REVISED

SUPPLEMENTARY MATERIAL

Experimental Section

Reagents and solvents were purified by standard procedures. Dimethyldioxirane in acetone solution was prepared according to reported procedures.[1] Diluted solutions of DMDO (**2**) are not known to decompose violently, but the usual precautions for handling peroxides should be applied, including the use of a shield. All reactions should be performed in a fume hood to avoid exposure to the volatile oxidants.[2]

Preparation of iodohydrines. General procedure. To a solution of iodomethane (1.19 mmol, 075 mL) in acetone cooled to –70 °C (acetone/CO_2 cooling bath) an aliquot of a DMDO acetone solution (1.13 mmol) was added under stirring. After few seconds the formation of a white solid was observed. The mixture was allowed to stand for 1 h and then a solution of 0.56 mmol of the olefin in 2 mL of acetone was added at once. The reaction was allowed to warm up slowly to room temperature (usually 18 h). Along this period the white solid dissolved forming an intense orange color solution which faded slowly with the passage of the time to reach a pale yellow color in the final solution. The solvent was removed under vacuum and the residue redissolved in 20 mL of dichloromethane. The solution was washed with sodium thiosulfate (1 N, 2 x 15 mL) and distilled water (1 x 15 mL). The organic layer was dried over anhydrous magnesium sulfate and the solvent removed under vacuum. Column chromatography over silica (hexane:ethyl acetate 95:5) of the residue yielded the pure iodohydrine.

***trans* 2-Iodocyclohexanol (6a).** Pale yellow solid mp: 35 °C. ^{1}H-NMR ($CDCl_3$): 1.2-1.5 (4H, m), 1.8-2-2 (3H, m), 2.4-2.6 (2H, m), 3.46 (1H, m), 4.02 (1H, ddd, 13.9, 9.7, 4.3 Hz); ^{13}C-NMR($CDCl_3$): 24.4 (t), 27.9 (t), 33.6 (d), 38.5 (t), 43.4 (t), 73.9 (d); HRMS(EI+): 225.9850 Exact mass: 225.9855.

1-Iodo-2-methyl-2-pentanol (6b). Pale yellow oil. ^{1}H-NMR ($CDCl_3$): 0.93 (3H, t, 7Hz), 1.2-1.4 (5H,m), 1.55-1.65 (2H, m), 1.75 (1H,s), 3.3 (2H,s); ^{13}C-NMR: 14.4(q), 17.6(t), 23.3(t), 25.7(q), 42.9(t), 70.6(s); HRMS (EI+): 228.0007 Exact mass: 228.0011.

3-Iodo-4-nonanol and 4-iodo-3-nonanol (6c). 1:1 Mixture of isomers. Pale yellow oil. ^{1}H-NMR ($CDCl_3$): 0.8-1.8 (32H,m), 2.08 (2H,s), 3.15-3.27 (2H, m), 4.15-4.2 (2H, m); ^{13}C-NMR:10.3 (q), 13.9 (q), 14.8 (q), 22.4 (t), 22.5 (t), 25.4 (t), 27.6(t), 28.0 (t), 29.6 (t), 30.8 (t), 31.7 (t), 34.5 (t), 34.6 (t), 49.4 (d), 51.9 (d), 75.12 (d), 76.8 (d).

1-Iodo-3-phenyl-2-propanol and 2-iodo-3-phenyl-1-propanol (6d). Mixture or isomers (65:35 by gc). Pale yellow oil. ^{1}H-NMR ($CDCl_3$): 3.17 (2H, m), 3.15-3.45 (5H, m), 3.6-3.8 (2H, m), 4.4-4.65 (1H, m), 7.1-7.4 (10H, m). ^{13}C-NMR: 14.9 (t), 39.9 (d), 42.7 (t), 41.8 (t), 67.2 (t), 71.6 (d), 126.8 (d), 126.9 (d), 128.5 (d), 128.6 (d), 128.9 (d), 129.2 (d), 137.0 (s), 138.8 (s).

2-Iodo-1-indanol (6e). Pale yellow solid mp: 119-120°C; ^{1}H-NMR($CDCl_3$): 2.64 (1H, d, 5.7Hz), 3.28 (1H,dd, 16.2, 8.0Hz), 3.56 (1H, dd, 16.2, 7.3Hz), 4.16 (1H, ddd, 8.0, 7.3, 6.2Hz), 5.37 (1H, m), 7.2-7.45 (4H, m); ^{13}C-NMR: 30.1 (d), 42.2(t), 84.9 (d), 123.8 (d), 124.3 (d), 127.5 (d), 128.7 (d), 140.9 (s), 141.9 (s); HRMS (EI+): 259.9695 Exact mass: 259.9698.

1-Iodo 2-phenyl–2-ethanol (6f). Pale yellow solid mp: 30°C. ^{1}H-NMR (CDCl3): 2.6 (1H, s), 3.28 (1H, dd, 10.25, 8.5 Hz), 3.37 (1H, dd, 10.25, 3.8 Hz), 4.7 (1H, m), 7.2-7.3 (5H, m); ^{13}C-NMR: 15.2 (t), 73.9 (d), 125.7 (d), 128.3 (d), 128.6 (d), 141.05 (s); HRMS (CI+): 247.9706 Exact mass: 247.9698.

1-Iodo-2-phenyl-2-methyl 2-ethanol (6g). Pale yellow oil. ^{1}H-NMR (CDCl$_3$): 1.72 (3H, s), 2.4 (1H, s), 3.6 (2H, m), 7.2-7.5 (4H, m); ^{13}C-NMR:24.2 (t), 28.4 (q), 72.6 (s), 124.6 (d), 127.4 (d), 128.4 (d), 144.2 (s); HRMS (CI+): 261.9857 Exact mass: 261.9855.

