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$AlCl_3$-Promoted Conjugate Reduction of α,β-Unsaturated Carbonyl Compounds with 1,3-Dimethyl-2-phenylbenzimidazoline

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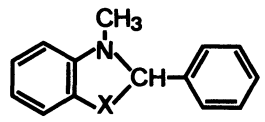
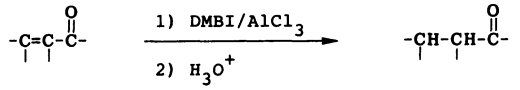
The reduction of a variety of α,β-unsaturated carbonyl compounds, except for α,β-unsaturated aldehyde, to the corresponding saturated carbonyl compounds was effectively performed by using 1,3-dimethyl-2-phenylbenzimidazoline (DMBI) as a reducing agent with the aid of $AlCl_3$. The reduction is discussed on the basis of the hydride-donating ability of DMBI, together with the role of $AlCl_3$ as an electrophilic activator for the substrates. The catalytic efficiency of Lewis acids was found to be proportional to the efficiency to form a complex with a carbonyl group. The reduction of 2-cinnamoylpyridine with 2-deuterated DMBI revealed that in the reduction product, a deuterium atom was located at the β-position with respect to the carbonyl group. On the other hand, the reduction of the same substrate with DMBI followed by quenching with D_2O gave a reduced product which contained a deuterium label at the α-position. These results were interpreted in terms of a mechanism involving an enolate intermediate produced by either a one-step hydride transfer or a sequential transfer of an electron (e) and a hydrogen atom (H·) from the reducing agent to the substrate.

Many useful methods for obtaining functionalizing organic compounds have been developed in recent years by employing various types of heterocyclic compounds, either as mediate or immediate reagents.[1] On the other hand, the selective reduction of organic functional groups is one of the important and frequently encountered synthetic subjects in organic syntheses. However, despite much work in these fields, little attention has been given to the use of heterocycles having a hydrogen-donating ability as practical reducing agents for such selective reductions. Therefore, it could become one of the useful methods in this field if such heterocycles could be used as direct and selective reducing agents. Although more recently, several reports[2] have appeared concerning the use of 1,4-dihydropyridine derivatives (so-called NAD(P)H model compounds) such as 1,4-dihydronicotinamides or 3,5-bis(ethoxycarbonyl)-1,4-dihydro-2,6-dimethylpyridine as reducing agents from an above synthetic viewpoint, reductions with NAD(P)H-models have, so far, been mainly investigated with regard to biological, biomimetic, or mechanical interests. To the best of our knowledge, there has only been two sources[3] concerning the synthetic utility of other heterocycles as practical and selective reducing agents. In previous papers from our laboratory, it was revealed that dihydrobenzazoles such as 2-phenylbenzimidazoline or 2-phenylbenzothiazoline were useful reducing agents for the selective reduction of carbon–carbon double bonds of α,β-unsaturated dinitriles,[4] 2-aryl-1-nitroalkenes,[5] and α,β-unsaturated carbonyl compounds.[6] As a continuation of this work, we have investigated the potential reducing ability of *N*-methylated 2-phenylbenzazolines in a reduction of α,β-unsaturated carbonyl compounds in the presence of a Lewis acid. We found that 1,3-dimethyl-2-phenylbenzimidazoline (DMBI) is the most powerful component in this reaction relative to the other heterocycles. In this paper, we report on the details of an $AlCl_3$-promoted conjugate reduction of α,β-unsaturated carbonyl compounds with DMBI and show the mechanical features of these reactions.



DMBI : X = N-CH$_3$
MBT : X = S
MBO : X = O

Scheme 1.



Scheme 2.

