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$FeCl_3(Py)_4$, $FeCl_3[(NH_2)_2CO]_6$ and $FeCl_3[(NH_2)_2CS]_6$ as Efficient Catalysts for the Efficient Reduction of Carbonyl Compounds with $NaBH_4$ under Aprotic Condition

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$FeCl_3(Py)_4$, $FeCl_3[(NH_2)_2CO]_6$ and $FeCl_3[(NH_2)_2CS]_6$ are used as efficient catalysts for reduction of a variety of carbonyl compounds such as aldehydes, ketones, acyloins, α-diketones and conjugated carbonyl compounds with $NaBH_4$ under aprotic condition. The corresponding alcohols are obtained in high to excellent yields. Reduction reactions are performed in CH_3CN at room temperature or reflux.

Key Words: Carbonyl compounds, Catalyst, Iron(III) compounds, Sodium borohydride.

INTRODUCTION

During the past decades, sodium borohydride as a key reagent has played an important role in the reduction of organofunctional groups in modern organic synthesis[1]. This reagent is a relatively mild reducing agent and mostly used for the reduction of aldehydes and ketones in protic solvents. In order to control the reducing power of $NaBH_4$, hundreds of substituted boron hydrides have been made and introduced in chemical literature and many of them are now commercially available. In fact, advances in such field have been realized by: a) substitution of the hydride(s) with other constituents which may exert marked steric or electronic influences upon the reactivity of substituted complex ion[2], b) variation of alkali-metal cation and metal cation in the hydride complex[3], c) a concurrent cation and hydride exchange[4], d) use of amin or phosphin ligands to alter behaviour of the metal hydroborates[5], e) combination of tetrahydroborates with Lewis acids, additives and mixed solvent systems[6], f) changing the cation to quaternary ammonium and phosphonium tetrahydroborates[7], g) use of polymers or solid supports for supporting the hydride species[8]. In this context, the preparations and applications of modified hydroborate agents in organic synthesis[5c,d,9] were extensively reviewed.

The application of Fe(III) in organic synthesis is well known. In the line of outlined strategies, although the reducing properties of sodium borohydride in combination with transition metal salt systems have been intensively investigated[6,9], it was realized that for the use of this reducing agent in the presence of an acidic catalysts or reagents, as far as known, there is no report. So, this subject and efforts for the introduction of modified hydroborate agents in organic synthesis[5c-e,6e,10] encouraged the present investigation into this kind of combination system. This study reported for the first time the use of sodium borohydride in the presence of $FeCl_3$ anhydrous complexes, can reduce efficiently varieties of carbonyl compounds such as aldehydes, ketones, conjugated carbonyl compounds, α-diketones and acyloins to their corresponding alcohols under aprotic condition in acetonitrile at room temperature or reflux.

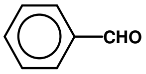
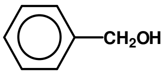
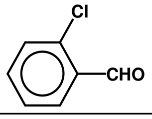
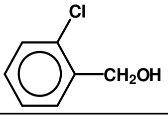
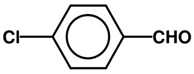
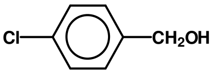
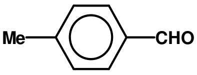
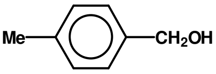
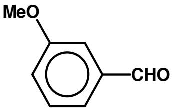
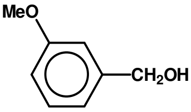
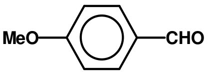
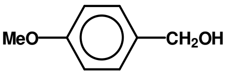
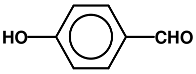
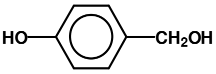
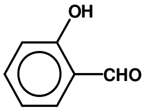
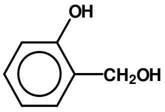
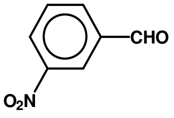
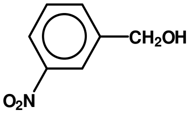
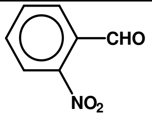
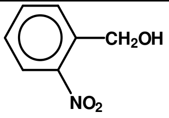
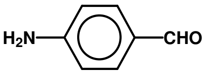
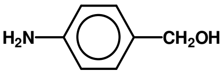
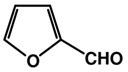
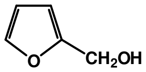
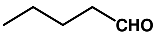
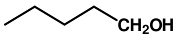
EXPERIMENTAL

