**Table 1.** $KMnO_4$ Oxidation of Alcohols using various setups[a]

| Entry | Alcohol | Product | New reactor[b] | Ultrasound[c] Lab. Cleaner | Mechanical[c] Stirrer |
|---|---|---|---|---|---|
| | | | Yield (%, time in hr) | | |
| 1 | Cyclohexanol | Cyclohexanone | 87(3)[d] | 53.2(5) | 4.2(5) |
| 2 | 2-Octanol | 2-Octanone | 93(1) | 93(5) | 2.6(5) |
| 3 | Cyclododecanol | Cyclododecanone | 45(2)[d] | 84.1(32) | |
| 4 | $PhCH=CHCH_2OH$ | $PhCH=CHCHO$ | 90(2)[e] | 82.8(3) | 4.5(3) |
| 5 | 1-Octanol | Octanal | 92(1) | 80.5(14)[f] | |
| 6 | $PhCH_2OH$ | PhCHO | 90(0.5) | 29.7(1.5) | |
| 7 | PhCH(OH)Ph | PhCOPh | 95(0.5) | 98.9(5) | |
| 8 | Cycloheptanol | Cycloheptanone | 85(1) | 45.1(5)[g] | 4.5(5)[h] |
| 9 | $4\text{-}ClC_6H_4CH_2OH$ | $4\text{-}ClC_6H_4CHO$ | 92(0.5) | 73.8(3)[g] | 16.5(5)[h] |
| 10 | 1-Octene-3-ol | 1-Octene-3-one | 21(12)[d] | 43.6(24) | |

[a] 2:12.8 mmole of alcohol : $KMnO_4$ were employed at 15 °C in 6 m*l* of benzene. [b] isolated yield, otherwise noted. [c] same reaction conditions except temperature (50 °C) and solvent (entry 1,2,5) used hexane repectively. see : ref. 7b. [d] GC yields. [e] carried out with 80 watt. [f] octanoic acid. [g] our results at same reaction condition. [h] our results with magnetic stirrer.

transducer. Alcohol (0.01 mole), 2g (0.0128 mole) of powdered and dried $KMnO_4$ and 6 m*l* of benzene were added to the flask under nitrogen and the mixture was sonicated for 1–12 hrs. Reaction vessel temperature was maintained at 15 °C by using a running water bath.

A strong atomization phenomena (fogginess) was occurred during sonication. The reactions were monitored by GC. Isolation involved filtering to remove $KMnO_4$, ether washes of $KMnO_4$. The major product was isolated by simple distillation under reduced pressure or crystallization. The products were identified by GC, IR and NMR spectra. We are currently exploring a number of applications of this reactor and will report on them in due course.

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# Enantioselective Inhibition Effect on Esterolytic Activity of β-Cyclodextrin by Inclusion with N-Benzoxycarbonyl-L-histidine

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Fine processes in which substrates bind into cyclodextrin cavities and then undergo reactions with one of the secondary cyclodextrin's hydroxyl groups have attracted great attention as models of enzymatic reactions[1]. To improve the reaction rates[2-4] and stereoselectivities[3,4] for many types of reactions, particularly for the cleavage of activated esters, the derivatives of cyclodextrins[5-7] have also been studied. In those systems catalytic or reactive functional groups such as imidazole are present to attack the bound substrate. However, the alteration of cyclodextrins' own catalytic activity

