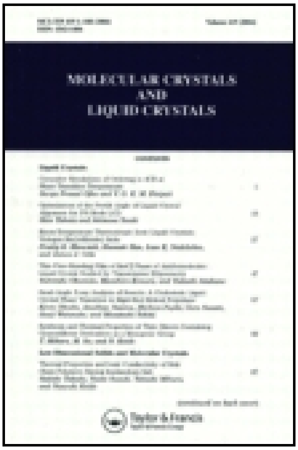

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Selective Reactions in Crystalline Inclusion Compounds

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Selective Reactions in Crystalline Inclusion Compounds

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Abstract.

1,1,6,6-Tetraphenylhexa-2,4-dyine-1,6-diol and it's chiral derivative 1,6-bis(o-chlorophenyl)-1,6-diphenyl-2,4-dyine-1,6-diol form inclusion compounds with various potentially reactive guest molecules. Photochemical reactions of α-oxoamides imbedded within the matrix of the host molecules afforded in stereo and enantiospecific ß-lactam derivatives. Similar reactions with α-tropolone alkyl ether reveal, in 100% e.e. (enantiomeric excess), a bicyclic product. Over 40% e.e. of phenylalcohols were obtained by solid state reduction of the corresponding phenylketones as the guest molecules.

Introduction

Traditionally, most of the investigations of chemical reactions as well as chemical syntheses have been carried out in solvent media. In solution or in the gas-phase the molecules have many degrees of freedom expressed by intramolecular rotations, leading to various conformations, as well as by molecular mobility. As a result many possible chemical reactions may occur and a mixture of products is a common result. The need for specific reactions leading to unique products cause the search for reactions which will occur in other media. In recent years much effort was devoted to the study of chemical reactivity, especially photochemistry, in organized media such as liquid crystals[1], micelles, monolayers[3], zeolites[4], crystals of the neat compounds[5], and host-guest assemblies.[6]

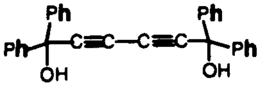
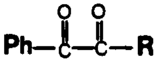
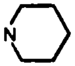
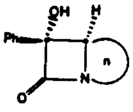
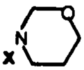
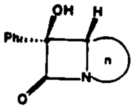
The main purpose for using organized media is to induce special arrangements as well as to control specific conformations to minimize the degrees of freedom of the reactant molecules, thereby allowing specific reactions. The present work describes the results from a study of chemical reactions in solid inclusion compounds composed of 1,1,6,6-tetraphenylhexa-2,4-dyine-1,6-diol[7] and its chiral dichlorophenyl derivative[8] as the host compound.

Results and Discussion

1,1,6,6-Tetraphenylhexa-2,4-dyine-1,6-diol is an achiral molecule which forms inclusion compounds with a variety of guest molecules possessing carbonyl groups. The guest molecules are hydrogen bonded to the host matrix. It was shown[9] that potentially photoreactive guest molecules undergo [2+2] or [4+4] photocyclodimerization to a single head-to-tail isomer. The crystal structures of three of such inclusion compounds with benzilideneacetophenone, 9-anthraldehyde and 2-pyridone as the guest molecules have been described.[9,10] It was suggested that the ability of the host molecule to occupy a crystallographic inversion centre is the property which controls the packing of the guest molecules in pairs related by inversion centres. This special arrangement leads to the head-to-tail isomers.

The same host molecule was found to be useful for carrying out intramolecular reactions as well. A summary of the various reactions is shown in Table 1. The first two parts of the table show the results of photochemical reaction of α-oxoamides imbedded within the matrix of the achiral and the chiral host molecule. Although the specificity of each of the reactions is not fully explained we would like to point out the factors which in our mind would be the key to the undestanding of the expected behavior. The photochemical reaction is initiated by excitation of a carbonyl oxygen atom followed by H abstraction to the excited oxygen and ring closure to the corresponding ß-lactam system. During the reaction two asymmetric carbon centres are formed and may result in four different diastereoisomers as shown in Fig. 1. The first asymmetric site is the carbon bearing the OH and Ph groups. The handedness of this site is dependent upon the relative orientation of this carbon atom and the carbon atom bearing the abstracted H atom. The orientation is controlled by the conformation of the moelcule, thus by the crystal packing. The second site is the carbon atom bearing the abstracted H hydrogen. The handedness of this atom depends on which atom out of the two possible atoms that is abstracted. It was assumed that the use of chiral host molecule will ensure chiral packing in which only one of the two possible conformations of the

Table 1. Summary of results of solid state reactions of host:guest inclusion compounds.