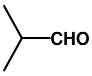
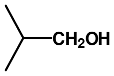
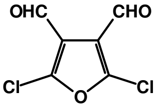
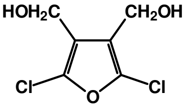
All reagents and substrates of highest quality were obtained from commercial sources and used without further purification. Acetonitrile and other solvents were dried, prior to use, by standard methods. The products were characterized by a comparison with authentic samples (melting or boiling point) and their ^1H NMR or IR spectral data. Molar ratio of $NaBH_4$ used in this study were the minimum amounts for reaching complete conversion of the reactions. The reaction times were the optimum ones. Organic layers were dried with anhydrous sodium sulfate before concentration *in vaccuo*. All yields referred to isolated pure products. TLC accomplished the purity determination of the substrates and products over silica gel PolyGram SILG/UV-254 plates. The progress of reaction was determined by disappearing of the spot of substrates on TLC.

A typical procedure for reduction of aldehydes to alcohols with $NaBH_4/FeCl_3$ anhydrous complexes system: In a round-bottomed flask (15 mL) equipped with magnetic stirrer, charged with a solution of benzaldehyde (0.106 g, 1 mmol) in CH_3CN (3 mL), $NaBH_4$ (0.038 g, 1 mmol) was added. To this mixture, $FeCl_3(py)_4$ (0.034 g, 0.07 mmol) was added immediately and the resulting brown mixture was stirred at room temperature for 1 min. TLC monitored the progress of the reaction (eluent; CCl_4/Et_2O: 5/2). After completion of the reaction, distilled water (3 mL) was added to the mixture and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2 (3 mL × 8 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel (eluent; CCl_2/Et_2O:5/2) affords the pure liquid benzyl alcohol (0.103 g, 96 % yield, Table-1).

A typical procedure for reduction of ketones to alcohols with $NaBH_4$/ $FeCl_3$ anhydrous complexes system: In a round-bottomed flask (15 mL) equipped with a magnetic stirrer and a condenser,to a solution of benzophenone (0.182 g, 1 mmol) in CH_3CN (3 mL), $NaBH_4$ (0.076 g, 2 mmol) was added. To this mixture, $FeCl_3(py)_4$ (0.034 g, 0.07 mmol) was

TABLE-1
REDUCTION OF ALDEHYDES TO ALCOHOLS WITH
$NaBH_4$/Fe(III) COMPLEX SYSTEM[a]

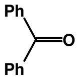
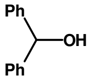
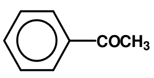
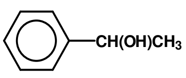
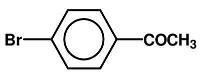
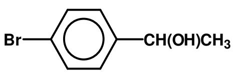
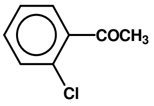
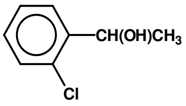
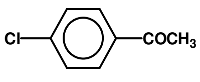
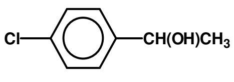
Entry	Substrate	Product	Molar ratio	Time (min)	Yield (%)[b]
1			[c](1:1:0.07) [d](1:0.5:0.04) [e](1:0.5:0.05)	1 6 6	96 97 95
2			[c](1:1:0.07) [d](1:0.5:0.04) [e](1:0.5:0.05)	3 2 1	98 97 98
3			[c](1:1.5:0.07) [d](1:1.5:0.04) [e](1:1:0.05)	4 2 3	96 97 95
4			[c](1:1:0.07) [d](1:1:0.04) [e](1:0.5:0.05)	6 2 7	96 97 95
5			[c](1:1:0.07) [d](1:0.5:0.04) [e](1:0.5:0.05)	5 4 1	96 97 95
6			[c](1:1.5:0.07) [d](1:1:0.04) [e](1:1:0.05)	6 6 1	96 97 95
7			[c](1:1:0.07) [d](1:1.5:0.04) [e](1:1:0.05)	6 9 9	96 97 95
8			[c](1:1:0.07) [d](1:1:0.04) [e](1:1:0.05)	1 1 5	96 97 95
9			[c](1:1:0.07) [d](1:0.5:0.04) [e](1:0.5:0.05)	1 2 2	96 97 95
10			[c](1:1:0.07) [d](1:0.5:0.04) [e](1:0.5:0.05)	1 2 1	96 97 95
11			[c](1:1.5:0.07) [d](1:1:0.04) [e](1:1:0.05)	15 7 7	96 97 95
12			[c](1:1:0.07) [d](1:1:0.04) [e](1:0.5:0.05)	2 4 6	96 97 95
13			[c](1:1:0.07) [d](1:0.5:0.04) [e](1:0.5:0.05)	1 5 5	96 97 95

