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Inclusion of α-phenyl-*N*-*p*-methylphenyl Nitrone in β-Cyclodextrin: Formation of 1G : 1H and 1G : 2H Complexes and the Remarkably Fast 1,3-Dipolar Cycloaddition of the 1G : 2H Complex with Olefins in the Solid State

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Abstract. The nitrone is found to be included in the β-cyclodextrin cavity in two different stoichiometries viz., 1G : 1H and 1G : 2H – the existence of which is proved by physical methods. The 1G : 2H complex of the nitrone serves as a good potent dipolarophile in the 1,3-dipolar cycloaddition reactions with olefins resulting in rate acceleration and regioselection.

Key words: α-phenyl-*N*-*p*-methylphenylnitrone, β-Cyclodextrin-Nitrone complexes [1G : 1H and 1G : 2H], 1,3-dipolar Cycloaddition reactions, rate acceleration, regioselectivity

1. Introduction

The control and modification of reactivity through incorporation of molecules into organized assemblies such as guest-host systems remains an area of considerable interest. Cyclodextrins (CDs), the cyclic oligomers consisting of 6(α), 7(β) and 8(γ) glucose units linked together in α-1,4 linkages, are the most well studied systems of this kind as they possess hydrophobic cavities that are able to include in aqueous solution a variety of organic molecules whose character may vary from hydrophobic to ionic [1] and catalyze various reactions [2]. Internal diameters and depths of α-CD (4.2–5.8 and 7.8 Å), β-CD (5.6–7.8 and 7.8 Å) and γ-CD (6.8–12.0 and 7.8 Å) provide cavities for appropriate sized guest molecules. The reactions catalyzed by CDs have been categorized either as covalent catalysis, conformational catalysis or microsolvent catalysis [3]. Geometrical factors are decisive in determining the kind of guest which can penetrate into the CD cavity [4–5]. Due to this, CDs can be used as microreactor vessels for a variety of thermal and photochemical reactions.

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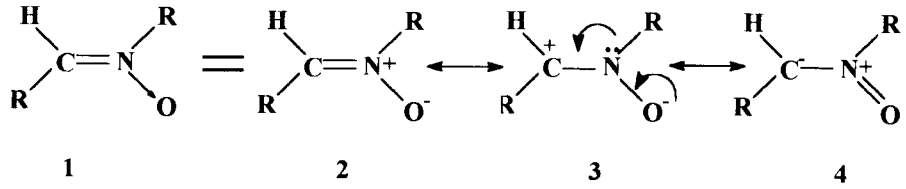


Figure 1. Canonical representations of nitrones.

Nitrones represented by formulae **1** or **2** (Figure 1) have a positive charge delocalized between the nitrogen and the α-carbon resulting in a 1,3-dipolar structure. The 1,3-dipolar cycloaddition of nitrones with olefins is by far the most studied area. Most cycloadditions of nitrones with monosubstituted olefins lead to 5-substituted isoxazolidines. Only with olefins substituted with strong electron withdrawing groups such as NO_2 and CN, 4-substituted isoxazolidines (where the electron withdrawing group occupies the 4th position) are the predominant products. The synthetic utility of the 1,3-dipolar reaction is well known and it serves as a key step in a number of natural product syntheses [6]. These reactions usually require much activation and thus take enormously long periods for completion. The use of catalysts for improving the speed and selectivity of these reactions has also been an active area of research. These reactions have been catalyzed by Lewis acids such as $BF_3{\cdot}Et_2O$, $ZnCl_2$, $ZnBr_2$ and $Ti(OPr\text{-}i)_2Cl_2$ catalysts [7–8]. The use of β-CD in improving the stereoselectivity of Diels-Alder reactions has been reported and here the conformational catalysis has been attributed to enhanced stereoselectivity as the compact transition state can be easily realized [9]. As a part of our study on the inclusion of nitrones in various host molecules such as calix[8]arene [10] here we report on the study of the inclusion of nitrones in β-CD and the 1,3-dipolar cycloaddition reaction of the nitrones in their included form.

