

Advanced
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Supporting Information

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Supplementary Information to

'Heterogeneous Raney Nickel and Cobalt catalysts for Racemization and Dynamic Kinetic Resolution of Amines'

by

Andrei N. Parvulescu, Pierre A. Jacobs and Dirk E. De Vos

The enantiomeric excess and enantiomeric purities of the reactants and products were determined with GC(HP-6890) on a CP-CHIRASIL-DEX CB chiral column (25m) with an FID detector using racemic mixtures or pure chiral compounds as references. In the analysis of the racemization reactions, the aliphatic amines were typically transformed to the corresponding amides by adding two drops of acetic anhydride and two drops of triethylamine to the GC vial (2ml). The corresponding amides were also identified with a Agilent 6890-N GC-MS and an Agilent 5973 mass spectrometer on a 30 m HP-5MS column.

1-phenylethylamine: chiral GC analysis: 25 min at 70°C, heating at 15°C per min to 150°C, and finally 10 min at 150°C; t_S = 14.3 min, t_R = 13.4 min. **N-(1-phenylethyl)-2-methoxyacetamide:** t_S = 31.3 min, t_R = 31.6 min; m/z 77 (21%), 79 (15%), 89 (1%), 91 (5%), 105 (100%), 119 (10%), 132 (10%), 146 (4%), 161 (12%), 163 (6%), 178 (7%), 193 (10%).

1-(p-methoxyphenyl)ethylamine: chiral GC analysis: 15 min at 80°C, heating at 2°C per min to 98°C, keeping at 98°C for 10 min, heating at 10°C per min to 150°C and finally 10 min at 150°C; t_S = 28.5 min, t_R = 28.1 min.

1-(p-tolyl)ethylamine: chiral GC analysis: 5 min at 100°C, heating at 3°C per min to 155°C, keeping at 155°C for 5 min, heating at 20°C per min to 200°C and finally 5 min at 200°C; t_S = 4.3 min, t_R = 4.1 min. **N-1-(p-tolyl)ethyl methoxyacetamide:** t_S = 19.0 min, t_R = 19.9 min; m/z 77(11%), 79(3%), 89(3%), 91(32%), 105(12%), 115(6%), 119(100%), 132(10%), 146(7%), 160(25%), 174(6%), 192(10%), 207(15%)

1-(p-fluorophenyl)ethylamine: chiral GC analysis: 25 min at 70°C, heating at 15°C per min to 150°C, and finally 10 min at 150°C; t_S = 19.5 min, t_R = 18.4 min.

N-methyl-N-(1-phenylethyl)amine: chiral GC analysis: 25 min at 70°C, heating at 15°C per min to 150°C, and finally 10 min at 150°C; t_S = 10.9 min, t_R = 12.0 min.

1-(1-Naphthyl)ethylamine: chiral GC analysis: 25 min at 80°C, heating at 15°C per min to 170°C, and finally 20 min at 170°C; t_S = 31.0 min, t_R = 31.3 min.

1-(2-Naphthyl)ethylamine: chiral GC analysis: 5 min at 100°C, heating at 3°C per min to 155°C, keeping at 155°C for 5 min, heating at 20°C per min to 200°C and finally 5 min at 200°C; t_S = 18.6 min, t_R = 18.4 min.

1-Aminotetralin: chiral GC analysis: 5 min at 100°C, heating at 3°C per min to 155°C, keeping at 155°C for 5 min, heating at 20°C per min to 200°C and finally 5 min at 200°C; t_S = 12.4 min, t_R = 12.7 min. **N-(1,2,3,4-tetrahydro-1-naphthalenyl)-2-methoxyacetamide:** t_S = 25.7 min, t_R = 26.1 min; m/z 77(6%), 91(26%), 103(4%), 115(18%), 120(2%), 130(100%), 146(9%), 159(8%), 186(8%), 219(3%).

2-Phenylglycinol: chiral GC analysis: 5 min at 100°C, heating at 3°C per min to 155°C, keeping at 155°C for 5 min, heating at 20°C per min to 200°C and finally 5 min at 200°C. This compound was acetylated before analysis: t_S = 23.4 min, t_R = 23.1 min.

1-Cyclohexylethylamine: chiral GC analysis: 5 min at 100°C, heating at 3°C per min to 155°C, keeping at 155°C for 5 min, heating at 20°C per min to 200°C and finally 5 min at 200°C. This compound was transformed to the corresponding acetamide before analysis: t_S = 13.0 min, t_R = 13.9 min. **N-(1-cyclohexylethyl)-2-methoxyacetamide,** t_S = 15.6 min, t_R = 16.2 min; m/z 79(1%), 81(5%), 85(6%), 88(2%), 90(25%), 95(2%), 111(3%), 116(100%), 154(6%), 169(1%).

2-Hexylamine: chiral GC analysis: 5 min at 100°C, heating at 3°C per min to 155°C, keeping at 155°C for 5 min, heating at 20°C per min to 200°C and finally 5 min at 200°C. This compound was transformed to the corresponding acetamide before analysis: t_S = 4.0 min, t_R = 4.8 min. **N-(2-hexyl)-2-methoxyacetamide:** t_S = 6.0 min, t_R = 6.8 min; m/z 72(1%), 84(4%), 85(26%), 86(6%), 88(4%), 90(15%), 91(1%), 98(4%), 114(1%), 116(100%), 128(26%), 130(4%), 143(16%), 158(3%).

2-Heptylamine: chiral GC analysis: 5 min at 100°C, heating at 3°C per min to 155°C, keeping at 155°C for 5 min, heating at 20°C per min to 200°C and finally 5 min at 200°C. This compound was transformed to the corresponding acetamide before analysis: t_S = 6.7 min, t_R = 7.9 min. **N-(2-heptyl)-2-methoxyacetamide:** t_S = 9.3 min, t_R = 10.4 min; m/z

72(2%), 86(7%), 88(3%), 90(19%), 92(1%), 99(4%), 112(3%), 116(100%), 130(3%), 142(27%), 144(2%), 157(6%), 172(5%).

2-Octylamine: chiral GC analysis: 5 min at 100°C, heating at 3°C per min to 155°C, keeping at 155°C for 5 min, heating at 20°C per min to 200°C and finally 5 min at 200°C. This compound was transformed to the corresponding acetamide before analysis: t_S = 9.9 min, t_R = 10.9 min. ***N*-(2-octyl)-2-methoxyacetamide:** t_S = 12.7 min, t_R = 13.3 min. *m/z* 71(28%), 85(11%), 90(11%), 116(100%), 156(45%), 172(10%), 201(5%).

1-Methyl-3-phenylpropylamine: chiral GC analysis: 5 min at 100°C, heating at 3°C per min to 155°C, keeping at 155°C for 5 min, heating at 20°C per min to 200°C and finally 5 min at 200°C. This compound was acetylated before analysis: t_S = 19.8 min, t_R = 20.4 min. ***N*-(1-methyl-3-phenylpropyl)-2-methoxyacetamide:** t_S = 22.4 min, t_R = 22.8 min. *m/z* 72(1%), 77(10%), 79(6%), 85(46%), 87(3%), 91(100%), 104(8%), 117(69%), 120(1%), 130(4%), 132(17%), 176(42%), 191(2%), 221(4%).

2-Methylpiperidine: chiral GC analysis: 5 min at 100°C, heating at 3°C per min to 155°C, keeping at 155°C for 5 min, heating at 20°C per min to 200°C and finally 5 min at 200°C. This compound was acetylated before analysis: t_S = 9.2 min, t_R = 8.7 min.