Results and Discussion

In contrast to 2-phenylbenzimidazoline, which should be prepared in situ from *o*-phenylenediamine and benzaldehyde in a solvent because it is an unstable intermediate and rapidly oxidized automatically to 2-phenylbenzimidazole in the absence of an appropriate hydrogen acceptor, DMBI can be prepared by a reaction of *N,N'*-dimethyl-*o*-phenylenediamine with benzaldehyde or the quaternization of 2-phenylbenzimidazole followed by a reduction with lithium aluminum hydride or sodium borohydride. It can be isolated as a handlable substance consisting of colorless needles.[7] DMBI is very stable in an atmospheric environment and can be stored in a sealed bottle for a long time.

For preliminary assays of the present study, we chose benzylideneacetone as a model compound and the reaction of the enone with DMBI in the presence or absence of a Lewis acid was carried out under the conditions shown in Table 1. Although the reduction of the enone with DMBI did not occur without a Lewis acid (Run 1), it was found that the reduction can proceed with 1 equivalent of DMBI in the presence of a slight excess of a Lewis acid in dry acetonitrile

Table 1. Reduction of Benzylideneacetone to Benzylacetone with DMBI in the Presence or Absence of Lewis Acid

Run	Lewis acid	Molar ratio[a] Enone:Lewis acid	Temp/°C	Time/h	Yield/%[b]
1	None	—	80	0.5	0
2	$ZnCl_2$	1:1.2	80	0.5	16
3	$SnCl_4$	1:1.2	80	0.5	36
4	$FeCl_3$	1:1.2	80	0.5	49
5	$AlCl_3$	1:1.2	80	0.5	100
6		1:1.2	r.t.	4	98
7		1:0.5	80	0.5	49
8		1:0.25	80	0.5	23

a) 1:1 Molar ratio of DMBI to the enone was used. b) Yield determined by GLC analysis.

Table 2. Reduction of Benzylideneacetone to Benzylacetone with MBT and MBO in the Presence or Absence of Lewis Acid[a]

Run	Reductant	Lewis acid	Molar ratio[b] Enone:Lewis acid	Time/h	Yield/%[c]
1	MBT	None	—	0.5	0
2		$ZnCl_2$	1:1.2	0.5	0
3		$FeCl_3$	1:1.2	0.5	34
4		$AlCl_3$	1:1.2	0.5	75
5		$AlCl_3$	1:1.2	48	100
6		$AlCl_3$	1:0.5	0.5	41
7		$AlCl_3$	1:0.25	0.5	20
8	MBO	$AlCl_3$	1:1.2	0.5	0

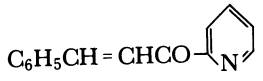
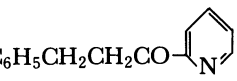
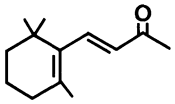
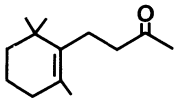
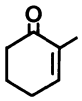
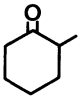
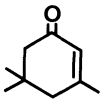
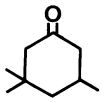
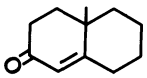
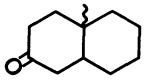
a) All the reactions were carried out in acetonitrile at 80°C. b) 1.2:1 Molar ratio of MBT and MBO to the enone was used. c) Yield determined by GLC analysis.

at 80°C. In all cases, the conjugate reduction product, 3-phenyl-2-butanone, was obtained in complete selectivity, and none of 4-phenyl-3-buten-2-ol, corresponding to the 1,2-reduction product, or 4-phenyl-2-butanol was detected. The change in the Lewis acid did not change the selectivity of the reduction, but the reaction employing $AlCl_3$ was very rapid and was completed within 30 min to give the product in quantitative yield (Run 5). In addition, this $AlCl_3$-promoted reduction proceeded well even at room temperature to give a nearly quantitative yield of the product (Run 6). As to the catalytic efficiency of the Lewis acid, Table 1 indicates that it is proportional to its efficiency to form a complex with a carbonyl group:[8] the latter efficiency increases in the order $ZnCl_2<SnCl_4<FeCl_3<AlCl_3$. Thus, a Lewis acid can be regarded as an electrophilic activator to polarize a carbon–carbon double bond due to the formation of a complex with a carbonyl group of the enone. The use of a 1.2 equivalent of $AlCl_3$ to the enone is sufficient to promote the reaction, while the use of 0.5 or 0.25 equivalents of $AlCl_3$ to the enone gave the reduced product in 49 and 23% yields, respectively (Runs 7 and 8). This shows that the present conjugate reduction requires a stoichiometric amount of the Lewis acid.

