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Note

A cleaner approach for reduction of some symmetric diimines using $NaBH_4$

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Symmetric diimines have been reduced to their corresponding amines by means of $NaBH_4$ using THF as a solvent at room temperature. The reaction time and yield are 3-4 hr and 77-93%, respectively. Reduction process is very effective, inexpensive and clean for the synthesis of symmetric diamines in good yield. The structures of the compounds are supported by FTIR, mass spectrometry, ^1H and ^{13}C NMR spectral data.

Keywords: $NaBH_4$ reduction, symmetric diamines, symmetric diimines, spectral data

Schiff bases constitute an area of rapidly growing interest because they form the basis of novel chemistry[1,2], interesting physical properties[3,4] and important biological activity[5,6]. Imines can be effectively reduced to amines by several reducing agents[7-9]. Sodium borohydride is a powerful reducing agent and has been employed in the reduction of a range of functional groups[10-11]. In the present work an effort has been made to reduce some symmetric double Schiff bases by $NaBH_4$, which is a simple, safe and inexpensive reagent, and reduction can be achieved within 3-4.5 hr.

Results and Discussion

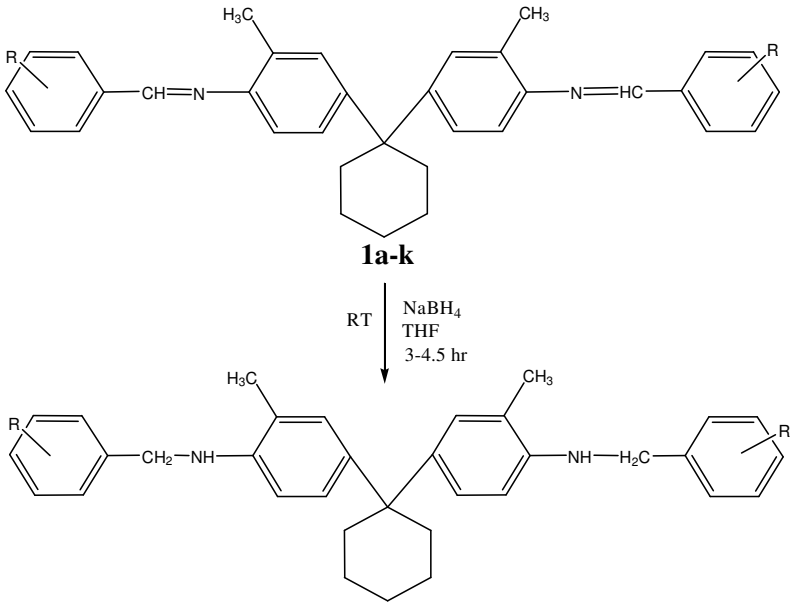
This article describes very simple methodologies developed for effective reduction of various symmetric diimines using sodium borohydride as a reducing agent. Similar methodologies have been found effective in reducing ketones to alcohols in an aprotic solvent[12]. Several structurally varied and symmetrical aldimines underwent reduction by this procedure to produce the corresponding secondary amines in high yields[13]. Sodium borohydride thus appears to be a very efficient reagent for the reduction of imines to the corresponding amines in high yields. Moreover, the easy availability of the reagent, operational simplicity and generality makes this procedure extremely attractive. The procedure does not require anhydrous conditions, is inexpensive and avoids the use of inert atmosphere.

Experimental Section

Solvents and chemicals used in the present investigation were of LR grade and used either as such or purified by fractional distillation. Symmetric double Schiff bases **(1a-k)** were synthesized and recrystallized according to procedures described in a recent work[14]. Melting points were determined in open capillary tubes and are uncorrected. Homogeneity of the compounds was checked by TLC and purified by column chromatography by using ethyl acetate:hexane (40:60 v/v) solvent system. IR spectra (KBr pellets) were scanned on a Shimadzu FTIR-8400 spectrometer. The ^1H and ^{13}C NMR spectra were scanned on a Brucker FTNMR (400 MHz) spectrometer by using $CHCl_3$ as a solvent and TMS as an internal standard. Mass spectra were scanned on a Shimadzu GC-MS-QP 2010 spectrometer by using E.I. (0.7 kV) detector. The ion source temperature was 220°C and interface temperature was 240°C.