1-Iodo-2-(*para*-methoxyphenyl)-2-ethanol (6h). Pale yellow solid mp: 45 °C. ^{1}H-NMR (CDCl$_3$): 2.7 (1H, s), 3.28-3.37 (2H, m), 3.72 (3H, s), 4.69 (1H, dd, 8.3, 4.1 Hz), 6.79-7.25 (4H, m); ^{13}C-NMR: 15.4 (t), 55.2 (q), 73.6 (d), 113.9 (d), 126.9 (d), 133.2 (s), 159.4 (s); HRMS(CI+): 277.9802 Exact mass: 277.9804.

1-Iodo-2-(*para*-chlorophenyl)-2-ethanol (6i). Pale yellow solid mp: 78°C. ^{1}H-NMR (CDCl$_3$): 2.58 (1H, d, 2.9 Hz), 3.16 (1H, dd, 10.3, 8.4 Hz), 3.27 (1H, dd, 10.3, 3.8 Hz), 4.6 (1H, m), 7.0-7.2 (4H, m); ^{13}C-NMR (CDCl$_3$) : 14.9 (t), 73.2 (d), 127.1 (d), 128.7 (d), 133.9 (s), 139.4 (s); HRMS (CI+): 282.9347 Exact mass: 282.9357.

1-Iodo-2-(*para*-methylphenyl)-2-ethanol (6j). Pale yellow solid mp: 41°C. ^{1}H-NMR(CDCl$_3$): 2.38 (3H, s), 3.38 (1H, dd, 10.1, 8.3 Hz), 3.46 (1H, dd, 10.1, 4.12 Hz), 4.8 (1H, m), 7.1-7.3 (4H, m); ^{13}C-NMR:15.2 (t), 21.1 (q), 73.7 (d), 125.6 (d), 129.2 (d), 137.9 (s), 138.1 (s); HRMS (CI+): 261.9859 Exact mass: 261.9855.

1-Iodo-2-(*para*-trifluoromethyl)-2-ethanol (6k). Pale yellow solid mp: 38°C. ^{1}H-NMR (CDCl$_3$): 2.60 (1H, d, 3.6 Hz), 3.30 (1H, dd, 10.1, 8.3 Hz), 3.43 (1H, dd, 10.1, 3.6 Hz), 4.8 (1H, m), 7.4-7.6 (4H, m); ^{13}C-NMR:14.7 (t), 73.2 (d), 121.8 (s), 125.6 (q, 14 Hz), 126.12 (d), 130.4 (m, 32 Hz), 144.8 (m); HRMS (CI+): 315.9563 Exact mass: 315.9572.

***cis*-7-Iodobicyclo [2.2.1] heptan-*exo*-2-ol (6l):** Pale yellow solid; mp: 49°C. ^{1}H-NMR (CDCl$_3$): 1-1.52 (4H, m), 1.52-1.65 (2H, m), 2.03 /1H, m), 2.3 (1H, m), 2.4 (1H, m), 2.5 (1H, m), 3.7 (1H, s, 3.84 (1H, m); ^{13}C-NMR: 24.8 (t), 25.6 (t), 30.3 (d), 42.6 (t), 43.9 (d), 49.8 (d), 76.5 (d); HRMS (CI+): 237.9858 Exact mass: 237.9855.

Competitive experiments. To a suspension of iodosomethane in acetone prepared as reported above at –70 °C, a mixture of styrene (0.16 mmol), *para*-substituted styrene (0.16 mmol) and methyl *para*-chlorobenzoate (0.16 mmol) as internal standard dissolved in 1 mL of acetone were added. The reaction was allowed to warm up slowly to room temperature over 18 h. The mixture was analyzed by gas-liquid chromatography and the values k_X/k_H plotted *vs.* the substituent constant σ_p. The slope of the Hammett plot was $\rho = -5.65$.

Epoxidation of *trans*-3-nonene with DMDO. To a solution of *trans*-3-nonene (0.47 mmol) in 1 mL of acetone cooled to –15 °C, an aliquot (0.57 mmol) of a DMDO solution in acetone was added. The reaction mixture was stirred at –15 °C for 3 h. The solvent was removed under vacuum to yield *trans*-3,4-epoxynonane as the only product (>99% yield). ^{1}H NMR (CDCl$_3$): 0.8-1.0 (6 H, m), 1.2-1.6 (10 H, m), 2.62 (2H, m). ^{13}C (NMR) (CDCl$_3$): 9.8 (q), 22.54 (t), 25.14 (t), 25.69 (t), 31.56 (t), 32.01 (t), 32.01 (t), 58.60 (d), 59.93 (d).

Determination of the stereochemistry of the addition of hypoiodous acid to *trans*-3-nonene. A methanol (5 mL) solution of 3-iodo-4-nonanol y 4-iodo-3-nonanol (**6c**) obtained as reported above, was treated with 3 equivalents of potassium carbonate (1.41 mmol). The mixture was stirred for 24 h at room temperature. The solvent was removed under vacuum and the residue partitioned into water and dichloromethane. The aqueous layer was further extracted with two portions of 10 mL of dichloromethane and the organic phase was dried over anhydrous magnesium sulfate. The solvent was removed under vacuum to yield a colorless oil which was identified as the *trans*-4,5-epoxynonane (91% isolated yield) by comparison with the authentic sample obtained by direct epoxidation of *trans*-3-nonene with DMDO.

References

1) Adam, W.; Bialas, J.; Hadjiarapoglou, L. *Chem. Ber.* **1991**, *124*, 2377.
2) Crandall, J. K. in *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: New York, 1995; Vol. 3, pp. 2061-2064.