A brief survey of the potential reducing ability of a series of *N*-methylated 2-phenylbenzazolines on the reduction of benzylideneacetone was conducted. As shown in Table 2, the reduction with 3-methyl-2-phenylbenzothiazoline (MBT) also proceeded in the presence of a Lewis acid with a similar trend shown on the DMBI-reduction (Runs 1—7) while the reduction with 3-methyl-2-phenylbenzoxazoline (MBO) did not occur at all (Run 8). Although the reaction with MBT proceeded well in the presence of $AlCl_3$ to give 3-phenyl-2-butanone in quantitative yield after a reaction time of 48 h (Run 5), it is apparent from Tables 1 and 2 that DMBI is superior to MBT in terms of its power.

We have demonstrated the general applicability of the present DMBI-reduction regarding a variety of α,β-unsaturated ketones. The results are summarized in Table 3. Generally, the reduction of linear enones by the present method can be performed easily to give nearly quantitative yields of the corresponding saturated ketones (Runs 1—7). β-Ionone, corresponding to an α,β:γ,δ-unsaturated carbonyl compound, was selectively reduced to dihydro-β-ionone in quantitative yield (Run 7). 1,2-Dibenzoylethylene, corresponding to an α,β-unsaturated diketone, was also reduced with no difficulty to 1,4-diphenyl-1,4-butanedione in quantitative yield (Run 3). In all cases, the conjugate reduction products were obtained in complete selectivity, and other by-products were not detected at all. Compared with a similar reduction with 2-phenylbenzothiazoline,[6] the present DMBI-reduction of linear enones is more rapid. In addition, 3-methyl-4-phenylbutenone could be effectively reduced with DMBI within 4 h, in contrast to the reduction by 2-phenylbenzothiazoline in which the butenone was

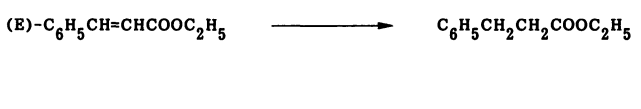
Table 3. Conjugate Reduction of α,β-Unsaturated Ketones with DMBI in the Presence of $AlCl_3$[a)]

Run	Enone	Product	Time/h	Yield/%[b)]	Bp or mp/°C/Torr[c)]
1	$C_6H_5CH=CHCOCH_3$	$C_6H_5CH_2CH_2COCH_3$	0.5	100	115—118/16[22)]
2	$C_6H_5CH=CHCOC_6H_5$	$C_6H_5CH_2CH_2COC_6H_5$	0.5	100	72.5—73.5[23)]
3	$C_6H_5COCH=CHCOC_6H_5$	$C_6H_5COCH_2CH_2COC_6H_5$	0.5	100	145—146[24)]
4	$(CH_3)_2C=CHCOCH_3$	$(CH_3)_2CHCH_2COCH_3$	1	96	45.5—46/80[25)]
5	$C_6H_5CH=C(CH_3)COCH_3$	$C_6H_5CH_2CH(CH_3)COCH_3$	4	94	104—105[22)]
6			1[d)]	69[e)]	—
7			1	96	105—107/3[26)]
8			24	55	46.5—47/12[27)]
9			19	71	54—56/12[28)]
10			24	26[f)]	(*cis*)175—176.5[g),29)] (*trans*)178.5—180[g),29)]

a) 1.2:1 Molar ratio of DMBI and $AlCl_3$ to enone was used. b) Yield determined by GLC analysis. c) Spectral data of the reduced products were in satisfactory agreement with those of the corresponding authentic samples or expected values. d) Reaction at 60°C. e) Yield of isolated, pure product. f) Yield of isomeric mixture. g) Mp of 2,4-dinitrophenylhydrazone derivative.

