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In Situ Generation and Synthetic Application of 2-Phenylbenzimidazoline to the Selective Reduction of Carbon-Carbon Double Bonds of Electron-Deficient Olefins

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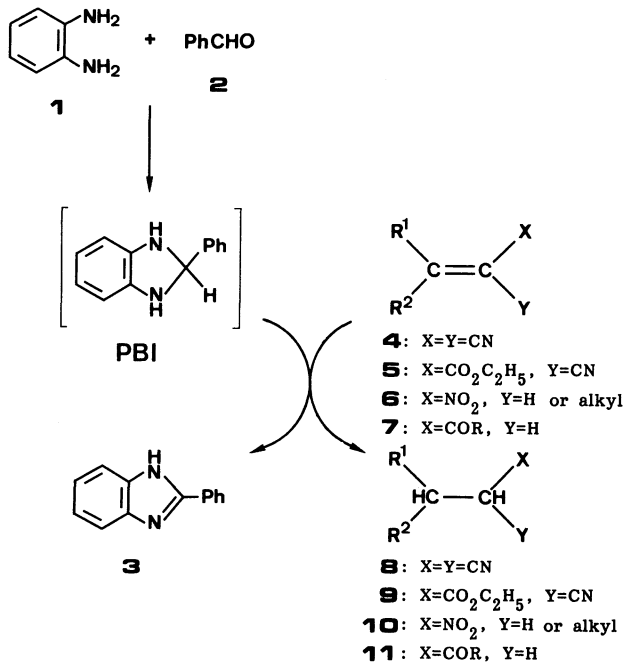
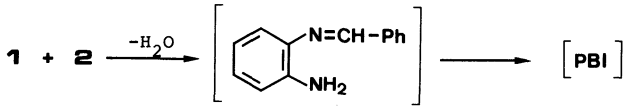
2-Phenylbenzimidazoline (PBI) as a mild, selective, and convenient reducing agent was efficiently generated in situ from *o*-phenylenediamine and benzaldehyde in alcohols. A generally applicable method for the selective reduction of carbon-carbon double bonds of a variety of electron-deficient olefins with an alcoholic solution of PBI is described. The reduction of α,β-unsaturated ketones to the corresponding saturated ketones could also be accomplished (but, less effectively) with PBI with the aid of a Lewis-acid catalyst. 1-Methyl-2-(*o*-nitrophenyl)benzimidazoline prepared and isolated by the reaction of *o*-nitrobenzaldehyde with *N*-methyl-*o*-phenylenediamine reduced benzylidenemalononitrile to give benzylmalononitrile and 1-methyl-2-(*o*-nitrophenyl)benzimidazole in high yields. This shows the validity of PBI to be the actual reducing species in the present reduction system. From a mechanistic study, the present reductions could be interpreted in terms of a mechanism involving a synchronous transport of a pair of hydrogens or a sequential transfer of a hydride and a proton from PBI to the olefins.

The selective reduction of organic functional groups is an important and frequently encountered synthetic operation in organic syntheses. Many methods have been developed toward this goal and many types of "selective reductions" have been accepted as being synthetically useful. In recent years, heterocyclic compounds having a hydrogen-donating ability, such as dihydrobenzazoles[1,2] or 1,4-dihydropyridines,[3] have been shown to be useful as such selective reducing agents. One such reagent developed in our laboratory is 2-phenylbenzimidazoline (PBI). The development of methods applicable to the selective reductions of carbon-carbon double bonds conjugated with electron-withdrawing groups such as cyano, nitro, or carbonyl group has been a synthetic subject. We have recently indicated the reducing and selective properties of PBI in the reduction of benzylidenemalononitriles and β-nitrostyrenes.[1a] However, the initial reaction mode has been shown to be disadvantageous from a synthetic viewpoint since a half molar amount of the olefins is consumed to form PBI. Due to this disadvantage, a convenient alternative method for in situ generation of PBI has been reported in a previous communication.[1b] This method includes the use of *o*-phenylenediamine (**1**) and benzaldehyde (**2**) in ethanol. In this paper, we report on details regarding the selective reduction of carbon-carbon double bonds of a variety of electron-deficient olefins with a reagent system of diamine (**1**) and aldehyde (**2**); discuss the scope, limitations, and general applicability of this simple reduction method, and show the mechanistic features of these reactions together with evidence that PBI is the actual reducing species (Scheme 1).



Scheme 1.

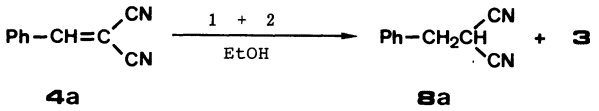
In Situ Generation and Properties of PBI. Recently, we have found that benzylmalononitriles or (2-nitroethyl)benzenes were obtained in good yields by a reaction of benzylidenemalononitriles or β-nitrostyrenes with a half molar amount of diamine (**1**); we indicated that the products resulted from a reduction of the olefins by PBI which was formed by the reaction of the olefins with equimolar amount of diamine (**1**).[1a] However, in order to synthetically utilize the reducing ability of PBI to the selective reduction of carbon-carbon double bonds of electron-deficient olefins, PBI should be prepared independently. In our attempts to prepare PBI conveniently, we have found that diamine (**1**) rapidly reacts with aldehyde (**2**) in ethanol at room



Scheme 2.

temperature to produce a mixture of *N*-benzylidene-*o*-phenylenediamine (**12**) and PBI, expected to be formed through the intramolecular cyclization of **12** (Scheme 2). Although these compounds could not be isolated, the formation of **12** and PBI were indicated by the appearance of signals at 8.57 and 5.74 ppm, assigned to methine protons of **12** and PBI, respectively, in the ^{1}H NMR spectra of an equimolar mixture of diamine (**1**) and aldehyde (**2**) in methanol-d_4 at room temperature. When the reaction mixture was allowed to warm to 50 °C, the complete disappearance of the above mentioned methine signals was observed after 24 h; also 2-phenylbenzimidazole (**3**) was isolated from the reaction mixture in 95% yield. This indicates that PBI is an unstable intermediate and is readily oxidized automatically to benzimidazole (**3**) in the absence of an appropriate hydrogen acceptor. The unstability of PBI is in sharp contrast to the high stability of *N,N'*-dimethylated PBI.[1f,h] In addition, Schiff's base (**12**), formed simultaneously, was inert to PBI in this mild reaction system, in contrast to the system reported by Smith et al.[4]

Upon a treatment of diamine (**1**) and aldehyde (**2**) in ethanol at room temperature, when benzylidenemalononitrile (**4a**) coexisted in the reaction system, a mixture of benzylmalononitrile (**8a**) and benzimidazole (**3**) was obtained in high yields (Scheme 3). As shown in



Scheme 3.

