Tetrahedron Vol. 42, No. 21, pp. 5753 to 5839, 1986
Printed in Great Britain.

0040-4020/86 $5.00+.00
Pergamon Journals Ltd.

TETRAHEDRON REPORT NUMBER 211

ORGANIC PHOTOCHEMISTRY IN ORGANIZED MEDIA

V. RAMAMURTHY
Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India

(*Received in U.K.* 10 *June* 1986)

CONTENTS

1. INTRODUCTION

Among many interesting and important problems of organic chemistry, the "selectivity of chemical reactions" is now undoubtedly one of the most promising and productive areas of investigation. The increasing number of publications, patents filed, symposia conducted,[1] books[2] and popular articles published[3] shows that this field took off rapidly during the past several years and some successful applications to the synthetic, analytical, pharmaceutical and industrial chemistry have been made. It is an active area with contributions from many laboratories around the world.

In biological systems enzymes conduct chemical synthesis with remarkable efficiency and speci-

ficity. Organic chemists' efforts have been much less successful than nature's synthetic activity. The style of laboratory organic chemistry differs from that used in living systems. In general, organic chemists allow small reagents to attack a free substrate randomly from solution. Any selectivity achieved is the result of the selective reactivity of particular sections of the substrate (electronic factor) or due to blocking certain approach directions (steric effect). By contrast, biochemical reactions involve enzymes which bind and orient the reactants. The most important factor is the tight binding of substrate into the active site of the enzyme when the resulting complex has unidimensional mobility, i.e. motional freedom only in the direction of the reaction coordinate. This contrasts with the complete three-dimensional mobility and consequent random collisional orientation, of a reacting pair of molecules in an isotropic fluid medium. Most enzyme catalysed reactions are stereoselective, selective in the choice of substrates, selective in the type of chemical reaction performed, and selective in the region of the molecule attacked when there are several possibilities.

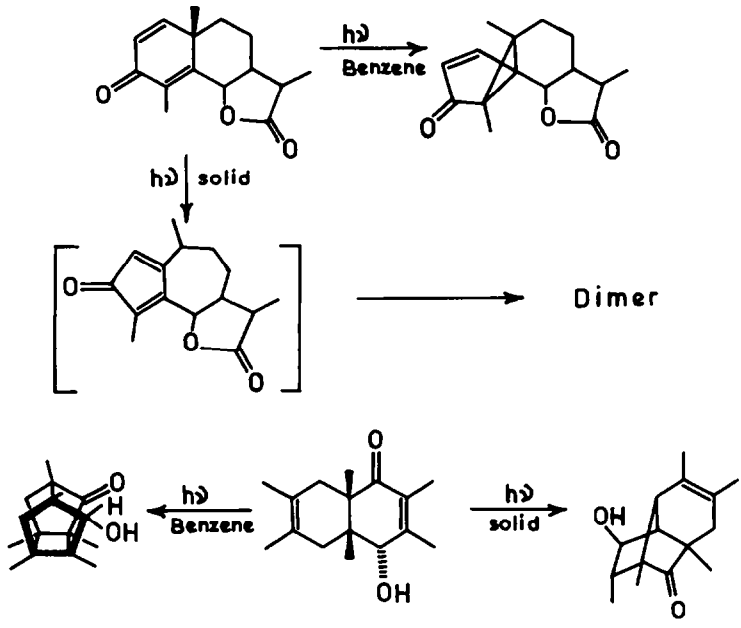
In this context, organic chemists have long recognized the important role the reaction media plays in controlling rates, product distributions and stereochemistry. Recently, much effort has been directed toward the use of organized media to modify reactivity (especially photochemical), as compared to that in isotropic liquids. A major goal of such studies is to utilize the order of the medium so as to increase the rate and selectivity of the chemical process involved in much the same way that enzymes modify the reactivity of the substrates to which they are bound. Among the many ordered or constrained systems utilized to organize the reactants, the notable ones are micelles, microemulsions, liquid crystals, inclusion complexes, monolayers and solid phases such as adsorbed surfaces and crystals. With these media partial constraints are imposed upon the reactants, limiting the overall number of possible transition states which can be formed, subsequently decreasing the number of products formed. Judicious selection of a given organized system for a given application requires a sufficient understanding and properties of the organized media themselves and those of the substrate interactions therein. The current state of art in reactivity control in organized systems will be the subject of this review. The article is primarily concerned with *organic photoreactions* in crystalline state, inclusion complexes (in solution and solid state), liquid crystals, micelles and on surfaces. Photophysical studies have been excluded.

2. PHOTOCHEMICAL REACTIONS OF ORGANIC CRYSTALS

Although reactions of many organic compounds in the solid state have been reported regularly over the last 50 years[4] and in spite of the fact that many organic compounds are crystalline solids at ambient temperatures, organic solid state chemistry has not been a subject of systematic study till recently. The science of solid state organic chemistry and particularly the area of lattice control over reaction pathways now seems to be entering a period of flowering and growth. There is no doubt that with deeper understanding of packing effects and of topochemistry, solid state organic reactions could be planned and exploited in organic chemistry. Following the pioneering contributions of Schmidt *et al.*,[5] several groups have attempted to understand organic solid state transformations on the basis of crystal structure. In this section we highlight with selected examples the role of solid state structure in controlling solid state reactions. It is not our aim to provide here a comprehensive review of solid state organic photochemistry. We intend to provide the readers a feel for what "solid state" can do in achieving selectivity in organic transformations. Various features of organic crystals are highlighted so that the similarity and differences between solid state and other media can be easily seen. For indepth survey of this field the readers are referred to two of the most recent reviews.[6]

2.1. *Difference in reactivity between solid and solution phases*

In general, unimolecular and bimolecular reactions occurring in the solid state differ from the same reactions in the fluid phase. This arises due to the fact that physical restraints on a given set of atomic and molecular motions by the environment can prevent drastic conformational, configurational, translational and rotational changes along the reaction coordinate and lead to alternate reaction pathways. With organic molecular crystals, environmental and crystallographic factors hold sway. The intrinsic reactivity of a molecule is frequently of secondary importance—sometimes it is of no consequence—compared with such features as site symmetry, nearest neighbour

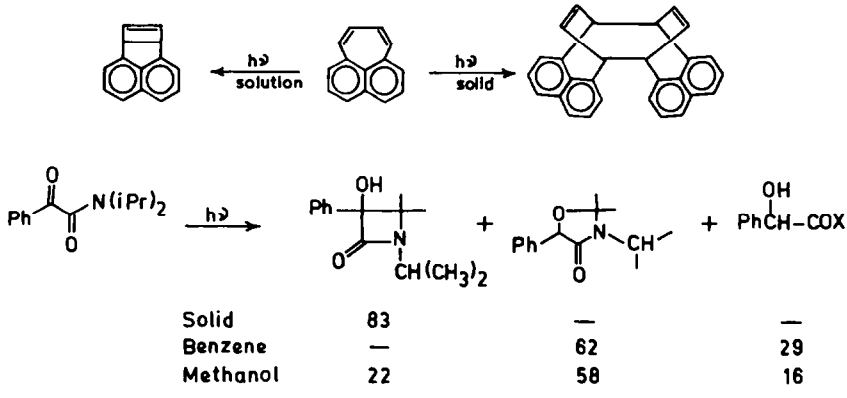


Scheme 1.

separation and other topochemical considerations. The products of an organic solid state reaction are almost invariably fewer in number than, and frequently very different from those produced from the same materials in fluid phases. Electronic and dipolar effects which are so familiar in solution chemistry are replaced by structural and topological factors with a resulting selectivity and stereospecificity of product formation that in many cases is virtually unknown in solution. Three examples provided in Schemes 1–3[7,8] highlight the differences between solution and solid state photochemistry. In the following sections the various unique features of crystal that influence the reactivity of organic molecules in crystals are briefly presented.