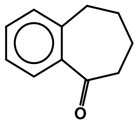
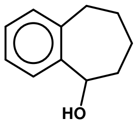
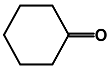
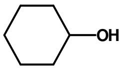
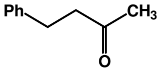
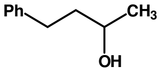
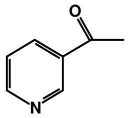
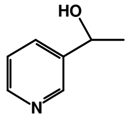
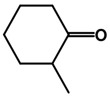
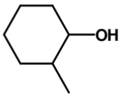
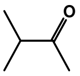
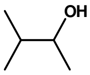
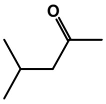
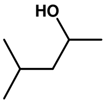
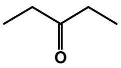
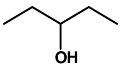
Entry	Substrate	Product	Molar ratio	Time (min)	Yield (%)[b]
14			[c](1:1:0.07) [d](1:0.5:0.04) [e](1:0.5:0.05)	2 6 6	96 97 95
15			[c](1:1:0.07) [d](1:0.5:0.04) [e](1:0.5:0.05)	3 5 4	96 97 95

a) All reactions were performed in CH_3CN at room temperature.
b) Yields refer to isolated pure products.
c) Molar ratio as Subs./$NaBH_4$/$FeCl_3(py)_4$.
d) Molar ratio as Subs./$NaBH_4$/$FeCl_3[(NH_2)_2CS]_6$.
e) Molar ratio as Subs./$NaBH_4$/$FeCl_3[(NH_2)_2CO]_6$.

added immediately and the resulting brown mixture was heated to gentle reflux with stirring. TLC monitored the progress of the reaction (eluent; CCl_4/Et_2O:5/2). After completion of the reaction in 0.5 h, distilled water (3 mL) was added to the reaction mixture and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2 (3 mL × 8 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel (eluent; CCl_4/E_2O:5/2) affords the pure crystals of 1-phenyl benzol (0.178 g, 97 % yield, Table-2).

TABLE-2
REDUCTION OF KETONES TO ALCOHOLS WITH $NaBH_4$/Fe(III) COMPLEX SYSTEM[a]

Entry	Substrate	Product	Molar ratio	Time (min)	Yield (%)[f]
[a]1			[c](1:2:0.07) [d](1:2:0.06) [e](1:2:0.05)	1.25 0.91 0.66	97 96 97
[a]2			[c](1:2:0.07) [d](1:2:0.06) [e](1:2:0.05)	1.50 0.66 1.50	67 96 75
[a]3			[c](1:2:0.07) [d](1:2:0.06) [e](1:2:0.05)	1.41 1.16 1.66	96 97 95
[a]4			[c](1:2:0.07) [d](1:2:0.06) [e](1:2:0.05)	0.08 0.05 0.08	98 97 98
[a]5			[c](1:2:0.07) [d](1:2:0.06) [e](1:2:0.05)	0.83 1.00 1.58	97 96 96