2. Experimental

2.1. MATERIALS

The nitrones under study viz., α-phenyl-*N*-(*p*-methylphenyl) nitrone, α-(*o*-methylphenyl)-*N*-phenyl nitrone, α-(*p*-methylphenyl)-*N*-(*p*-methylphenyl) nitrone, α-(*o*-methylphenyl)-*N*-(*p*-methoxyphenyl) nitrone were synthesized by condensing the corresponding hydroxylamines (obtained by the Zn/NH_4Cl reduction of the corresponding nitro compound) with benzaldehyde or *o*/*p*-tolualdehyde. They were recrystallized from ethanol prior to use. Olefins used in this study were obtained employing known procedures [11–12]. β-CD (Leochem, India), and acrylonitrile (S.D. Fine, India) were used as received. 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 β-CD-NITRONE COMPLEXES

The complexation was carried out using the standard method [13]. The 1G : 1H (G-guest; H-host) complex was obtained by stirring an equimolar quantity of the guest to a saturated solution of the host in distilled water at 20 °C for 2–5 hours, while the 1G : 2H complex was obtained by stirring at 35 °C for 36–40 hours. One important inference during the formation of the complex was that the nitrone which initially floats upon the water surface disappears into the solution making it turbid. Only after some time was the powdery complex precipitated. It was filtered off, washed with cold ether to remove any uncomplexed guest and dried in an air oven at 65 °C for 6–12 hours. The complex was stored at 0–4° under refrigeration in a moisture free environment.

A physical mixture of the nitrone and β-CD in the molar ratio 1 : 1 and 1 : 2 were prepared by thoroughly mixing the well ground components in an agate mortar.

The guest–host stoichiometry was determined by subjecting a known amount of the complex to quantitative soxhlet extraction with $CHCl_3$ and estimating the amount of the guest by gravimetry.

2.3. 1,3-DIPOLAR CYCLOADDITION OF THE β-CD COMPLEXES IN THE SOLID STATE

Equimolar quantities of the 1G : 2H complex and the olefin were thoroughly homogenized in an agate mortar and subjected to the reaction conditions as given in Table IV. After monitoring the product formation with TLC, the product was isolated by extraction with warm $CHCl_3$. The product was purified by column chromatography (silica gel, eluent 1 : 1 petroleum ether-chloroform). The products were compared with products obtained by normal solvent phase reactions as reported [6].

Control experiments in the absence of β-CD complexation were also carried out by subjecting a physical mixture of the reactants in the presence of β-CD to the identical experimental conditions.

2.4. ANALYTICAL METHODS

Powder X-ray patterns were obtained using a PW1820 diffractometer using a Cu source, operating at 40 KV/30mA. 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 ^1H and ^{13}C] were recorded on a JEOL-GSX 400 spectrometer at 23 °C in D_2O and DMSO-d_6 respectively with TMS as the internal standard. HPLC analyses were done on a Shimadzu LC8A instrument using a reverse phase ODS column with 70% methanol as the mobile phase.

2.5. DETERMINATION OF FORMATION CONSTANTS

A stock solution of CD [10^{-3} M in DMSO] and the nitrones [10^{-2} M in DMSO] were prepared. DMSO was used because in water, turbidity did not allow spectrophotometric study. 25 μL of the nitrone solution was taken in 5 mL standard measuring flasks. To this, ten various quantities of the CD solution [10 μL–1000 μL] 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 [ϵ_{max}] for the nitrone at 322 nm in DMSO were observed. Using the Benesi-Hildebrand plot [14] ($a_0 b_0/\Delta$OD versus $1/a_0$ where a_0 and b_0 are the concentration of CD and nitrone respectively) the dissociation constants K_{d1} and K_{d2} were determined. From these, the formation constants K_f ($1/K_{d1}$ and $1/K_{d2}$) for the 1G : 1H and 1G : 2H complexes were thus arrived at.

3. Results and Discussion

3.1. CHARACTERIZATION OF β-CD-NITRONE COMPLEX

Prominent physical methods which are often used for the identification of inclusion complexes are powder X-ray diffraction, FT-IR, NMR and kinetic methods such as formation constants and these are all employed in characterizing the inclusion complexes under study.