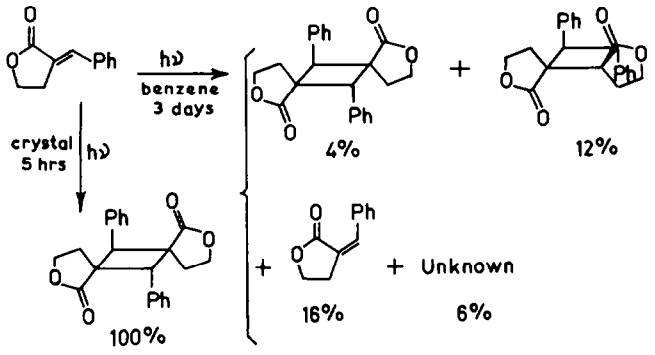
2.2. *Consequences of restricted motions in the solid state*

2.2.1. *General.* The crystalline state of organic systems is characterized by relatively large intermolecular forces which effectively restrict the rotational and translational motions of the constituent molecules. These lattice restraints can influence reactions occurring in the solid state. If the molecular packing in the crystal is such that adjacent molecules are favourably oriented with respect to one another for reaction to occur, then one may expect that this reaction will predominate in the solid state in contrast to more mobile phases where different geometries of approach may be favoured leading to different products. Further, in so far as the molecules making up the lattice are held in specific conformations which in turn predispose the molecules to specific reaction pathways, solid



Solid	83	—	—
Benzene	—	62	29
Methanol	22	58	16

Scheme 2.



Scheme 3.

state reactions will differ from those observed for the same molecules in solution if these conformations are either not present or are involved in rapid conformational isomerism with other reactive conformers in the liquid state. This is expected to be of particular importance for intramolecular reactions which are often sensitive to conformational changes. Finally, the crystal can constrain the movements of the reactants and thus gives rise to the specificity of the solid state reactions via "cage effects".

In general, the course of solid state reactions are determined by the geometry of the reactant lattice. This concept was originally formulated by Kohlschutter[9] and was termed "topochemical postulate". According to Kohlschutter, a topochemical reaction is one in which both the nature and properties of the products of the reaction are governed by the fact that it takes place under the constraining influence of the three dimensionally periodic environment. Schmidt and co-workers studied systematically the factors that govern the course of organic solid state, especially photo-induced, reactions.[10] As a result of their extensive studies on the photodimerization of cinnamic acids, they confirmed the topochemical postulate. The topochemical postulate is a landmark in organic solid state photochemistry and are used as rules as they provide an understanding of a large number of reactions.

Cohen introduced the concept of "reaction cavity", an extension of the topochemical postulate as an aid to interpret the course of a variety of solid state reactions.[11] According to this, the molecules taking part in a reaction occupy a certain size and shape in the crystal. This space occupied by the molecules is the "reaction cavity" and is surrounded by other molecules. The atomic movements constituting the reaction would cause "pressure" on the cavity wall which may tend to become distorted. However, any such distortion in shape would be resisted by the close packed environment, as a result only those reactions which involve minimal change in the external contacts of the reacting molecules would be energetically feasible. Therefore, the topochemical postulate can be redefined as "reactions proceeding under lattice control do so with minimal change or distortion of the surface of the reaction cavity". This concept is valuable in predicting the course of a reaction especially when more than one reaction is topochemically permitted. If there is more than one topochemically permitted product, the preformed one will be that for which the transition state involves the least change in shape of the reaction cavity (Fig. 1). Examples of the various effects discussed above are available in the literature and a few of these are presented below.

2.2.2. *Bimolecular reactions.* The reactions of *trans*-cinnamic acids in the crystalline state are well-known examples of [2+2] photodimerization and the classic studies by Schmidt and co-workers have demonstrated[12–14] that such reactions are strictly controlled by the packing arrangement of the molecules in the crystal. Among the several examples of solid state photodimerizations those have been reported since the original contributions of Schmidt, recent investigations on coumarins[15–20] and benzylidene cyclopentanones[21–26] are noteworthy. While studies on cinnamic acids resulted in very important correlation between molecular alignment in the reactant crystal and steric configuration of the product, analyses of the behaviour of benzylidene cyclopentanones (Scheme 4) and coumarins (Scheme 5) in the solid state have provided an opportunity to reexamine the subtler aspects of the topochemical postulates.

Based on extensive crystallographic and photochemical studies on cinnamic acids, Schmidt deduced the following conclusions. (a) The nature of the crystal structure determines whether or

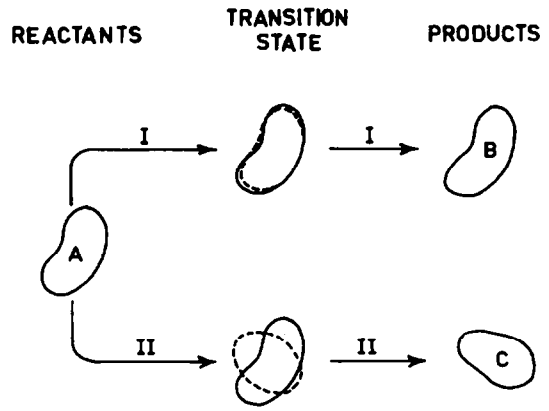
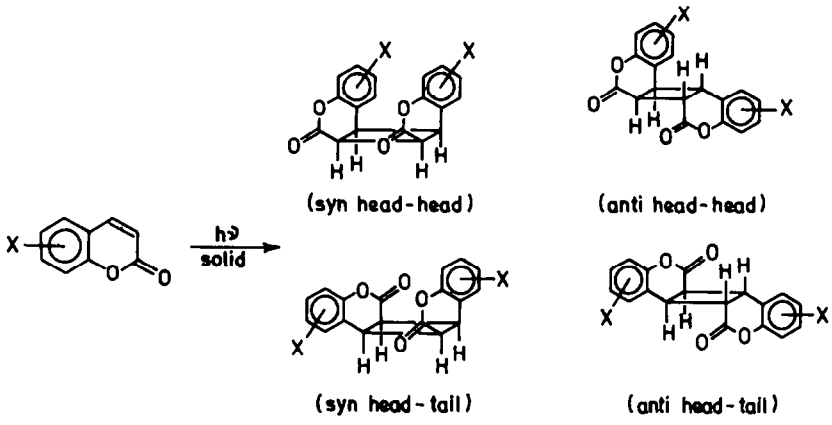


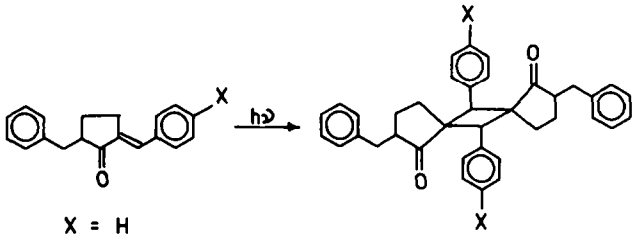
Fig. 1. Pictorial representation of "reaction cavity" concept.

