

REDUCTION OF O-ACYL OXIMES WITH
SODIUM BOROHYDRIDE / IODINE SYSTEM

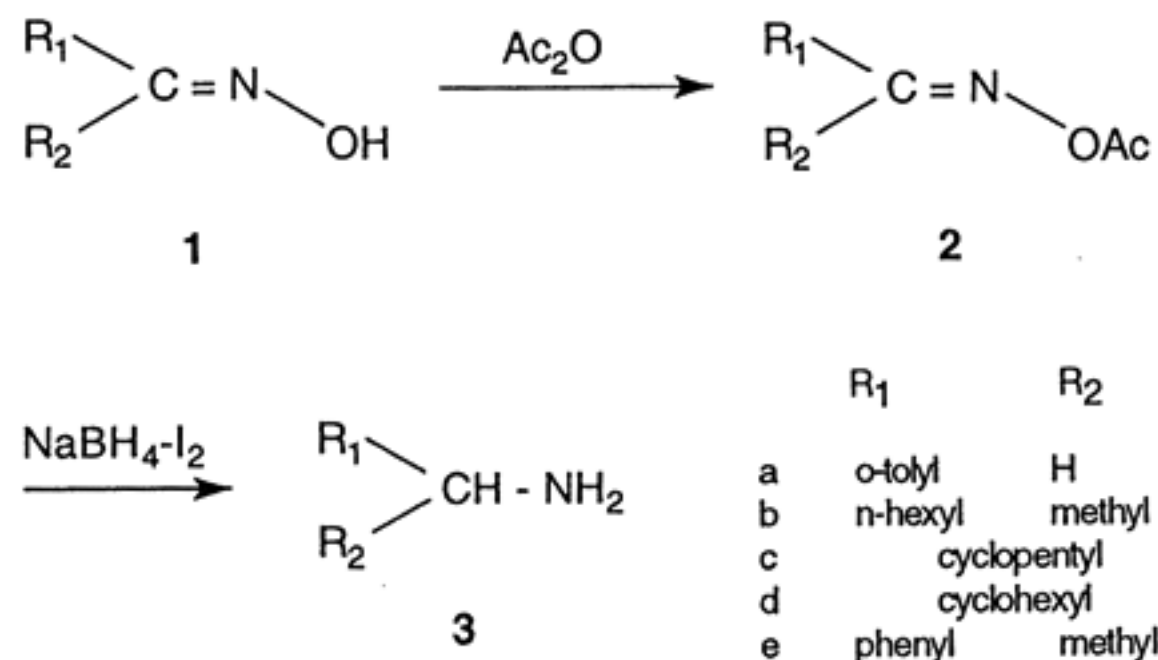
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ABSTRACT: O-acyl derivatives of aldoximes and ketoximes are reduced in good yields to the corresponding amines with sodium borohydride-iodine system.

Recent paper¹ on the reduction of aromatic oximes with borohydride system prompts us to report our results on the transformation of oximes to amines.

This reaction is widely used and the subject has recently been reviewed². Sodium borohydride does not reduce oximes under ambient conditions but efforts have been made to increase its reactivity with additives. So Periasamy et al³ have recently reported the reduction of carboxylic acids and derivatives using the sodium borohydride / iodine system.



We here report our work to reduce oximes with this system. Whereas it leads to a mixture of compounds with oximes, the reduction of O-acyl oximes with sodium borohydride / iodine affords good yields of the corresponding amines whatever the structure of the starting carbonyl compound (aldehydes like aliphatic, cyclic and aromatic ketones). This method avoids the preliminary preparation of diborane which is the better reagent for this reaction. Results are summarised in table.

EXPERIMENTAL

NMR spectra are recorded on a Bruker AC 300 spectrometer in deuteriochloroform. High resolution mass spectrum is recorded on a Kratos Concept II HH instrument.

O-acetylation of oxime **1b** (typical procedure)

A mixture of 2-octanone oxime **1b** (1g, 7 mmol), acetic anhydride (10.82g, 105 mmol) and pyridine (20 ml) is stirred at 0°C for twelve hours, diluted with 20 ml of chloroform and 40 ml of water. The acetic acid is neutralised with sodium hydrogenocarbonate and the organic layer is washed until neutrality; after drying over magnesium sulfate and removal of the solvent, the residue is distilled.

Table - Reduction of O-acyl oximes with sodium borohydride / iodine system

oxime	2 → 3 %	1 → 3 %
1a	73	59
1b	90	86
1c	64	60
1d	79	69
1e	65	59

Reduction of O-acetyl oxime **2b** (typical procedure)

A mixture of 2-octanone O-acetyloxime **2b** (0.96g, 6.7 mmol), sodium borohydride (1.2g, 32 mmol) and 20 ml tetrahydrofuran is cooled at 0°C. A solution of iodine (3g, 12 mmol) in tetrahydrofuran (20 ml) is slowly added at this temperature and the mixture is then refluxed for three hours. After cooling at 0°C, the mixture is acidified with a 3 N solution of hydrochloric acid and concentrated. The residue is diluted with chloroform (30 ml) and water (20 ml); the solution is made alkaline with potassium hydroxide and the aqueous layer is extracted with 20 ml of chloroform. The organic layers are dried on potassium carbonate and distilled.