It has been found that only α-phenyl-*N*-*p*-methylphenyl nitrone precipitated CD in the form of both 1G : 1H and 1G : 2H complexes, while the other guests formed only the 1G : 2H complexes. An important observation is the effect of substitution on the aryl part in the azomethine carbon on the formation of the complex. When the *C*-side aryl part is unsubstituted, whatever the substitution on the *N*-side, complex formation occurs under both 1G : 1H and 1G : 2H stoichiometries. No complex is isolable when the aryl residue of the *C*-side of the nitrone is substituted in *o*-or *p*- positions, irrespective of the substitution on the *N*-side under 1G : 1H conditions. But addition of another mole of CD and continued stirring for a much longer period and at a slightly higher temperature results in the formation of a 1G : 2H complex. This means that the *N*-aryl ring first enters the cavity along with the azomethine system forming the 1G : 1H complex and upon continued stirring for a longer duration, increasing the concentration of CD and warming up leads to the 1G : 2H complex.

3.2. X-RAY POWDER DIFFRACTION

A true inclusion complex will have its diffraction pattern altered from those of the pure components [15]. The powder X-ray patterns for the individual components, complex (1G : 2H) and the physical mixture are reported in Figure 2. Comparing the patterns for the β-CD nitrone complex with that of the physical mixture reveals marked differences. Peaks for the nitrone at 2θ 10.75°, 19.33°, 24.85° and 29.71°

are found to be absent in the complex. Also peaks for β-CD at 2θ 13.95°, 17.99°, 20.5° and 25.7 are not present in the complex. Some of the peaks are also shifted. For example, peaks at 16.73° and 19.79° for β-CD and 16.55° and 21.52° for the nitrone are shifted. This may be attributed to the insertion of the aromatic residues of the nitrone into the CD cavity. The intensities of certain peaks in the complex are also enhanced thereby confirming complex formation. Similar changes are also seen in the case of the 1G : 1H complex associated with comparably higher shifts and enhanced intensities (Figure 2). The diffraction patterns of the physical mixture of the host and guest can be interpreted as an approximate superposition of the components.

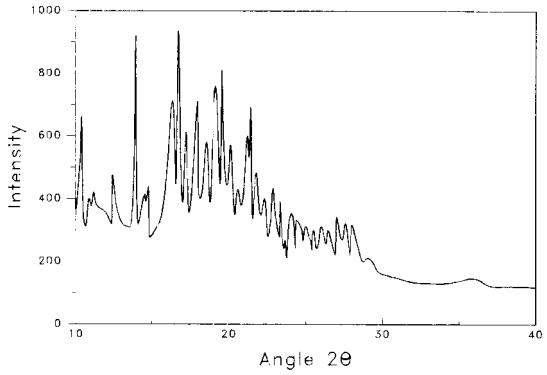
3.3. IR STUDIES

IR studies are not usually used for the characterization of inclusion complexes due to the superimposition of the bands of the guest and the host. In the present case, the peaks for the stretching of C—N and N—O for the nitrone originally observed at 1549 cm^{-1} and 1067 cm^{-1} are not significantly altered in the 1G : 2H complex with changes of only 10 cm^{-1} while in the 1G : 1H complex there is a change in the frequencies towards the high energy side and they vibrate at 1590 cm^{-1} and 1099 cm^{-1} respectively. The absence of remarkable shifts in the vibrational frequencies of the 1G : 2H complex proves the insertion of the two aryl rings inside two CD cavities leaving the $C{=}N^{+}O^{-}$ exposed. In the case of the 1G : 1H complex since the $C{=}N^{+}O^{-}$ systems remains inside the CD cavity near the wider C-2, C-3 hydroxyl face of β-CD, the C—N and N—O frequencies are changed due to possible hydrogen bonding interactions with the hydroxyl groups.

3.4. ^{1}H NMR SPECTRA

Clinching evidence regarding the formation of the inclusion complex in solution has been obtained from the ^{1}H NMR spectra of the complexes in D_2O. The specific coupling patterns of the β-CD protons make it easy for the identification of the individual protons. Table I illustrates the changes upon complex formation.