Table 1, this reduction also occurred by the treatment of the olefin (**4a**) with diamine (**1**) and other aldehydes under the same reaction conditions to give the same reduced product **8a** in good yields, although it is apparent that aldehyde (**2**) is the most effective among the aldehydes employed. In these reactions, benzimidazolines could not be isolated as well as PBI but the corresponding benzimidazoles were obtained in practically quantitative yields. These results indicate that the olefin (**4a**) was effectively reduced by benzimidazolines produced in situ from diamine (**1**) and aldehydes, and that compensating reactions are oxidations of benzimidazolines to benzimidazoles.

General Applicability of the PBI-Reduction to a Variety of Electron-Deficient Olefins. We have extended this simple reduction technique to a variety of electron-deficient olefins (**4—6**) which have a carbon-carbon double bond conjugated with one or two highly electron-withdrawing groups such as -CN, -NO_2, or -CO_2Et. The results are summarized in Table 2. In general, the yields of products (**8—10**) were consistently high and no other by-products were obtained at all. Benzimidazole (**3**) formed by the reactions is almost insoluble in low-polar organic solvents and could be easily removed from the reaction mixture by simple filtration after removing the solvent. A characteristic feature of the reduction is the steric effect at the β-position on the rate of reduction (Fig. 1). The results obtained by the reduction of a series of α-cyano-β-substituted cinnamonitriles (**4a—d, 4h, 4i**) indicate that the reduction was sensitive to a steric hinderance at the β-position associated with group R^1, revealing the following order:

$$R^1=H > CH_3 > C_2H_5 > n\text{-}C_3H_7 > i\text{-}C_3H_7 \sim t\text{-}C_4H_9 \quad \text{(no reaction)}$$

Table 1. The Reduction of **4a** to **8a** with Diamine (**1**) and Aldehyde[a]

Aldehyde	Yield of **8a**/%[b]
Benzaldehyde (**2**)	96
Acetaldehyde	88
Propionaldehyde	90
Butyraldehyde	89
2-Phenylpropionaldehyde	87
2-Furaldehyde	61

a) All the reactions were carried out in ethanol at room temperature using the reagent system; **4a**: diamine (**1**): aldehyde=1:1:1 (molar ratio). b) All yields were determined by GLC using benzyl cyanide as an internal standard.

Table 2. Reduction of Electron-Deficient Olefins (**4—6**) with Diamine (**1**) and Aldehyde (**2**)[a]

Product	R^1	R^2	X	Y	Reaction time/h	Yield/%[b]
8b	CH_3	C_6H_5	CN	CN	9	88
8c	C_2H_5	C_6H_5	CN	CN	9.5	88
8d	n-C_3H_7	C_6H_5	CN	CN	12	72
8e	CH_3	CH_3	CN	CN	7	80
8f	CH_3	C_2H_5	CN	CN	8	63
8g	-$(CH_2)_5$-		CN	CN	5	71
9	H	C_6H_5	$CO_2C_2H_5$	CN	11	90
10a	H	C_6H_5	NO_2	H	24	72
10c	H	p-ClC_6H_4	NO_2	H	24	65
10d	H	p-$CH_3C_6H_4$	NO_2	H	24	50
10e	H	p-$CH_3OC_6H_4$	NO_2	H	24	61

a) All the reactions were carried out in ethanol at room temperature using the reagent system; olefin: diamine (**1**): aldehyde (**2**)=1:1:1 (molar ratio). b) Yield of isolated, pure product.

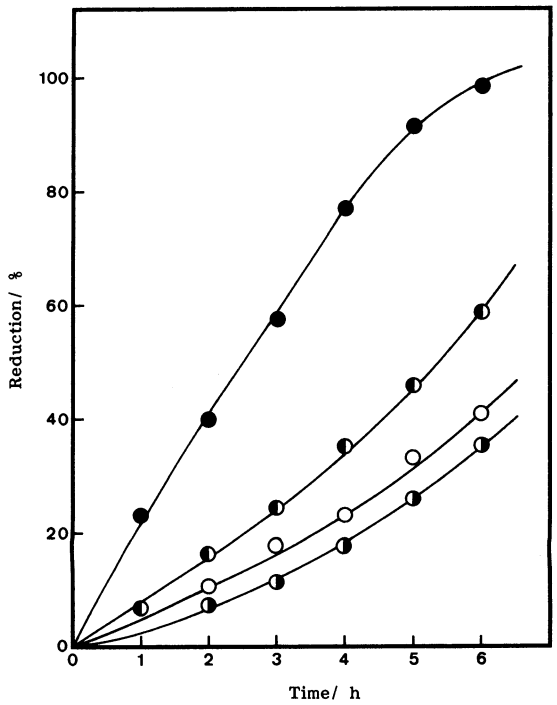
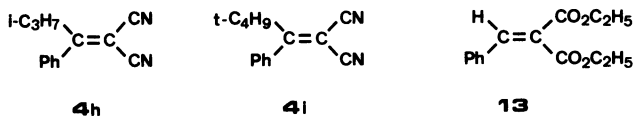


Fig. 1. Rate of reduction of β-substituted benzylidenemalononitriles with **1** and **2** in ethanol at room temperature. Olefins: **4a**(●), **4b**(◐), **4c**(○), and **4d**(◑).

Thus, a highly hindered olefin such as α-cyano-β-isopropylcinnamonitrile (**4h**) or α-cyano-β-(*t*-butyl)-cinnamonitrile (**4i**) could not be reduced at all in the present reduction system. The another feature is the electronic effect of groups X and Y on the reactivity of the olefins. Increasing the sum of the electron-withdrawing abilities of the groups X and Y resulted in a substantial increase in the reactivity of the olefin, revealing the following order:

$$\text{X, Y} = \text{CN, CN} > \text{CN, } CO_2C_2H_5 > NO_2\text{, H} > CO_2C_2H_5\text{, } CO_2C_2H_5 \text{ (no reaction)}$$

Thus, diethyl benzylidenemalonate (**13**) could not be reduced at all.



