Synthesis of Aromatic (*E*)- or (*Z*)- α,β -Unsaturated Amides with Total or very High Selectivity from α,β -Epoxyamides and Samarium Diiodide

José M. Concellón, and Eva Bardales

Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Julián Clavería, 8, 33071 Oviedo, Spain.

SUPPORTING INFORMATION

Spectroscopic data of compounds 1	2S
Spectroscopic data of compounds 3	4S
(<i>Z</i>)-(<i>N,N</i>)-Diethyl-2-methyl-3-phenylpropenamide (2a).....	6S
(<i>Z</i>)-2-Butyl-(<i>N,N</i>)-diethyl-3-phenylpropenamide (2b).....	7S
(<i>Z</i>)-(<i>N,N</i>)-Diethyl-3-[4-(methoxy)phenyl]-2-methylpropenamide (2c).....	8S
(<i>Z</i>)-(<i>N,N</i>)-Diisopropyl-3-[4-(methoxy)phenyl]-2-methylpropenamide (2d).....	9S
(<i>Z</i>)-(<i>N,N</i>)-Diisopropyl-3-[4-(chloro)phenyl]-2-methyl propenamide (2e).....	10S
(<i>E</i>)-(<i>N,N</i>)-Diethyl-3-phenylpropenamid (4a).....	11S
(<i>E</i>)-(<i>N,N</i>)-Diethyl-3-[4-(methoxy)phenyl]propenamide (4b)	12S
(<i>E</i>)-(<i>N,N</i>)-Diethyl-2-methyl-3-phenylbut-2-enamide (4c)	13S
(<i>E</i>)-(<i>N,N</i>)-Diethyl-2-methyl-3-phenylpent-2-enamide (4d)	14S
(<i>E</i>)-(<i>N,N</i>)-Diisopropyl-2-methyl-3-phenylpent-2-enamide (4e).....	15S

SPECTROSCOPIC DATA OF COMPOUNDS 1

2,3-Epoxy-(*N,N*)-diethyl-2-methyl-3-phenylpropanamide (1a): ^1H NMR (200 MHz, CDCl_3): δ = 7.38-7.17 (m, 10 H), 4.13 (s, 1 H), 3.93 (s, 1 H), 3.57-3.25 (m, 8 H), 1.63 (s, 3 H), 1.24 (s, 3 H), 1.23 (t, J = 6.9 Hz, 3 H), 1.11 (t, J = 6.9 Hz, 3 H), 0.88-0.67 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 169.3 (C), 166.8 (C), 134.6 (C), 134.0 (C), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 126.2 (CH), 125.8 (CH), 64.3 (C), 64.2 (CH), 62.9 (C), 61.9 (CH), 41.0 (CH_2), 40.3 (CH_2), 39.0 (CH_2), 37.9 (CH_2), 20.5 (CH_3), 14.6 (CH_3), 14.0 (CH_3), 13.2 (CH_3), 12.3 (CH_3), 11.7 (CH_3); IR (neat): $\tilde{\nu}$ = 2974, 1634, 1462, 1383, 1071 cm^{-1} ; R_f = 0.4 (hexane/AcOEt 1/1).

2-Butyl-2,3-epoxy-(*N,N*)-diethyl-3-phenylpropanamide (1b): ^1H NMR (200 MHz, CDCl_3): δ = 7.42-7.08 (m, 10 H), 4.13 (s, 1 H), 3.70 (s, 1 H), 3.38-3.06 (m, 8 H), 3.07-1.27 (m, 12 H), 1.26-1.08 (m, 6 H), 0.91 (t, J = 6.9 Hz, 6 H), 0.81-0.62 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 168.5 (C), 166.0 (C), 134.3 (C), 134.0 (C), 127.7 (CH), 127.5 (CH), 126.0 (CH), 125.8 (CH), 67.2 (C), 65.9 (C), 62.8 (CH), 61.9 (CH), 40.8 (CH_2), 39.7 (CH_2), 39.0 (CH_2), 37.2 (CH_2), 33.6 (CH_2), 28.2 (CH_2), 26.6 (CH_2), 26.1 (CH_2), 22.3 (CH_2), 22.1 (CH_2), 13.9 (CH_3), 13.5 (CH_3), 13.3 (CH_3), 12.8 (CH_3), 12.2 (CH_3), 11.4 (CH_3); IR (neat): $\tilde{\nu}$ = 2960, 1644, 1462, 1381, 1131 cm^{-1} ; R_f = 0.3 (hexane/AcOEt 3/1).

