



## Inclusion Complexes of Conjugated Nitroolefins in $\beta$ -Cyclodextrin

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**Abstract.** Physical studies such as Powder X-ray, FT-IR, UV,  $^1\text{H}$  and  $^{13}\text{C}$  NMR clearly identify a 1 : 1 inclusion complex formed between  $\beta$ -cyclodextrin and nitroolefins such as  $\beta$ -nitrostyrene, 1-nitrocyclohexene in the solid state as well as in solution. The olefins lie shallow inside the cavity leaving the nitro group outside the torus. It has been found that the complex is capable of reacting with a  $\alpha$ -phenyl-*N*-*p*-methylphenyl nitron in a 1,3-dipolar cycloaddition with excellent rate acceleration and regioselection. The  $\text{NaBH}_4$  reduction of the complex in the solid state leads to the corresponding nitroalkane.

**Key words:**  $\beta$ -CyD,  $\beta$ -nitrostyrene, 1-nitrocyclohexene, 1 : 1 complexes, 1,3-dipolar cycloadditions,  $\text{NaBH}_4$  reduction.

### 1. Introduction

The cyclodextrins (CyDs), the cyclic oligomers of glucose linked by  $\alpha,1,4$ -bonds are doughnut shaped molecules with a definite cavity. The interior of the cavity is sufficiently hydrophobic and thus CyDs serve as host for a range of organic molecules [1–2]. The inclusion complexes of CyDs are useful in controlled chemical synthesis [3–4].

The nitro group, as a powerful electron withdrawing group, dominates the chemistry of all compounds bearing it. They are useful synthetic intermediates in organic synthesis because of their excellent ability to form carbon-carbon bonds and their easy transformation into a variety of functional groups [5–6]. They have found potent application in the field cycloadditions as they are quite reactive and they decide the course of the reaction as a dienophile [7–8]. The reduction reactions of the nitroolefins are quite interesting as the reduction is reagent sensitive [9].

Recently, we have reported that the  $\alpha$ -phenyl-*N*-*p*-methylphenyl nitron forms an inclusion complex with  $\beta$ -CyD in two different stoichiometries namely 1G:1H and 1G:2H and that the 1G:2H complex is found to be an excellent dipole in the 1,3-dipolar cycloadditions with electron deficient olefins [10]. In continuation of this work, we have now embarked upon a strategy of including electron deficient

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nitroolefins in CyD and to observe the effect of inclusion complexation on the rate and selectivity in the cycloaddition reaction with nitrones.

## 2. Experimental

### 2.1. MATERIALS

The nitroolefins under study viz.,  $\beta$ -nitrostyrene (NS) and 1-nitrocyclohexene (NC) were synthesized by the reported procedures [7, 11]. They were purified prior to use.  $\beta$ -CyD (Leochem, India) was used after drying at 60 °C in a vacuum oven at 10 mm for 24 hours. All the common solvents used were of laboratory grade and purified according to standard procedures. Millipore distilled water was used throughout the study.

### 2.2. PREPARATION OF THE $\beta$ -CYD NITROOLEFIN COMPLEXES

The complex was obtained by stirring a equimolar quantity of the nitroolefin (0.045 g, 0.3 mmol of NS and 0.037 g, 0.3 mmol of NC) in chloroform (20 mL) layered over by a saturated solution of the  $\beta$ -CyD in water (0.33 g, 0.3 mmol in 25 mL) at 20 °C for 24–30 hours. The chloroform was separated off and the precipitate in the aqueous layer was filtered under the pump and dried in air. Any uncomplexed guest that might have adhered was removed by washing with a small quantity of cold chloroform. The complex was dried in an vacuum oven at 45 °C/10 mm for 2–5 hours. The complex was then stored at 0–4° under refrigeration in a moisture free environment. The guest-host stoichiometry was determined by subjecting a known amount of the complex to quantitative soxhlet extraction with chloroform and estimating the amount of the guest by gravimetry.

