

A Mild and Convenient Method for the Reduction of Carbonyl Compounds with NaBH_4 in the Presence of Catalytic Amounts of MoCl_5

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NaBH_4 with catalytic amounts of MoCl_5 can readily reduce a variety of carbonyl compounds such as aldehydes, ketones, acyloins, α -diketones and conjugated enones to their corresponding alcohols in good to excellent yields. Reduction reactions were performed under aprotic condition in CH_3CN at room temperature or reflux. In addition, the chemoselective reduction of aldehydes over ketones was accomplished successfully with this reducing system.

Key Words : Reduction, Sodium borohydride, MoCl_5 , Carbonyl compounds, Alcohols

Introduction

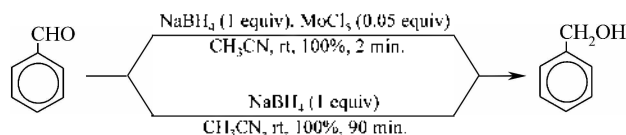
The discovery of NaBH_4 in 1942 brought about revolutionary changes in the procedures for the reduction of functional groups in organic synthesis. However, it should be pointed out that in spite of their great convenience, this reagent suffers from certain limitations: NaBH_4 is a remarkably mild reducing agent and reduces only aldehydes and ketones in protic solvents. Consequently, the rate of reductions is sometimes slow and a relatively low selectivity is accompanied with the reactions. This situation made it desirable to develop means for controlling the reducing power of such reagent. Therefore, controlling the reducing power of sodium borohydride has been one of the main interests for organic chemists in many years. In fact, advances in such a field have been realized by: a) substitution of the hydride(s) with other groups which may exert marked steric and electronic influences upon the reactivity of the substituted complex ion, b) variation in the alkali metal cation and metal cation in the complex hydride which would alter the reducing power of the reagent, c) by concurrent cation and hydride exchange, d) use of ligands to alter behavior of the metal hydrides, e) combination of borohydrides with metal, metal salts, Lewis acids, mixed solvent systems or some other agents, f) changing the cation to quaternary and phosphonium borohydrides, and g) finally use of the polymers and solid beds for supporting the hydride species. Modification of borohydride agents and their applications in organic synthesis have been extensively reviewed.¹⁻⁵ In the line of outlined strategies, although the reducing properties of sodium borohydride in combination with metal halides have been intensively investigated,⁶ in our literature survey we could not find any report for the combination of NaBH_4 with MoCl_5 . Therefore, in continuation of our efforts towards the development of new borohydride systems,^{2-4,7} we decided to investigate the reducing properties of NaBH_4 in the presence of MoCl_5 for

the reduction of a variety of carbonyl compounds with the hope that this system shows good selectivity and/or efficiencies. Now we wish to report a mild and efficient method for reduction of aldehydes, ketones, α -diketones, acyloins and α,β -unsaturated carbonyl compounds to their corresponding alcohols with a $\text{NaBH}_4/\text{MoCl}_5$ system.

Results and Discussion

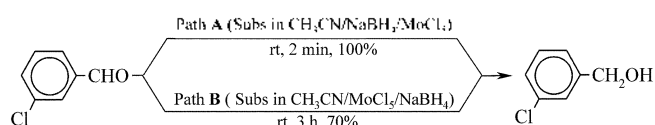
Reduction of Aldehydes and Ketones. Sodium borohydride is usually used for the reduction of aldehydes and ketones to their corresponding alcohols in protic solvents, especially ethanol or isopropyl alcohol. In our preliminary experiment we observed that by NaBH_4 in the presence of catalytic amount of MoCl_5 accelerated remarkably the rate of reduction of benzaldehyde under aprotic condition at room temperature (Scheme 1). Although NaBH_4 alone is very slightly soluble in CH_3CN , but in the presence of MoCl_5 its solubility increases tremendously accompanied by the color change to deep brown.