2,3-Epoxy-(*N,N*)-diethyl-3-[4-(methoxy)phenyl]-2- methylpropanamide (1c): ^1H NMR (200 MHz, CDCl_3): δ = 7.19 (d, J = 8.7 Hz, 2 H), 7.14 (d, J = 8.5 Hz, 2 H), 6.85 (d, J = 8.7 Hz, 2 H), 6.76 (d, J = 8.5 Hz, 2 H), 4.06 (s, 1 H), 3.86 (s, 1 H), 3.74 (s, 3 H), 3.70 (s, 3 H), 3.22-2.41 (m, 8 H), 1.59 (s, 3 H), 1.23 (s, 3 H), 1.20 (t, J = 6.9 Hz, 3 H), 1.09 (t, J = 6.9 Hz, 3 H), 0.82-0.67 (m, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 169.4 (C), 167.1 (C), 159.4 (C), 159.1 (C), 127.4 (CH), 127.1 (CH), 126.6 (C), 125.9 (C), 113.4 (CH), 113.3 (CH), 64.2 (C), 64.1 (CH), 62.9 (C), 61.8 (CH), 54.9 (CH_3), 41.0 (CH_2), 40.2 (CH_2), 39.0 (CH_2), 37.5 (CH_2), 20.4 (CH_3), 14.5 (CH_3), 13.9 (CH_3), 13.1 (CH_3), 12.3

(CH₃), 11.8 (CH₃); IR (neat): $\tilde{\nu}$ = 2936, 1645, 1464, 1383, 1032 cm⁻¹; R_f = 0.4 (hexane/AcOEt 1/1).

2,3-Epoxy-(*N,N*)-diisopropyl-3-[4-(methoxy)phenyl]-2-methyl propanamide (1d):

¹H NMR (200 MHz, CDCl₃): δ = 7.24-7.17 (m, 4 H), 6.81 (d, *J* = 8.7 Hz, 4 H), 4.61-4.54 (m, 1 H), 3.89 (s, 2 H), 3.80-3.64 (m, 1 H), 3.70 (s, 6 H), 3.35-3.20 (m, 1 H), 3.15-3.01 (m, 1 H), 1.64 (s, 3 H), 1.59 (s, 3 H), 1.36 (d, *J* = 6.9 Hz, 3 H), 1.30 (d, *J* = 6.9 Hz, 3 H), 1.21 (d, *J* = 6.9 Hz, 3 H), 1.18 (d, *J* = 6.9 Hz, 3 H), 1.08 (d, *J* = 6.9 Hz, 3 H), 1.02 (d, *J* = 6.9 Hz, 3 H), 0.18 (d, *J* = 6.9 Hz, 6 H); ¹³C NMR (50 MHz, CDCl₃): δ = 166.5 (C), 159.6 (C), 127.5 (CH), 126.2 (C), 113.3 (CH), 113.2 (CH), 64.6 (C), 64.3 (CH), 54.9 (CH₃), 48.0 (CH₂), 47.9 (CH₂), 45.2 (CH₂), 45.1 (CH₂), 20.3 (CH₃), 20.2 (CH₃), 19.6 (CH₃), 19.5 (CH₃); IR (neat): $\tilde{\nu}$ = 2970, 1637, 1439, 1304, 1171 cm⁻¹; R_f = 0.4 (hexane/AcOEt 1/1).