HOST	GUEST	R	PRODUCT	E.E.
				0
		2x 		0
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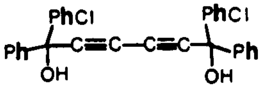
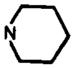
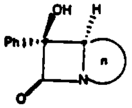
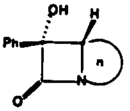
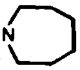
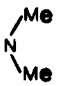
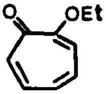
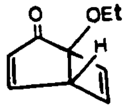
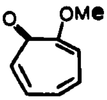
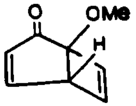
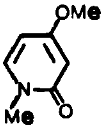
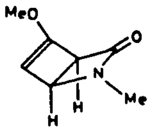
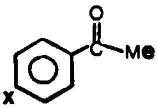
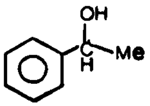
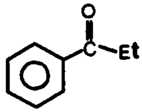
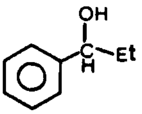
				62.5; 95
				55.8; ?
		2x 		11.2; 0
				100; –
				100
				100
				100
	2x 			45
				42

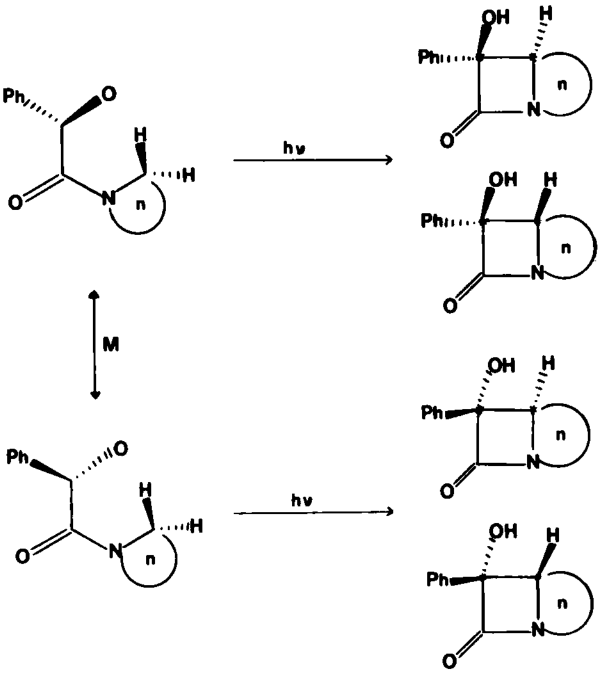


Figure 1. Possible diastereoisomers of ß-lactam derivatives obtained by irradiation of α-oxoamides.

guest molecule will exist. Hence, it will lead to products in which the first asymmetric carbon will have a preferred handedness. This assumption is found to be correct in inclusion compounds where the host to guest ratio is 1:1, as shown in Figure 2.[11] However when the host to guest ratio is 1:2 the two guest molecules, although in a chiral space group, are found to be related by a non-crystallographic inversion centre as shown in Fig. 3. The outcome is that the two mirror related conformations were present in the same crystal lattice and the reaction cannot be enantiospecific. The possible specificity regarding the other asymmetric carbon atom is found to be more confusing. The six and seven-membered rings of the

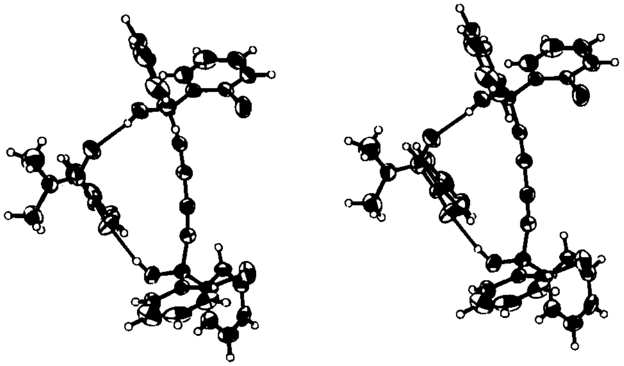


Figure 2. Stereoscopic drawing of the chiral host with N,N-dimethyl-α-oxobenzena-cetamide. (1:1).

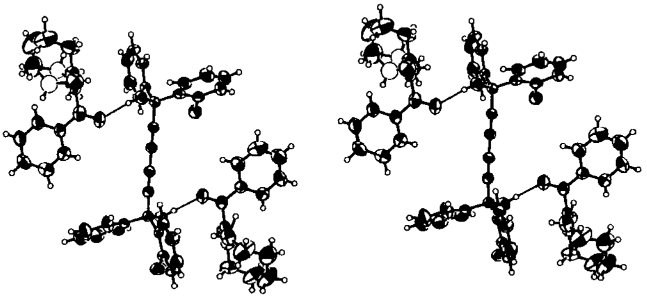


Figure 3. Stereoscopic drawing of the chiral host with an α-oxoamide derivative (1:2). (Showing disorder at the seven-membered ring).