Compound **2a**: mp = 55-56°C; bp = 100 / 1,5; ¹H RMN: 2.12 (s, 3H, CH₃CO), 2.34 (s, 3H, CH₃Ar), 7.12 (t, 2H, H-3, H-5), 7.23 (t, 1H, H-4), 7.72 (d, 1H, H-6), 8.50 (s, 1H, CH=N); ¹³C RMN: 19.6 (2 CH₃), 128.4 and 138.1 (C-1 and C-2), 126.2, 128.0, 131.0, 131.3 (C-3, C-4, C-5, C-6), 154.7 (C=N), 168.8 (C=O). Mass spectrum (FAB) calculated for C₁₀H₁₂NO₂: 178.0868; Found: 178.0861.

Compound **2b**⁴: bp = 96°C / 10; ¹H RMN: 0.74 (t, 3H, H-8), 1.15 (m, 6H, H-5, H-6, H-7), 1.40 (m, 2H, H-4), 1.83 and 1.88 (s, 3H, H-1 E and Z), 2.01 (s, 3H, CH₃CO), 2.19 and 2.27 (m, 2H, H-3 E and Z).

Compound **2c**⁵ : bp = 140°C / 12 ; ¹H RMN : 1.58 (m, 4H, H-3 and H-4), 1.90 (s, 3H, CH₃CO), 2.30 (m, 4H, H-2 and H-5) ; ¹³C RMN : 19.3 (CH₃), 24.3 and 24.8 (C-3 and C-4), 28.9 and 31.1 (C-2 and C-5), 168.5 (CO), 175.0 (C-1).

Compound **2d**⁶ : bp = 127°C / 18 ; ¹H RMN : 1.26 (m, 6H, H-3, H-4 and H-5), 1.73 (s, 3H, CH₃CO), 1.93 and 2.13 (2m, 4H, H-2 and H-6).

Compound **2e**⁷ : bp = 112°C / 1.5 ; ¹H RMN : 2.21 (s, 3H, CH₃CO), 2.34 (s, 3H, CH₃C=N), 7.38 (m, 3H, H-3, H-4, H-5), 7.70 (m, 2H, H-2 and H-6) ; ¹³C RMN : 14.4 (CH₃CN), 19.8 (CH₃CO), 127.0 (C-2 and C-6), 128.5 (C-3 and C-5), 130.6 (C-4), 134.8 (C-1), 162.4 (C=N), 168.9 (C=O).

Compound **3a**⁸ : bp = 96°C / 10 ; ¹H RMN : 1.88 (bs, 2H, NH₂), 2.31 (s, 3H, CH₃), 3.80 (s, 2H, CH₂), 7.14-7.29 (m, 4H, aromatic) ; ¹³C RMN : 18.8 (CH₃), 44.0 (CH₂), 126.2 (C-5), 126.9 and 127.0 (C-4 and C-6), 130.3 (C-3), 135.4 (C-2), 141.0 (C-1).

Compound **3b**⁹ : bp = 76°C / 15 ; ¹H RMN : 0.65 (t, 3H, H-8), 0.83 (d, 3H, H-1), 1.05 (m, 10H, H-3, H-4, H-5, H-6, H-7), 1.52 (s, 2H, NH₂), 2.66 (m, 1H, H-2) ; ¹³C RMN : 13.8 (C-8), 22.4 (C-7), 23.6 (C-4), 26.2 (C-1), 29.2 (C-5), 31.6 (C-6), 39.9 (C-3), 46.7 (C-2).

Compound **3c**¹⁰ : bp = 24°C / 18 ; ¹H RMN : 1.10-1.80 (m with bs at 1.87, 10H, H-2, H-3, H-4, H-5, NH₂), 3.20 (m, 1H, H-1) ; ¹³C RMN : 23.7 (C-3 and C-4), 36.0 (C-2 and C-5), 53.1 (C-1).

Compound **3d**¹¹ : bp = 41°C / 20 ; ¹H RMN : 0.85-1.85 (m with bs at 1.27, 12H, H-2, H-3, H-4, H-5, H-6, NH₂), 2.5 (m, 1H, H-1) ; ¹³C RMN : 25.1 (C-3 and C-5), 25.6 (C-4), 36.8 (C-2 and C-6), 50.4 (C-1).

Compound **3e**¹² : bp = 85°C / 10 ; ¹H RMN : 1.32 (d, 3H, CH₃, J = 6.7), 2.01 (bs, 2H, NH₂), 4.02 (q, 1H, CH), 7.17-7.30 (m, 5H, aromatic) ; ¹³C

RMN : 25.6 (CH₃), 51.2 (CH), 125.7 (C-2 and C-6), 126.8 (C-4), 128.5 (C-3 and C-5), 147.6 (C-1).

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