These results prompted us to investigate the optimum reaction conditions for the reduction of a variety of carbonyl compounds. For the selection of appropriate solvents in such reactions, we examined Et_2O , CHCl_3 , CH_2Cl_2 , CH_3CN and THF in which 3-chlorobenzaldehyde and benzophenone were adopted as model compounds. Our observations reveal that THF and CH_3CN are suitable for the reduction, but the reductions in CH_3CN provides faster and more efficient than in THF. In addition, we found that addition order of reaction components plays a role in these reactions. We observed that in all addition modes in which a stepwise addition of sodium borohydride and MoCl_5 to a solution of 3-chlorobenzaldehyde in acetonitrile (Path A), the reduction is much



Scheme 1

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Scheme 2

faster than that in a reverse mode of MoCl₅ and sodium borohydride to a solution of substrate (Path B). In the later case, no further conversion than 70% in even 3 h at room temperature could be observed (Table 1, entry 3) (Scheme 2). However, in case where aldehyde is added to the mixture of MoCl₅ and sodium borohydride in acetonitrile, the reaction is completed in 10 min. Therefore, we choose the addition order of the reaction components in Path A (Subs in CH₃CN/NaBH₄/MoCl₅) for all other reactions.

Table 1. Reduction of Aldehydes with NaBH₄/MoCl₅ System^a

Entry	Substrate	Product	Molar Ratio NaBH ₄ /MoCl ₅ /Subs.	Time (min)	Yield (%) ^b
1			0.5:0.05:1	2	96
2			0.5:0.05:1	3	98
3			0.5:0.05:1	2	95
4			0.5:0.05:1	3	97
5			0.5:0.05:1	4	90
6			0.5:0.05:1	2	99
7			1:0.1:1	4	90
8			0.5:0.05:1	5	99
9			0.5:0.05:1	1	97
10			0.5:0.05:1	1	98
11			1:0.1:1	2	96
12			0.5:0.05:1	4	98
13			1:0.1:1	3	95
14			0.5:0.05:1	2	93
15			1:0.1:1	3	93
16			1:0.1:1	2	95
17			0.8:0.1:1	2	89
18			0.5:0.05:1	3	85

^aAll reactions were performed in CH₃CN at room temperature. ^bYields referred to isolated pure products.

Table 2. Reduction of Ketones with NaBH₄/MoCl₅ System^a

Entry	Substrate	Product	Molar Ratio NaBH ₄ /MoCl ₅ /Subs.	Time (h)	Yield (%) ^b
1			2:0.1:1	0.8	99
2 ^c			2:0.1:1	6	30
3			2:0.1:1	5	94
4			2:0.1:1	0.6	93
5			2:0.1:1	0.35	97
6			2:0.1:1	0.5	98
7			3:0.2:1	0.75	99
8 ^c			2:0.1:1	6	50
9			2:0.1:1	0.6	97
10			3:0.2:1	0.35	92
11			1.5:0.1:1	0.42	95
12			2:0.1:1	0.67	97
13			2:0.1:1	0.25	94
14			6:0.2:1	4	91
15			2:0.1:1	1.1	98

^aAll reactions were performed in CH₃CN under reflux condition. ^bYields referred to isolated pure products. ^cReduction of these compounds under the same condition with 4 molar equivalents of NaBH₄ in the absence of MoCl₅ only has 5-10% conversions in 24 h.

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 molar equivalent of NaBH₄ and in the presence of 5-10 mole % of MoCl₅ in CH₃CN at room temperature. The yields are high to excellent (85-99%). 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 NaBH₄ and MoCl₅ (1.5-3 and 0.1-0.2 molar equivalents, respectively) in refluxing acetonitrile are required (Table 2). The yields are generally higher than 90% except for acetophenone (30%). The work-up procedure is simple: distilled water was added to the reaction mixture and the resulting mixture was extracted with CH₂Cl₂. The crude products were further purified by a short column chromatography on silica gel.

To highlight the efficiency of our reducing system, we compared our results with those of achieved by other reported reagents such as NaBH₄/Dowex1-x8, ^{7a}[Zn(BH₄)₂(bpy)], ²[Zn

Table 3. Comparison of Reductions of Aldehydes and Ketones with NaBH₄/MoCl₅ System and Other Reported Reducing Systems

