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# Formation of the Boron Chelates in the Sodium Borohydride Reduction of the Schiff Bases

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Billman and Diesing[1] reported that the C=N bond of *o*- or *o*′-hydroxy Schiff bases could not be reduced with sodium borohydride in boiling methanolic solutions. Failure of the reduction was ascribed to the resonance stabilization of the Schiff bases (VIIa↔VIIb) in alkaline media. For the purpose of synthesizing the chelating reagents for the spectrophotometric determination of the metal ions,[2] the reduction of a number of Schiff bases with sodium borohydride in the methanolic solutions at 50°C, was attempted and the results are summarized.

When *o*- or *o*′-monohydroxy compounds are reduced, the expected benzylaniline derivatives are precipitated as crystals merely by the acidification of the reaction mixture with dilute acetic acid (procedure A). The Schiff bases having hydroxyl groups on *o*- and *o*′-positions such as Ig and Ih could also be reduced with sodium borohydride, as evidenced by the disappearance of the orange color of the Schiff bases. However, the expected product IIIg or IIIh does not crystallize upon the acidification of the reaction mixture with acetic acid. Therefore, the isolation of the soluble reaction products from the acidified solution was attempted, and the boron chelate *O,O,N*-(*o,o*′-dihydroxybenzylanilino)-borane (Va) was obtained as crystals by the evaporation of the solvents in a vacuum at room temperature (procedure C). The chelate Va was easily dehydrated to give VIa by sublimation in a vacuum at 130—135°C, indicating a weakly coordinated water molecule of Va. The mass spectral data of Va and VIa, and the structures of the ionic species involved are listed in Table 3. The structure of Va and VIa were proved by the *m/e* of 223 and other *m/e* values. Some differences were observed in the mode of fragmentation between Va and VIa.

The normal reduction products *o*-, *o*′-dihydroxybenzylaniline derivatives were also obtained by evaporating methanol from the reaction mixture prior to dilution and acidification (procedure B).

The IR spectra of IIIg, Va and Vb are given in Fig. 2. The 3600 cm$^{-1}$ O-H stretching of Va was ascribed to the coordinated water molecule.[3] Two

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[1] J. H. Billman and A. C. Diesink, *J. Org. Chem.*, **22**, 1068 (1957).

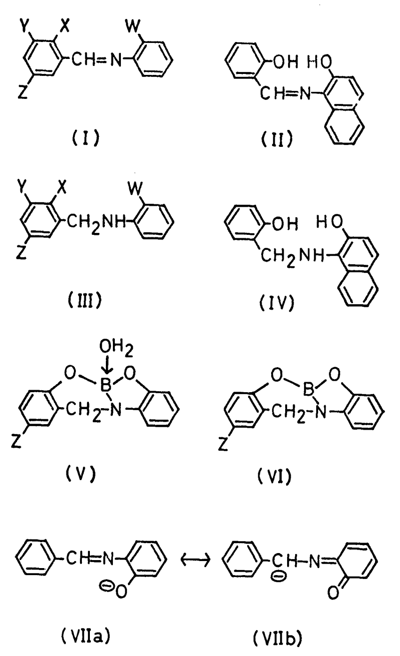
[2] T. Tanaka, This Bulletin, **41**, 1277 (1968).

[3] I. Gamo, *ibid.*, **34**, 761 (1961).

IR peaks of 3490 and 3060 cm$^{-1}$ seem to be due to the vibration related to the boron chelates. The peaks of 1470, 1280, and 1125 cm$^{-1}$ of the boron chelate were ascribed to the B-N,[4] B-O,[5] and C-N stretching vibrations, respectively, in comparison with the IR spectrum of IIIg.

From the results, it was concluded that the isolation of the normal reduction products of Ig and Ih was prevented by the formation of soluble boron chelates in weakly acidic solutions.

The Schiff base II did not yield the boron chelate but gave the normal reduction product. The yellow color of II is also in contrast with the orange-red color of Ig and Ih. It is deduced that the naphthalene ring is prohibited by the steric hindrance from being in a plane containing the C=N double bond and the phenyl ring of II.



| | X | Y | Z | W |
|---|---|---|---|---|
| Ia | OH | $CH_2$-$CH_2$-COOH | $CH_3$ | OH |
| Ib, IIIb | OH | $CH_2$-$CH_2$-COOH | $CH_3$ | H |
| Ic | OH | $CH_2$-$CH_2$-COOH | Cl | OH |
| Id, IIId | OH | $CH_2$-$CH_2$-COOH | Cl | H |
| Ie | OH | $CH_2$-COOH | Br | OH |
| If, IIIf | OH | $CH_2$-COOH | Br | H |
| Ig, IIIg | OH | H | H | OH |
| Ih, IIIh | OH | H | $CH_3$ | OH |
| Ii, IIIi | H | H | H | OH |
| IIIj | OH | H | H | H |

Va, VIa: Z=H; Vb, VIb: Z=$CH_3$

Fig. 1.