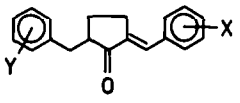
not reaction occurs and the molecular structures of products, if any. (b) The reaction involves a combination between nearest neighbour molecules in a stack, and occurs with a minimum of atomic and molecular movements. Schmidt has drawn attention to the fact that not only must the double bonds of the reacting monomers of cinnamic acids be within ~4.2Å, they must also be aligned parallel for cycloaddition to occur. However, very recent studies on the photodimerization of several olefinic crystals have brought out examples which deviate significantly from the above well-accepted conclusions.[27,28] Exceptions to original topochemical principles are summarized in Tables 1 and 2. Exceptions observed in recent studies should not be construed as serious violations of original



Coumarin Irradiated	Nature of Dimer
6 - Methoxy	syn HH (60%)
7 - Methoxy	syn HT (90%)
8 - Methoxy	anti HT (50%)
6 - Acetoxy	syn HH (70%)
7 - Acetoxy	syn HH (90%)
4 - Methyl 7-Acetoxy	syn HH (80%)
4 - Chloro	anti HH and syn HT (25%)
6 - Chloro	syn HH (100%)
7 - Chloro	syn HH (70%)
4 - Methyl 6 - Chloro	syn HH (50%)
4 - Methyl 7 - Chloro	syn HH (80%)
7 - Methyl	syn HH (65%)

Scheme 4.





Bp-Cl BCP	Y = H, X = p-Cl	No	
Bp-Me BCP	Y = H, X = p-Me	No	
p-Cl BBCP	Y = p-Cl, X = H	Yes	Centrosymmetric dimer
p-Me BBCP	Y = p-Me, X = H	Yes	
p-Cl Bp-Br BCP	Y = p-Cl, X = p-Br	No	
p-Me Bp-Br BCP	Y = p-Me, X = p-Br	Yes	

Scheme 5.

concepts but should be integrated into the original basic ideas by widening apparent limitations and scope.

Restricted motion does not imply that reaction in the crystal will not occur unless the reactants are in the ideal geometry for the reaction. It is important to note that a certain amount of motion of various atoms in the crystal lattice is tolerable. To give the reader a feel for this flexibility we refer to the recent reports on the photodimerization of coumarins.[15–20] Geometrical parameters that are useful in addition to centre–centre distance are θ_1, θ_2, θ_3 and the displacement of double bonds with respect to each other (Fig. 2). Here θ_1 corresponds to the rotational angle of one double bond

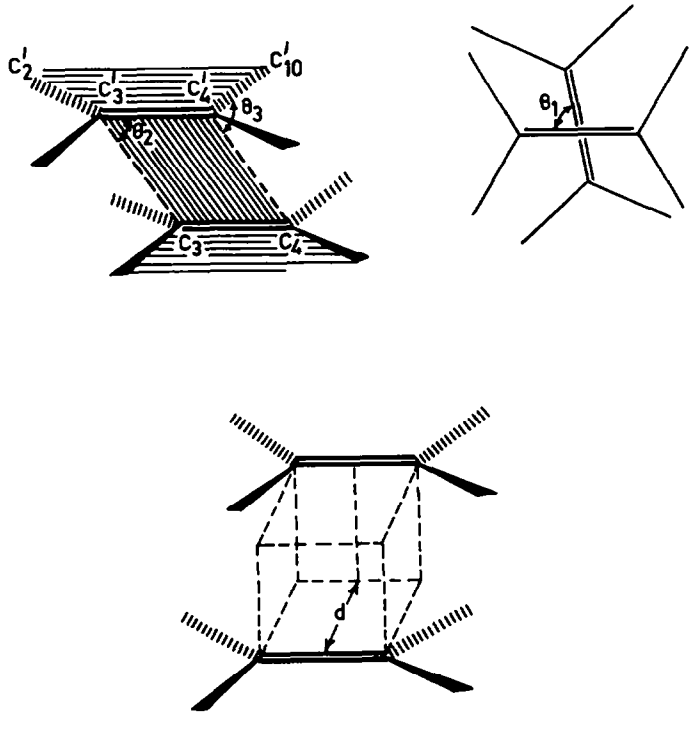


Fig. 2. Geometrical parameters used in the relative representation of reactant double bonds.

Chart 1. (For Tables 1 and 2.)