A physical mixture of the nitroolefins and  $\beta$ -CyD in the molar ratio 1 : 1 was prepared by thoroughly mixing the well ground components in an agate mortar.

### 2.3. 1,3-DIPOLAR CYCLOADDITION OF THE INCLUDED NITROOLEFINS WITH $\alpha$ -PHENYL-*n*-*p*-METHYLPHENYL NITRONE IN THE SOLID STATE

Equimolar quantities of the inclusion complexes of NS or NC (2 g, 1.6 mmol) and  $\alpha$ -phenyl-*N*-*p*-methylphenyl nitrone (0.3 g, 1.6 mmol) were thoroughly homogenized in an agate mortar and shaken in a mechanical shaker at 65–75 °C. The product formation was monitored by TLC and the product was isolated by extraction with warm chloroform. The precipitated cyclodextrin was removed by filtration and washed several times with warm chloroform to remove any adhering product. The reaction conditions were optimized after a number of trials and the optimum condition was found to be 60 °C/3 hours. The filtrates were evaporated and the products obtained were purified by column chromatography (silica gel/hexane) and their physical data are comparable to products obtained by normal reactions in solution as reported [12].

Control experiments in the absence of the  $\beta$ -CyD complex were also carried out by subjecting a physical mixture of the reactants in the presence of  $\beta$ -CyD under the identical experimental conditions.

## 2.4. $\text{NaBH}_4$ REDUCTION OF THE INCLUDED NITROOLEFINS

### 2.4.1. *Reduction in THF-MeOH medium*

The CyD complex (1 g, 0.8 mmol) was suspended in 50 mL of THF-MeOH (10 : 1 v/v) and  $\text{NaBH}_4$  (2.5 g, 50 mmol) was added in portions and the mixture stirred for 4–6 hours. The reaction mixture was carefully decomposed in crushed ice and the products were extracted with warm chloroform.

### 2.4.2. *Reduction in the solid state*

Dry  $\text{NaBH}_4$  (2.5 g, 50 mmol) was mixed thoroughly with the complex (1 g, 0.8 mmol) in a dry mortar and kept at 20 °C after flushing the flask with a stream of dry nitrogen. The sealed flask was shaken in a mechanical shaker for 48 hours at 20 °C. The product was isolated after careful dissolution of the reaction mixture in ice cold water followed by extraction with warm chloroform. Its physical characteristics were compared with the product obtained from a reported method [13].

## 2.5. ANALYTICAL METHODS

Powder X-ray patterns were obtained using a PW1820 diffractometer using a Cu source, operating at 40 KV/30 mA. FT IR spectra were recorded on a Perkin–Elmer 1900 spectrometer by mounting the samples in KBr discs. UV studies were carried out using a Shimadzu 160 spectrophotometer with either HPLC or analytical grade DMSO as solvent. The NMR [both  $^1\text{H}$  and  $^{13}\text{C}$ ] were recorded on a Bruker AC-200 spectrometer in  $\text{D}_2\text{O}$  (60 °C) and  $\text{DMSO } d_6$  (room temperature) respectively. HPLC analyses were done on a Shimadzu LC8A instrument using a reverse phase ODS column with 70% methanol as the mobile phase.

## 2.6. DETERMINATION OF FORMATION CONSTANTS

A stock solution of CyD [ $10^{-3}\text{M}$  in DMSO] and the nitroolefins [ $10^{-2}\text{M}$  in DMSO] were prepared.  $25\mu\text{L}$  of the nitroolefin solution was taken in 5 mL standard measuring flasks. To this, ten various quantities of the  $\beta$ -CyD solution [10–1000  $\mu\text{L}$ ] were added. The solutions were made to 5 mL with DMSO. The flasks were shaken for 4–6 hours and equilibrated well. The changes in the absorbances [ $\epsilon_{\text{max}}$ ] for the nitroolefin at 289 and 282 nm respectively for NS and NC in DMSO were observed. Using the Benesi–Hildebrand plot [14] ( $a_0b_0/\Delta\text{OD}$  versus  $1/a_0$ , where  $a_0$  and  $b_0$

are the concentration of  $\beta$ -CyD and nitroolefin respectively) the dissociation constant  $K_d$  was determined. From these, the formation constant  $K_f$  ( $1/K_d$ ) for the complex was arrived at.