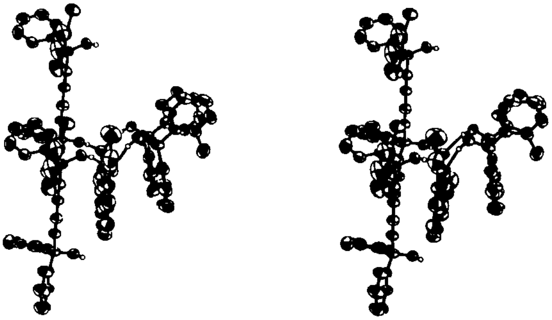


Figure 4. Stereoscopic drawing of the chiral host with α-tropolone ethylether.

α-oxoamide molecules are found to be disordered. Thus both hydrogen atoms have a chance to be abstracted and therefore the reaction will not be so specific.

The second type of reaction shown in Table 1 is the photochemical conversion of α-tropolone alkyl ethers[11] or pyridone[12] to the corresponding bicyclic product. This reaction occurring in the crystalline inclusion compound of the chiral host is specific and the product is obtained in 100% e.e.[8] Remembering that the host to guest ratio is 1:1, that the compound crystallizes in a chiral space group and that there is no disorder, the specificity is clear. An example of the crystal structure of the inclusion compound with α-tropolone ethylether is shown in Figure 4. The guest molecule is held by bifurcated hydrogen bonds to two host molecules. The chiral environment of the guest molecule and the differences between the space available at both sides of the planar molecule cause bending to produce the bicyclic product in just one way.[11,12]

The last type of reaction is a reduction of phenylketones to the corresponding alcohols in over 40% e.e. by mixing the solid inclusion compounds with solid reducing reagent. We have determined the crystal structure of two such compounds with the chiral host molecule to guest ratios of 1:1 (with phenylpropanone) and 1:2 (with phenylethanone). The packings in the crystal lattice are shown in Figures 5 and 6 respectively. It is too early to give an explanation to the specificity of the reaction based on the crystal structure, but it seems that the reaction occurs on the surface of the small particle size sample obtained by grinding the solid compound.

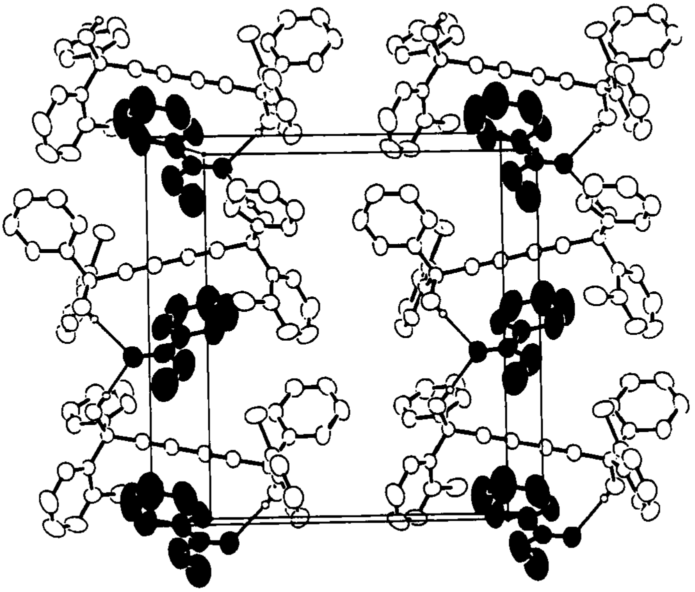


Figure 5. Packing of the chiral host with phenylpropanone (1:1).

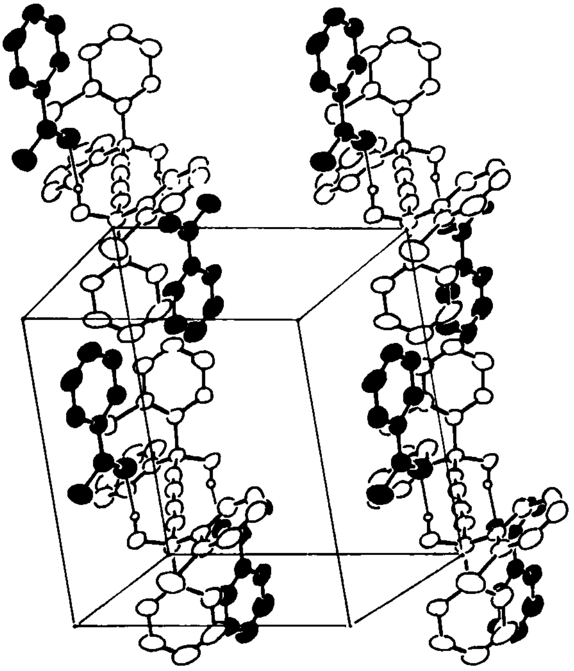


Figure 6. Packing of the chiral host with phenylethanone (1:2).

Conclusions

It was shown that chemical reactions in solid inclusion compounds may be specific. The specificity depends upon the packing of the guest molecules within the crystal lattice. The use of a chiral host molecule has the advantage of providing a chiral environment at the reaction sites which may lead by enantiospecific reactions to unique products.

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