General procedure for reduction of symmetric double Schiff bases

Into a 100 mL flask 0.01 mole symmetric Schiff base **(1a-k)** and 20 mL THF were placed in an ice bath and 0.03 mole $NaBH_4$ was added pinch wise during 15 min with stirring. After complete addition of $NaBH_4$, the reaction mixture was stirred at RT for 3-4 hr. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mass was transferred to a 250 mL separating funnel containing 20 mL diethyl ether and washed repeatedly with water till $NaBH_4$ was removed completely. The separated organic layer was dried over anhydrous sodium sulphate and the solvent was evaporated to dryness. The products **(2a-k**, **Scheme I)** were purified by column chromatography using ethyl acetate:hexane (40:60 v/v) as eluent. The homogeneity of **(2a-k)** was checked by TLC using appropriate solvent system. Analytical data of **2a-k** are presented in **Table I**.



1a, **2a** : R=H
1b, **2b** : R= 2-OH
1c, **2c** : R= 4-OH
1d, **2d** : R= 4-OCH_3
1e, **2e** : R= 2- NO_2
1f, **2f** : R= 3- NO_2
1g, **2g** : R= 4- NO_2
1h, **2h** : R= 4-N $(CH_3)_2$
1i, **2i** : R= 2-Cl
1j, **2j** : R= 3-Cl
1k , **2k** : R= 4-Cl

Scheme I

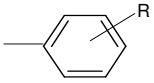
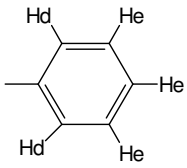
2a: ^{1}H NMR ($CDCl_3$): δ 1.258 (s, 6H, β + γ -CH_2-), 2.024 (s, 10H, α -CH_2- + -CH_3 h), 4.245 (s, 4H, -CH_2-), 6.148-6.165 (d, 2H, -NH, *J* = 8), 6.738-6.764 (d-d, 2H, Ar-Ha, *J* = 4), 6.857 (s, 2H, Ar-Hb), 7.358-7.401 (q, 2H, Ar-Hc, *J* = 8), 7.569-7.584 (d, 4H, Ar-Hd, *J* = 8) , 7.725-7.746 (d, 6H, Ar-He, *J* = 8); ^{13}C NMR ($CDCl_3$): δ 12.4, 21.9, 27.7, 39.7, 40.3, 57.4, 112.7, 122.0, 126.2, 126.5, 127.1, 128.3, 129.9, 131.3, 141.7, 142.4; IR (KBr): 3358.6, 2930.2, 2856.4, 1512.5, 1454.2, 1142.9, 1025.3, 982.1, 751.3 cm^1; MS: *m/z* 475, 474, 437, 470, 428, 401, 323, 323, 194, 168, 129, 115, 104, 91, 77.

2b: ^{1}H NMR ($CDCl_3$): δ 1.528-1.536 (d, 6H, β + γ -CH_2-), 2.159-2.206 (d, 10H, α -CH_2- + -CH_3 h), 3.656 (s, 2H, -NH), 4.388 (s, 4H, –CH_2-), 6.786-6.807(d, 2H, Ar-Hc, *J* = 8.4), 6.853-6.898 (d-d, 4H, Ar-Ha+b, *J* = 5.1), 7.037-7.062 (d, 4H, Ar-Hg+e, *J* = 10.4), 7.143-7.161 (d, 2H, Hf, *J* = 7.2), 7.201-7.243 (m, 2H, Hd), 8.654 (s, 2H, Ar-OH); ^{13}C NMR ($CDCl_3$): δ 18.0, 23.0, 26.4, 37.1, 44.8, 48.5, 113.3, 116.6, 119.9, 123.0, 125.0, 125.6, 128.8, 129.1, 129.2, 141.1, 142.4, 157.0; IR (KBr): 3560.7, 3323.6, 2914.5, 2852.8, 1587.4, 1454.3, 1151.5, 1031.9, 976.0, 723.3 cm^{-1}; MS: *m/z* 506, 400, 357, 331, 294, 279, 251, 223, 144, 132, 120, 107, 94, 77.

2c: ^{1}H NMR ($CDCl_3$): δ 1.142 (s, 6H, β + γ -CH_2-), 2.015 (s, 10H, α -CH_2- + -CH_3 h), 4.256 (s, 4H, -CH_2-), 6.148-6.150 (t, 2H, -NH *J* = 8), 6.628-6.634 (m, 4H, Ar-Ha+b), 6.841-6.862 (m, 2H, Ar-Hc), 7.154-7.156 (d-d, 4H, Ar-Hd, *J* = 4), 7.245-7.274 (d-d, 4H, Ar-He, *J* = 4),8.248 (s, 2H, Ar-OH); ^{13}C NMR ($CDCl_3$): δ 16.0, 21.5, 28.5, 39.7, 42.1, 45.8, 112.3, 115.4, 117.8, 123.4, 125.3, 128.1, 129.8, 132.4, 140.9, 158.2; IR (KBr): 3545.7, 3318.4, 2925.6, 2852.1, 1592.6, 1442.8, 1140.1, 1024.5, 965.3, 725.9 cm^{-1}; MS: *m/z* 506, 400, 357, 331, 294, 279, 251, 223, 144, 132, 120, 107, 94, 77.