sluggishly reduced to the same in 26% yield after a 24 h reaction. On the other hand, the reduction of cyclic enones was generally slower than that of linear enones but afforded moderate yields of saturated cyclic ketones (Runs 8—10). As pointed out regarding the reduction of linear enones, DMBI also seems to be more powerful in the reduction of cyclic enones than 2-phenylbenzothiazoline. In short, the $AlCl_3$-promoted conjugate reduction of a variety of α,β-unsaturated ketones can be practically performed in good yields with complete regiospecificity together with no side reactions. Thus, although there are several methods available to bring about such conversions, we consider the present method to be a useful addition. The relative reactivities of the enones were found to decrease in the order α,β-disubstituted linear enone>α,β,β-trisubstituted linear enone>α,α,β-trisubstituted linear enone>cyclic enone.

The conjugate reduction of an α,β-unsaturated ester and a similar aldehyde were also examined under similar conditions (Scheme 3). Methyl cinnamate

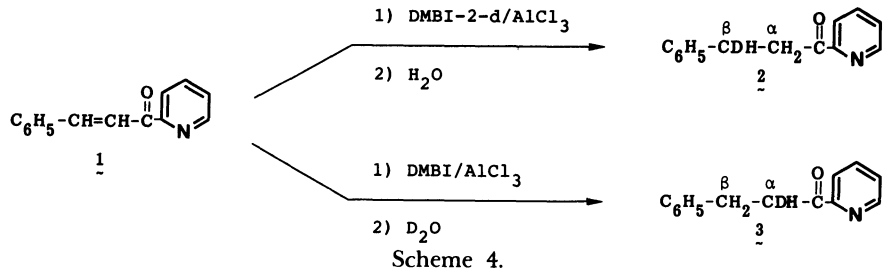


Scheme 3.

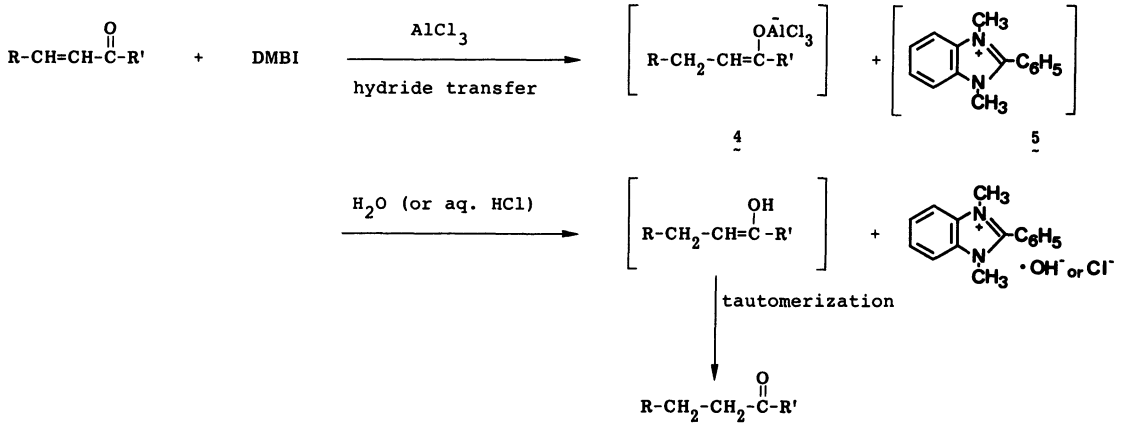
was less effectively reduced to the corresponding 3-phenylpropionate in 30% yield after a reaction time of 30 min. However, the reduction of cinnamaldehyde under the same conditions gave only a trace amount of the expected saturated aldehyde, 3-phenylpropanal. The latter result may show that the present method is, as yet, inapplicable to the conjugate reduction of α,β-unsaturated aldehydes.