3-[4-(Chloro)phenyl]-2,3-epoxy-(*N,N*)-diisopropyl-2-methyl propanamide (1e): ¹H NMR (200 MHz, CDCl₃): δ = 7.39-7.12 (m, 8 H), 4.47-4.42 (m, 1 H), 3.94 (s, 1 H), 3.93 (s, 1 H), 3.80-3.62 (m, 1 H), 3.39-3.21 (m, 1 H), 3.16-3.02 (m, 1 H), 1.74 (s, 3 H), 1.64 (s, 3 H), 1.41-1.12 (m, 18 H), 0.11 (d, *J* = 6.4 Hz, 6 H); ¹³C NMR (75 MHz, CDCl₃): δ = 165.9 (C), 133.9 (C), 133.5 (C), 128.0 (CH), 127.7 (CH), 127.1 (CH), 64.8 (C), 63.9 (CH), 63.6 (CH), 48.1 (CH₂), 47.8 (CH₂), 45.6 (CH₂), 45.2 (CH₂), 20.6 (CH₃), 20.1 (CH₃), 19.6 (CH₃), 19.5 (CH₃); IR (neat): $\tilde{\nu}$ = 2974, 1637, 1464, 1374, 1078 cm⁻¹; R_f = 0.2 (hexane/AcOEt 3/1).

SPECTROSCOPIC DATA OF COMPOUNDS 3

2,3-Epoxy-(*N,N*)-diethyl-3-phenylpropanamide (3a): ^1H NMR (200 MHz, CDCl_3): δ = 7.50-7.21 (m, 10 H), 4.21 (d, J = 4.4 Hz, 1 H), 4.05-4.01 (m, 1 H), 3.84 (m, 1 H), 3.58-3.56 (m, 1 H), 3.52-3.20 (m, 8 H), 1.17 (t, J = 7.2 Hz, 3 H), 1.13 (t, J = 7.2 Hz, 3 H), 0.99 (t, J = 7.2 Hz, 3 H), 0.74 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 165.5 (C), 164.0 (C), 135.5 (C), 133.5 (C), 128.5 (CH), 128.4 (CH), 128.2 (CH), 127.9 (CH), 126.1 (CH), 125.4 (CH), 57.6 (CH), 57.4 (CH), 57.3 (CH), 56.9 (CH), 41.3 (CH₂), 40.7 (CH₂), 40.3 (CH₂), 39.0 (CH₂), 14.6 (CH₃), 13.7 (CH₃), 12.7 (CH₃), 12.0 (CH₃); IR (neat): $\tilde{\nu}$ = 2962, 1652, 1460, 1377, 1149 cm^{-1} ; R_f = 0.3 (hexane/AcOEt 1/1).

2,3-Epoxy-(*N,N*)-diethyl-3-[4-(methoxy)phenyl]propanamide (3b): ^1H NMR (200 MHz, CDCl_3): δ = 7.26 (d, J = 8.5 Hz, 2 H), 7.23 (d, J = 8.5 Hz, 2 H), 6.88 (d, J = 8.7 Hz, 2 H), 6.82 (d, J = 8.7 Hz, 2 H), 4.18 (d, J = 4.4 Hz, 1 H), 4.01 (d, J = 2.1 Hz, 1 H), 3.83 (d, J = 4.4 Hz, 1 H), 3.79 (s, 3 H), 3.76 (s, 3 H), 3.57 (d, J = 2.1 Hz, 1 H), 3.52-3.03 (m, 8 H), 1.23 (t, J = 7.2 Hz, 3 H), 1.15 (t, J = 7.2 Hz, 3 H), 1.02 (t, J = 7.2 Hz, 3 H), 0.83 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 165.6 (C), 164.2 (C), 159.8 (C), 159.6 (C), 127.5 (CH), 127.4 (CH), 126.8 (C), 125.4 (C), 113.9 (CH), 113.4 (CH), 57.7 (CH), 57.4 (CH), 57.3 (CH), 56.9 (CH), 55.1 (CH₃), 55.0 (CH₃), 41.3 (CH₂), 40.7 (CH₂), 40.4 (CH₂), 39.2 (CH₂), 14.7 (CH₃), 13.8 (CH₃), 12.8 (CH₃), 12.4 (CH₃); IR (neat): $\tilde{\nu}$ = 2976, 1653, 1460, 1304, 1032 cm^{-1} ; R_f = 0.2, 0.3 (hexane/AcOEt 1/1).