### 3. Results and Discussion

#### 3.1. CHARACTERIZATION OF $\beta$ -CYD-NITROOLEFIN COMPLEXES

Prominent physical methods, which are often used, for the identification of inclusion complexes are powder X-ray diffraction and FT-IR (solid state), NMR and kinetic methods such as the determination of formation constants (solution). These were all employed in characterizing the inclusion complexes under study.

#### 3.2. X-RAY POWDER DIFFRACTION

A true inclusion complex will have its diffraction patterns altered from those of the pure components [2]. Comparing the patterns for the  $\beta$ -CyD, NS, its complex and the NC complex with that of the physical mixture reveals marked differences. Peaks for the NS in the region  $2\theta$  5.2–28.09° are found to be absent or shifted in the complex and decreased intensities. In addition, peaks for  $\beta$ -CyD between 10.4–19.1° are absent in the complex. Similar shifts in the peaks of the CyD are also visible in the case of the  $\beta$ -CD-NC complex. Changes also are observed in the NC complex. However, the diffraction patterns of the physical mixture of the host and guest have been found to be the approximate superposition of the X-ray patterns of the two components. This clearly shows that the precipitated solids are true inclusion complexes.

#### 3.3. IR STUDIES

In the present case, bands due to C=C, C-NO<sub>2</sub> (assym. str) and C-NO<sub>2</sub>(sym. str) observed at 1632 cm<sup>-1</sup> for NS, 1513 cm<sup>-1</sup> 1342 cm<sup>-1</sup>, are found at 1635 cm<sup>-1</sup>, 1522 cm<sup>-1</sup> and 1347 cm<sup>-1</sup> respectively in the complexes with reduced intensities.

#### 3.4. <sup>1</sup>H NMR SPECTRA

Because of the magnetic screening environment of aromatic molecules, their inclusion should be particularly susceptible to detection by <sup>1</sup>H NMR [15]. All the six CyD protons can be identified by their specific coupling pattern. According to Connors [16], a typical inference is that if only H(3) undergoes a shift, then the cavity penetration is shallow, whereas if H(5) is also shifted, the penetration is deep.

In the case of the precipitated  $\beta$ -CyD NS and NC complexes dissolved in D<sub>2</sub>O at 60 °C, as seen from Figure 1A, although all the CyD protons are shifted upfield, remarkable shifts occur only for H(3). The splitting patterns for all the six protons

are also changed. The H(3) peak moves upfield and appears under the H(6) signal. Thus the one hydrogen triplet is absent and a four hydrogen unresolved multiplet is only observable. The H(5) peak whose multiplicity is not directly observable even in free CyD, as it merges with the H(6) signal, does not shift much in the complex and appears almost at the same position. The shift for the H(3) peak is more marked in the case of the  $\beta$ -CyD-NC complex (almost 25 Hz) while it is around 12–15 Hz in the case of  $\beta$ -CyD-NS complex. This clearly proves that the complex is shallow in nature. In the case of the  $\beta$ -CyD-NC complex, the shifts can be accounted for by the van der Waals interactions with the more protruding alicyclic methylene hydrogens and it must be noted that the bonds here are having  $\sigma$  character. Here also the H(2) and H(6) signals are not shifted very much indicative of the mode of penetration of NC through the wider secondary hydroxyl side leaving the nitro group outside the torus to be surrounded by the aqueous phase. The fact that the H(6) proton does not undergo any nitro group induced shifts as seen in some earlier cases such as nitrophenyl acetate [17] proves the existence of the same outside the torus in the aqueous phase [15–18]. In both the cases, it has been found that the coupling of the anomeric H(1) to H(2) has been changed by 0.6 Hz as reported earlier [18]. No conformational change occurs upon inclusion which is indicated by the absence of any dramatic change in the H(1) position (Figure 1B).