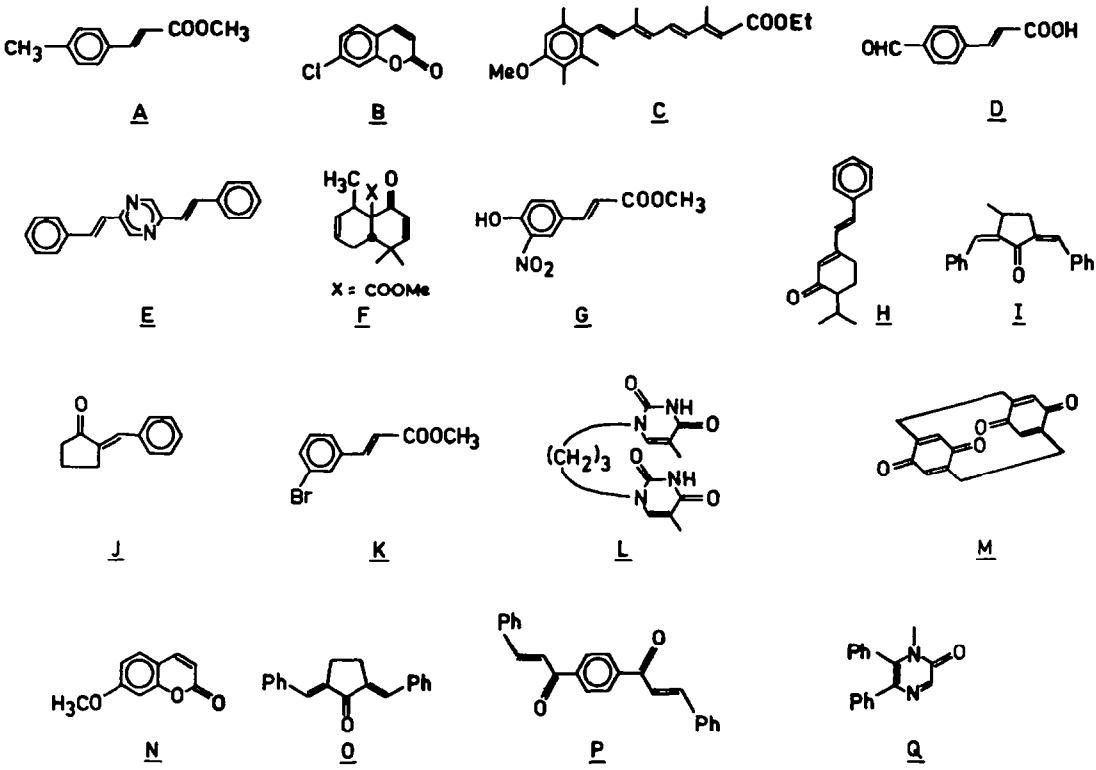


Table 1. Examples of exceptions to original topochemical principles regarding distance[a]

Compound	Distance between reactive double bonds	Reactivity	Nature of dimer
Methyl-*p*-iodocinnamate (**A**)	β-type 4.3 Å	Yes	minor symmetric
7-Chlorocoumarin (**B**)	β-type 4.45 Å	Yes	*syn*-head–head
Eteretinate (**C**)	4.4 Å	Yes	—
p-Formyl cinnamic acid (**D**)	β-type 4.825 Å	Yes	Minor symmetric
Distyryl pyrazine (**E**)	<4.19 Å	No	—
Enone (**F**)	3.79 Å	No	
4-Hydroxy-3-nitrocinnamate (**G**)	3.78 Å	No	—
Benzylidene-*dl*-pipertone (**H**)	<4.0 Å	No	—
(+)-2,5-Dibenzylidene-3-methyl cyclopentanone (**I**)	3.87 Å	No	—
2-Benzylidene cyclopentanone (**J**)	4.14 Å	No	—

[a] For structures of compounds see Chart 1.

Table 2. Examples of exceptions to original topochemical principles regarding parallelism of double bonds[a]

Compound	Rotational angle of one double bond with respect to the other	Reactivity–dimerization
Methyl *m*-bromo cinnamate (**K**)[b]	28°	No
1,1′-Trimethylene-bis-thymine (**L**)	6°	Yes
[2,2](2,5)-Benzoquinophane (**M**)	3°	Yes
7-Methoxycoumarin (**N**)	65°	Yes
2,5-Dibenzylidene cyclopentanone (**O**)	56°	Yes
1,4-Dicinnamoyl benzene (**P**)	6°	Yes
1-Methyl-5,6-diphenylpyrazine-2-one (**Q**)	24°	Yes

[a] For structures of compounds see Chart 1.
[b] The postulate was formulated on the basis of the compound.

with respect to the other, θ_2 corresponds to the obtuse angle of the parallelogram formed by double bond carbons C_3, C_4, C'_3 and C'_4, whereas θ_3 measures the angle between the least square plane through the reactive bonds C_3, C_4, C'_3 and C'_4 and that passing through the reactive C_2, C_3, C_4 and C_{10}. While θ_2 reflects the displacement along the double bond axis, θ_3 is a measure of its displacement in the molecular plane. Perusal of Table 3 reveals that in all the four reactive coumarins the reactive double bonds are not ideally placed. Although they are coplanar and parallel the two double bonds are displaced with respect to each other both in the molecular plane as well as along the double bond axis. In all the four cases the configuration of the dimers obtained in high yield corresponds to the one that is expected based on molecular packing in the crystal. This suggests that the motion of molecules in the molecular plane and along the double bond axis, in addition to toward each other, are required and indeed occur. Thus a certain amount of flexibility in the motions of the molecules in the crystal is to be expected. The above analysis illustrates that packing permitting some amount of molecular movements at no great loss of lattice energy can assist the topochemically allowed reactions.

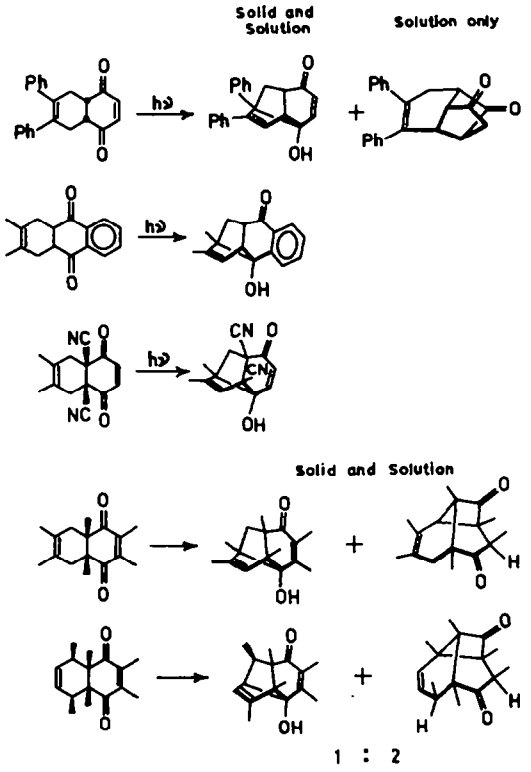
2.2.3. *Unimolecular rearrangements.* Scheffer has recently elucidated how the ground state conformations influence the excited state behaviour of tetrahydronaphthoquinones and their derivatives in the solid state.[29] Following these pioneering contributions, work related to the intramolecular hydrogen abstraction in the case of arylalkyl ketones[30] and aromatic nitro compounds[31] have appeared in the literature. In general, all these studies are aimed at answering the questions concerning the factors which influence the photochemical intramolecular hydrogen abstraction. Before going into the details it can be stated that these unimolecular photorearrangements appear to be controlled by a reaction cavity that allows a minimum of atomic and molecular motions. That is, the crystal forms an environment in which motion is restricted and products that have a shape similar to that of the starting materials are favoured. In solution where numerous conformers are present, different products are formed. Of the many available examples, only two are presented below.