4h **4i** **13**

Scheme 4.

Nitroalkanes have recently been demonstrated to be useful synthetic intermediates for a variety of transformations of the nitro functionality to other functional groups.[5] Especially, aromatic nitroalkanes are of importance in connection with the synthesis of a variety of biochemically and pharmacologically interesting compounds.[6] They also have been used as a synthetically equivalent to enamines and enolates.[7] A combination of preparation of nitroalkenes from aldehydes by the Knoevenagel condensation and subsequent reduction of them to the corresponding nitroalkanes is the most desirable method for the synthesis of nitroalkanes; this is useful in connection with the elongation of aldehydes or the elongating transformation of aldehydes to ketones.[8] A widely employed method[9] for the reduction of nitroalkenes to the corresponding nitroalkanes involves a $NaBH_4$ reduction. Although this type of reduction of nitroalkenes derived from aliphatic aldehydes[9b] or ketones[10] usually proceeds smoothly in good yields, the reduction of aromatic nitroalkenes (**6**) with $NaBH_4$ produces low yields of products due to undesired side reactions such as dimerization.[9] With these considerations in mind, we studied the general applicability of the PBI-reduction method to the selective reduction of a variety of aromatic nitroalkenes (**6**).

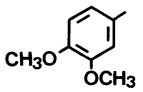
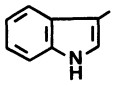
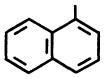
Although the reduction of aromatic nitroalkenes (**6**) with diamine (**1**) and aldehyde (**2**) proceeded in ethanol at room temperature (Table 2), it is desirable to optimalize the reaction conditions in order to obtain the products in higher yields. Thus, the reduction of β-nitrostyrene (**6a**) with diamine (**1**) and aldehyde (**2**) was preliminary examined in a variety of solvents. As shown in Table 3, the reduction with PBI could be accelerated by the use of an alcoholic solvent; however, the kind of alcohol used did not influence the rate of reduction at 65 °C. The change in solvent does not change the specificity of the reduction, as no products other than the (2-nitroethyl)benzene (**10a**) was detected. However, the reaction in 1-butanol at reflux temperature gave the best results in terms of rapidity, due to a rise in the reaction temperature. Thus, the reduction of various aromatic nitroalkenes (**6**) were demonstrated with diamine (**1**) and aldehyde (**2**) in 1-butanol at reflux temperature. The results are summarized in Table 4. Although the kind of aromatic substituent in nitroalkenes (**6**) influenced the rate of the reduction, a variety of nitroalkenes employed here were reduced to the corresponding nitroalkanes (**10**) in excellent yields. In particular, the successful conversion of 3-(2-nitrovinyl)indole (**6k**) to the corresponding 3-(2-nitroethyl)indole (**10k**) is of interest in connection with the synthesis of substituted 3-(2-nitroethyl)-indoles which have proven to be valuable as intermediates in the synthesis of functionalized polycyclic indoles and natural products of the ergoline class.[11b] Similarly, β-nitrostyrenes (**6a—h**) without or with a substituent of nitro, chloro, methyl, methoxyl, or hydroxyl group were effectively converted to the corresponding (2-nitroethyl)benzenes (**10a—h**) in high yields by the same method. In addition, the reduction of β-nitrostyrenes (**6m—o**) possessing alkyl substitution at the α-carbon was more sluggish than that of **6a** but afforded high yields of 1-phenyl-2-nitroalkanes (**10m—o**) after the reaction time of 6—9 h. In all cases, carbon-carbon double bonds of nitroalkenes (**6**) were reduced with complete selectivity and no formation of dimer or other by-products could be observed. The use

Table 3. Rates of Reduction of β-Nitrostyrene (**6a**) with Diamine (**1**) and Aldehyde (**2**) in Various Solvents[a,b]

Solvent	Reduction/%[c,d]			
	1 h	3 h	5 h	8 h
1-Butanol	35(100)	57	66	100
1-Propanol	35 (88)	57(100)	65	100
Ethanol	37 (57)	57 (79)	66 (87)	100(100)
Methanol	38 (52)	59 (74)	64 (86)	100(100)
DMF	0	trace	42	76
Acetonitrile	trace	22	30	44

a) In all cases, solutions were 0.20 M (1 M=mol dm^{-3}) in the olefin (**6a**) and 0.24 M in diamine (**1**) and aldehyde (**2**). b) The reactions were carried out at 65 °C. c) All yields were determined by GLC using pentylbenzene as an internal standard. d) The values in parentheses indicate the yields of the reactions at reflux temperature.

Table 4. Reduction of Nitroalkenes (**6**) to Nitroalkanes (**10**) with Diamine (**1**) and Aldehyde (**2**)[a]

Product	R^1	R^2	Y	Reaction time/h	Yield/%[b]
10a	C_6H_5	H	H	1	88
10b	p-$NO_2C_6H_4$	H	H	1	91
10c	p-ClC_6H_4	H	H	1	82
10d	p-$CH_3C_6H_4$	H	H	3	85
10e	p-$CH_3OC_6H_4$	H	H	3	93
10f	p-HOC_6H_4	H	H	6	78
10g		H	H	6	85
10h		H	H	3	82
10i		H	H	2	81
10j		H	H	3	89
10k		H	H	15	70
10l		H	H	1	80
10m	C_6H_5	H	CH_3	6	91
10n	C_6H_5	H	C_2H_5	8	87
10o	C_6H_5	H	n-C_3H_7	9	84

a) All the reactions were carried out in 1-butanol at reflux temperature using the reagent system; nitroalkene (**6**): diamine (**1**): aldehyde (**2**)=1:1.2:1.2 (molar ratio). b) Yield of isolated, pure product.

of 1.2 equivalent of diamine (**1**) and aldehyde (**2**) was sufficient to conduct the reduction, and benzimidazole (**3**) formed by the reaction could be easily removed from the reaction mixture as described previously. Compared with several other methods[11] currently used for the reduction of aromatic nitroalkenes, the present method is advantageous on account of its simplicity and general applicability to a wide range of aromatic nitroalkenes.