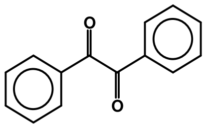
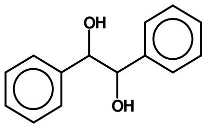
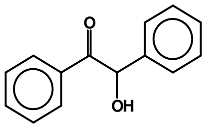
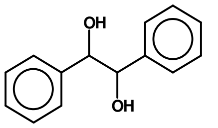
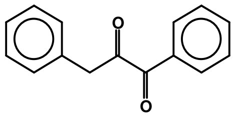
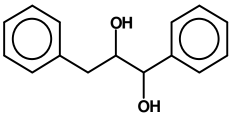
Entry	Substrate	Product	Molar ratio	Time (min)	Yield (%)^f
^{a}6			^{c}(1:2:0.07) ^{d}(1:2:0.06) ^{e}(1:2:0.05)	0.16 0.18 0.16	96 96 96
^{b}7			^{c}(1:2:0.07) ^{d}(1:2:0.06) ^{e}(1:2:0.05)	0.08 0.06 0.08	97 97 98
^{a}8			^{c}(1:2:0.07) ^{d}(1:2:0.06) ^{e}(1:2:0.05)	0.06 0.10 0.08	97 98 96
^{a}9			^{c}(1:2:0.07) ^{d}(1:2:0.06) ^{e}(1:2:0.05)	0.08 0.06 0.05	98 98 98
^{b}10			^{c}(1:2:0.07) ^{d}(1:2:0.06) ^{e}(1:2:0.05)	0.03 0.01 0.03	96 97 98
^{b}11			^{c}(1:2:0.07) ^{d}(1:2:0.06) ^{e}(1:2:0.05)	0.05 0.03 0.10	97 97 98
^{b}12			^{c}(1:2:0.07) ^{d}(1:2:0.06) ^{e}(1:2:0.05)	0.03 0.01 0.08	98 97 98
^{b}13			^{c}(1:2:0.07) ^{d}(1:2:0.06) ^{e}(1:2:0.05)	0.05 0.01 0.03	96 97 96

a) All reactions were performed in CH_3CN under reflux condition.
b) All reactions were performed in CH_3CN at room temperature.
c) Molar ratio as Subs./$NaBH_4$/$FeCl_3(py)_4$.
d) Molar ratio as Subs./$NaBH_4$/$FeCl_3[(NH_2)_2CS]_6$.
e) Molar ratio as Subs./$NaBH_4$/$FeCl_3[(NH_2)_2CO]_6$.
f) Yields refer to isolated pure products.

A typical procedure for reduction of α-diketones and acyloins with $NaBH_4$/$FeCl_3$ anhydrous complexes system: In a round-bottomed flask (15 mL) equipped with magnetic stirrer, $NaBH_4$ (0.057 g, 1.5 mmol) was added to a solution of benzil (0.21 g, 1 mmol) in CH_3CN (3 mL). To this mixture, $FeCl_3(py)_4$ (0.034 g, 0.07 mmol) was added immediately and the resulting brown mixture was stirred at room temperature for 6 min. TLC monitored the progress of the reaction (eluent; CCl_4/Et_2O:5/2). After completion of the reaction, distilled water (3 mL) was added to the mixture and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2 (3 mL

× 8 mL) and dried over anhydrous sodium sulfate. Evaporation of all the volatile materials and short column chromatography of the resulting crude material over silica gel (eluent; CCl_4/Et_2O: 5/2) affords the pure crystals of hydrobenzoin (0.203 g, 96 % yield, Table-3).

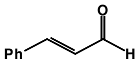
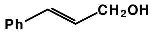
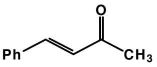
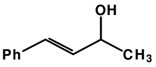
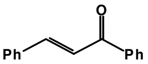
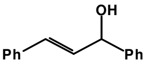
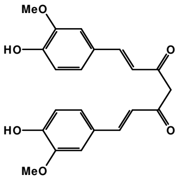
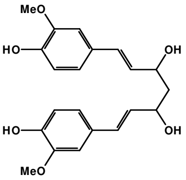
TABLE-3
REDUCTION OF ACYLOINS AND α-DIKETONES WITH $NaBH_4$/Fe(III) COMPLEX SYSTEM[a]