Entry	Substrate	Molar Ratio (Reag./Subs.), Time (h) and Yield (%)						
		I	II ^{7a}	III ²	IV ³	V ⁸	VI ⁹	VII ¹⁰
1		(0.5:0.05) ^a (0.03)(96)	1 ^b (0.05)(96)	0.25(0.02)(95)	1(0.5)(91)	–	1(<i>d</i>)(90)	1(0.25)(90)
2		(0.05:0.05) ^a (0.05)(98)	1 ^b (0.15)(99)	0.25(0.08)(98)	1(0.2)(99)	1(<i>d</i>)(88)	1(<i>d</i>)(86)	1(0.23)(90)
3		(0.5:0.05) ^a (0.06)(90)	1.5 ^b (3)(99)	0.35(0.17)(99)	1(1.3)(96)	1(0.17)(89)	1(<i>d</i>)(83)	2(0.8)(85)
4		(0.5:0.05) ^a (0.08)(99)	–	0.25(0.13)(99)	1(0.8)(95)	1.5(<i>d</i>)(100)	1(<i>d</i>)(100)	1(0.25)(90)
5		(2:0.1) ^a (0.8)(99)	3 ^c (3.2)(98)	1(0.75)(99)	2(4.3)(97)	–	–	2(21.5)(90)
6		(1.5:0.1) ^a (0.42)(95)	1.5 ^c (1.25)(90)	0.5(0.15)(88)	2(2)(89)	1(1)(95)	1(10)(95)	–
7		(3:0.2) ^a (0.75)(99)	2 ^c (1.8)(94)	1(1.5)(94)	2(5.3)(98)	2(0.33)(85)	1.6(18)(80)	–
8		(2:0.1) ^a (0.25)(97)	2 ^c (0.17)(96)	0.5(0.08)(91)	0.5(0.5)(97)	–	–	–

¹NaBH₄/MoCl₅; ²NaBH₄/Dowex I-x8; ³[Zn(BH₄)₂(bpy)]; ⁴[Zn(BH₄)₂(py)]; ⁵[Zn(BH₄)₂(Ph₃P)₂]; ⁶Ph₃PMe(BH₄); ⁷[PhClI₂(dabco)]BH₄; ⁸Molar ratio as NaBH₄/MoCl₅/Subs.; ⁹Referred to using of 10 and 20 mg of Dowex I-x8 per one mmole of substrate respectively. ^aImmediately.

Table 4. Competitive Reduction between Aldehydes and Ketones with NaBH₄/MoCl₅ System^a

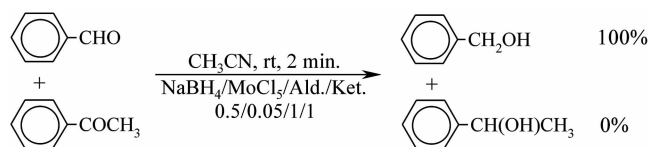
Entry	Substrate 1	Substrate 2	Molar Ratio ^b	Condition	Time (h)	Conv. 1 (%) ^c	Conv. 2 (%) ^c
1			0.5:0.05:1:1	RT	0.03	100	0
2			0.5:0.05:1:1	RT	0.08	100	5
3			2:0.1:1:1	Reflux	1.2	100	0
4			0.5:0.1:1:1	RT	0.35	100	0
5			0.5:0.1:1:1	RT	0.4	100	0
6			0.5:0.1:1:1	Reflux	1.7	100	10

^aAll reactions were performed in CH₃CN. ^bMolar ratio as NaBH₄/MoCl₅/Subs. 1/Subs. 2. ^cConversions referred to TLC monitoring and isolated pure products.

(BH₄)₂(py)]₃,³ [Zn(BH₄)₂(Ph₃P)₂],⁸ Ph₃PMeBH₄,⁹ and 4-aza-*N*-benzylbicyclo[2.2.2]octylammonium tetrahydroborate¹⁰ (Table 3).

As shown in Tables 1 and 2, aldehydes are generally much reactive than ketones with NaBH₄/MoCl₅ system and we investigated a chemoselective reduction of aldehydes over ketones. We examined a chemoselectivity in the reduction of molar equivalent mixture of a pair of carbonyl compounds with this system at room temperature. We observed that the aldehyde was completely reduced in an excellent selectivity without any attack on ketone (Scheme 3).

Reduction of α -diketones and acyloins. Reduction of α -hydroxy ketones and α -diketones to vicinal diols and/or acyloins has attracted a great deal of attention in organic synthesis. Reduction of α -diketones usually gives a mixture

**Scheme 3**

of α -hydroxy ketones and vicinal diols. Selective reduction of α -diketones to acyloins¹¹ or vicinal diols¹² can undergo with some chemical or biochemical reagents. Reduction of α -diketones with modified borohydride agents is also the subject of interests^{2-4,7b} and can be easily achieved by NaBH₄/MoCl₅ system. Sodium borohydride in the presence of catalytic amount of MoCl₅ reduces readily α -diketones to their vicinal diols in CH₃CN at room temperature (Table 5).