Recently, 2-phenylbenzothiazoline has been reported to be a good reducing agent with the aid of $AlCl_3$ for the conjugate reduction of α,β-unsaturated carbonyl compounds.[1c,g] Using this reagent, olefins **4a—c**, **5**, and **6a** could also be reduced to the corresponding reduced products **8a—c**, **9**, and **10a** in 80—98% yields.[1g] However, these reductions with 2-phenylbenzothiazoline were apparently more sluggish than that involving the PBI-reduction method.

Throughout the reductions (Tables 2 and 4), the cyano, nitro, alkoxycarbonyl, hydroxyl, and arylic

chloro groups were inert to the PBI-reduction. In addition, we have found that other functional groups such as carbonyl, unactivated carbon-carbon double bond, carbon-carbon triple bond, and common carbon-halogen bond are inert under the present reduction conditions. These high chemoselectivities are of great importance and enhance the utility of the present reagent.

Lewis Acid-Promoted Conjugate Reduction of α,β-Unsaturated Ketones (7) with PBI. In order to demonstrate the propensity of PBI regarding a reduction of carbon-carbon double bond systems conjugated with electron-withdrawing groups, we finally examined the reduction of α,β-unsaturated ketones (**7**) to the corresponding saturated ketones (**11**). When benzylideneacetone (**7a**) was dissolved in methanol and allowed to react with 2 equivalents of the reagents, **1** and **2**, at 50 °C, no trace of reduction occurred even after 24 h. However, when the same reaction was carried out in the presence of a Lewis acid, the reduction to 4-phenyl-2-butanone (**11a**) proceeded in 6% ($AlCl_3$)—64% ($ZnCl_2$) yields (Table 5). Among the solvent tested, methanol gave the best results while the reduction in acetonitrile, which is recognized as a good medium in the reduction with 1,3-dimethyl-2-phenylbenzimidazoline[1f] or NAD(P)H-model compounds,[3] gave low yield of the product. Thus, although the enone (**7a**) itself should resist a reduction, the increased electron-deficiency of the enone due to the coordination of the carbonyl group with a Lewis acid allowed the reaction to be possible. It should be noted that the catalytic efficiency is not proportional to the efficiency in forming a complex with a carbonyl group, in contrast to the similar Lewis acid-promoted conjugate reduction with 2-phenylbenzothiazoline[1c,g] or 1,3-dimethyl-2-phenylbenzimidazoline.[1f] The latter efficiency denotes the intensity of a Lewis acid and increases in the order $ZnCl_2<FeCl_3<AlCl_3$.[12] This is probably due to the complex action of a Lewis acid on both the producing step of PBI from **1** and **2** and the actual reduction step. To survey the generality, a series of representative enones (**7b—e**) were treated in the same fashion with the reagent system of diamine (**1**), aldehyde (**2**), and $ZnCl_2$. The results are summarized in Table 6. Although conjugate reductions were accomplished in 11—44% yields with complete regiospecificity, these reactions were apparently more sluggish and less effective compared with similar reductions with 2-phenylbenzothiazoline[1c,g] or 1,3-dimethyl-2-phenylbenzimidazoline.[1f] Accordingly, the synthetic utility of PBI in the conjugate reduction of α,β-unsaturated ketones seems to be rather low.

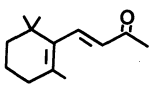
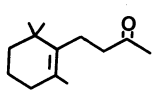
Table 5. Conjugate Reduction of Benzylideneacetone (**7a**) with Diamine (**1**) and Aldehyde (**2**) in the Presence or Absence of Lewis Acid[a]

Lewis acid	Solvent	Yield/%[b]
None	Methanol	0
$AlCl_3$	Methanol	6
$FeCl_3$	Methanol	12
$ZnCl_2$	Methanol	64
$ZnCl_2$	Acetonitrile	10

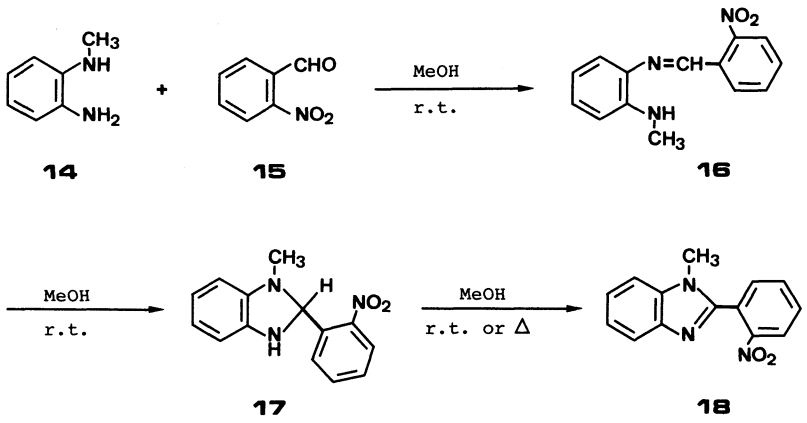
a) All the reactions were carried out at 50°C for 24 h by using the reagent system; **7a**: Lewis acid: diamine (**1**): aldehyde (**2**)=1:1:2:2 (molar ratio). b) Yield determined by GLC.

Mechanisms. In order to obtain clear evidence of the reducing ability of PBI to electron-deficient olefins, we tried to prepare and isolate the structurally related benzimidazoline (**17**) according to the Scheme 5. When *N*-methyl-*o*-phenylenediamine (**14**) was treated under stirring with the same molar amount of *o*-nitrobenzaldehyde (**15**) in methanol at room temperature, Schiff's base (**16**) could be separated soon from the reaction mixture as orange colored needles. This compound could be directly isolated in high purity by a simple filtration from the reaction mixture; any attempt to purify it was unsuccessful due to its unstability. When **16** was heterogeneously stirred in methanol at room temperature, the orange color of **16** turned to pale brown. This was indicative of the formation of imidazoline (**17**) by the intramolecular cyclization of **16**. This compound, which was isolated by filtration, was also unstable; the continuous stirring of its methanol solution at room temperature led to the formation of a stable benzimidazole (**18**) by autoxida-

Table 6. Conjugate Reduction of α,β-Unsaturated Ketones (**7**) with Diamine (**1**) and Aldehyde (**2**)[a]

	Enone		Product	Yield/%[b]
7b	$C_6H_5CH=CHCOC_6H_5$	**11b**	$C_6H_5CH_2CH_2COC_6H_5$	44
7c	$C_6H_5COCH=CHCOC_6H_5$	**11c**	$C_6H_5COCH_2CH_2COC_6H_5$	36
7d		**11d**		23
7e		**11e**		11

a) All the reactions were carried out at 50°C for 24 h by using the reagent system; enone (**7**): $ZnCl_2$: diamine (**1**): aldehyde (**2**)=1:1:2:2 (molar ratio). b) Yield determined by GLC.