Entry	Substrate	Product	Molar ratio	Time (min)	Yield (%)[b]
1			[c](1:1.5:0.07) [d](1:1.5:0.04) [e](1:1.5:0.05)	6 6 6	96 98 96
2			[c](1:1:0.07) [d](1:1:0.04) [e](1:1:0.05)	1 5 4	98 97 98
3			[c](1:1.5:0.07) [d](1:1.5:0.04) [e](1:1.5:0.05)	5 7 5	96 97 97

a) All reactions were performed in CH_3CN at room temperature.
b) Yields refer to isolated pure products.
c) Molar ratio as Subs./$NaBH_4/FeCl_3(py)_4$.
d) Molar ratio as Subs./$NaBH_4/FeCl_3[(NH_2)_2CS]_6$.
e) Molar ratio as Subs./$NaBH_4/FeCl_3[(NH_2)_2CO]_6$.

A typical procedure for regioselective 1,2-reduction of conjugated enones with $NaBH_4/FeCl_3$ anhydrous complexes system: In a round-bottomed flask (15 mL) equipped with a magnetic stirrer and a condenser, $NaBH_4$ (0.057 g, 1.5 mmol) was added to a solution of benzylideneacetone (0.146 g, 1 mmol) in CH_3CN (3 mL). To this mixture, $FeCl_3(py)_4$ (0.034 g, 0.07 mmol) was added immediately and the resulting brown mixture was stirred at room temperature. TLC monitored the progress of the reaction (eluent; CCl_4/Et_2O:5/2). After completion of the reaction in 55 min, distilled water (3mL) was added to the reaction mixture and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2 (3 mL × 8 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel (eluent; CCl_4/E_2O:5/2) affords the pure 4-phenyl-3-buten-2-ol (0.141 g, 95 % yield, Table-4).

TABLE-4
REDUCTION OF CONJUGATED CARBONYL COMPOUNDS WITH $NaBH_4Fe(III)$ COMPLEX SYSTEM[a]

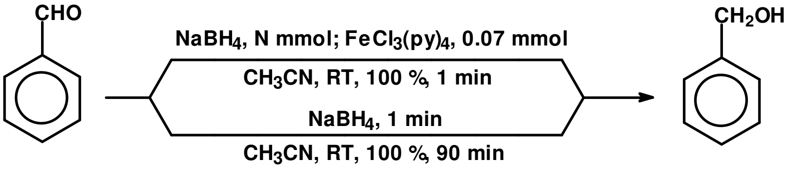
Entry	Substrate	Product	Molar ratio $NaBH_4$/ Subs.	Condition	Ratio 1,2:1,4	Time (min)	Yield (%)[b]
1			[c](1:1:0.07) [d](1:1:0.04) [e](1:1:0.05)	RT	100:0 100:0 100:0	10 10 3	95 96 98
2			[c](1:1.5:0.07) [d](1:2:0.07) [e](1:1.5:0.05)	RT	70:30 80:20 80:20	55 43 55	94 95 94
3			[c](1:1.5:0.07) [d](1:2:0.07) [e](1:1.5:0.05)	RT	75:25 80:20 75:25	104 40 100	95 96 96
4			[c](1:2:0.07) [d](1:2:0.06) [e](1:2:0.05)	RT	100:0 100:0 100:0	11 5 10	94 97 96

a) All reactions were performed in CH_3CN at room temperature.
b) Yields refer to isolated pure products.
c) Molar ratio as Subs./$NaBH_4$/$FeCl_3(py)_4$.
d) Molar ratio as Subs./$NaBH_4$/$FeCl_3[(NH_2)_2CS]_6$.
e) Molar ratio as Subs./$NaBH_4$/$FeCl_3[(NH_2)_2CO]_6$.

RESULTS AND DISCUSSION

Preparation of $FeCl_3$ anhydrous complexes: Three complexes of $FeCl_3$ anhydrous with ligands containing oxygen and nitrogen donor atoms were prepared[11-13] and their formation characterized by infrared spectra and color with those of reported in the literatures[14].