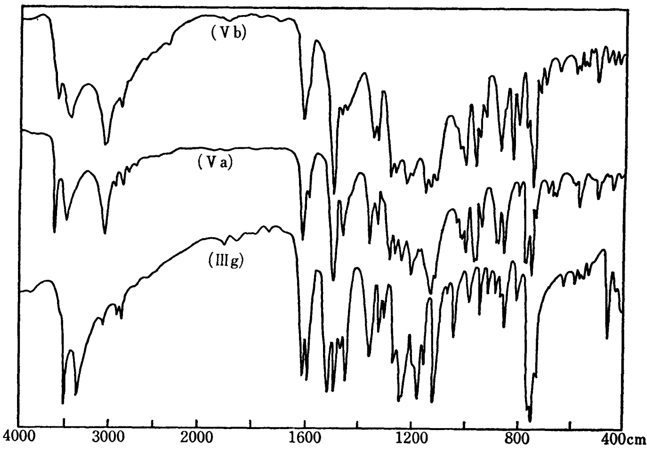


Fig. 2. The IR spectra of (IIIg), (Va), and (Vb).

Table 1. The Schiff bases to be reduced

| | Mp °C | Yield % | Anal. Found (%) C | H | N | Calcd (%) C | H | N |
|---|---|---|---|---|---|---|---|---|
| Ia[a)] | 145—147 | 80 | 64.84 | 6.04 | 4.44 | 64.34 | 6.03 | 4.41[b)] |
| Ib | 110—111 | 81 | 71.95 | 6.11 | 4.88 | 72.02 | 6.05 | 4.94 |
| Ic[a)] | 185—186 | 97 | 60.05 | 4.49 | 4.33 | 60.10 | 4.41 | 4.38 |
| Id | 108 | 99 | 63.48 | 4.72 | 4.62 | 63.27 | 4.65 | 4.61 |
| Ie[a)] | 217 | 55.3 | 51.44 | 3.43 | 3.95 | 51.45 | 3.45 | 4.00 |
| If | 165 | 85.5 | 54.00 | 3.61 | 4.00 | 53.91 | 3.62 | 4.19 |
| II | 195—198[c)] | 54 | 76.65 | 4.85 | 5.22 | 76.38 | 4.90 | 5.24 |

Ig, Ih, Ii: known compounds.

a) The reduction products of these Schiff bases were not identified. They were neither the boron chelate nor the expected reduction product but were a mixture of deoxygenated products.

b) Analytical values of monohydrate.

c) Reported[6)] melting point 230°C.

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4) H. Steinberg and R. J. Brotherton, "Organoboron Chemistry," John Wiley and sons, New York, 1966, vol. 2. pp. 7—8.

5) J. A. Blau, W. Gerrard, M. F. Lappert, B. A. Mountifield, and H. Pyszora, *J. Chem. Soc.*, **1960**, 380.

6) Z. Holzbecher, *Chem. Abstr.*, **48**, 3198d (1952).

TABLE 2. REDUCTION PRODUCTS

| | Procedure | Mp °C | Yield % | Anal. Found (%) | | | Calcd (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | C | H | N |
| IIIb | A | 131—132 | 90 | 71.34 | 6.74 | 4.85 | 71.55 | 6.72 | 4.91 |
| IIId | A | 110 | 69.5 | 62.65 | 5.59 | 4.57 | 62.85 | 5.27 | 4.59 |
| IIIf | A | 142—143 | 62.5 | 53.28 | 4.30 | 4.03 | 53.59 | 4.20 | 4.17 |
| IIIg | B | 88—90 | 86 | | | | | | |
| IIIh | B | 95—96 | 72 | 73.14 | 6.58 | 6.13 | 73.34 | 6.59 | 6.11 |
| IIIi[7] | A | 79 | 50 | | | | | | |
| IIIj | A | 45—46 | 72 | | | | | | |
| IV | A<br>B | 129—131 | 63.3<br>75 | 72.02 | 5.36 | 4.60 | 67.66 | 5.34 | 4.65[a] |
| Va | C | 145—146 | 84.5 | 64.44 | 5.08 | 5.72 | 64.78 | 5.02 | 5.81 |
| | | | | B 4.43[b] | | | B 4.70 | | |
| VIa | | 131—133 | | 69.60 | 4.67 | 6.12 | 70.01 | 4.52 | 6.28 |
| Vb[c] | C | 119—127 | 67 | 67.35 | 5.73 | 5.45 | 65.92 | 5.53 | 5.49 |
| VIb[c] | | 108—112 | | 69.81 | 5.17 | 6.04 | 70.93 | 5.10 | 5.91 |