Table 5. Reduction of Acyloins and α -Diketones with NaBH₄/MoCl₅ System^a

Entry	Substrate	Product	Molar Ratio NaBH ₄ /MoCl ₅ /Subs.	Time (min)	Yield (%) ^b
1			2:0.1:1	6	99
2			2:0.1:1	5	95
3			2:0.1:1	12	97
4			2:0.1:1	10	98
5			2:0.1:1	8	96
6			2:0.1:1	15	97
7			2:0.1:1	20	99
8			2:0.1:1	22	96
9			2:0.1:1	15	94
10			2:0.1:1	12	95

^aAll reactions were performed in CH₃CN at room temperature. ^bYields referred to isolated pure products.

Our attempts to reduction of α -diketones to acyloins were unsatisfactory and only vicinal diols were identified as the sole products (95-99%). In addition, the reduction of acyloins to vicinal diols is also the subject of interests. The using of non-hydridic reductants¹³ and modified borohydride agents^{2-4,7b} has been reported for this achievement. We also applied our system to this goal. We observed that benzoin was efficiently reduced to hydrobenzoin at room temperature. A variety of acyloins were readily reduced to their corresponding vicinal diols in excellent yields (94-99%) (Table 5). The results in Table 5 show that the rate of reductions for acyloin compounds is generally slower than α -diketones under the same conditions. The hydrogen evolution from the reaction of hydroxy group of acyloin and sodium borohydride, and hence the formation of alkoxy moiety bound to boron atom may play a role in part to the rate being diminished.

Regioselective 1,2-reduction of conjugated enones. A regioselective reduction of α,β -unsaturated aldehydes and ketones is an easy way to obtain allylic alcohols which are important synthetic materials in organic synthesis. Such achievement with NaBH₄ is highly solvent-dependent and

generally the results does not show a useful regioselectivity.¹⁴ Regioselective 1,2-reduction of conjugated enones is usually achieved using modified borohydride agents, which are formed a) by the replacement of hydride with sterically bulky substituents or electron-withdrawing/releasing groups in order to discriminate between the structural and electronic environments of the carbonyl groups, b) by changing the metal cation, c) by combination with metal salts and mixed solvents, and d) finally immobilization on polymeric supports.^{7b} Recently, non-free hydride reducing systems achieved a perfect conversion.¹⁵ For this purpose, NaBH₄ in combination with catalytic amount of MoCl₅ is also efficient to provide the corresponding allylic alcohols at room temperature in high to excellent yields (89-98%) (Table 6).

The chemo- and regioselectivity of this reducing system are also demonstrated by the competitive reduction of cinnamaldehyde in the presence of benzalacetone (Scheme 4). To highlight the efficiency of our system, we compared our results with those of achieved by other reported reagents such as NaBH₄/Dowex1-x8,^{7b} NaBH₄,^{7b} Li-*n*-BuBH₃,¹⁶ (*i*-PrO)₂LiBH₄,¹⁷ [Zn(BH₄)₂(bpy)]₂,² [Zn(BH₄)₂(py)]₃,³ Ph₃PMeBH₄.⁹ Investigation of the results shows that in most

Table 6. Reduction of α,β -Unsaturated Carbonyl Compounds with $\text{NaBH}_4/\text{MoCl}_5$ System^d

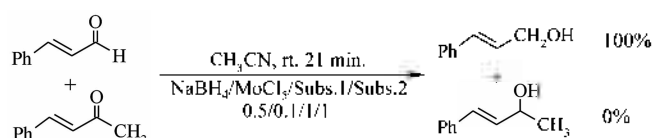
Entry	Substrate	Product	Molar Ratio $\text{NaBH}_4/\text{MoCl}_5/\text{Subs.}$	Ratio 1.2:1.4	Time (h)	Yield (%) ^b
1 ^c			0.5:0.1:1	100:0	0.3	98
2			2:0.1:1	100:0	0.9	96
3			2:0.1:1	100:0	1	97
4			2:0.1:1	100:0	1.2	90
5			2:0.1:1	100:0	1.1	89
6			0.5:0.1:1	100:0	1.5	95
7			2:0.1:1	100:0	1.4	98
8			2:0.1:1	100:0	2.6	94

^aAll reactions were performed in CH_3CN under reflux condition. ^bYields referred to isolated pure products. ^cThis reaction was performed at room temperature.