Photolysis of *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone derivatives yields a plethora of products. Impressive differences in the nature and yields of products were noticed between the solution and solid state irradiations and these are summarized in Schemes 6 and 7.[32,33] The mechanism of formation of these products can be understood on the basis of three primary reactions, namely, β-H abstraction by the carbonyl oxygen, γ-H abstraction by the enone double bond and inter- and intramolecular cycloadditions (Schemes 8 and 9). Although the X-ray crystal structures of these substrates revealed a common ground state conformation irrespective of substitution, four different reactivity patterns emerged. (a) Intermolecular [2+2] cycloaddition for substrates in which the reacting double bonds are parallel and a centre–centre separation of <4.04 Å. (b) Intramolecular hydrogen abstraction by an oxygen of an excited carbonyl moiety through a five-membered cyclic transition state (Scheme 8), in cases where the substrates lacked the intermolecular orientation necessary for dimerization but which had β-H in the carbonyl plane at a distance of <2.58 Å from the oxygen. The H_β—O—C angle in all cases was very close to the optimum angle (90°) for efficient

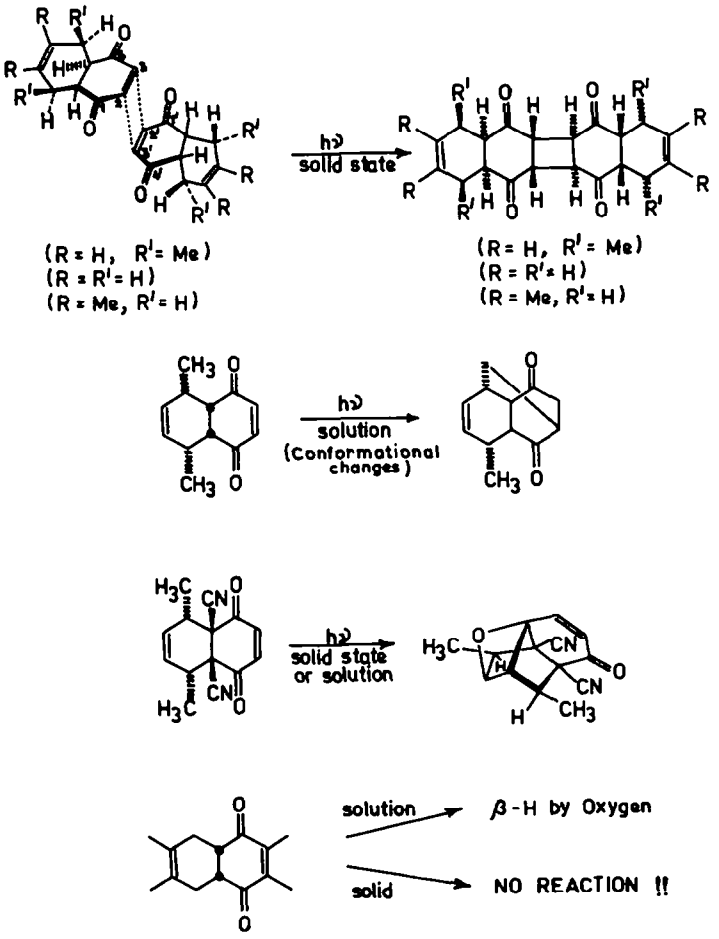
Table 3. Relative orientations of reactive double bonds in coumarins[a,b]

Coumarin	Centre to centre distance between the reactive double bonds (Å)	θ_1 (deg.)	θ_2 (deg.)	θ_3 (deg.)	Displacement of double bonds upon projection (Å)
7-Chlorocoumarin					
pair I (translation)	4.45	0	131.4	85.3	0.287
pair II (centrosymm)	4.12	0	127.9	107.0	0.936
4-Methyl 7-chlorocoumarin	4.08	0	121.4	88.53	0.011
7-Acetoxycoumarin	3.83	0	106.4	125.45	1.329
8-Methoxycoumarin					
pair I	4.07	0	122.4	63.77	1.565
pair II	3.86	0	117.4	112.88	1.333
7-Methoxycoumarin	3.83	65	—	—	—
Ideal values	4.2	0	90	90	0.0

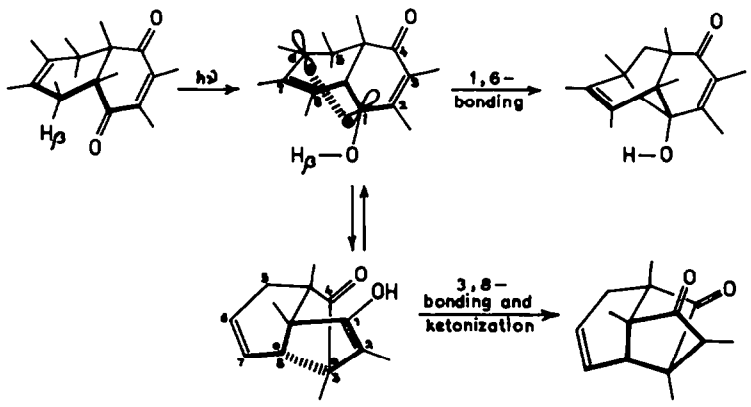
[a] For definition of geometrical parameters see Fig. 2.
[b] Taken from: K. Gnanaguru, N. Ramasubbu, K. Venkatesan and V. Ramamurthy, *J. Org. Chem.* **50**, 2337 (1985).



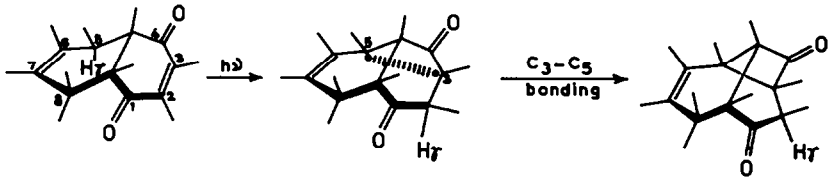
Scheme 6.



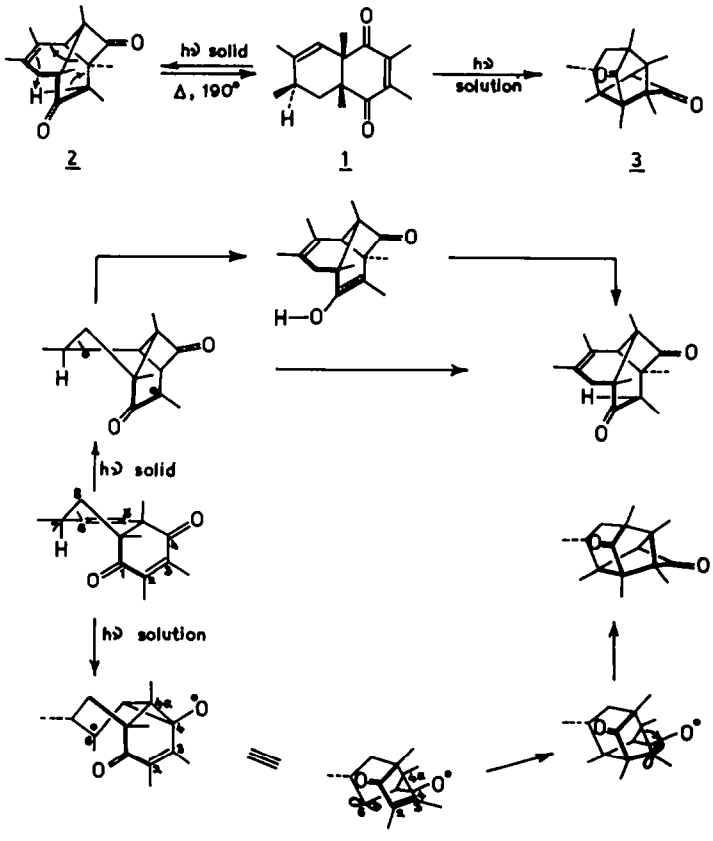
Scheme 7.



