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Supporting Information

Olefin Epoxidations Using the Dicyclohexylcarbodiimide-H₂O₂ System

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Styrene Oxide. The general procedure was followed to give a residue which was chromatographed on the Chromatotron (centrifugal chromatography) to give a colorless liquid. The product was identified by comparing its NMR data with those in the literature⁸ and on the basis of the following data: ¹H NMR (CDCl₃) δ 2.76 (dd, 1H), 3.11 (dd, 1H), 3.83 (dd, 1H), 7.24-7.35 (m, 5H). ¹³C NMR (CDCl₃): δ 51.31, 52.50, 125.53, 128.20, 128.52, 137.63. Mass spectrum (EI, 70 eV): 120 (M⁺, 31.44), 91 (base peak), calcd for C₈H₈O: 120.15.

α-Methylstyrene Oxide. The general procedure was followed to give a residue which was chromatographed on the Chromatotron to give a colorless liquid. The product was identified by comparing its NMR data with those in the literature⁸ and on the basis of the following data: ¹H NMR (CDCl₃): δ 1.73 (s, 3H), 2.81(d, 1H), 2.98 (d, 1H), 7.27-7.41 (m, 5H). ¹³C NMR (CDCl₃): δ 22.11, 56.98, 57.25, 125.43, 127.57, 128.45, 141.29. Mass spectrum (EI, 70 eV): 134 (M⁺, 18.72), 133 (base peak), calcd. for C₉H₁₀O: 134.18.

trans-β-Methylstyrene Oxide. The general procedure was followed to give a residue which was chromatographed on the Chromatotron to give a colorless liquid. The

product was identified by comparing its NMR data with those in the literature⁹ and on the basis of the following data: ¹H NMR (CDCl₃): δ 1.45 (d, 3H), 3.01-3.07 (m, 1H), 3.5 (d, 1H), 7.25-7.37 (m, 5H). ¹³C NMR (CDCl₃): δ 18.32, 59.35, 59.85, 125.80, 128.25, 128.66, 137.99. Mass spectrum (EI, 70 eV): 134 (M⁺, 34.37), 90 (base peak), calcd. for C₉H₁₀O: 134.18.

Cyclohexene Oxide. The general procedure was followed to give a residue which was chromatographed on the Chromatotron to give a colorless liquid. The product was identified by comparing its NMR data with those in the literature⁹ and on the basis of the following data: ¹H NMR (CDCl₃): δ 1.15-1.32 (m, 2H), 1.37-1.51 (m, 2H), 1.79-1.87 (m, 2H), 1.91-2.01 (m, 2H), 3.13 (m, 2H). ¹³C NMR (CDCl₃): δ 19.68, 24.68, 52.28. Mass spectrum (EI, 70 eV): 98 (M⁺, 2.43), 83 (base peak), calcd for C₆H₁₀O: 98.14

1-Methyl-1-cyclohexene Oxide. The general procedure was followed to give a residue which was chromatographed on the Chromatotron to give a colorless liquid. The product was identified by comparing its NMR data with those in the literature¹⁰ and on the basis of the following data: ¹H NMR (CDCl₃): δ 1.10 (m, 2H), 1.33 (s, 3H), 1.34-1.50 (m, 2H), 1.64-1.74 (m, 2H), 1.85-1.96 (m, 2H), 2.97 (d, 1H). ¹³C NMR (CDCl₃): δ 19.82, 20.20, 24.09, 24.92, 30.04, 57.62, 59.64. Mass spectrum (EI, 70 eV): 112 (M⁺, 2.88), 97 (base peak), calcd. for C₇H₁₂O: 112.19.

Ethyl *trans*-cinnamate Oxide. The general procedure was followed to give a residue which was found to contain two products. The products were separated by chromatography on the Chromatotron to give two colorless liquids. One of these products was identified as methyl *trans*-cinnamate oxide, the product transesterified with solvent methanol, by comparing its NMR and mass spectral data with those in the

literature¹¹ and on the basis of the following data: ¹H NMR (CDCl₃): δ 3.56 (d, 1H), 3.88 (s, 3H), 4.14 (d, 1H), 7.32-7.45 (m, 5H). ¹³C NMR (CDCl₃): δ 52.87, 56.90, 58.24, 125.9, 128.8, 129.2, 135.0, 168.7. Mass spectrum (EI, 70 eV): 178 (M⁺, 0.78), 121 (base peak), calcd. for C₁₀H₁₀O₃: 178.19. The second product was identified as ethyl *trans*-cinnamate oxide by comparing its NMR and mass spectral data with those in the literature¹² and on the basis of the following data: ¹H NMR (CDCl₃): δ 1.35 (t, 3H), 3.53 (d, 1H), 4.11 (d, 1H), 4.25-4.36 (m, 2H), 7.29-7.39 (m, 5H). ¹³C NMR (CDCl₃): δ 14.35, 56.93, 58.04, 61.90, 125.9, 128.7, 129.0, 135.1, 168.1. Mass spectrum (EI, 70 eV): 192 (M⁺, 1.55), 135 (base peak), calcd. for C₁₁H₁₂O₃: 192.21. With ethanol solvent only the ethyl ester was present.