These shifts are comparatively small when compared to other substrates. But it should be mentioned that these are studies involving precipitated solid complexes dissolved in D<sub>2</sub>O at 60 °C, while most of the previous work [15–19] involved the NMR study of the CyD in the presence of added guest.

### 3.5. <sup>13</sup>C NMR STUDIES

The conformational nature of the complex in solution is best established by the <sup>13</sup>C NMR spectra of the complex in DMSO *d*<sub>6</sub>. The <sup>13</sup>C NMR chemical shifts of different carbons are given in Table 1 and Table 2. The shifts are assigned using the DMSO signal as the internal standard and the chemical shifts are measured relative to Me<sub>4</sub>Si using the correction  $-\delta(\text{Me}_4\text{Si}) = \delta\text{DMSO} + 40.5$ .

In the case of the CyD-NS complex, the <sup>13</sup>C NMR shifts complement the results obtained from the <sup>1</sup>H NMR studies. The C(2), C(3) and C(4) carbons experience a smaller shielding effect compared to C(5) and C(6) which experience a large shielding effect. In the case of NS, the carbons C(4), C(5) and C(6) are deshielded to a lesser extent when compared to carbons C(1), C(2) and C(3) which experience more deshielding. These are indicative of the inclusion of the phenyl ring although not deep inside leaving carbons 1, 2 and 3 outside the cavity. The shift recorded for C(3) clearly outlines its presence in the borderline between the non polar CyD cavity and the polar DMSO phase [22].

In the case of the NC complex, (Table 2) introduction of the carbons C(3), C(4) and C(5) into the cavity leaving the C(1)–C(2) double bond along with the nitro group outside the doughnut can be inferred from the shifts. Here also the maximum

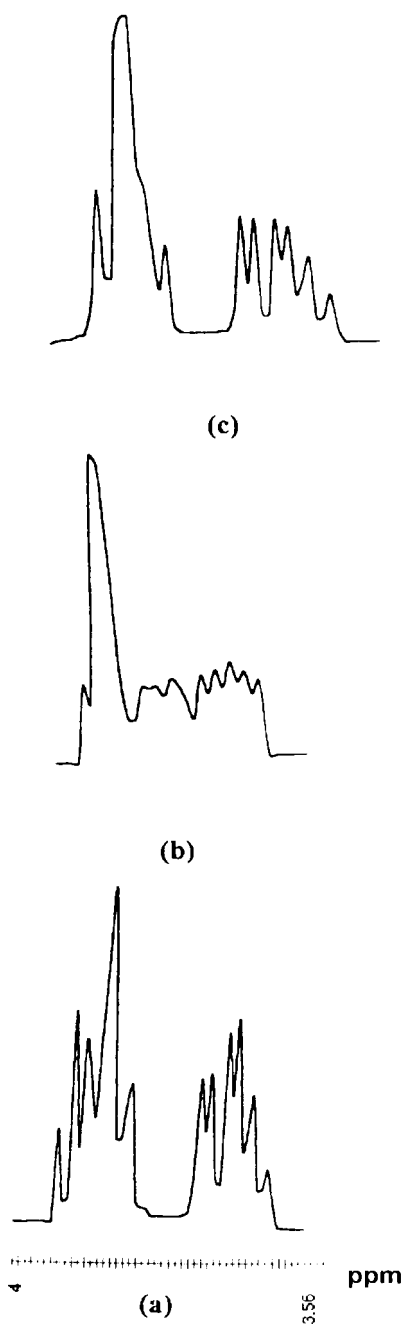


Figure 1A. (a)  $^1\text{H}$  NMR of  $\beta\text{CyD}$ , (b)  $\beta\text{-CyD-NS}$  complex, (c)  $\beta\text{-CyD-NC}$  complex.