Scheme 8.



Scheme 9.



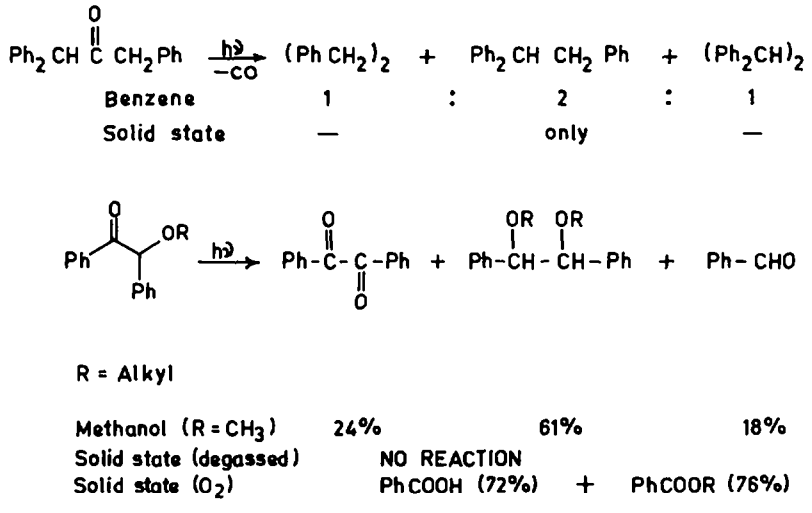
Scheme 10.

hydrogen abstraction by the n-orbital of oxygen. (c) Intramolecular γ-H abstraction by the β-C of an excited enone system was the predominant reaction in substrates having low lying $\pi\pi^*$ excited states (Scheme 9). The distance between the hydrogen and the abstracting carbon was <2.89 Å. Since the abstracting orbital in this case is the 2p orbital of carbon, the optimum geometry for efficient abstraction differs from that of the β-process. (d) Intramolecular oxetane formation occurs for substrates which lack the pre-requisites for the other three processes.

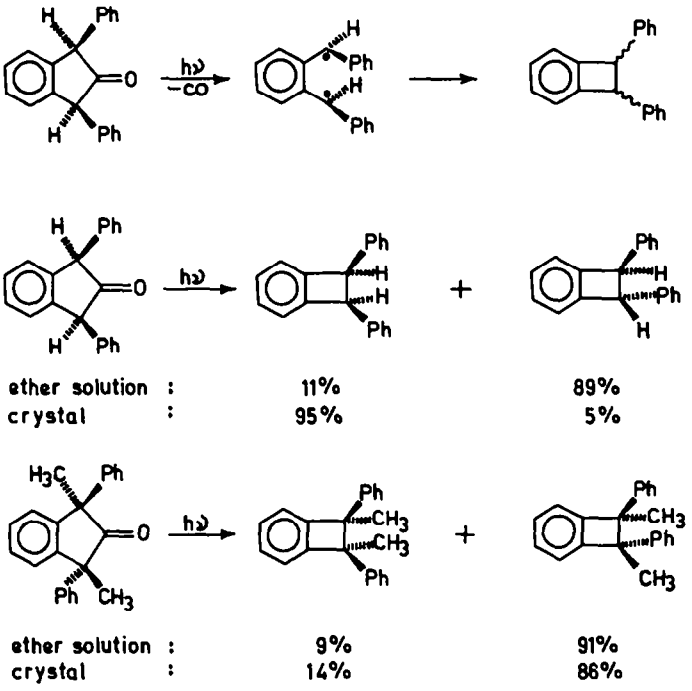
The same authors reported an elegant comparison of the solid state and solution behaviour of a β,γ-unsaturated ketone **1** (Scheme 10).[34] In solution, the ketone is conformationally mobile; in solid it is frozen into a single conformation. The photochemical consequences of this simple fact illustrate well the unparalleled opportunities that certain organic solids offer for the construction of detailed unimolecular structure–reactivity relationships. As shown in Scheme 10, the β,γ-unsaturated ketone **1** yields different products in solution and in the solid state upon photolysis. The solution product originates via oxa-di-π-methane rearrangement. It is to be noted that tetrahydronaphthoquinone **1** adopts a conformation in the solid state in which the cyclohexane ring is half chair-like and the methyl group at C(7) is pseudoquatorial. A key feature of this conformation is that the hydrogen atom at C(7) is pseudoaxial and in a position to be transferred to the ene-dione ring at some stage in the formation of the photoproduct. In terms of overall atomic motions, formation of **2** requires only the relatively minor processes of rehybridization of carbon atoms 2, 3, 5 and 7 plus a decrease in the C(3) to C(5) contact. The basic molecular shape remains constant throughout the transformation. In contradistinction, the shape of solution photoproduct **3** bears little resemblance to that of the starting compound **1** and is formed via a sequence of steps each of which requires substantial atomic motion and molecular deformation.

2.2.4. *Effects on reaction intermediates.* A factor of considerable topochemical and practical importance in unimolecular reactions in crystals is the fact that the crystal reaction cavity can constrain the movements of the contents of the cavity and thus give rise to the specificity of the solid state reaction. Not only are fragments constrained to stay close together, but their rotational motions may also be restricted. Examples of such an effect are also available in the literature.

The two examples reported by Quinkert *et al.*[35,36] illustrate the restriction brought about by the lattice on the diradicals generated via decarbonylation. Photolysis of 1,1,3-triphenyl acetone in the crystal gives selectively only one product while in solution a statistical mixture of products is obtained (Scheme 11). The presence of such a "super cage" effect has also been reported during the photolysis of benzoin ethers.[37] Benzoin ethers undergo photochemical α-cleavage to form a benzoyl–benzyl radical pair which subsequently undergoes free radical reaction in solution to give benzaldehyde, benzil and pinacol ethers. However, when the irradiation of these crystals was conducted in the absence of oxygen, the starting material was recovered unchanged.[37] Presumably the radical pair generated in the crystalline phase cannot diffuse apart and result in recombination. Indeed this was demonstrated by photolyzing the above crystals in an oxygen atmosphere. Under these con-



Scheme 11.



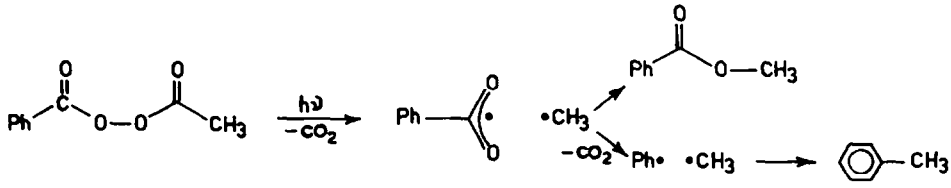
Scheme 12.

ditions benzoic acid and alkyl benzoates, the products resulting from the trapping of the radical pair, were obtained in high yield (Scheme 11).