Table 7. Comparison of Regioselective 1,2-Reduction of Conjugated Enones with $\text{NaBH}_4/\text{MoCl}_5$ System and Other Reducing Systems

Entry	Substrate	Molar Ratio: ^d Time (h) and Yield (%)							
		I	II ^{7b}	III ^{7b}	IV ¹⁶	V ¹⁷	VI ²	VII ³	VIII ⁹
1		(0.5:0.1) ^b (0.3)(98) (100:0) ^c	I(0.7)(96) (100:0) ^c	I(3)(93) (95:5) ^c	—	I(5 ^d)(90) (>99:<1) ^c	0.5(0.03)(92) (100:0) ^c	I(1.5)(97) (100:0) ^c	I(^e)(95) (100:0) ^c
2		(2:0.1) ^b (0.9)(96) (100:0) ^c	I(1.4)(98) (100:0) ^c	I(2.8)(96) (95:5) ^c	I(2)(98) (100:0) ^c	I(5 ^d)(97) (>99:<1) ^c	I(1.3)(97) (100:0) ^c	2(1)(97) (100:0) ^c	I(3.5)(90) (100:0) ^c
3		(2:0.1) ^b (1)(97) (100:0) ^c	I(0.7)(95) (100:0) ^c	I(1.7)(95) (90:10) ^c	I(2)(99) (100:0) ^c	—	I(3)(98) (100:0) ^c	2(3)(94) (100:0) ^c	1.2(6)(90) (100:0) ^c
4		(0.5:0.1) ^b (1.5)(95) (100:0) ^c	I(1.3)(94) (100:0) ^c	I(2.8)(90) (99:1) ^c	—	I(5 ^d)(95) (>99:<1) ^c	0.5(1)(95) (100:0) ^c	1(1.8)(93) (100:0)	—
5		(2:0.1) ^b (1.4)(98) (100:0) ^c	I(2.2)(91) (100:0) ^c	I(3)(80) (95:5) ^c	I(2)(98) (100:0) ^c	—	I(1.6)(96) (100:0) ^c	2(1.5)(92) (100:0) ^c	I(6)(71) (100:0) ^c
6		(2:0.1) ^b (1.2)(90) (100:0) ^c	I(0.8)(89) (100:0) ^c	I(1)(85) (80:20) ^c	I(2)(84) (92:8) ^c	—	0.5(0.5)(90) (100:0) ^c	—	—

¹ $\text{NaBH}_4/\text{MoCl}_5$; ² $\text{NaBH}_4/\text{Dowex 1-x8}$; ³ NaBH_4 ; ⁴1, n-n-BuBH₃; ⁵(*t*-PrO)₂TiBH₃; ⁶[Zn(BH₄)₂(bpy)]; ⁷[Zn(BH₄)₂(py)]; ⁸Ph₃PMeBH₄; ⁹Reducing agent/Substrate; ^bMolar ratio as $\text{NaBH}_4/\text{MoCl}_5/\text{Subs.}$; ^cRatio of 1.2:1.4-reduction; ^dTime in minute; ^eImmediate reaction.

**Scheme 4**

cases, this new reducing system is more efficient or comparable (Table 7).

The catalytic effect of MoCl_5 in the reduction reactions with sodium borohydride has not been cleared, but we thought that one or two of the following factors may play a role in the catalytic function of MoCl_5 : a) Lewis acidity character of MoCl_5 , b) formation of the new reductant

species as $\text{MoCl}_{5-x}(\text{BH}_4)_x$, or c) formation of the molybdenum boride that actively catalyzes the decomposition of borohydride. The capability of this system for the reduction of other functional groups as well as the reducing potential of NaBH_4 in the presence of other Lewis acids or metal chlorides is extensively investigated in our laboratory.

In conclusion, we have shown that $\text{NaBH}_4/\text{MoCl}_5$ 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.

Experimental Section

General. All reagents and substrates were obtained from commercial sources of highest quality 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 points) and their $^1\text{H-NMR}$ or IR spectral data. Molar ratios of NaBH_4 used in this study are the minimum amounts for reaching to complete conversion of the reactions. The reaction times are the optimum ones. Organic layers were dried with anhydrous sodium sulfate before concentration *in vacuo*. 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 reactions was determined by disappearing of the spot of substrates on TLC.

