol three times. The filtrate was evaporated under reduced pressure. The crude products were chromatographed on silica gel to give 3-(3',4'-dichlorophenyl)-3-buten-1-ol in 99% yield.

3-(3',4'-Dichlorophenyl)-3-buten-1-ol:¹

IR (CCl_4) 3628, 3393, 3087, 2951, 2881, 1626, 1549, 1473, 1384, 682 cm^{-1} . ^1H NMR (CDCl_3): δ 1.55 (s, 1H), 2.72 (dt, J = 1.1 and 6.5 Hz, 2H), 3.73 (t, J = 6.5 Hz, 2H), 5.21 (d, J = 1.1 Hz, 1H), 5.41 (d, J = 1.1 Hz, 1H), 7.24 (dd, J = 2.2 and 8.6 Hz, 1H), 7.40 (d, J = 8.6 Hz, 1H), 7.49 (d, J = 2.4 Hz, 1H). ^{13}C NMR (CDCl_3): δ 38.2, 60.8, 115.9, 125.3, 128.0,

130.2, 131.4, 132.4, 140.5, 142.7. HRMS: Calcd for $C_{10}H_{10}OCl_2$ (M^+) 216.0109. found 216.0103. Anal: Calcd for $C_{10}H_{10}OCl_2$: C, 55.33; H, 4.64; Cl, 32.66. found: C, 55.18; H, 4.62; Cl, 32.74.

3-Phenyl-3-buten-1-ol:¹

IR (CCl_4) 3628, 3365, 3084, 3059, 3026, 2948, 2880, 1627, 1574, 1495, 1445, 705 cm^{-1} . 1H NMR ($CDCl_3$) δ 1.47 (s, 1H), 2.79 (dt, $J = 1.4$ and 6.5 Hz, 2H), 3.73 (t, $J = 6.5$ Hz, 2H), 5.16 (d, $J = 1.4$ Hz, 1H), 5.41 (d, $J = 1.4$ Hz, 1H), 7.25-7.44 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 38.6, 61.0, 114.5, 126.0, 127.6, 128.3, 140.2, 144.7. HRMS: Calcd for $C_{10}H_{12}O$ (M^+) 148.0888. found 148.0887. Anal: Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. found: C, 80.91; H, 8.36.

2-Butyl-3-methyl-3-buten-1-ol:

IR (CCl_4) 3294, 3157, 2943, 2851, 1630, 1470 cm^{-1} . 1H NMR ($CDCl_3$) δ 0.89 (t, $J = 0.7$ Hz, 3H), 1.20-1.36 (m, 6H), 1.67 (s, 3H), 2.24-2.30 (m, 1H), 3.45-3.59 (m, 2H), 4.91 (d, $J = 5.5$ Hz, 2H). ^{13}C NMR ($CDCl_3$) 14.0, 18.5, 22.7, 28.9, 29.4, 50.0, 64.0, 113.7, 145.4. HRMS: Calcd for $C_9H_{18}O$ (M^+) 142.1358. found 142.1351.

Ene reaction with 1-methylcyclohexene.² The isomeric ratio of three ene products were determined to be 50:50 by 1H NMR.

2-Mehtylenecyclohexylmethanol:

1H NMR ($CDCl_3$) δ 1.20-2.40 (m, 8H), 3.57-3.60 (m, 1H), 3.76-3.80 (m, 1H), 4.72 (d, $J = 6.0$ Hz, 2H).

2-Mehtylcyclohex-2-enylmethanol:

1H NMR ($CDCl_3$) δ 1.50-2.00 (m, 4H), 1.70 (s, 3H), 1.98 (m, 2H), 2.24 (m, 1H), 3.63-3.70 (m, 2H), 5.58 (m, 1H).

Ene reaction with Limonene.² The isomeric ratio of three ene products were determined to be 20:13:67:0 by 1H NMR.

5-Isopropenyl-2-methylcyclohex-2-enylmethanol:

1H NMR ($CDCl_3$) δ 1.37 – 2.32 (m, 7H), 1.66 (s, 3H), 1.70 s, 3H), 3.6 – 3.8 (m, 2H), 4.71 (s, 2H), 5.56 (s, 1H).

References and Notes

1. Okachi, T.; Fujimoto, K.; Onaka, M. *Org. Lett.* **2002**, *4*, 1667.
2. (a) Maruoka, K.; Concepcion, A. B.; Murase, N.; Oishi, M.; Hirayama, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1993**, *115*, 3943. (b) Snider, B. B.; Rodini, D. J.; Kirk, C.; Cordova, R. *J. Am. Chem. Soc.* **1982**, *104*, 555.

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