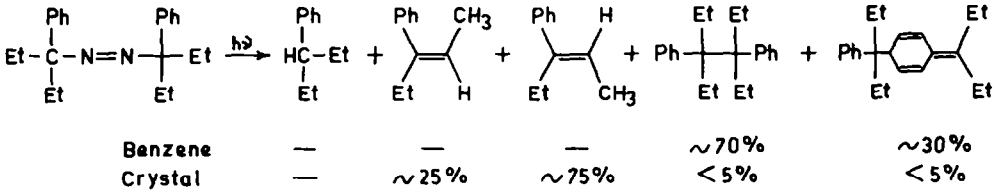
An example of rotational restriction imposed by the crystalline medium has also been provided by the investigations of Quinkert *et al.*[35] Photolysis of indanones in solution results in smooth decarbonylation to give isomeric benzocyclobutanes. The stereoselectivity observed during the photo-elimination of carbon monoxide from *cis*- and *trans*-1,3-diphenyl substituted 2-indanones show a striking increase on going from the solution phase to the crystal as illustrated in Scheme 12.

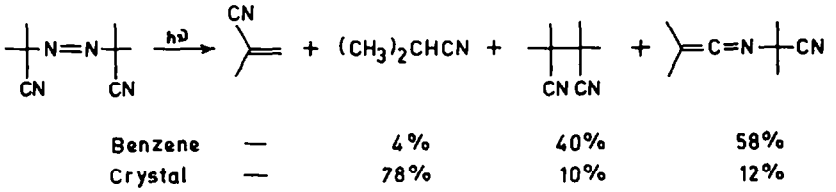
Further interesting examples of the topochemical effect on radical reactions have been provided by McBride and co-workers.[38-47] For example, decomposition of acetylbenzoylperoxide (ABP) in solution gave more than one dozen products among which no single compound accounted for more than 25%. Partial photolysis of crystalline ABP, however, gave only products methylbenzoate from loss of one CO_2, and toluene from loss of both, which are expected from the cage effect in the reaction (Scheme 13). There are several examples of radical pairs which yield coupling products in solution but give predominantly disproportionation products in the solid state. The photolysis of azobis-3-phenyl-3-pentane in solution gives 3,4-diethyl-3,4-diphenylhexane and a photostable product (Scheme 14). However, in the crystalline state at $-78°$ disproportionation products 3-phenylpentane and 3-phenyl-2-pentene as a 3 : 1 mixture of *E* and *Z* isomers were obtained. It was observed that azobisisobutyronitrile upon photolysis accounts for only 5% radical–radical reactions in the solution phase whereas 95% in the crystalline phase (Scheme 14).

The above examples illustrate the influence of the lattice on the constitution and configuration of the products. Examples of the role of the lattice in generating radicals in a given conformation and in selecting one among many nominally degenerate pathways have been described.



Scheme 13.





Scheme 14.

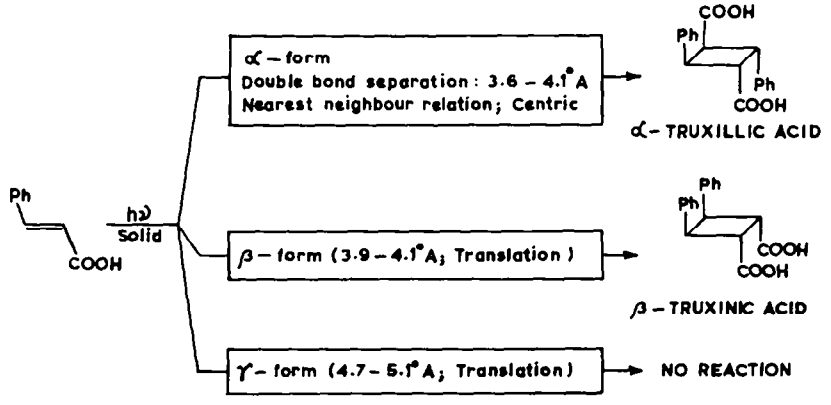
2.3. *Polymorphism and reactivity*

Organic crystals are known to display diverse polymorphic forms. It has been very well established that different polymorphic forms of a given compound may show significant differences in reactivity and photochemical behaviour. A few illustrative examples are provided below.

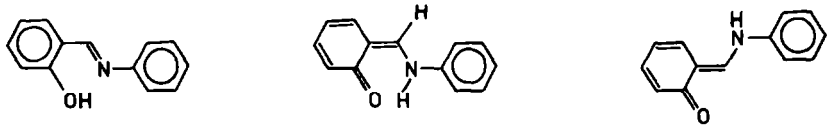
A classic example that shows polymorphic form dependent reactivity is cinnamic acid. Substituted cinnamic acids crystallize in three polymorphic forms namely α, β and γ and show photochemical behaviour which is characteristic of the structural type (Scheme 15).[12–14] It has been shown that the symmetry of the product could be derived from the crystallographic symmetry relating the nearest neighbours. Another class of molecules which exhibits reactivity dependent on polymorphism is anils. Photochromism is the salient feature of this class of molecules. Based on extensive studies, Schmidt and co-workers[48–51] have identified two major crystalline forms in the case of anils— α and β types. The α-type is photochromic and not thermochromic and the β-type is thermochromic but not photochromic. It is suggested that the α-type permits the photochemical formation of the *trans*-keto structure, whereas the β-type packing prevents this but does permit thermal formation of the *cis*-keto structure (Scheme 16).

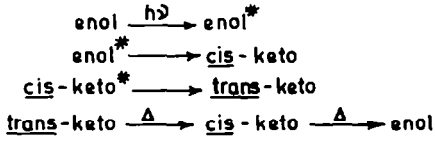
One of the crystal structure dependent interesting cyclizations reported recently is that of tetrabenzoylethylene.[52] Only one of the dimorphic modifications gives rise to a product upon photolysis while the other is inert to UV radiation (Scheme 17). It has recently been reported by Scheffer and co-workers[53] that α-admantyl-*p*-chloroacetophenone undergoes solid state Norrish type II cyclobutanol formation with different stereoselectivity from the dimorphic forms (Scheme 18).

The most remarkable example is provided by Lahav and co-workers.[54] The resolved monomer **4** (Fig. 3) is polymorphic. Crystallization under different conditions from the melt or from solution

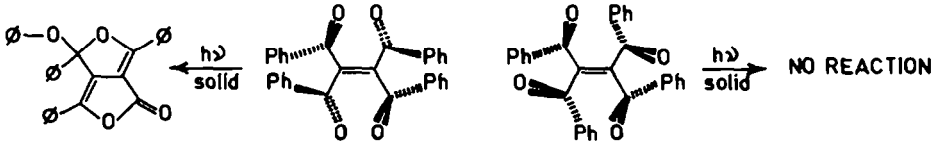


Scheme 15.