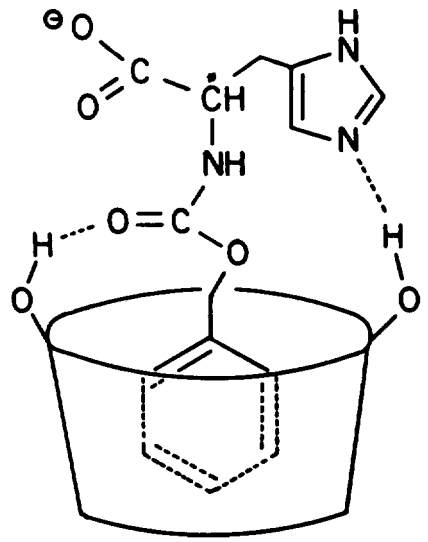

**Figure 1.** The simplified structure of possible inclusion complex of β-CD and N-Cbz-His.

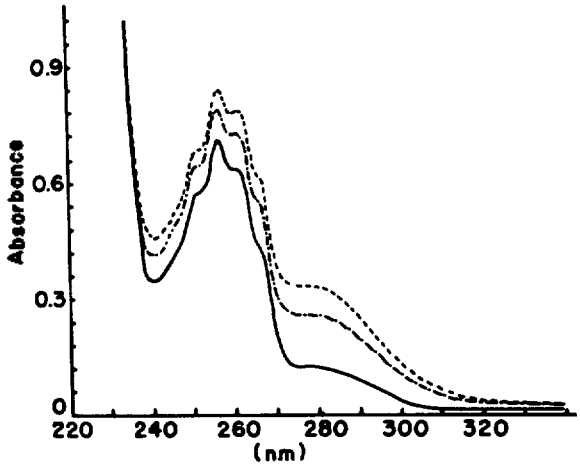


**Figure 2.** Spectra of N-Cbz-His at β-CD concentrations of $1.59 \times 10^{-2}$ (---), $8.51 \times 10^{-3}$ (···), and 0 (—) M (concentration of N-Cbz-His: $3.13 \times 10^{-3}$ M; Tris buffer, pH 10.0). The secondary band of N-Cbz-His is represented.

along with stereochemistry caused by binding other kinds of chiral molecules containing catalytic functional group has virtually never been reported. Only from the recent work of Ohkubo and coworkers[7], slightly favored inhibition effect to D-substrate could be found in hydrolysis of N-acylamino acid esters by equimolar mixtures of β-cyclodextrin (β-CD) and L-histidine.

In this communication we report the remarkable enantioselective effect on the esterolytic activity of β-CD by inclusion with N-carbobenzoxy-L-histidine (N-Cbz-His). Even though the N-Cbz-His possesses catalytically active imidazole group, the cyclodextrin has showed the decreased activity toward the optically active activated esters rather than synergistically improved activity by complexing with N-Cbz-His. The inclusion of benzyl group into the hydrophobic cavity of the cyclodextrin (Figure 1) was confirmed by UV absorption and NMR spectra.

Figure 2 shows the secondary band of absorption spectra

**Table 1.** Apparent Catalytic Rate Constants of Solvolyses of Optically Active Substrates[a] in Catalytic Systems of m-CD and N-Cbz-His[b] in 0.02 M Tris Buffer at 25 °C (pH 10.0)

| Catalytic System[c] | $k_{cat}$ (1/mole·sec) | | | | | |
|---|---|---|---|---|---|---|
| | NBP | | | NDP | | |
| | D | L | L/D | D | L | L/D |
| N-CBz-His | 0.35 | 0.36 | 1.02 | 0.008 | 0.008 | 1.00 |
| β-CD | 0.58 | 1.62 | 2.78 | 0.14 | 0.20 | 1.42 |
| β-CD+N-Cbz-His[d] | 0.20 | 0.85 | 4.25 | 0.02 | 0.04 | 2.00 |

[a]The concentration of substrates: $1.07 \times 10^{-5}$ M. [b]N-Carbobenzoxy-L-histidine. [c]The concentration of the β-CD: $5.86 \times 10^{-4}$ M. [d]The molar ratio ([β-CD]/[N-Cbz-His]) employed was 0.97. The calculation of $k_{cat}$ was executed according to the concentration of m-CD.

of N-Cbz-His measured at different concentrations of β-CD between $1.59 \times 10^{-2}$M and 0 M in aqueous solution. The increase in absorption coefficient at 256 nm was used to determine the association constant according to the Bender method[2a]. The analysis gave the value of *ca.* 15 for β-CD as the association constant. The 300 MHz $^1$H-NMR spectra also confirmed the formation of inclusion complex from the change in chemical shifts at different concentration of β-CD. A simplified presentation of the possible structure of inclusion complex is represented in Figure 1.

