Supporting Informations

Beckmann Rearrangement of Oximes under Very Mild Conditions

Lidia De Luca, Giampaolo Giacomelli, and Andrea Porcheddu

All solvents and reagents were used as obtained from commercial source. The oximes were prepared according standard methods and their purities were established before utilization by melting point. Standard ^1H NMR and ^{13}C NMR were recorded at 300 and 75.4 MHz, from CDCl_3 solutions. All runs were conducted at least in duplicate. The structures of the acyclic amides were confirmed by saponification and identification of the acid and/or amine components. The nitrile were identified by comparison with samples prepared according to known procedures too. In particular, ϵ -caprolactam, benzonitrile and 2-hydroxybenzonitrile were identified by comparison with commercial products (Aldrich).

Acetanilide: from acetophenone oxime, m. p. $114\text{ }^\circ\text{C}^1$ (1.35 g, 100%).

***N*-(2-hydroxyphenyl)acetanilide:** (from 2-hydroxyacetophenone oxime) m. p. $209\text{ }^\circ\text{C}^1$ (1.13 g, 75%), ^1H NMR δ 9.03 (bs, 1H), 8.79 (s, 1H), 7.38 (m, 1H), 7.02 (m, 2H), 6.85 (m, 1H), 2.24 (s, 3H); ^{13}C NMR δ 169.5, 147.5, 126.1, 124.6, 121.2, 116.6, 22.8.

***N*-(3-hydroxyphenyl)acetanilide:** (from 3-hydroxyacetophenone oxime) m. p. $149\text{ }^\circ\text{C}^1$ (1.51 g, 100%), ^1H NMR δ 9.23 (bs, 1H), 8.94 (s, 1H), 7.33 (s, 1H), 7.05 (t, 1H), 6.89 (d, 1H), 6.54 (d, 1H), 2.08 (s, 3H); ^{13}C NMR δ 169.1, 157.5, 139.6, 129.3, 111.0, 110.7, 107.2, 24.2.

***N*-(4-hydroxyphenyl)acetanilide:** (from 4-hydroxyacetophenone oxime) m. p. $168\text{ }^\circ\text{C}^1$ (1.21 g, 80%), ^1H NMR δ 9.39 (bs, 1H), 8.92 (s, 1H), 7.55 (d, 1H), 6.95 (d, 1H), 2.04 (s, 3H); ^{13}C NMR δ 167.4, 153.0, 130.1, 120.9, 115.0, 24.3.

***N*-(2-nitrophenyl)acetanilide:** (from 2-nitroacetophenone oxime) m. p. $94\text{ }^\circ\text{C}^1$ (1.08 g, 60%), ^1H NMR δ 9.94 (s, 1H), 8.04 (d, 1H), 7.62 (d, 1H), 7.53 (t, 1H), 7.38 (d, 1H), 2.26 (s, 3H); ^{13}C NMR δ 170.1, 142.5, 134.6, 131.3, 130.0, 128.5, 124.2, 23.2.

***N*-(3-nitrophenyl)acetanilide:** (from 3-nitroacetophenone oxime) m. p. $155\text{ }^\circ\text{C}^1$ (1.44 g, 80%), ^1H NMR δ 8.82 (s, 1H), 8.37 (s, 1H), 8.08 (t, 1H), 7.80 (d, 1H), 7.47 (d, 1H), 2.27 (s, 3H); ^{13}C NMR δ 170.0, 150.5, 140.8, 132.6, 129.5, 124.7, 121.4, 20.2.

2-methyl-*N*-phenylpropanamide: (from *iso*-propyl phenyl ketone oxime) m. p. $105\text{ }^\circ\text{C}^1$ (1.38 g, 85%), ^1H NMR δ 8.38 (s, 1H), 7.54 (m, 2H), 7.23 (m, 2H), 7.00 (t, 1H), 2.52 (m, 1H), 1.15 (d, 6H); ^{13}C NMR δ 175.2, 138.1, 128.8, 124.0, 120.0, 36.5, 19.5.³

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¹ Vogel's *Textbook of Practical Organic Chemistry* Longman Ed. 5th ed, **1989**.

² Maran, F.; Vianello, E: *J. Chem. Soc. Perkin Trans. II* **1987**, 33.

³ Metz, P.; Mues, C. *Tetrahedron* **1988**, *44*, 6841.

2,2-dimethyl-*N*-benzoylethylamine: (from *tert*-butyl phenyl ketone oxime) (1.60 g, 91%), ¹HNMR δ 8.45 (s, 1H), 7.64-7.41 (m, 4H), 7.15 (t, 1H), 1.35 (s, 9H); ¹³CNMR δ 166.8, 133.6, 131.1, 128.0, 127.6, 51.5, 28.2.⁴

2,2-dimethyl-*N*-acetylethylamine: (from *tert*-butyl methyl ketone oxime) (1.06 g, 91%), ¹HNMR δ 8.55 (s, 1H), 1.92 (s, 3H), 1.35 (s, 9H); ¹³CNMR δ 171.2, 53.4, 28.7, 24.4.⁵

***N*-(2-naphtyl)acetamide:** (from 2-naphtyl methyl ketone oxime) (1.84 g, 100%), ¹HNMR δ 8.58 (s, 1H), 8.17 (s, 1H), 7.73 8m, 3H), 7.42-7.38 (m, 3H), 2.20 (s, 3H); ¹³CNMR δ 169.2, 135.5, 133.8, 130.6, 128.6, 127.6, 127.5, 126.4, 125.0, 120.2, 117.0, 24.4.⁶

ϵ -Caprolactam: (from cyclohexanone oxime) m. p. 72°C (1.13 g, 100%).

1,3,4,5-tetrahydrobenzo[*b*]azepin-2-one: (from ϵ -tetralone oxime) (1.61 g, 100%), m. p. 141 °C, ¹HNMR δ 8.85 (bs, 1H), 7.24-7.01 (m, 4H), 2.85-2.70 (m, 2H), 2.35-2.16 (m, 4H); ¹³CNMR δ 137.8, 134.0, 129.5, 127.4, 125.5, 121.8, 32.7, 30.3, 28.5.⁷

Benzonitrile: (from benzaldehyde oxime) (1.03 g, 100%).

4-hydroxybenzonitrile: (from 4-hydroxybenzaldehyde oxime) m. p. 111°C⁸ (1.19 g, 100%).

2-hydroxybenzonitrile: (from 2-hydroxybenzaldehyde oxime) m. p. 93°C (1.19 g, 100%).

4-chlorobenzonitrile: (from 4-chlorobenzaldehyde oxime) m. p. 96°C¹ (1.37 g, 100%).

3,7-dimethyloct-6-enenitrile: (from citronellal oxime) (1.61 g, 100%), b. p. 96 °C/ 12 mm.⁹

⁴ Tsutsui, H.; Ichikawa, T.; Narasaka, K.: *Bull. Chem. Soc. Jpn.* **1999**, 72, 1869.

⁵ Yadav, V. K.; Babu, K. G.; Mittal, M. *Tetrahedron* **2001**, 57, 7047.

⁶ Boykin, D. W.; Deadwyler, G. H.; Baumstark, A. L. *Magn. Reson. Chem.* **1988**, 26, 19.

⁷ Grunewald, G. L.; Dahanukar, V. H. *J. Heterocyclic Chem.* **1994**, 31, 1609.

⁸ Konvar, D. Boruah, R. C., Sandhu, S. *Tetrahedron Lett.* **1990**, 31, 1063.

⁹ Herschmann, C. *Helv. Chim. Acta* **1949**, 32, 2537.