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Didier Barbry [a] & Philippe Champagne [a]
[a] Laboratoire de Chimie Organique et Environnement, Université des Sciences et Technologies de Lille, B[acaron]timent C4, 59655, Villeneuve d'Ascq Cédex, France

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

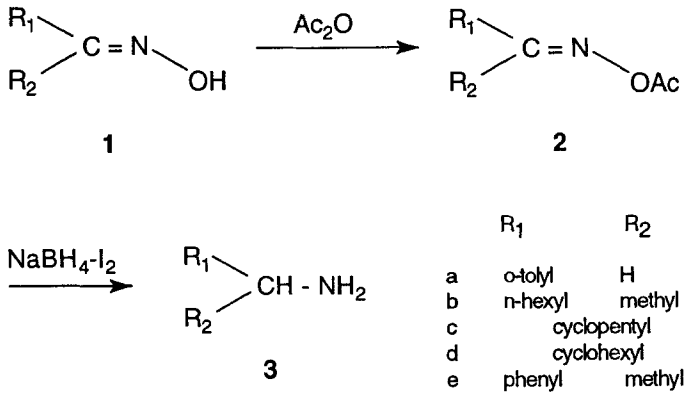
Didier Barbry * and Philippe Champagne

Laboratoire de Chimie Organique et Environnement
Bâtiment C4
Université des Sciences et Technologies de Lille
59655 Villeneuve d'Ascq Cédex - France

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

Recent paper[1] 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 reviewed[2]. Sodium borohydride does not reduce oximes under ambient conditions but efforts have been made to increase its reactivity with additives. So Periasamy et al[3] 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 deuterochloroform. 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 ; ^{1}H RMN : 2.12 (s, 3H, CH_3CO), 2.34 (s, 3H, CH_3Ar), 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) ; ^{13}C RMN : 19.6 (2 CH_3), 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 $C_{10}H_{12}NO_2$: 178.0868 ; Found : 178.0861.

Compound **2b**[4] : bp = 96°C / 10 ; ^{1}H 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, CH_3CO), 2.19 and 2.27 (m, 2H, H-3 E and Z) .

Compound **2c**[5] : bp = 140°C / 12 ; ^{1}H RMN : 1.58 (m, 4H, H-3 and H-4), 1.90 (s, 3H, CH_3CO), 2.30 (m, 4H, H-2 and H-5) ; ^{13}C RMN : 19.3 (CH_3), 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 ; ^{1}H RMN : 1.26 (m, 6H, H-3, H-4 and H-5), 1.73 (s, 3H, CH_3CO), 1.93 and 2.13 (2m, 4H, H-2 and H-6).

Compound **2e**[7] : bp = 112°C / 1.5 ; ^{1}H RMN : 2.21 (s, 3H, CH_3CO), 2.34 (s, 3H, $CH_3C{=}N$), 7.38 (m, 3H, H-3, H-4, H-5), 7.70 (m, 2H, H-2 and H-6); ^{13}C RMN : 14.4 ($\underline{C}H_3CN$), 19.8 ($\underline{C}H_3CO$), 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 ; ^{1}H RMN : 1.88 (bs, 2H, NH_2), 2.31 (s, 3H, CH_3), 3.80 (s, 2H, CH_2), 7.14-7.29 (m, 4H, aromatic) ; ^{13}C RMN : 18.8 (CH_3), 44.0 (CH_2), 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 ; ^{1}H 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, NH_2), 2.66 (m, 1H, H-2) ; ^{13}C 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 ; ^{1}H RMN : 1.10-1.80 (m with bs at 1.87, 10H, H-2,H-3, H-4, H-5, NH_2), 3.20 (M, 1H, H1) ; ^{13}C 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 ; ^{1}H RMN : 0.85-1.85 (m with bs at 1.27, 12H, H-2,H-3, H-4, H-5, H-6, NH_2), 2.5 (m, 1H, H-1) ; ^{13}C 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 ; ^{1}H RMN : 1.32 (d, 3H, CH_3, J= 6.7), 2.01 (bs, 2H, NH_2), 4.02 (q, 1H, CH), 7.17-7.30 (m, 5H, aromatic) ; ^{13}C

RMN : 25.6 (CH_3), 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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