In the case of the 1G : 1H complex where we expect the insertion of the one aryl ring and the azomethine system, the shifts are relatively large. The H_1 proton of β-CD suffers a significant downfield shift while other protons (namely H_2, H_3, H_4, H_5 and H_6) are shifted upfield. The effect is more pronounced on the H_3 and H_5 protons. The stronger shifts in the case of these protons are quite unusual and they may be attributed to the anisotropic effects of the induced magnetic field of the aryl ring as well as the horizontally lying dipolar $C{=}N^{+}{-}O^{-}$ system. The relatively smaller upfield shift for H_6 may be attributed to their presence at the periphery and the rotation of the CH_2OH group. Thus it is away from the aryl and the azomethine system. Only the *p*-CH_3 will be closer to it and its influence will be marginal. This clearly demonstrates the insertion of the guest deep into the cavity



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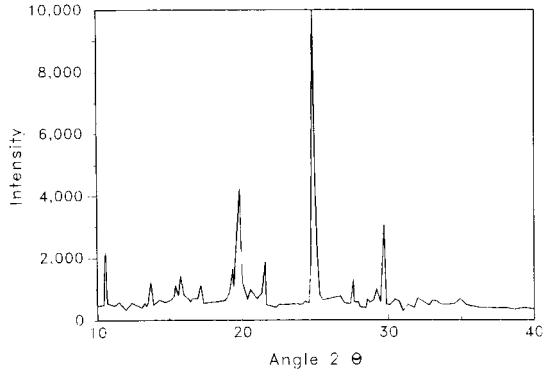

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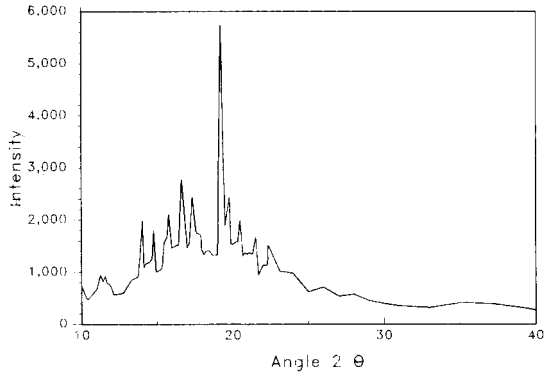
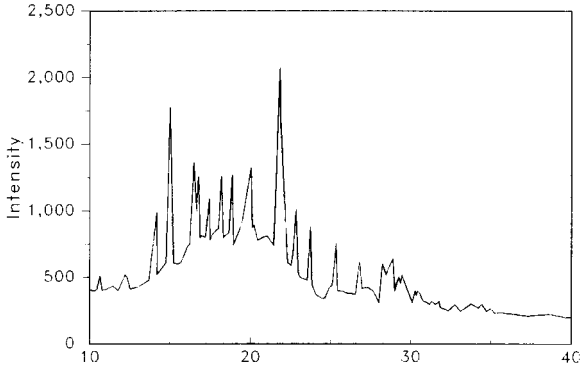


(c)

Figure 2. Powder X-ray patterns of (a) β-CD, (b) α-phenyl-*N*-*p*-methylphenyl nitrone, (c) 1G : 1H complex of a and b, (d) 1G : 2H complex of a and b, (e) Physical mixture of a and b in the molar ratio 2 : 1.



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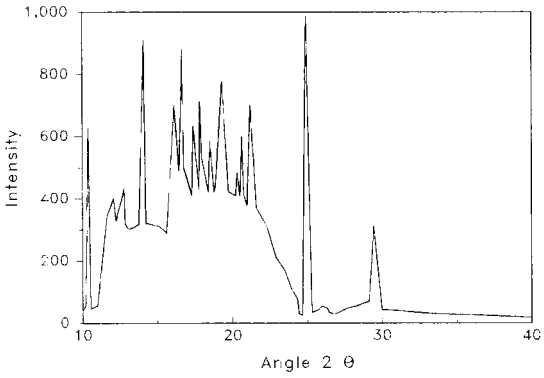


(e)

Figure 2. Continued.