The functional selectivity of the present DMBI-reduction should be noted since it is of importance in an organic synthesis and of interest to organic chemists. We have found that functional groups such as carbonyl, carboxylic ester, acid, nitro, isolated C=C, isolated C≡C, and the common carbon-halogen bond are inert to the present reducing system. These selective properties might enhance the utility of the present reducing method.

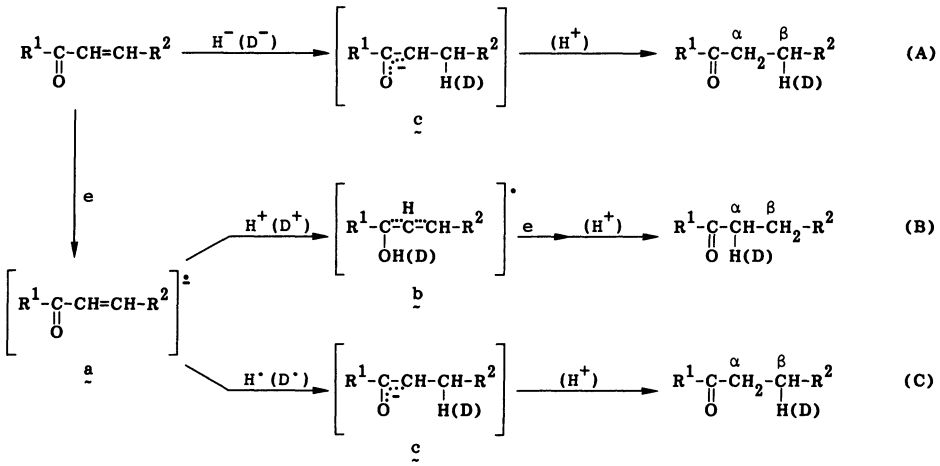
Mechanism. In an attempt to determine the destination of a hydrogen atom at the C-2 carbon of DMBI, we reduced 1-(2-pyridyl)-3-phenyl-2-propen-1-one (**1**) with 2-deuterated DMBI which can be easily prepared by the reduction of 2-phenylbenzimidazolium iodide with lithium aluminum deuteride (Scheme 4). The product of this reaction was found to be the saturated ketone (**2**) containing one deuterium atom at its β-carbon to the carbonyl group. This result shows that the hydrogen atom at C-2 carbon of DMBI surely transfers to the β-carbon of the substrate as a hydride, because the carbon at the β-position of the substrate is very nucleophilic due to the formation of a complex of $AlCl_3$ with the carbonyl group of the enone (**1**) and the pathway involving an isomerization of an allylic



Scheme 4.



Scheme 5.



Scheme 6.

intermediate produced by the 1,2-reduction can be excluded according to the results reported by Gase et al.[9] When azachalcone (**1**) was reduced by DMBI, the α-deuterated ketone (**3**) was obtained in 65% yield after a workup with D_2O (Scheme 4). This indicates that the incorporation of a hydrogen atom from the water of the workup takes place and shows that the hydrogen atom at the α-position of the reduced product comes from the water for the workup after completion of the reaction. Considering these facts, a mechanism involving the hydride transfer followed by protonation of the aluminum enolate (**4**) by quenching water can be proposed for the present conjugate reduction as shown in Scheme 5. These processes fully conform to the driving force of the formation of stable benzimidazolium ion (**5**).