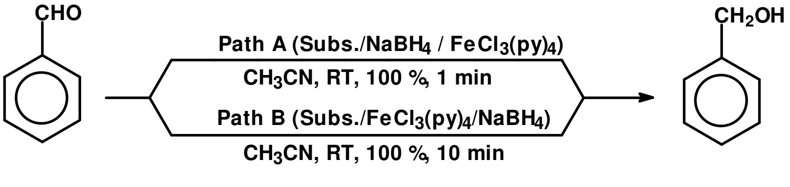
Reduction of aldehydes and ketones: The transformation of aldehydes and ketones to their alcohols is one of the most encountered reactions in the total synthesis of organic molecules[1]. Sodium borohydride is usually used for the reduction of aldehydes and ketones to their corresponding alcohols in protic solvents, especially ethanol or isopropyl alcohol. In the preliminary experiment, it was observed that $NaBH_4$ in the presence of catalytic amount of $FeCl_3(Py)_4$, $FeCl_3[(NH_2)_2CO]_6$ and $FeCl_3[(NH_2)_2CS]_6$ accelerated remarkably the rate of reduction of benzaldehyde under aprotic condition at room temperature (**Scheme-I**).



Scheme-I

These results prompted the present investigation of the optimum reaction conditions for reduction of a variety of carbonyl compounds. For selection of appropriate solvents in such reactions, CH_2Cl_2, THF, CH_3CN and C_6H_6 in which benzaldehyde and acetophenone were adopted as model compounds were examined. The present observations revealed that CH_3CN is a suitable solvent for the reduction.

In addition, it was found that addition order of reaction components plays a role in these reactions. It was observed that in all addition modes in which a stepwise addition of sodium borohydride and $FeCl_3(py)_4$ to a solution of benzaldehyde in acetonitrile (path A), the reduction is much faster than that in a reverse mode of $FeCl_3(py)_4$ and sodium borohydride to a solution of substrate (path B). In the later case, conversion 100 % in 10 min at room temperature could be observed (**Scheme-II**). However, in case where aldehyde is added to the mixture of $FeCl_3(py)_4$ and sodium borohydred in acetonitrile, the reaction is completed in 6 min. Therefore, the addition order of the reaction components in path A (subs in CH_3CN/ $NaBH_4$/$FeCl_3(Py)_4$) was chosen for all other reactions. The same results have also been observed for other Fe(III) catalysts ($FeCl_3[(NH_2)_2CS]_6$ and $FeCl_3[(NH_2)_2CO]_6$) and functional groups. Therefore, the precise order of the reaction components as $NaBH_4$ then $FeCl_3$ anhydrous complex to the solution of substrates were used for all of reduction reactions (path A).



Scheme-II

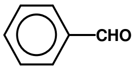
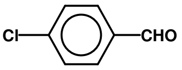
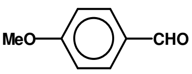
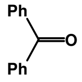
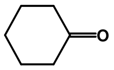
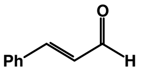
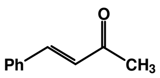
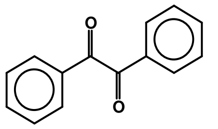
Reduction of a variety of structurally different aromatic and aliphatic aldehydes to their corresponding alcohols is performed efficiently with this reducing system (Table-1). Aldehydes are reduced rapidly with 0.5-1.5 molar equivalent of $NaBH_4$ and in presence of 4-7 mole % of $FeCl_3$ anhydrous complex in CH_3CN at room temperature. The yields are high to excellent (95-98 %). In general, the reduction of aromatic aldehydes bearing an electron-withdrawing group is faster than that of bearing an electron-releasing group. The reduction of ketones requires more drastic conditions: a larger amount of $NaBH_4$ and $FeCl_3$ anhydrous complexes (2 and 0.05-0.07 molar equivalents, respectively) in refluxing acetonitrile are required (Table-2). In the case of $FeCl_3(Py)_4$ and $FeCl_3[(NH_2)_2CO]_6$ no further conversion than 70 and 80 % respectively in even 1.5 h at refluxing could be observed (Table-2, entry 2).The yields are generally higher than 95 % except for acetophenone (67 and 75 %, respectively). The work-up procedure is simple: distilled water was added to the reaction mixture and the resulting mixture was extracted with CH_2Cl_2. The crude products were further purified by a short column chromatography on silica gel. To highlight the efficiency of our reducing system, the results were compared with those achieved by other reported reagents such as $NaBH_4/MoCl_5$[6c], $NaBH_4/TiO(acac)_2$[6d], $NaBH_4$/dowexl-x8[10b], $[Zn(BH_4)_2(bpy)]$[5d] and $[Zn(BH_4)_2(py)]$[5e] (Table-5).