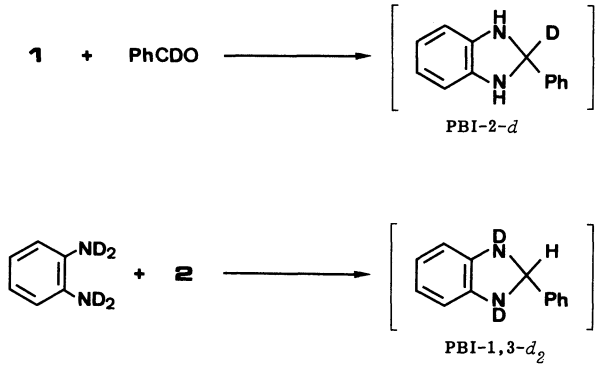


Scheme 5.

tion. The spectral and analytical data of these compounds (**16**—**18**) were entirely consistent with the proposed structures. For an examination of the reducing ability of **17**, a reaction with same molar amount of the olefin (**4a**) was carried out in ethanol at room temperature. Expectedly, the reduced product (**8a**) was obtained in 85% yield together with **18** (97% yield). This result strongly supports the validity of the existence of the reducing ability of PBI to an electron-deficient olefin.

When an ethanol solution of an equimolar mixture of **4a** and **17** was kept standing at room temperature for 12 h, a spectral change gradually occurred in which a new spectrum was reached with four clear isosbestic points at 207, 225, 291, and 331 nm (Fig. 2). The presence of these points indicates that no intermediate is present during a reaction in sufficient concentration for its own spectrum to become apparent, superimposed on those of reactants and products.

In an attempt to determine the destination of a hydrogen atom at the C-2 carbon of PBI, we reduced the olefin **6a** with PBI-2-*d* and PBI-1,3-d_2, which were prepared with the reagent system of diamine (**1**) and benzaldehyde-*d* or *o*-phenylenediamine-d_4 and aldehyde (**2**), respectively (Scheme 6). The product of the



Scheme 6.

reduction with PBI-2-*d* in 1-butanol was found to be (2-nitroethyl)benzene (**19**); it contained one deuterium atom at its β-carbon (Scheme 7). This result shows that the hydrogen atom at the C-2 carbon of PBI surely transfers to the β-carbon of the olefin as a hydride,

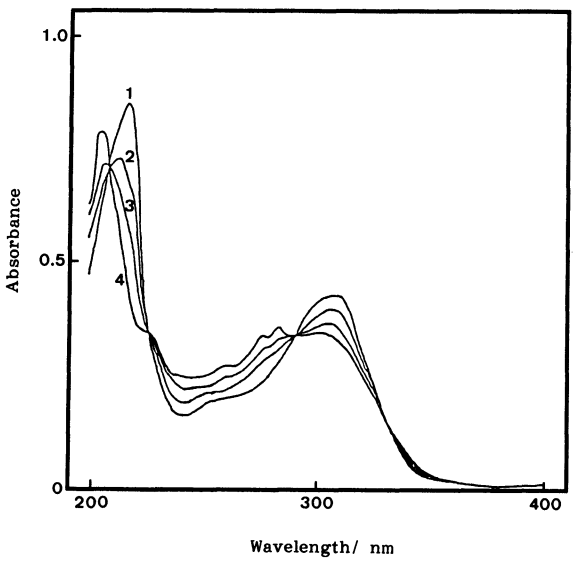
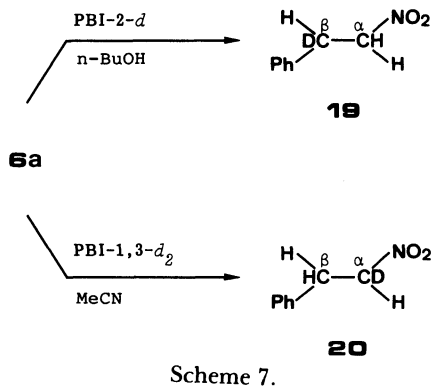


Fig. 2. Spectral change as a function of time for reaction between olefin **4a** and imidazoline **17** in ethanol at 25°C. $[\mathbf{4a}]_0=[\mathbf{17}]_0=2\times10^{-5}$ mol dm^{-3}. Time (h): 1, 0; 2, 4; 3, 8; 4, 12.



Scheme 7.

since the carbon at the β-position of **6a** is very electrophilic. When the same olefin was reduced in acetonitrile with PBI-1,3-d_2, the α-deuterated product (**20**) was selectively obtained in 83% yield (Scheme 7). This shows that the olefin incorporated the hydrogen atom at the nitrogen of PBI at its α-position probably as a proton.

Table 7. Rates of Reduction of β-Nitrostyrene (**6a**) with diamine (**1**) and *p*-Substituted Benzaldehyde in Refluxing 1-Butanol[a)]

Substituent	Reduction/%[b)]		
	1 h	3 h	5 h
NO_2	63	81	100
Cl	77	100	—
H	100	—	—
CH_3	78	100	—
CH_3O	70	85	100

a) In all cases, solutions were 0.20 M in the substrate and 0.24 M in diamine (**1**) and *p*-substituted benzaldehyde. b) All yields were determined by GLC using pentylbenzene as an internal standard.