Recently, the mechanism of a hydride-equivalent transfer in a reduction with 1,4-dihydropyridine derivatives has been extensively discussed, and it has been proposed in some cases[10] that the reduction is most likely composed of an initial electron transfer followed by the transfer of a hydrogen nucleus or radical. Although the initial hydride transfer shown in Scheme 5 may be viewed as simply a one-step hydride transfer (mechanism A), schemes involving sequential transfers of e+H$^\cdot$ (mechanism C) and e+H$^+$+e (mechanism B) are also possible in theory (Scheme 6). The transfer of a hydride ion to the unsaturated ketone system (mechanism A) should give the saturated ketone in which the hydrogen atom of DMBI would be introduced at the β-carbon. In considering mechanisms B and C, it is expected that the radical

anion intermediate **a** formed by the addition of an electron to the substrate would undergo protonation (mechanism B) at the oxygen site to give the allylic intermediate **b**, while the addition of a hydrogen atom to the same (mechanism C) should result in anion **c**. As a consequence, upon completion of the reaction, the hydrogen atom of DMBI would be introduced at the α-carbon of the product obtained via mechanism B and that found via mechanism C would carry at the β-position. Thus, in light of the forementioned observation that the reduction of azachalcone (**1**) with 2-deuterated DMBI leads to the corresponding saturated ketone (**2**) which contains one deuterium atom at the β-carbon, mechanisms A and C are both candidates for the initial hydride transfer shown in Scheme 5. In addition, the role of the Lewis acid in the present reduction can be well understood according to these mechanisms as follows. First, a Lewis acid activates the substrate as an electrophilic activator. Second, a Lewis acid stabilizes the resulting enolate anion **c** by coordination.

Experimental

Melting points were recorded on a Yanagimoto micro melting-point apparatus and are uncorrected. ^{1}H NMR spectra were measured with a JEOL PMX-60 spectrometer at 60 MHz using tetramethylsilane as an internal reference. IR spectra were recorded on a JASCO A-202 spectrophotometer. Mass spectra were obtained on a JMS-QH100 GC-Mass spectrometer. GLC analyses were carried out on a Shimadzu Gas Chromatograph GC-6AM equipped with a hydrogen flame ionization detector using glass columns (1.5 m) packed with 2% Silicone OV-7 on Uniport HP (60—80 mesh). The yields by quantitative GLC were measured on the same columns by internal standard method, using pentylbenzene as an internal standard. Silica gel (Wakogel C-300) was used for short column chromatography.

Materials. DMBI, mp 97.5—98.5 °C (lit,[11] 96 °C) was prepared from 2-phenylbenzimidazole by the slight modification of the method of Craig et al.[12] DMBI-2-*d*, mp 97—98 °C was prepared by the reduction of 2-phenylbenzimidazolium iodide with $LiAlD_4$ according to the same procedure, that was fully deuterated material by ^{1}H NMR; no azomethine proton absorption was detected. MBT, mp 113—114.5 °C (lit,[13] 112—113 °C), and MBO, bp 151—152 °C/3 mmHg (lit,[14] 146—149 °C/2 mmHg (1 mmHg= 133.322 Pa)) were prepared according to the literature procedures.[13,14] Commercially available $AlCl_3$, $FeCl_3$, $SnCl_4$, and $ZnCl_2$ were used without purification. Acetonitrile was distilled three times on phosphorus pentaoxide before use. Mesityl oxide, β-ionone, isophorone, methyl cinnamate, and cinnamaldehyde were commercially supplied and purified by distillation. The following derivatives were prepared according to the literature and identified by spectroscopic (NMR and IR) methods: benzylideneacetone, bp, 110—112 °C/4.5 mmHg; mp 40—42 °C (lit,[15] bp 123—128 °C/8 mmHg; mp 40—42 °C); benzylideneacetophenone, mp 55—57 °C (lit,[16] 55—57 °C); (*E*)-1,2-dibenzoylethylene, mp 109—110 °C (lit,[17] 109—110 °C); (*E*)-3-methyl-4-phenyl-3-buten-2-one, bp 91 °C/2 mmHg (lit,[18] 80—93 °C/1 mmHg); 4a-methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one, bp 109—111 °C/1 mmHg (lit,[19] 112—115 °C/5 mmHg); 2-methyl-2-cyclohexen-1-one, bp 64.5—65.5 °C/16 mmHg (lit,[20] 83—85.5 °C/35 mmHg); 2-cinnamoylpyridine, mp 71—72 °C (lit,[21] 71—72 °C).