As shown in Tables 1 and 2, aldehydes are generally much reactive than ketones with $NaBH_4/FeCl_3$ complexes system.

Reduction of α-diketones and acyloins: Synthetic application of α-hydroxy ketones and α-diketones are well known and their reductions to vicinal diols[15] and/or acyloins[16] are the subjects of interest in organic synthesis[5c-e]. Reduction of α-diketones usually gives a mixture of α-hydroxy ketones and vicinal diols. In spite of this, some chemical or biochemical reagents can undergo selective reduction of α-diketones to only one of the mentioned products.

Reduction of α-diketones with modified tetrahydroborate agents is also subject of the interest[5c-e,10b] and this goal was easily achieved by $NaBH_4$/Fe(III) catalysts systemes. Sodium borohydride in the presence of catalytic amounts of $FeCl_3$ anhydrous complexes reduces readily α-diketones to their vicinal diols in CH_3CN at room temperature and short reaction times. The present attempts for reduction of α-diketones to acyloins were unsatisfactory and only vicinal diols were detected as products (Table-3) (96-98 %). In addition to the reduction of α-diketones, reduction of acyloins to vicinal diols is also important in organic synthesis. For this transformation using $H_2/CuCr_2O_4$[17], *Saccharomyces cerevisiae* (bakers yeast)[18] and modified tetrahydroborate agents[5c] have been reported. In continuation of this study, this goal was also easily achieved by $FeCl_3$ anhydrous complexes and it was observed that benzoin is reduced to hydrobenzoin efficiently at room temperature in CH_3CN by utilizing $NaBH_4$/Fe(III) complex 1.0-1.5 and 0.04-0.07 molar equivalent, respectively (Table-3). The yields are high to excellent (95-99 %). The results in Table-3 show that the rate of reductions for acyloin compounds is generally faster than α-diketones under the same conditions. In Table-5, a comparison can be seen for reduction of this compound with Fe(III)complexes and other reported reagents.

TABLE-5
COMPARISON OF REDUCTION OF ALDEHYDES AND KETONES TO ALCOHOLS WITH $NaBH_4$/Fe(III) COMPLEX AND OTHER REPORTED REAGENTS

Entry	Substrate	Molar ratio Reag./Subs., Time (min)/Yield (%)							
		I	II	III	IV	V	VI	VII	VIII
1		1^{a}/1/96	0.5^{a}/6/97	0.5^{a}/6/95	$1/^{b}15/93$	1^{c}/3/96	0.25/1/95	1/30/91	0.5/3/96
2		1^{a}/4/98	0.5^{a}/2/95	0.5^{a}/3/96	1^{b}/5/97	1^{c}/9/99	0.25/5/98	1/12/99	0.5/3/98
3		1.5^{a}/6/97	1^{a}/6/96	1^{a}/12/98	1.2^{b}/90/98	1.5^{c}/180/99	0.35/10/99	1/78/96	1/3/98
4		2^{a}/75/97	2^{a}/55/96	2^{a}/40/97	2^{b}/180/98	3^{c}/192/98	1/45/99	2/258/97	2/48/99
5		2^{a}/5/98	2^{a}/4/97	2^{a}/5/97	1^{b}/5/90	1.5^{d}/75/90	0.5/9/88	2/120/89	1.5/25/95
6		1/10/96	1/10/96	1.5/3/98	–	1/42/96	0.5/2/92	1/90/97	0.5/18/98
7		1.5/55/93	2/43/97	1.5/55/96	–	1/84/98	1/78/97	260/97	2/54/96
8		1.5/6/96	1.5/6/98	1.5/5/96	–	–	–	0.5/30/97	2/15/97

I = $NaBH_4/FeCl_3(py)_4$; II = $NaBH_4/FeCl_3[(NH_2)_2CS]_6$; III = $NaBH_4/FeCl_3[(NH_2)_2CO]_6$; IV = $NaBH_4$/TiO(acac)$_2$; V = $NaBH_4$/Dowex 1-x8; VI = Zn $(BH_4)_2$(bpy); VII = $Zn(BH_4)_2$(Py); VIII = $NaBH_4/MoCl_5$

a) In the presence of 5-7 mol % Fe(III) complexes.

b) In the presence of 5-20 mol % TiO(acac)$_2$.

c,d) Referred to using of 10 and 20 mg of Dowex1-x8 per one mmol of substrate, respectively.