α-Ionone Oxide. The general procedure was followed to give a residue which was chromatographed on the Chromatotron to give a colorless liquid. The Hetero Multi Bond Correlation (HMBC) NMR spectrum of this material shows a correlation between the carbonyl signal and two olefinic protons thus indicating that the oxirane ring is on the cyclohexane ring. Confirmation of this assignment comes from a comparison of NMR data with those in the literature¹³ and on the basis of the following data: ¹H NMR (CDCl₃): δ 0.75 (s, 3H), 0.93 (s, 3H), 0.9-1.6 (m, 2H), 1.25 (s, 3H), 1.80-2.1 (m, 2H), 2.05 (d, 1H), 2.30 (s, 3H), 3.1 (t, 1H), 6.08 (d, 1H), 6.72 (dd, 1H). ¹³C NMR (CDCl₃): δ 22.02, 24.33, 26.70, 27.79, 28.14, 28.73, 31.47, 52.69, 59.02, 59.71, 134.2, 146.5, 198.8. Mass spectrum (EI, 70 eV): 208 (M⁺, 0.782), 109 (base peak), calcd. for C₁₃H₂₀O₂: 208.29.

exo-2,3-Epoxybornane. The general procedure was followed to give a residue which was chromatographed on the Chromatotron to give a colorless solid. The product

was identified by comparing its NMR data with those in the literature¹⁴ and on the basis of the following data: ¹H NMR (CDCl₃): δ 0.70 (d, 1H), 1.17-1.24 (m, 2H), 1.28-1.34 (m, 1H), 1.44-1.51 (m, 2H), 2.44 (br s, 2H), 3.05 (s, 2H). ¹³C NMR (CDCl₃): δ 25.36, 26.48, 36.87, 51.60. Mass spectrum (EI, 70 eV): 110 (M⁺, 3.20), 81 (base peak), calcd. for C₇H₁₀O: 110.15.

Cyclododecene Epoxide (*cis* + *trans*). The general procedure was followed to give a colorless liquid residue. The isomeric epoxide products could not be separated by preparative GLC. The mixture was collected and analyzed by NMR. The product mixture was identified by comparing its NMR data with those in the literature¹⁵ and on the basis of the following data: ¹H NMR (CDCl₃): δ 1.04-1.12 (m, 2H), 1.25-1.7 (m, 20H), 1.79-1.89 (m, 1H), 2.17-2.24 (m, 2H), 2.70-2.75 (m, 2H), 2.88-2.93 (m, 1H). ¹³C NMR (CDCl₃): δ 22.73, 23.74, 23.92, 24.16, 24.30, 24.36, 25.33, 25.84, 26.21, 26.94, 31.67, 58.33, 60.09. Mass spectrum (EI, 70 eV): 182 (M⁺, 0.11), 55 (base peak), calcd. for C₁₂H₂₂O: 182.31.

References and Notes

- (8) Bloodworth, A.J.; Bylina, G.S. *J. Chem. Soc. Perkin Trans. 1* **1972**, 2433.
- (9) Denmark, S.E.; Forbes, D.C.; Hays, D.S.; DePue, J.S.; Wilde, R.G. *J. Org. Chem.* **1995**, *60*, 1391.
- (10) Kaneda, K.; Itoh, T.; Fujiwara, Y.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3810.
- (11) Borredon, M.E.; Delmas, M.; Gaset, A. *Tetrahedron*, **1987**, *43*, 3945.
- (12) Conan, A.; Sibille, S.; Perichon, J. *J. Org. Chem.* **1991**, *56*, 2018.
- (13) Haag, A.; Eschenmoser, W.; Eugster, C.H. *Helv. Chim. Acta* **1980**, *63*, 10.

(14) Lambert, J.B.; Greifenstein, L.G. *J. Am. Chem. Soc.* **1974**, *96*, 5120.

(15) Kurkchi, G.A.; Furman, V.M.; Dement'eva, L.A.; Levina, O.V.; Vazinger, N.V.;
Volovoi, V. A.; Guttman, N.A.; Samoilenko, A.A.; Golovistikov, Yu. N. *Neftekhimiia*
1977, *17*, 101.