A Typical Procedure for Reduction of Aldehydes to Alcohols with $\text{NaBH}_4/\text{MoCl}_5$ System. In a round-bottom flask (15 mL) equipped with magnetic stirrer, charged with a solution of benzaldehyde (0.106 g, 1 mmol) in CH_3CN (5 mL), NaBH_4 (0.019 g, 0.5 mmol) was added. To this mixture, MoCl_5 (0.014 g, 0.05 mmol) was added immediately and the resulting brown mixture was stirred at room temperature for 2 min. TLC monitored the progress of the reaction (eluent: $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2). After completion of the reaction, distilled water (5 mL) was added to the mixture and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2 (3×10 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2 affords the pure liquid benzyl alcohol (0.104 g, 96% yield, Table 1).

A Typical Procedure for Reduction of Ketones to Alcohols with $\text{NaBH}_4/\text{MoCl}_5$ System. In a round-bottom flask (15 mL) equipped with a magnetic stirrer and a condenser, to a solution of benzophenone (0.182 g, 1 mmol) in CH_3CN (5 mL), NaBH_4 (0.076 g, 2 mmol) was added. To this mixture, MoCl_5 (0.027 g, 0.1 mmol) was added immediately and the resulting brown mixture was heated to

gentle reflux with stirring. TLC monitored the progress of the reaction (eluent: $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2). After completion of the reaction in 48 min, distilled water (5 mL) was added to the reaction mixture and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2 (3×10 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2 affords the pure crystals of benzhydrol (0.182 g, 99% yield, Table 2).

A Typical Procedure for Competitive Reduction of Aldehydes and Ketones with $\text{NaBH}_4/\text{MoCl}_5$ System. In a round-bottom flask (15 mL) equipped with a magnetic stirrer, to a solution of benzaldehyde (0.106 g, 1 mmol) and acetophenone (0.12 g, 1 mmol) in CH_3CN (5 mL), NaBH_4 (0.019 g, 0.5 mmol) was added. To this mixture, MoCl_5 (0.014 g, 0.05 mmol) was added immediately and the resulting brown mixture was stirred at room temperature. TLC monitored the progress of the reaction. After 2 min, the reaction is quenched by addition of distilled water (5 mL) and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2 (3×10 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent of $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2 affords the pure liquid benzyl alcohol as a sole product of reduction and acetophenone as an intact material (Table 4).

A Typical Procedure for Reduction of α -Diketones and Acyloins with $\text{NaBH}_4/\text{MoCl}_5$ System. In a round-bottom flask (15 mL) equipped with magnetic stirrer, to a solution of benzil (0.21 g, 1 mmol) in CH_3CN (5 mL), NaBH_4 (0.076 g, 2 mmol) was added. To this mixture, MoCl_5 (0.027 g, 0.1 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: $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2). After completion of the reaction, distilled water (5 mL) was added to the mixture and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2 (3×10 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 by eluent of $\text{CCl}_4/\text{Et}_2\text{O}$: 5/3 affords the pure crystals of hydrobenzoin (0.212 g, 99% yield, Table 5).

A Typical Procedure for Regioselective 1,2-Reduction of Conjugated Enones with $\text{NaBH}_4/\text{MoCl}_5$ System. In a round-bottom flask (15 mL) equipped with a magnetic stirrer and a condenser, to a solution of benzylideneacetone (0.146 g, 1 mmol) in CH_3CN (5 mL), NaBH_4 (0.076 g, 2 mmol) was added. To this mixture, MoCl_5 (0.027 g, 0.1 mmol) was added immediately and the resulting brown mixture was heated to gentle reflux with stirring. TLC monitored the progress of the reaction (eluent: $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2). After the completion of the reaction in 55 min, distilled water (5 mL) was added to the reaction mixture and stirred for additional 5 min. The mixture was extracted with CH_2Cl_2 (3×10 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent and short column chromatography of the resulting crude material over silica gel by eluent

of $\text{CCl}_4/\text{Et}_2\text{O}$: 5/2 affords the pure 4-phenyl-3-buten-2-ol (0.142 g, 96% yield, Table 6).

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