2d: ^{1}H NMR ($CDCl_3$): δ 1.442 (s, 6H, β + γ -CH_2-), 2.025 (s, 10H, α -CH_2- + -CH_3 h), 2.751 (s, 6H, Ar-OCH_3) 4.328 (s, 4H, -CH_2-), 6.382- 6.435 (t, 2H, -NH, *J* = 8), 6.886-7.014 (m, 4H, Ar-Ha+b), 7.107-7.179 (m, 2H, Ar-Hc), 7.511-7.540 (d-d, 4H, Ar-Hd, *J* = 4), 8.165-8.195 (d-d, 4H, Ar-He, *J* = 4); ^{13}C NMR ($CDCl_3$): δ 13.1, 20.5, 28.6, 38.1, 40.5, 58.4, 60.4,

Table I — Analytical data of 1,1′-bis[4-N(R-benzyl)-3-methylphenyl]cyclohexane **2a-k**

Compd		m.p.	TLC data		Reaction	Yield
		°C	Solvent system v/v	R_f value	time hr	(%)
2a		115	CF: MeOH 90 : 10	0.62	3.5	79
2b		80	CF : MeOH 90 : 10	0.71	3.0	80
2c		104	CF : MeOH 90 : 10	0.78	4.0	80
2d		165	CF : MeOH 90 : 10	0.74	4.0	82
2e		160	EA-Hex. 20:80	0.54	4.0	82
2f		98	EA-Hex. 20:80	0.63	3.0	77
2g		127	EA-Hex. 20:80	0.47	3.0	82
2h		143	EA-Hex. 20:80	0.46	3.5	82
2i		138	EA-Hex. 20:80	0.59	4.0	80
2j		120	EA-Hex. 20:80	0.50	3.5	93
2k		124	EA-Hex. 20:80	0.58	4.0	83

CF = Chloroform; EA = Ethylacetate

113.5, 115.8, 123.1, 126.2, 128.6, 129.3, 131.0, 134.7, 140.1, 160.0; IR (KBr): 3493.2, 2929.9, 2848.9, 1572.4, 1452.4, 1251.8, 1182.4, 1030.0, 1014.5, 976.0, 746.8 cm^{-1}; MS: *m/z* 535, 534, 533, 530, 487, 396, 379, 353, 262, 238, 223, 121, 91, 77.

2e: ^{1}H NMR ($CDCl_3$): δ 1.364 (s, 6H, β + γ -CH_2-), 2.275 (s, 10H, α -CH_2- + -CH_3h), 4.354 (s, 4H, -CH_2-), 6.146-6.168 (d, 2H, -NH, *J* = 8), 6.874-6.893 (d, 2H, Ar-Ha, *J* = 4, 6.924 (s, 2H, Ar-Hb), 7.102-7.127 (d, 2H, Ar-Hc, *J* = 8, 7.265-7.281 (d, 2H, Ar-Hf, *J* = 8), 7.426-7.446 (d, 2H, Ar-He, *J* = 8), 7.668-7.673 (d-d, 2H, Ar-Hg, *J* = 4), 8.015 (s, 2H, Ar-Hd); ^{13}C NMR ($CDCl_3$): δ 12.0, 21.9, 27.7, 39.7, 40.3, 48.8, 112.7, 124.3, 125.8, 127.2, 128.9, 129.4, 130.2, 132.5, 134.4, 137.5, 141.7, 147.0; IR (KBr): 3491.8, 2935.7, 2854.7, 1516.1, 1453.4, 1344.4, 1141.9, 1014.5, 991.4, 746.8 cm^{-1}; MS: *m/z* 564, 563, 562, 519, 493, 384, 368, 234, 207, 144, 130, 120, 106, 91, 78.