Table I. ^{1}H NMR chemical shifts of β-CD protons in complexes.[#]

Compound	H_1	H_2	H_3	H_4	H_5	H_6
β-CD	2095.7	1522.9	1638.6	1461.4	1599.9	1607.4
β-CD Nitrone complex 1G : 1H	2189.8	1489.8	1488.0	1433.8	1462.9	1573.9
β-CD Nitrone complex 1G : 2H	2169.5	1509.2	1603.5	1454.2	1531.0	1579.4

[#] Chemical shifts are expressed in Hz; Solvent D_2O. The nitrone used is α-phenyl-*N*-*p*-methylphenyl nitrone. In the case of other nitrones poor solubility prevented us from running the spectra. Numbering of carbon atoms of β-CD is given in Figure 3. Recorded on a 400 MHz instrument.

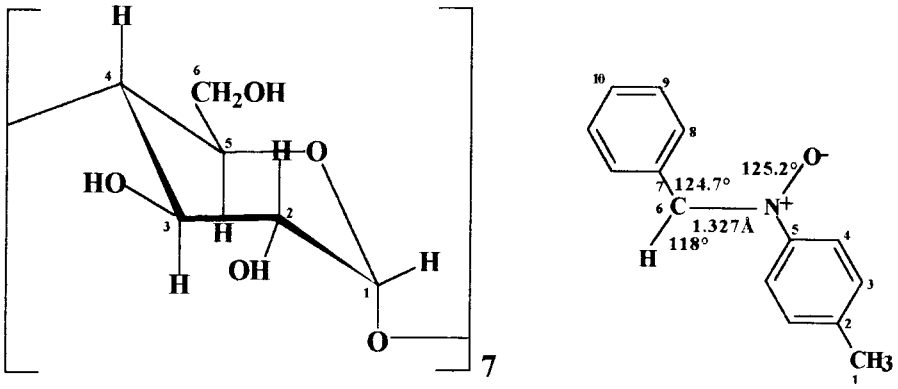
and leads to a conclusion regarding the insertion of the guest from the wider C-2, C-3 hydroxyl face and not through the narrow primary hydroxyl face. These results are in agreement with the observations of Ramamurthy et al. [13] and Demarco et al. [16] where they have attributed the sensing of the screening environment only by the inner hydrogens H_3 and H_5 rather than by the outer hydrogens H_2, H_4 and H_6. The shifts are quite large when compared to other substrates [17–19]. In the case of the 1G : 2H complex where one would expect each aryl ring to be bound to one CD cavity, the influence of only aryl rings on the CD protons are manifested in the NMR spectrum. The main inference is that smaller shifts occur for all the protons. This proves the shallow nature of the complex wherein only the aryl ring gets into the cavity but not that much deeper as in the case of the 1G : 1H complex leaving the $C{=}N^{+}O^{-}$ outside the cavity. Here also the smaller upfield shift in the case of H_3 compared to H_5 may be due to the opposing magnetic anisotropic effect of the aryl ring and the azomethine dipolar system.

3.5. ^{13}C NMR SPECTRA

The conformational nature of the complex in solution is best established by ^{13}C NMR spectra of the complex in DMSO-d_6. There are only a few reports on the ^{13}C NMR study of the inclusion complexes of β-CD [17–20]. The ^{13}C NMR chemical shifts of different carbons are given in Table II. The shifts are assigned using the DMSO signal as the internal standard and the chemical shifts are measured relative to Me_4Si using the correction

$$(Me_4Si) = DMSO + 40.5.$$

The carbons of the β-CD in the 1G : 1H complex undergo strong deshielding at most positions with the shifts ranging from 0.137 to 0.727 while the carbons of the nitrone show slight shielding. When the dipolar nitrone enters the β-CD cavity, the lowest deshielding occurs for the C-3 and C-5 which remain inside the cavity whereas C-2, C-4 have larger deshielding as they remain outside the cavity. This deshielding effect is exactly the reverse of the shielding that occurs during the incorporation of guests such as chalcones, coumarin, β-phenyl propiolic acid, benzene sulfonanilide and substituted anilines [17–20]. In all these cases, the diamagnetic anisotropic effect of the phenyl rings cause the shielding of the β-CD carbons. In the present case, the 1,3-dipole causes the reverse effect on the β-CD carbons as it enters the cavity. In the case of the nitrone carbons C-3, C-4, C-5, C-6 undergo significant shielding while C-8, C-9, C-10 experience a small deshielding effect. This emphasizes the presence of the C-3, C-4, C-5, C-6 in the interior of the cavity making them sterically more hindered while the other carbons remain outside the cavity. This is in agreement with the results obtained for coumarin. The same result is corroborated by the fact that any nitrone substituted at C-8 is not able to form this 1G : 1H complex. This may be due to the steric hindrance caused by the C-8 substituent.



a) β-CD b) Nitrone

Figure 3. (a) β-Cyclodextrin and (b) α-phenyl-*N*-*p*-methylphenyl nitrone.