General Procedure for the Conjugate Reduction of α,β-Unsaturated Carbonyl Compounds with DMBI. A solution of an unsaturated carbonyl compound (1.0 mmol) in dry acetonitrile (2 ml) and $AlCl_3$ (0.16 g, 1.2 mmol) were mixed in a glass tube under ice-water cooling. After the $AlCl_3$ was completely dissolved, DMBI (0.27 g, 1.2 mmol) was added and the mixture was degassed several times in vacuo. The tube was sealed in vacuo and kept at 80 °C for the appropriate time (see Tables). After 0.1 M HCl (2 ml (1 M= 1 mol dm^{-3})) was added to the mixture in the tube under ice-water cooling, the aqueous mixture was extracted with chloroform. The chloroform extract was washed thoroughly with water and the organic layer was analyzed by quantitative GLC. The results are given in Tables. An identification of the products isolated by short-column chromatography on silica gel was performed by spectroscopic (NMR, IR, and MS) methods. These spectral data were in satisfactory agreement with those of the corresponding authentic samples or expected values.

In a large-scale synthesis, the reaction could be carried out in a three-necked flask under nitrogen and the same reaction conditions. After a workup, as previously described, the products could be isolated by distillation or short-column chromatography on silica gel.

Reduction of 2-Cinnamoylpyridine (1). A solution of azachalcone (**1**) (0.10 g, 0.5 mmol) in dry acetonitrile (1 ml) and $AlCl_3$ (0.08 g, 0.6 mmol) were mixed in a glass tube under ice-water cooling. After the $AlCl_3$ was completely dissolved, DMBI (0.13 g, 0.6 mmol) was added and the mixture was degassed several times in vacuo. The tube was sealed in vacuo and kept at 60 °C for 1 h. After water (1 ml) had been added to the mixture in the tube under ice-water cooling, the aqueous mixture was extracted with chloroform. The chloroform extract was thoroughly washed with water and dried with anhydrous Na_2SO_4. The oily residue obtained by evaporation of solvent was subjected to short column chromatography on silica gel to give 1-(2-pyridyl)-3-phenyl-1-propanone (73 mg, 69%), ^{1}H NMR ($CDCl_3$) δ=2.93 (t, 2H, β-CH_2), 3.43 (t, 2H, α-CH_2), 7.04 (s, 5H, Ph), and 7.17—8.42 (m, 4H, C_5H_4N); MS *m/z* 211 (M^+).

Azachalcone (**1**) (0.10 g, 0.5 mmol) was similarly reduced with DMBI-2-*d* (0.14 g, 0.6 mmol). The chromatographic purification of the crude product gave fully β-deuterated ketone (**2**) (81 mg, 76%), ^{1}H NMR ($CDCl_3$) δ=2.92 (t, 1H, β-CDH), 3.43 (d, 2H, α-CH_2), 7.04 (s, 5H, Ph), and 7.17—8.42 (m, 4H, C_5H_4N); MS *m/z* 212 (M^+).

Azachalcone (**1**) (0.10 g, 0.5 mmol) was similarly reduced with DMBI (0.13 g, 0.6 mmol). After quenching with D_2O (2 ml) under ice-water cooling, the aqueous mixture was extracted with chloroform and dried with anhydrous Na_2SO_4. Chromatographic purification of the crude product gave the fully α-deuterated ketone (**3**) (69 mg, 65%), ^{1}H NMR ($CDCl_3$) δ=2.92 (br, 2H, β-CH_2), 3.39 (t, 1H, α-CDH), 7.04 (s, 5H, Ph), and 7.17—8.42 (m, 4H, C_5H_4N); MS *m/z* 212 (M^+).

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