2f: ^{1}H NMR ($CDCl_3$): δ 1.325 (s, 6H, β + γ -CH_2-), 2.024 (s, 10H, α -CH_2- + -CH_3 h), 4.328 s, 4H, -CH_2-), 5.974-5.997 (d, 2H, -NH, *J* = 8), 6.847-6.875 9d, 2H, Ar-Ha, *J* = 4), 6.942 (s, 2H, Ar-Hb), 7.214-7.238 (d,

2H, Ar-Hc, *J* = 8), 7.542-7.564 (d, 2H, Ar-Hf, *J* = 8), 7.741-7.765 (d, 2H, Ar-He, *J* = 8, 7.918-8.937 (d, 2H, Ar-Hg, *J* = 4), 8.125 (s, 2H, Ar-Hd); ^{13}C NMR ($CDCl_3$): δ 12.8, 20.4, 26.2, 40.5, 42.1, 58.4, 111.3, 122.4, 123.0, 126.2, 129.2, 129.9, 131.3, 133.2, 141.7, 143.3, 148.2; IR (KBr): 3350.4, 2933.8, 2858.6, 1523.8, 1444.7, 1340.5, 1171.1, 1021.8, 983.1, 786.9 cm^{-1}; MS: *m/z* 564, 563, 562, 519, 493, 429, 384, 234, 220, 144, 130, 120, 106, 91, 78.

2g: ^{1}H NMR ($CDCl_3$): δ 1.491-1.499 (d, 6H, β + γ -CH_2-), 2.164 (s, 4H, α -CH_2-) 2.356 (s, 6H, -CH_3 h), 4.46 (s, 4H, -CH_2-), 6.339-6.377 (t, 2H, -NH *J* = 7.6), 6.886-7.014 (m, 4H, Ar-Ha+b), 7.107-7.18 (m, 2H, Ar-Hc), 7.511-7.540 (d-d, 4H, Ar-Hd, *J* = 2.8), 8.165-8.195(d-d, 4H, Ar-He, *J* = 3.2); ^{13}C NMR ($CDCl_3$): δ 12.4, 21.9, 27.7, 39.7, 40.3, 57.4, 112.7, 122.0, 123.4, 126.2, 128.0, 129.9, 131.3, 141.7, 148.5, 149.4; IR (KBr): 3491.2, 2935.7, 2854.7, 1516.1, 1446.6, 1344.4, 1141.9, 1014.5, 991.4, 746.4 cm^{-1}; MS: *m/z* 564, 563, 562, 519, 493, 429, 384, 234, 220, 144, 130, 120, 106, 91, 78.

2h: ^{1}H NMR ($CDCl_3$): δ 1.348 (s, 6H, β + γ -CH_2-), 2.347 (s, 10H, α -CH_2- + -CH_3 h), 2.864 (s, 12H, -$N(CH_3)_2$), 3.482 (s, 4H, -CH_2-), 4.327 (s, 2H, -NH), 6.421-6.446 (d, 2H, Ar-Ha, *J* = 8.4), 6.586-6.604 (d-d, 4H, Ar-Hb+c, *J* = 5.1), 6.954-6.983 (d, 4H, Ar-Hd *J* = 10.4), 7.128-7.146 (d, 4H, Ar-He *J* = 7.2); ^{13}C NMR ($CDCl_3$): δ 13.5, 20.2, 28.6, 40.3, 42.1, 43.6, 58.6, 113.4, 114.5, 122.3, 125.7, 127.9, 129.4, 130.2, 131.3, 140.2, 141.7; IR (KBr): 3452.4, 2954.9, 2850.2, 1518.7, 1461.1, 1372.5, 1170.3, 1025.4, 984.1, 752.4 cm^{-1}; MS: *m/z* 561, 560, 559, 556, 513, 487, 366, 251, 236, 147, 134, 122, 107, 91, 77.

2i: ^{1}H NMR ($CDCl_3$): δ 1.503 (s, 6H, β + γ -CH_2-), 2.184 (s, 10H, α -CH_2- + -CH_3 h), 4.447 (s, 4H, -CH_2-), 6.395-6.415 (d, 2H, -NH, *J* = 8), 6.907-6.993 (m, 4H, Ar-Ha+b), 7.470-7.510 (m, 2H, Ar-Hc), 7.707-7.726 (d, 2H, Ar-Hg, *J* = 8), 7.821-7.842 (d, 2H, Ar-He, *J* = 8.4), 8.098-8.122 (d, 2H, Ar-Hf, *J* = 9.6), 8.216 (s, 2H, Ar-Hd); ^{13}C NMR ($CDCl_3$): δ 12.8, 23.4, 29.1, 37.6, 39.3, 55.4, 111.4, 120.0, 126.1, 127.4, 128.3, 129.4, 131.1, 131.9, 133.4, 134.8, 139.8, 141.3; IR (KBr): 3402.5, 2931.9, 2856.6, 1564.3, 1450.5, 1199.7, 1049.3, 995.8, 769.6, 752.1 cm^{-1}; MS: *m/z* 543, 542, 499, 471, 402, 359, 333, 268, 234, 206, 127, 125, 89, 77.