Table II. ^{13}C NMR chemical shifts in ppm of β-CD, nitrone and the 1G : 1H complex

β-CD Carbon atoms	β-CD δ	β-CD-nitrone complex 1G : 1H Δδ	Nitrone carbon atoms	Nitrone δ	β-CD nitrone complex 1G : 1H Δδ
C-1	102.231	+0.312	C-1	20.704	−0.073
C-2	73.072	+0.653	C-2	121.159	−0.082
C-3	73.632	+0.227	C-3	128.250	−0.165
C-4	81.991	+0.727	C-4	128.779	−0.113
C-5	72.070	+0.137	C-5	129.280	−0.124
C-6	60.215	+0.303	C-6	130.297	−0.119
			C-7	131.116	−0.043
			C-8	133.983	+0.039
			C-9	139.510	+0.027
			C-10	146.311	+0.023

+ and − signs refer to deshielding and shielding effects respectively. Numbering of β-CD and nitrone carbon atoms is given in Figure 3.

For the 1G : 2H complex, the ^{13}C NMR data is as given in Table III. All the CD carbons experience a shielding effect with the maximum shift for C-3 and C-5 while the nitrone carbons, especially the phenyl carbons experience a marginal deshielding effect. An important observation is the azomethine carbon C-6 being shielded by 1.513 ppm. This may be due to the sensitivity of the dipolar azomethine system to spatial interaction with the host. This is similar to the shift encountered by the alkyne carbon of β-phenyl propiolic acid [20]. Thus the conformation of the complex may be given as in Figure 4 and it is possible for us to distinguish the two types of complexes based on their ^{13}C NMR spectra.

Table III. ^{13}C NMR shifts for the 1G : 2H complex in DMSO d_6

β-CD carbon atoms	β-CD-nitrone complex 1G : 2H $\Delta\delta$	Nitrone carbon atoms	β-CD nitrone complex 1G : 1H $\Delta\delta$
C-1	−0.112	C-1	+0.073
C-2	−0.253	C-2	+0.082
C-3	−0.427	C-3	+0.065
C-4	−0.127	C-4	−0.013
C-5	−0.413	C-5	−0.024
C-6	−0.030	C-6	−1.513
		C-7	+0.043
		C-8	+0.042
		C-9	+0.038
		C-10	+0.041

3.6. FORMATION CONSTANTS

Based on the UV absorption measurements as described in the experimental section (using the Benesi–Hildebrand plot) the formation constants ($1/K_{d1}$ and $1/K_{d2}$) are evaluated as 41 M^{-1} and 133 M^{-1}. The higher value for the 1G : 2H complex is obviously due to the fact that this is the thermodynamically more favorable one. The plot is characterized by two isosbestic points, one at a low concentration of β-CD and another upon increasing the host concentration with no significant change in the λ_{max} of the guest.

The stoichiometries of the complexes are also determined using the gravimetric method and the values obtained for 1G : 1H is 1:1.2 and for the 1G : 2H is 1:1.87 and this is due to the presence of the other complex in minor amounts. This experiment also proves the non existence of any charge transfer complex and this is further evidenced by the non appearance of any new $\lambda_{max}$for the guest in the UV study.