Solvolytic rates were measured in aqueous solution buffered with 0.02 M tris(hydroxymethyl)aminomethane and hydrochloric acid with 0.02 M potassium chloride. N-Benzoxycarbonyl-D- and L-phenylalanine *p*-nitrophenyl esters (D-NBP and L-NBP) and N-dodecanoyl-D- and L-phenylalanine *p*-nitrophenyl esters (D-NDP and L-NDP) were used as substrates, which are optically active and possess hydrophobic side groups[9].

As indicated in Table 1, the introduction of chiral N-Cbz-His into aqueous β-CD reduced the hydrolytic rate of the substrates with the enhancement of enantioselectivity, *i.e.*, the reaction of D-enantiomer is more inhibited by β-CD complex than that of L-substrate. Similarly to other amino acid substrates reported[7], β-CD itself also showed enantioselective solvolytic activity to a certain degree toward D- and L-NBP and NDP. In case of D- and L-NBP pair, the enantioselectivity ($k_{cat}$(L)/$k_{cat}$(D)) of 2.78 was observed and this value was increased to 4.25 by introducing the N-Cbz-His. This effect was more pronounced compared with the case of D- and L-NDP. Taking the powerful nucleophilicity of imidazole group of N-Cbz-His into consideration, the reduced stereoselectivity of solvolytic rate also supports the catalytic action of the cyclodextrin via binding with substrates and the inhibitory complexing of N-Cbz-His into catalytic site of β-CD prior to the binding with substrates. Although the three functional groups such as hydroxyl, carboxyl, and imidazole, which are properly positioned together around the hydrophobic pocket in active site of chymotrypsin, are closely arranged, it was misfortune that we could not observe any contribution to the enhancement in the hydrolytic rate. Further examinations to explore the mechanistic relation between inclusion complex and stereochemistry of esterolysis are in progress.

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# Benzophenone Sensitized Photoisomerization of 1,2-Bispyrazinylethylene

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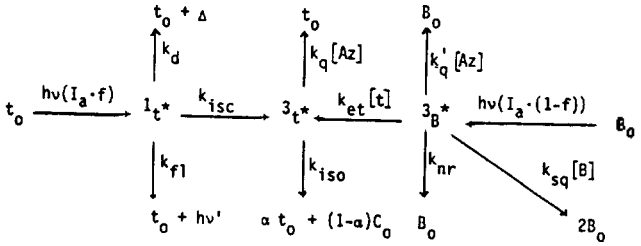
We have proposed a triplet mechanism for direct *trans*→*cis* photoisomerization of 1,2-bispyrazinylethylene(BPyE) on the basis of benzophenone sensitization and azulene quenching studies.[1] Benzophenone sensitizer, however, showed an anomalous concentration effect on the photoisomerization quantum yields[1b] which could not be clearly explained at that time. We now propose a plausible mechanism to explain this anomaly.

A simple analysis of the data[1b] shows a decrease of benzophenone sensitized *trans*→*cis* photoisomerization quantum yields as the concentration of benzophenone increases indicating that not all the benzophenone triplets generate the olefin triplets. The simplest mechanism which will account for this observation is shown in Scheme 1.

When the steady-state approximation is applied on the benzophenone sensitized *trans*→*cis* photoisomerization,

$$\Phi_{t\to c}^{obs}=f(1-\alpha)\Phi_{isc}+(1-f)(1-\alpha)\frac{k_{et}[t]}{k_{nr}+k_{et}[t]+k_{sq}[B]} \quad (1)$$

and when azulene is added as a triplet quencher, the following Stern-Volmer relationship can be derived,




**Scheme 1.** Mechanism of the *trans*→*cis* photoisomerization of *trans*-1,2-bispyrazinylethylene.

$$\Phi_{t\to c}^{\circ}/\Phi_{t\to c}=\frac{(1+k_q[Az]/k_{iso})(f\Phi_{isc}+\dfrac{(1-f)k_{et}[t]}{k_{nr}+k_{et}[t]+k_{sq}[B]})}{(f\Phi_{isc}+\dfrac{(1-f)k_{et}[t]}{k_{nr}+k_{et}[t]+k_{sq}[B]+k_q'[Az]})} \quad (2)$$

where, $f=E_t[t]$ which is the fraction of photons absorbed by *trans*-BPyE at 366 nm, $(1-\alpha)$ is the fraction of decay from $^3t^*$