a) Analytical values of hydrochloride mp 162—165°C.
b) Atomic absorption analysis of aqueous sodium hydroxide solution using aqueous sodium borohydride solution as a reference.
c) The analytical values were not satisfactory owing to difficulty in purification.

TABLE 3. THE MASS SPECTRA OF Va AND VIa

| m/e | Relative intensities (%)[a] | | Possible ionic species |
|---|---|---|---|
| | (Va)[b] | (VIa)[c] | |
| 224 | 7.6 | 19.9 | |
| 223 | 93 | 91 | $C_{13}H_{10}BNO_2^+$ |
| 222 | 100 | 100 | $C_{13}H_9BNO_2^+$ |
| 221 | 24 | 71 | |
| 111 | 11.8 | 24 | $C_{13}H_9BNO_2^{++}$ |
| 77 | | 27 | $C_6H_5^+$ |
| 60 | 29 | | $HBO_3^+$ |
| 45 | 37 | | $H_2BO_2^+$ |
| 43 | 33 | | $BO_2^+$ |
| 39 | | 11.1 | $CH_2BN^+$ |
| 28 | 20.5 | | $CO^+$ |
| 18 | 44 | | $H_2O^+$ |
| 17 | 45 | | $HO^+$ |

a) Ions having relative intensities less than 10% are omitted.
b) Ionizing voltage, 75 eV; ionizing current, 200 μA; sample temperature, 105°C; chamber temperature, 140°C.
c) Ionizing voltage, 75 eV; ionizing current, 100 μA; sample temperature, 135°C; chamber temperature, 110°C.

## Experimental

*Procedure A.* To a solution of 100 mg of the Schiff base Id in 15 m*l* of methanol heated to 50°C, crystals of 50 mg of sodium borohydride were gradually added in small portions after frothing had subsided. The reaction mixture was then cooled, filtered, diluted with 12 m*l* of water, and acidified with dilute acetic acid. The solution became turbid and after a while white crystals separated out. Recrystallization from benzene gave 70 mg of IIId with a melting point 110°C (69.5%).

*Procedure B.* A solution of 1 g of Ig in 20 m*l* of methanol was treated with 114 mg of sodium borohydride as in procedure A. After the reaction was over, methanol was evaporated off in a vacuum at room temperature. The residual purple oil was dissolved in water, and the solution was acidified with dilute acetic acid. White crystals then separated out. Recrystallization from methanol gave 860 mg of IIIg with a melting point 88—90°C (86%).

*Procedure C.* A solution of 4.5 g of Ig in 150 m*l* of methanol was treated with 3.4 g of sodium borohydride as in procedure A. After the reaction was over, the reaction mixture was cooled and diluted with 120 m*l* of water, when the color of the solution turned green. The solution was then acidified with dilute acetic acid, and the color of the solution turned reddish brown. Evaporation of the solvent at room temperature in a vacuum, yielded 4.3 g of gray precipitate of Va (84.5%). UV, λmμ (log ε); 203—5 (4.56), 207 (4.59), 244—5 (3.98), 277 (3.67),[8] 282 (3.70), 292 (3.59)[8] in ethanol; 218 (4.27), 230 (4.02), 275 (3.66),[8] 280 (3.70), 285 (3.66)[8] in cyclohexane.

One gram of Va was sublimed at 130—135°C in a vacuum (5 mmHg), to yield 570 mg of yellow crystals of VIa (61.3%). UV, λ mμ (log ε); 218—220 (4.10), 230 (3.92), 275 (3.53),[8] 280 (3.58), 284 (3.54)[8] in cyclohexane.

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7) B. Witkop and J. B. Patrick, *J. Amer. Chem. Soc.*, **74**, 3865 (1952).

8) These bands are obscure owing to overlapping.