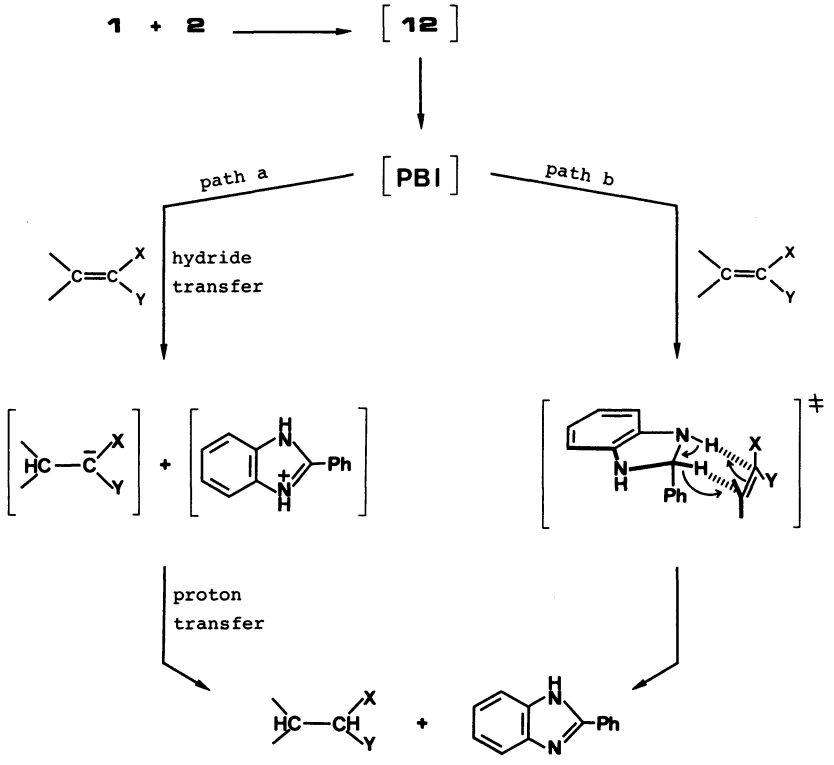
The substituent effect on the reduction of the olefin (**6a**) by PBI was studied with the reagent system of diamine (**1**) and *p*-substituted benzaldehyde. Thus, the reaction was monitored by GLC at a reflux temperature of 1-butanol. As shown in Table 7, when the aldehyde (**2**) was substituted by an electron-donating group, the rate of the reduction decreased in proportion to electron-donating ability of the substituent. On the other hand, the rate also decreased with an increase in the electron-withdrawing ability of the substituent. These results well match with a mechanism including a hydride transfer followed by a proton transfer from PBI to the olefin, since the rate of formation of PBI should decrease with an increase in electron-donating ability of the substituent and the rate on the actual reduction stage (hydride transfer) should also decrease with an increase in electron-withdrawing ability of the substituent.

Considering these facts, two possible reaction mechanisms for the present PBI-reduction can be proposed as shown in Scheme 8. They involve the sequential transfer of a pair of hydrogens of PBI (shown as path **a**) and a cyclic addition of two hydrogens of PBI in either exact or nearly exact concurrence (shown as path **b**). We consider that only the stereochemistry of the transfer of a pair of hydrogens of PBI to the carbon-carbon multiple bond of the conjugate olefin system can distinguish between path **a** and **b**. However, all of our attempts to determine such a stereochemical course were unsuccessful. Thus, paths **a** and **b** are, as yet, both candidates for the present PBI-reduction; however, path **b** seems to be more likely in light of the forementioned observation on UV-spectral change in the reduction of **4a** with **17** together with the previous results[1g)] that the hydrogen shift from 2-phenylbenzothiazoline to electron-deficient carbon-carbon double bonds of α,β-unsaturated carbonyl system is a synchronous transport of a pair of hydrogens.

Conclusion. The present study clearly reveals that PBI is a mild, selective and useful reducing agent for the reduction of carbon-carbon double bonds of electron-deficient olefins, and provides a unique and convenient method for this type of reaction. The advantages of the present method are summarized as follows:

(1) Easy preparation (in situ generation) of the reducing agent,

(2) operational simplicity,



Scheme 8.

(3) mild reaction conditions (moderate temperature, nonbasic, nonacidic, and no active ionic species present),
(4) complete selectivity,
(5) no side reactions,
(6) high chemoselectivity.

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 and UV spectra were recorded on a JASCO A-202 and a Simadzu UV-240 spectrophotometers, respectively. Mass spectra were obtained on a JEOL JMS-0lSG 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. Silica gel (Wakogel C-300) was used for short-column chromatography.

Materials. *o*-Phenylenediamine was purified by recrystallization from ethanol. *o*-Phenylenediamine-d_4 was prepared by continual recrystallization of pure *o*-phenylenediamine from D_2O, that was pure *o*-phenylenediamine-d_4 by ^{1}H NMR; no amino proton absorption was detected. Aldehydes were commercially supplied and purified by distillation or recrystallization. Benzaldehyde-*d* was prepared via deuteration of 2-lithio-2-phenyl-1,3-dithiane with D_2O,[13] that was pure benzaldehyde-*d* by ^{1}H NMR; no aldehyde proton absorption was detected. Commercially available $ZnCl_2$, $FeCl_3$, and $AlCl_3$ were used without purification. Alkylidenemalononitriles,[14] ethyl α-cyanocinnamate,[15] diethyl benzylidenemalonate,[16] and aromatic nitroalkenes[17] were prepared by a Knoevenagel condensation of the corresponding aldehydes or ketones with malononitrile, ethyl cianoacetate, diethyl malonate, or nitroalkanes, respectively. Benzylideneacetone[18] and (*E*)-1,2-dibenzoylethylene[19] were prepared according to methods described in the literature. Other α,β-unsaturated ketones and solvents were commercial materials which were purified by the usual methods.