Regioselective 1,2-reduction of conjugated enones: A regioselective reduction of α,β-unsaturated aldehydes and ketones to the allylic alcohols is a very important process in organic chemistry. Reduction of α,β-unsaturated carbonyl compounds by sodium borohydride can follow two pathways: addition to carbonyl group (1,2-reduction) to give allylic alcohols or addition to the conjugated double bond (1,4-addition) to give saturated carbonyl compounds.

In spite of substantial evidence, the tendency for sodium borohydride to reduce conjugated enones is highly solvent dependent and generally does not result in a useful regioselectivity[19a-c]. On the other hand, the need for reduction of conjugated enones to the corresponding allylic alcohols has led to the development of several new specific reagents[19d-i]. Selective 1,2-reduction is usually achieved by using modified tetrahydroborate agents,which are formed: a) by the replacement of hydride (s) with sterically bulky substituents or electron-withdrawing/releasing groups in order to discriminate between the structural and electronic environments of the carbonyl groups[20], b) combination with Lewis acids and mixed solvents[21], c) by use of transition metal tetrahydroborates and its new modifications[22], d) by use of quaternary ammonium and phosphonium tetrahydroborates[23] and e) finally, by immobilization on polymeric supports and anion exchange resins[24].

Reduction of α,β-unsaturated aldehydes and ketones by $FeCl_3$ anhydrous complexes proceeds with excellent regioselectivity and final allylic alcohol products are obtained in high yields. Aldehydes are reduced readily with 1.0-1.5 molar equivalent of $NaBH_4$ and 4-7 mol % of $FeCl_3$ anhydrous complexes in CH_3CN at room temperature (95-98 %), but the reduction of ketones required drastic reaction conditions of higher molar ratios of $NaBH_4$ and $FeCl_3$ anhydrous complexes (2-1.5 and 0.05-0.07 molar equivalents, respectively) in CH_3CN at room temperature. The efficiency of the reactions was also excellent to provide the corresponding secondary allylic alcohols in (94-98 %) (Table-4).

For showing the efficiency of Fe(III) complexes for 1,2-regioselective reduction of α,β-unsaturated carbonyl compounds, the results were compared with other reported reagents such as $NaBH_4/MoCl_5$, $NaBH_4/TiO(acac)_2$, $NaBH_4$/dowexl-x8, $[Zn(BH_4)_2(bpy)]$ and $[Zn(BH_4)_2(py)]$ (Table-5). Investigation of the results shows that in most cases, this new reducing systemes is more efficient or comparable (Table-5).

Conclusion

The catalytic effect of $FeCl_3$ complexes in the reduction reactions with sodium borohydride have not been cleared, but it was investigated that one or two of the following factors might play a role in the catalytic function of $FeCl_3(Py)_4$, $FeCl_3[(NH_2)_2CO]_6$ and $FeCl_3[(NH_2)_2CS]_6$: a) Lewis acidity character of $FeCl_3$ complexes, b) formation of the new reductant species as $FeCl_{3-x}(L)_{n-y}(BH_4)_{x+y}$, c) formation of the ferric boride that actively catalyzes the decomposition of borohydride.

In conclusion, the study has shown that $NaBH_4/FeCl_3$ anhydrous complex system reduces aldehydes and ketones to their corresponding alcohols and α,β-unsaturated carbonyl compounds to their corresponding allylic alcohols. This reducing system is also efficient for the reduction of α-diketones and acyloins to their corresponding vicinal diols. Excellent regioselectivity, convenient procedure, mild reaction conditions, high yields of the products as well as a simple work-up procedure affords this system to be an attractive method for a synthetically useful methodology.

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