3.7. REGIOSELECTIVE 1,3-DIPOLAR CYCLOADDITION OF INCLUDED NITRONE WITH OLEFINS

The included nitrone both in the 1G : 1H and 1G : 2H complexes are tested for their reactivity towards potential olefins. It has been found that the former is passive in the solid state while the latter is highly reactive. Even under comparatively milder conditions, the 1,3-dipolar cycloaddition takes place efficiently leading to 4-isoxazolidines (Figure 5) where the electron withdrawing substituent occupies the 4th position. Only in the case of the chalcone (entry 5 in Table IV) is a small

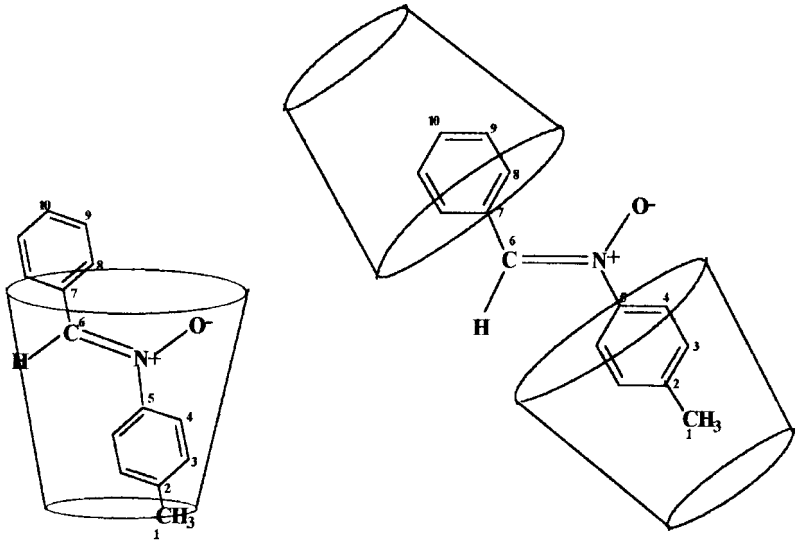
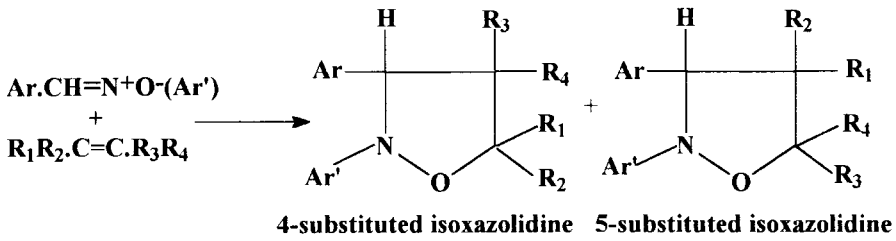


Figure 4. Preferred conformations of the 1G : 1H and 1G : 2H complexes.

Table IV. 1,3-Dipolar cycloaddition reactions of nitrone with olefins

Entry	Olefin	Reaction Conditions	Yield %*
1	β-Nitrostyrene	55 °C, 7.5 hrs	70
2	1-Nitrocyclohexene	45 °C, 10 hrs	79
3	Phenyl vinyl sulfone	40 °C, 7 hrs	89
4	Cyanoethylene	55 °C, 12 hrs	85
5	Benzalacetophenone	65 °C, 24 hrs	77**

* All the products are identified by NMR.
** Overall yield of the 4 and 5 isomers.



Ar = Ph, Ar' = *p*-$CH_3C_6H_4$
1. R_1 = Ph, R_2 = R_4 = H, R_3 = NO_2
2. R_1 = H, R_2 = R_4 = -$(CH_2)_4$-, R_3 = NO_2
3. R_1 = R_2 = R_4 = H, R_3 = $PhSO_2$
4. R_1 = R_2 = R_4 = H, R_3 = CN
5. R_1 = Ph, R_2 = R_4 = H, R_3 = COPh

Figure 5. 1,3-dipolar cycloaddition reactions of nitrone with olefins.

fraction of 5-isomer obtained. These interesting results may well be explained on the basis of the structure of the inclusion as given in Figure 4. In the 1G : 2H complex, the reaction site is held rigidly exposed for attack of the olefin whereas in the 1G : 1H complex, it is sterically hindered. Also in the 1G : 2H complex, the inclusion of both the aryl groups in the cavity might have disturbed the efficient delocalization of the π electrons and thus increasing the electron density around the C=N bond and thus making it more reactive. Control experiments i.e. by using physical mixtures of the individual components under the given experimental conditions showed no traces of products confirming the involvement of the complex in the reaction. Normally in solutions such as benzene/toluene, these additions take about 48-96 hours for completion at the boiling temperature.

Acknowledgements

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