General Procedure for the Reduction of Electron-Deficient Olefins (4 and 5) with PBI. To a stirred solution of the olefin (2.0 mmol) and benzaldehyde (0.21 g, 2.0 mmol) in ethanol (20 ml) under nitrogen at room temperature, *o*-phenylenediamine (0.22 g, 2.0 mmol) was added. After completion of the reaction (monitored by TLC; see Table 2), the solvent was evaporated under reduced pressure. Dichloromethane was added to the residue and insoluble imidazole (**3**) was filtered off. After removing dichloromethane under reduced pressure, the crude product was purified by short-column chromatography on silica gel to give the pure reduced product (**8** and **9**). In a large-scale synthesis, purification by distillation or recrystallization was also effective. Some physical and spectral data of the products are given as follows: **8a**: Mp 91—92 °C; IR (KBr) 2252 cm^{-1} (CN); ^{1}H NMR (CCl_4) δ=3.16 (d, 2H, CH_2, *J*=7 Hz), 3.70 (t, 1H, CH, *J*=7 Hz), and 7.18 (s, 5H, Ar); MS *m/z* 156 (M^+). **8b**: Bp 117—119 °C/6 mmHg (1 mmHg=133.322 Pa); IR (neat) 2250 cm^{-1} (CN); ^{1}H NMR (CCl_4) δ=1.49 (d, 3H, CH_3, *J*=7 Hz), 3.31 (m, 1H, CH), 3.71 (d, 1H, CH, *J*=6 Hz), and 7.15 (s, 5H, Ar); MS *m/z* 170 (M^+). **8c**: Bp 128—130 °C/5 mmHg; IR (neat) 2250 and 2230 cm^{-1} (CN); ^{1}H NMR (CCl_4) δ=0.83 (t, 3H, CH_3, *J*=6.2 Hz), 1.91 (m, 2H, CH_2), 2.98 (q, 1H, CH), 3.83 (d, 1H, CH, *J*=6 Hz), and 7.15 (s, 5H, Ar); MS *m/z* 184 (M^+). **8d**: Bp 108—111 °C/3 mmHg; IR (neat) 2249 cm^{-1} (CN); ^{1}H NMR (CCl_4) δ=0.88 (t, 3H, CH_3, *J*=5.6 Hz), 1.20 (m, 2H, CH_2), 1.87 (q, 2H, CH_2), 3.07 (q, 1H, CH), 3.73 (d, 1H, CH, *J*=6 Hz), and 7.15 (s, 5H, Ar); MS *m/z* 198 (M^+). **8e**: Bp 85—86 °C/5 mmHg; IR (neat) 2245 cm^{-1} (CN); ^{1}H NMR (CCl_4) δ=1.21 (d, 6H, $2CH_3$, *J*=7 Hz), 2.25 (m, 1H, CH), and 3.62 (d, 1H, CH, *J*=5 Hz); MS *m/z* 107 (M^+−1). **8f**: Bp 77—78 °C/7 mmHg; IR (neat) 2246 cm^{-1} (CN); ^{1}H NMR (CCl_4) δ=0.70—1.24 (m, 6H, $2CH_3$), 1.54 (m, 2H, CH_2), 2.02 (m, 1H, CH), and 3.72 (d, 1H, CH, *J*=4.6 Hz); MS *m/z* 121 (M^+−1). **8g**: Colorless oil; IR (neat) 2251 cm^{-1} (CN); ^{1}H NMR (CCl_4) δ=0.80—2.28 (br, 11H, *c*-C_6H_{11}) and 3.42 (d, 1H, CH, *J*=5.2 Hz); MS *m/z* 147 (M^+−1). **9**: Colorless oil; IR (neat) 2240 (CN) and 1740 (CO) cm^{-1}; ^{1}H NMR (CCl_4) δ=1.14 (t, 3H, CH_3, *J*=7 Hz), 3.10 (d, 2H, CH_2, *J*=6 Hz), 3.48 (t, 1H, CH, *J*=6 Hz), 4.05 (q, 2H, CH_2), and 7.10 (s, 5H, Ar); MS *m/z* 203 (M^+).

General Procedure for the Reduction of Aromatic Nitroalkenes (6) with PBI. To a stirred solution of nitroalkene (**6**) (5.0 mmol) and benzaldehyde (0.64 g, 6.0 mmol) in 1-butanol (25 ml) under nitrogen at room temperature, *o*-phenylenediamine (0.65 g, 6.0 mmol) was added. After refluxing for the appropriate time (monitored by TLC; see Table 4), the solvent was evaporated under reduced pressure. Dichloromethane was added to the residue and insoluble imidazole (**3**) was filtered off. The dichloromethane solution was thoroughly washed with 0.1M HCl, dried with $MgSO_4$, and concentrated to give a crude product. The crude product was purified by short-column chromatography on silica gel to give the pure reduced product (**10**). In a large-scale synthesis, purification by distillation or recrystallization was also effective. Some physical and spectral data of the products are given as follows: **10a**: Bp 78 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ=3.00 (t, 2H, β-CH_2, *J*=7 Hz), 4.27 (t, 2H, α-CH_2, *J*=7 Hz), and 6.97 (s, 5H, Ar). **10b**: Mp 96—97 °C; ^{1}H NMR ($CDCl_3$) δ=3.39 (t, 2H, β-CH_2, *J*=7 Hz), 4.63 (t, 2H, α-CH_2, *J*=7 Hz), 7.35 (d, 2H, Ar, *J*=8 Hz), and 8.09 (d, 2H, Ar, *J*=8Hz). **10c**: Bp 136 °C/3 mmHg; ^{1}H NMR ($CDCl_3$) δ=3.17 (t, 2H, β-CH_2, *J*=7 Hz), 4.43 (t, 2H, α-CH_2, *J*=7 Hz), and 7.07 (m, 4H, Ar). **10d**: Bp 96 °C/2 mmHg; ^{1}H NMR ($CDCl_3$) δ=2.25 (s, 3H, CH_3), 3.07 (t, 2H, β-CH_2, *J*=7 Hz), 4.30 (t, 2H, α-CH_2, *J*=7 Hz), and 6.90 (s, 4H, Ar). **10e**: Bp 123 °C/2 mmHg; ^{1}H NMR ($CDCl_3$) δ=3.03 (t, 2H, β-CH_2, *J*=7 Hz), 3.57 (s, 3H, OCH_3), 4.33 (t, 2H, α-CH_2, *J*=7 Hz), 6.93 (d, 4H, Ar). **10f**: Colorless oil; ^{1}H NMR (DMSO-d_6) δ=3.09 (t, 2H, β-CH_2, *J*=7 Hz), 4.43 (t, 2H, α-CH_2, *J*=7 Hz), 6.60 (d, 2H, Ar, *J*=8 Hz), and 6.86 (d, 2H, Ar, *J*=8 Hz). **10g**: Mp 50—51 °C; ^{1}H NMR ($CDCl_3$) δ=3.23 (t, 2H, β-CH_2, *J*=7 Hz), 3.80 (s, 6H, $2OCH_3$), 4.53 (t, 2H, α-CH_2, *J*=7 Hz), and 6.67 (s, 3H, Ar). **10h**: Colorless oil; ^{1}H NMR ($CDCl_3$) δ=3.13 (t, 2H, β-CH_2, *J*=7 Hz), 4.50 (t, 2H, α-CH_2, *J*=7 Hz), 5.80 (s, 2H, OCH_2O), and 6.57 (s, 3H, Ar). **10i**: Bp 61—63 °C/2 mmHg; ^{1}H NMR ($CDCl_3$) δ=3.30 (t, 2H, β-CH_2, *J*=7 Hz), 4.50 (t, 2H, α-CH_2, *J*=7 Hz), 5.97 (m, 2H, Ar), 6.13 (m, 1H, Ar), and 7.17 (s, 1H, Ar). **10j**: Bp 99—101 °C/3 mmHg; ^{1}H NMR ($CDCl_3$) δ=3.33 (t, 2H, β-CH_2, *J*=7 Hz), 4.30 (t, 2H, α-CH_2, *J*=7 Hz), and 6.80—7.03 (m, 3H, Ar). **10k**: Colorless oil; ^{1}H NMR ($CDCl_3$) δ=3.13 (t, 2H, β-CH_2, *J*=7 Hz), 4.30 (t, 2H, α-CH_2, *J*=7 Hz), 6.57 (d, 1H, Ar, *J*=4Hz), 6.97 (m, 3H, Ar), and 7.57 (br, 1H, NH). **10l**: Mp