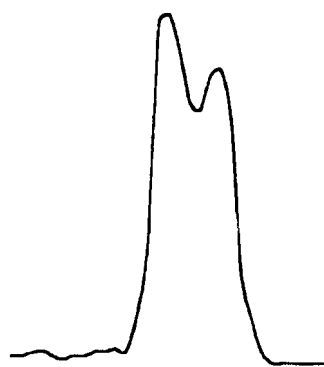


Figure 1B. (a)  $^1\text{H}$  NMR of  $\beta$ -CyD, (b)  $\beta$ -CyD-NS complex, (c)  $\beta$ -CyD-NC complex.

shift occurring for C(1) clearly shows its presence in the borderline just outside the cavity. The mode of the inclusion is also evident from the shifts in which the olefinic bond lie outside the cavity; instead, the saturated cyclic carbons have been trapped. From these results, it is possible to arrive at the structure of the inclusion complexes as depicted in Figure 3.

### 3.6. FORMATION CONSTANT DETERMINATION

Using the Benesi–Hildebrand plot, the dissociation constants of the NS and NC complex have been calculated. The values are 79 and 84  $\text{M}^{-1}$ . These very low values clearly account for the weak association in solution and thus for the minor

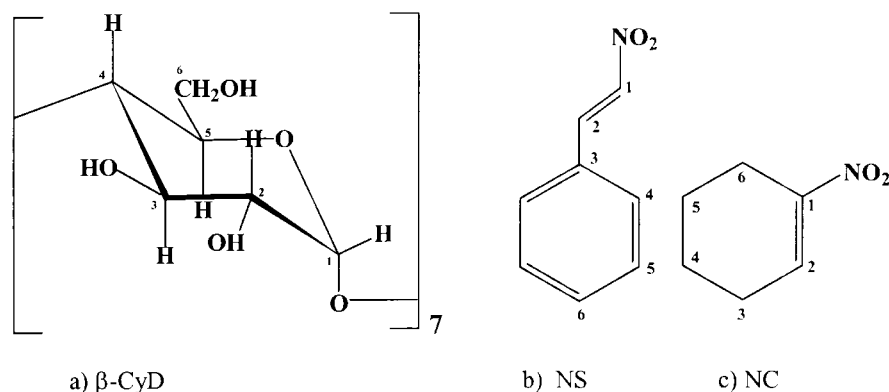


Figure 2. (a)  $\beta$ -cyclodextrin, (b)  $\beta$ -nitrostyrene and (c) 1-nitrocyclohexene.

Table I.  $^{13}\text{C}$  NMR Chemical shifts in ppm of  $\beta$ -CyD, NS, and the  $\beta$ -CyD-NS complex

$\beta$ -CyD carbon atoms	$\beta$ -CyD $\delta$	$\beta$ -CyD-NS complex $\Delta\delta$	NS carbon atoms	NS $\delta$	$\beta$ -CyD-NS complex $\Delta\delta$
C-1	102.217	-0.201	C-1	138.140	+0.252
C-2	72.654	-0.109	C-2	139.140	+0.279
C-3	73.348	-0.137	C-3	130.405	+0.283
C-4	81.800	-0.103	C-4	129.354	+0.128
C-5	72.321	-0.203	C-5	132.250	+0.184
C-6	60.269	-0.163	C-6	129.923	+0.162

+ And - signs refer to deshielding and shielding effects respectively. Numbering of  $\beta$ -CD and NS carbon atoms is as given in Figure 2.

Table II.  $^{13}\text{C}$  NMR Chemical shifts in ppm of  $\beta$ -CyD, NC, and the  $\beta$ -CyD-NC complex

$\beta$ -CyD carbon atoms*	$\beta$ -CyD $\delta$	$\beta$ -CyD-NS complex $\Delta\delta$	NC carbon atoms	NC $\delta$	$\beta$ -CyD-NC complex $\Delta\delta$
C-1	102.217	-0.085	C-1	135.413	+0.324
C-2	72.654	-0.071	C-2	149.318	+0.295
C-3	73.348	-0.083	C-3	23.633	+0.207
C-4	81.800	-0.089	C-4	20.348	+0.197
C-5	72.321	-0.102	C-5	21.509	+0.197
C-6	60.269	-0.120	C-6	24.592	+0.206

\* Numbering of  $\beta$ -CD and NC carbon atoms is given in Figure 2.