2,3-Epoxy-(*N,N*)-diethyl-2-methyl-3-phenylbutanamide (3c): ^1H NMR (200 MHz, CDCl_3): δ = 7.38-7.28 (m, 10 H), 3.79-3.23 (m, 8 H), 1.58 (s, 6 H), 1.28 (t, J = 7.1 Hz, 6 H), 1.21-1.14 (m, 6 H), 1.19 (s, 6 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 168.9 (C), 139.2 (C), 127.8 (CH), 127.0 (CH), 125.9 (CH), 66.2 (C), 66.1 (C), 41.2 (CH₂), 39.4 (CH₂), 22.4 (CH₃), 17.2 (CH₃), 13.9 (CH₃), 12.3 (CH₃); IR (neat): $\tilde{\nu}$ = 2973, 1644, 1463, 1381, 1103 cm^{-1} ; R_f = 0.2 (hexane/AcOEt 3/1).

2,3-Epoxy-(*N,N*)-diethyl-2-methyl-3-phenylpentanamide (3d): ^1H NMR (200 MHz, CDCl_3): δ = 7.41-7.21 (m, 10 H), 3.91-3.82 (m, 8 H), 2.25-2.05 (m, 2 H), 1.51-1.34 (m, 2 H), 1.27 (t, J = 6.9 Hz, 3 H), 1.25 (t, J = 6.9 Hz, 3 H), 1.20-1.12 (m, 6 H), 1.16 (s, 3 H), 1.15 (s, 3 H), 0.84 (t, J = 7.4 Hz, 3 H), 0.83 (t, J = 7.4 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ = 169.2 (C), 137.3 (C), 127.8 (CH), 127.1 (CH), 126.8 (CH), 70.2 (C), 67.2 (C), 41.5 (CH_2), 39.7 (CH_2), 28.8 (CH_2), 17.9 (CH_3), 14.3 (CH_3), 12.5 (CH_3), 8.9 (CH_3); IR (neat): $\tilde{\nu}$ = 2972, 1637, 1460, 1380, 1072 cm^{-1} ; R_f = 0.2 (hexane/AcOEt 3/1).

2,3-Epoxy-(*N,N*)-diisopropyl-2-methyl-3-phenylpentanamide (3e): ^1H NMR (200 MHz, CDCl_3): δ = 7.52-7.08 (m, 10 H), 4.56-4.45 (m, 1 H), 4.15-4.00 (m, 1 H), 3.49-3.30 (m, 2 H), 2.21-2.04 (m, 2 H), 1.61 (d, J = 6.4 Hz, 3 H), 1.49-1.19 (m, 23 H), 1.12 (s, 3 H), 1.07 (s, 3 H), 0.80 (t, J = 7.4 Hz, 6 H); ^{13}C NMR (50 MHz, CDCl_3): δ = 169.0 (C), 168.8 (C), 137.5 (C), 137.3 (C), 128.1 (CH), 127.8 (CH), 127.2 (CH), 127.0 (CH), 126.7 (CH), 126.3 (CH), 70.9 (C), 70.4 (C), 67.4 (C), 67.1 (C), 48.5 (CH), 48.4 (CH), 46.0 (CH), 45.5 (CH), 29.0 (CH_2), 27.7 (CH_2), 21.3 (CH_3), 20.9 (CH_3), 20.6 (CH_3), 20.5 (CH_3), 20.4 (CH_3), 20.2 (CH_3), 19.9 (CH_3), 19.7 (CH_3), 17.9 (CH_3), 16.7 (CH_3), 9.0 (CH_3), 8.8 (CH_3); IR (neat): $\tilde{\nu}$ = 2970, 1637, 1445, 1373, 1038 cm^{-1} ; R_f = 0.3 (hexane/AcOEt 5/1).

4a

4d