2j: ^{1}H NMR ($CDCl_3$): δ 1.124 (s, 6H, β + γ -CH_2-), 2.024 (s, 10H, α -CH_2- + -CH_3 h), 3.954 (s, 4H, -CH_2-), 5.128-5.143 (d, 2H, -NH, *J* = 8), 6.429-6.443 (d, 2H, Ar-Ha, *J* = 8), 6.642 (s, 2H, Ar-Hb), 6.926-6.948 (d, 2H, Ar-Hc, *J* = 8), 7.184-7.196 (d, 2H, Ar-Hf, *J* = 4.8), 7.296-7.315 (d, 2H, Ar-He, *J* = 7.6), 7.465-7.483 (d, 2H, Ar-Hg, *J* = 7.2), 7.953 (s, 2H, Ar-Hd); ^{13}C NMR ($CDCl_3$): δ 12.4, 20.8, 26.5, 37.6, 39.5, 48.3, 113.4, 123.6, 125.4, 125.9, 126.2, 129.6, 129.9, 130.7, 131.3, 135.2, 141.5, 142.8; IR (KBr): 3479.7, 2931.9, 2858.6, 1564.3, 1446.6, 1143.1, 1033.8, 984.2, 769.6, 738.1 cm^{-1}; MS: *m/z* 543, 542, 499, 471, 402, 359, 333, 268, 234, 206, 127, 125, 89, 77.

2k: ^{1}H NMR ($CDCl_3$): δ 1.154 (s, 6H, β + γ -CH_2-), 2.026 (s, 10H, α -CH_2- + -CH_3 h), 4.325 (s, 4H, -CH_2-), 6.238-6.271 (t, 2H, -NH *J* = 8), 6.725-6.764 (m, 4H, Ar-Ha+b), 7.065-7.102 (m, 2H, Ar-Hc), 7.261-7.293 (d-d, 4H, Ar-Hd, *J* = 4), 7.414 -7.442 (d-d, 4H, Ar-He, *J* = 4); ^{13}C NMR ($CDCl_3$): δ 14.3, 20.5, 28.6, 40.4, 42.6, 59.4, 111.9, 121.5, 125.4, 129.4, 129.8, 130.4, 133.1, 133.8, 140.5, 142.5; IR (KBr): 3446.9, 2931.9, 2860.5, 1514.1, 1452.4, 1180.4, 1012.6, 937.4, 748.5 cm^{-1}; MS: *m/z* 543, 542, 499, 471, 402, 359, 333, 268, 234, 206, 127, 125, 89, 77.

Conclusion

A convenient reduction procedure by means of $NaBH_4$ has been shown to convert aromatic diimines into corresponding amines. The structures of all the amines are supported by FTIR, ^{1}H and ^{13}C NMR and mass spectroscopic techniques. The developed method is simple, inexpensive and safe for the one-pot reduction of imines.

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References

1 Syamal A & Maurya M R, *Coord Chem Rev,* 95, **1989**,183.
2 Gibson V C & Spitzmesser S K, *Chem Rev,* 103, **2003**, 283.
3 Marcos M, Serrano J L & Sierra T, *Chem Mater,* 5, **1993**, 1332.
4 Ghedini M, Pucci D, Cesarotti E, Francescangeli O & Bartolino R, *Liq Cryst,* 15, **1993**, 331.
5 Gopinathan S, Deshpande S S & Gopinatha C, *Synth React Inorg Met-Org Chem,* 19, **1989**, 321.
6 Chan A S, Chen C C, Lin C W, Cheng M C & Peng S M, *J Chem Soc Chem Commun,* 17, **1995**, 1767.
7 Fujii M, Aida T, Yoshihara M & Ohno A, *Bull Chem Soc Japan,* 62, **1989**, 3845.
8 Schlesinger H I, Brown H C, Hoekstra H R & Rapp L R, *J Am Chem Soc,* 75, **1953**, 199.
9 Banik B K, Hackfeld L & Becker F F, *Synth Commun,* 31, **2001**, 1581.

10 Tsukinoki T, Mitoma Y, Nagashima S, Kawaji T, Hashimoto I & Tashiro M, *Tetrahedron Lett,* 39, **1998**, 8873.
11 Periasamy M, Devasagayaraj A, Satyanarayana N & Narayana C, *Synth Commun,* 19, **1989**, 565.
12 Yakabe S, Hirano M & Morimoto T, *Synth Commun,* 29, **1999**, 295.
13 Ranu B C, Sarkar A & Majee A, *J Org Chem,* 62, **1997,** 1841.
14 Gangani B J & Parsania P H, *Spect Lett,* 40, **2007**, 97.