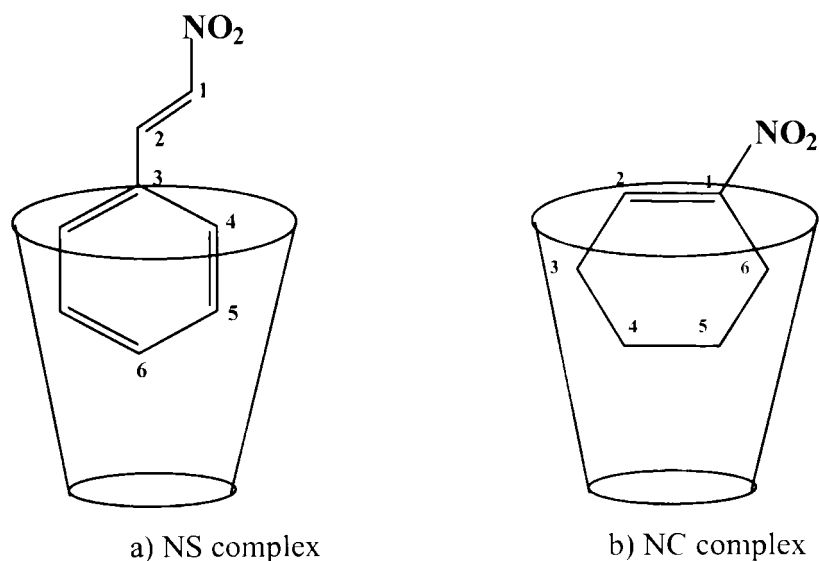


Figure 3. Preferred conformations of the NS and NC complexes.

changes happening in the case of the  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies. The nonappearance of any new band negates the formation of any charge transfer complex.

The stoichiometry of the solid state complex was determined using the gravimetric method and the values are in close agreement for a 1:1 complex. (0.97 and 0.98 respectively). This result is also complemented from the  $^1\text{H}$  NMR studies where the integration lengths of the CyD protons and the guest protons are nearly in the expected ratio, which clearly proves the exclusive formation of the 1:1 complex. The isolation of pure NS and NC from the complexes by this method proves the inclusion of the olefins without any chemical transformation.

### 3.7. REACTIONS OF THE COMPLEXED NITROOLEFINS

In order to find out how inclusion influences the property of the nitroolefins, it was decided to carry out some reactions characteristic of the nitroolefins namely a 1,3-dipolar cycloaddition and a reduction using  $\text{NaBH}_4$ .

#### 3.7.1. 1,3-Dipolar cycloaddition of the included nitroolefin with $\alpha$ -phenyl-*N*-*p*-methylphenyl nitron in the solid state

Since inclusion involves the restriction of freedom of the trapped molecule, the reactions of the included guest molecules assume interest and selectivity have been achieved in many cases [23]. In continuation of our earlier work [10], as a case study we have tested the reactivity of these complexes in the 1,3-dipolar cycloaddition with  $\alpha$ -phenyl-*N*-*p*-methylphenyl nitron which results are reported here.

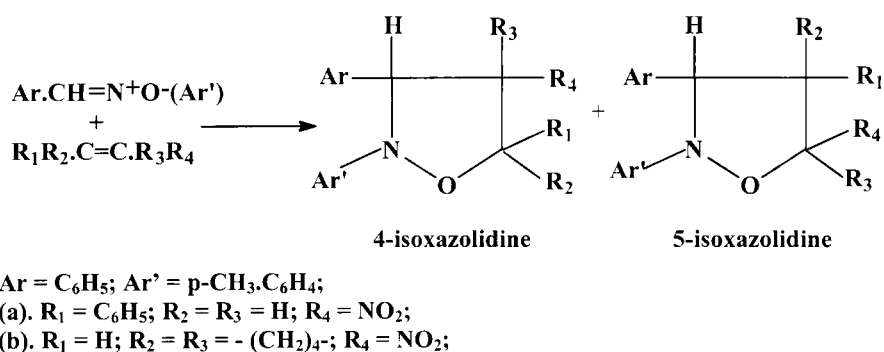


Figure 4.