45—46 °C; ^{1}H NMR ($CDCl_3$) δ=4.43 (t, 2H, β-CH_2, J=7 Hz), 5.30 (t, 2H, α-CH_2, J=7Hz), and 7.80—8.70 (m, 7H, Ar). **10m**: Bp 85 °C/2 mmHg; ^{1}H NMR ($CDCl_3$) δ=1.43 (d, 3H, CH_3, J=7 Hz), 3.00 (m, 2H, β-CH_2), 4.50 (m, 1H, α-CH), and 7.07 (s, 5H, Ar). **10n**: Bp 100 °C/2 mmHg; ^{1}H NMR ($CDCl_3$) δ=0.97 (t, 3H, CH_3, J=7.4 Hz), 1.90 (m, 2H, CH_2), 3.13 (q, 2H, β-CH_2), 4.60 (m, 1H, α-CH), and 7.17 (s, 5H, Ar). **10o**: Bp 81—82 °C/1 mmHg; ^{1}H NMR ($CDCl_3$) δ=0.70—2.20 (m, 7H, C_3H_7), 3.06 (m, 2H, β-CH_2), 4.67 (m, 1H, α-CH), and 7.06 (s, 5H, Ar).

Conjugate Reduction of α,β-Unsaturated Ketones (7) with PBI in the Presence of $ZnCl_2$. A solution of enone (**7**) (1.0 mmol) in dry methanol (3 ml) and $ZnCl_2$ (0.14 g, 1.0 mmol) were mixed in a glass tube under ice-water cooling. After the $ZnCl_2$ was completely dissolved, a solution of *o*-phenylenediamine (0.22 g, 2.0 mmol) and benzaldehyde (0.21 g, 2.0 mmol) in dry methanol (4 ml) was added and the mixture was degassed several times in vacuo. The tube was sealed in vacuo and kept at 50 °C for 24 h. After 0.1M HCl (15 ml) was added to the mixture in the tube under ice-water cooling, the aqueous mixture was extracted with dichloromethane. The dichloromethane solution was thoroughly washed with water, dried with $MgSO_4$, and analyzed by quantitative GLC. The results are given in Table 6. 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.

Preparation of 1-Methyl-2-(*o*-nitrophenyl)benzimidazoline (17). A solution of *o*-nitrobenzaldehyde (0.15 g, 1 mmol) and *N*-methyl-*o*-phenylenediamine (0.12 g, 1 mmol) in methanol was stirred at room temperature. After ca. 5 min, precipitated orange-colored needles were separated out, which were collected by filtration, washed with cold methanol, and dried in vacuo to give an almost pure Schiff's base (**16**) (0.22 g, 85%); mp 89—93 °C; IR (KBr) 1590 cm^{-1} (N=C); ^{1}H NMR ($CDCl_3$) δ=2.67 (s, 3H, CH_3), 8.93 (s, 1H, CH), and 7.00—8.00 (m, 8H, Ar).

Found: C, 65.59; H, 5.05; N, 16.41%. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46%.

Without further purification, Schiff's base (**16**) (0.26 g, 1 mmol) was added in methanol and heterogeneously stirred at room temperature for 6 h. During this period, the orange-color of the needles turned to light brown. Filtration, washing with cold methanol, and drying in vacuo gave almost pure benzimidazoline (**17**) as brown needles (0.24 g, 92%); mp 134—136 °C; IR (KBr) 1495 cm^{-1} (NH); ^{1}H NMR ($CDCl_3$) δ=2.97 (s, 3H, CH_3), 6.07 (s, 1H, CH), and 6.20—8.00 (m, 8H, Ar).

Found: C, 65.46; H, 5.06; N, 16.38%. Calcd for $C_{14}H_{13}N_3O_2$: C, 65.87; H, 5.13; N, 16.46%.

Reduction of Benzylidenemalononitrile (4a) with Benzimidazoline (17). The olefin **4a** (0.15 g, 1 mmol) was reduced with benzimidazoline (**17**) (0.26 g, 1 mmol) in ethanol (3 ml) for 12 h according to the general procedure. The usual work-up of the reaction mixture gave benzimidazole (**18**) (0.25 g, 97%). Chromatographic purification of the filtrate gave the pure reduced product (**8a**) (0.13 g, 85%).

Reduction of β-Nitrostyrene (6a) with PBI-2-*d*. Nitrostyrene **6a** (0.45 g, 3.0 mmol) was reduced for 1h with *o*-phenylenediamine and benzaldehyde-*d* according to the general procedure. A chromatographic purification of the crude product gave β-deuterated compound (**19**) as a colorless oil (0.42 g, 91%); ^{1}H NMR (CCl_4) δ=3.00 (t, 1H, β-CDH), 4.27 (d, 2H, α-CH_2), and 6.97 (s, 5H, Ar); MS m/z 152 (M^+).

Reduction of β-Nitrostyrene (6a) with PBI-1,3-d_2. Nitrostyrene **6a** (0.45 g, 3.0 mmol) was reduced with *o*-phenylenediamine-d_4 and benzaldehyde for 24 h according to the general procedure, except that acetonitrile was used in place of 1-butanol. A chromatographic purification of the crude product gave α-deuterated compound (**20**) as a colorless oil (0.38 g, 83%); ^{1}H NMR ($CDCl_3$) δ=3.07 (d, 2H, β-CH_2), 4.30 (t, 1H, α-CDH), and 7.00 (s, 5H, Ar); MS m/z 152 (M^+).

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