In the solid state, the reaction proceeded well even at milder conditions, to give exclusively the 4-nitro substituted isoxazolidines in yields more than 75%. (Table 3) This rate acceleration may be explained based on the structure of these complexes as shown in Figure 4. The catalytic activity may be explained on the possible activation of the olefinic double bond due to the stabilizing effect of the CyD cavity on the electron deficient aryl ring as a case of electrophilic catalysis [24]. In the case of the NC complex, the catalytic effect may be more due to conformational catalysis, as the included guest has no aromatic nucleus.

### 3.7.2. NaBH<sub>4</sub> reduction of the included nitroolefins

The direct reduction of nitroalkenes provides a convenient route to a variety of different functionalities including nitroalkanes, oximes, carbonyl compounds, hydroxylamines and alkyl amines. Perhaps the most well studied method is the reduction using sodium borohydride. Here it must be stated that the dimerization is a major obstacle in the synthetic utility of this reaction. However, modifications have resulted in better procedures [9].

Of the two methods, which have been employed to reduce the nitroolefins, in the case of the THF-MeOH medium, no product was obtained and the reaction is not synthetically useful. An interesting observation is that the solid state reaction reduces the nitroolefin to the corresponding nitroalkane; yields being 55–60%. These results are comparable with an earlier procedure using NaBH<sub>4</sub> in THF/MeOH solvent [13]. The formation of the nitro compound in considerable quantities when the reduction is carried out in the solid state can be explained on the basis of the structure of the complex as given in Figure 3 where the olefinic double bond along with the nitro group is held open for the attack of the reducing agent.

Table III. 1,3-dipolar cycloaddition reactions of NS and NC with  $\alpha$ -phenyl-*N*-*p*-methylphenyl nitron in the presence and absence of  $\beta$ -CyD

Substrate	Reaction conditions	Isolated yield (%)	Regio/stereo chemistry	Literature conditions (solvent reaction)/yield
$\beta$ -CyD-NS complex	Solid state/45°C, 3 hours	80	100% <i>trans</i> -4-nitro isoxazolidine*	80°C/benzene reflux, 85:15 <i>trans</i> and <i>cis</i> 4-nitro isoxazolidine/85% <sup>12</sup>
$\beta$ -CyD-NC complex	Solid state/45°C, 2 hours	85	100% <i>trans</i> -4-nitro isoxazolidine*	—
$\beta$ -CyD, NS, nitron physical mixture-	Solid state/45–70°C, 36 hours	—	No reaction	—
$\beta$ -CyD, NC, nitron physical mixture-	Solid state/45–70°C, 36 hours	—	No reaction	—

\* Single isomer as shown by HPLC.

Table IV. Sodium borohydride reduction of NS and NC in the presence and absence of  $\beta$ -CyD

Substrate	Reaction conditions	Product/Yield	Literature conditions/ Product/Yield <sup>13</sup>
$\beta$ -CyD-NS complex	1. Solid state*/20 °C, 48 hours	1-phenyl-2- nitroethane/60%	THF/MeOH, 20 °C 1-phenyl-2-nitroethane/64%
	2. THF-MeOH/ 20°C 1–48 hours	No product	
$\beta$ -CyD-NC complex	1. Solid state*/20°C, 48 hours	Nitrocyclohexane/57%	THF/MeOH/ Nitrocyclohexane/62%
	2. THF-MeOH/ 20°C 1–48 hours	No product	

\* 50 mmol of NaBH<sub>4</sub> used per mmol of the complex.

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