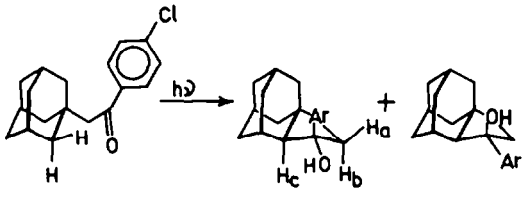




Scheme 16.



Scheme 17.



Reaction medium	cis : trans Cyclobutanol ratio
benzene (0.1 M)	27 : 73
moist acetonitrile (0.1 M)	36 : 64
dimorph (needles)	26 : 74
dimorph (plates)	0 : 100

Scheme 18.

yields α or β forms without any apparent preference for either. What is most interesting is that the two forms are chiral and are enantiomorphous $\{R\}_+$ and $\{R\}_-$. Irradiation of a polycrystalline sample of (*R*)-(−)-**4** of the form α yields dimer with absolute configuration (*RRRR*) and of the form β with (*SSSS*). It is important to note that the chiral s-butyl group which steers the crystal to either $\{R\}_+$ or $\{R\}_-$ crystals pack into conformations which are different from each other in the two forms. Thus no doubt this is an elegant example where conformational polymorphism has been exploited for the performance of asymmetric synthesis of either isomer on the same chiral molecule (Fig. 3).

It is clear, therefore, that the phenomenon of polymorphism, whereby the molecules that make up an organic crystal pack differently or exhibit conformational differences can be exploited intelligently to control solid state reactivity.

2.4. *Chiral crystals and absolute asymmetric synthesis in the solid state*

The achievement of an asymmetric synthesis starting from an achiral reagent and in the absence of any external chiral agent, has long been an intriguing challenge to chemists. The possibility of utilizing the chirality of crystals to achieve asymmetric synthesis was considered almost at the turn of this century. However, successful approaches awaited the better understanding of, and experience with, organic solid state reactions. On the basis of the vast amount of knowledge gained regarding

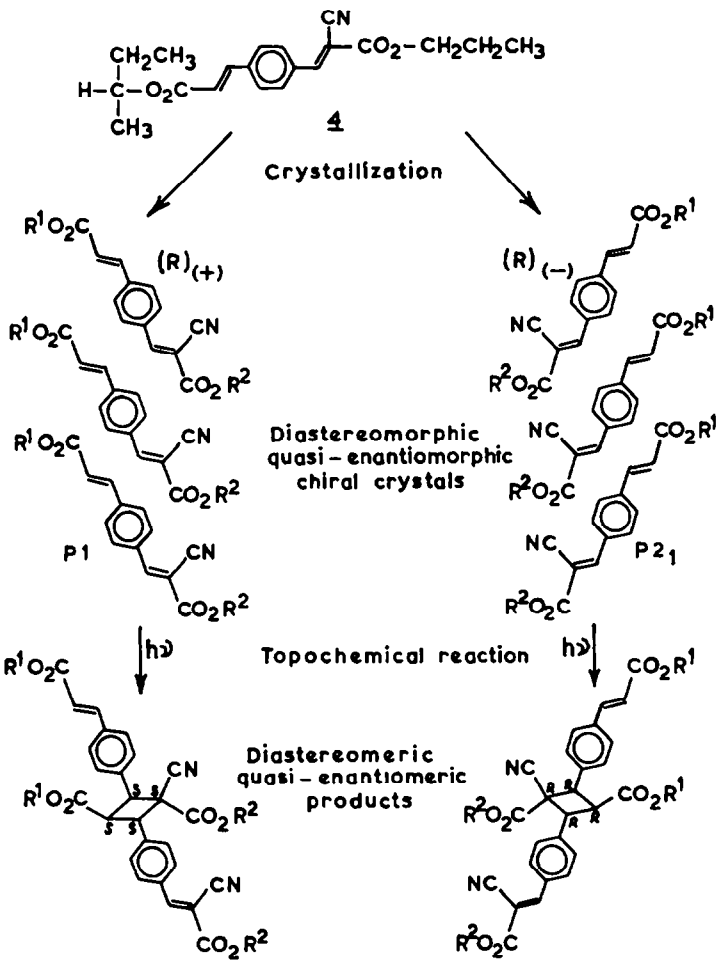


Fig. 3. Chiral synthesis of photodimers from polymorphic 4.

the photodimerization reactions in the solid state, Schmidt and co-workers extended their studies to design and perfom solid state asymmetric synthesis.[55,56] The strategy and the main results reported by these investigators are briefly summarized here.

Before describing the results of Schmidt and co-workers it would be appropriate to mention a few facts relating to the symmetry of crystals. There are 230 genera of space groups which can be divided into two categories: (a) the chiral space groups, 65 in number, have only symmetry elements of the first kind namely translations, rotations and a combination of these; and (b) the non-chiral space groups of which there are 165, may contain symmetry elements such as mirror plane, glide plane or centre of inversion. Thus the unit cell of a compound belonging to an achiral space group will contain both the object and its image. It is obvious that any attempt at achieving asymmetric synthesis via photochemical reactions should begin with a compound crystallizing in any one of the 65 chiral space groups. Optically active compounds must crystallize in chiral space groups; samples containing equal numbers of enantiomeric molecules can yield either racemic or chiral crystals, the latter case being known as spontaneous resolution. Of particular interest here is the observation that molecules which are achiral in solution can also spontaneously resolve and afford chiral crystals. In these instances, the chiral environment of the crystal forces the molecule to acquire a chiral conformation (e.g. benzophenone, benzil and binaphthyl).

A systematic solid state approach to asymmetric synthesis demands the design of chiral crystals having certain intermolecular and intramolecular features. Crystal engineering is not so advanced that any desired crystal environment can be prepared to order. In this context, the following observations are worthy of note. In a survey of some 5000 X-ray structure determinations of homomolecular crystals reported, it has been observed[57] that organic molecules tend to crystallize in the systems of low symmetry, namely monoclinic and orthorohmbic systems. Of the 219 distinct space

Table 4. The most common space groups of molecular crystals based upon a survey of some 5000 crystal structure determinations[a]

Space group	Number	Percentage
$P2_{1/c}$	1897	37.9
$P2_12_12_1$	839	16.8
$P\bar{1}$	449	9.0
$P2_1$	418	8.4
$C2/c$	310	6.2
Pbca	247	4.7

[a] Taken from: V. K. Blsky and P. M. Zorkii, *Acta Cryst.* **33A**, 1004 (1977).

groups (11 enantiomorphous groups excluded from the total of 230) the most commonly occurring space groups are $P2_{1/c}$, $P2_12_12_1$, $P\bar{1}$, $P2_1$, $C2/c$ and *Pbca*, the chiral ones being $P2_12_12_1$ and $P2_1$ (Table 4).

Two approaches were mainly used to achieve asymmetric photodimerization.[55,56] In the first approach the basic idea is to grow crystals containing two components. If there is appreciable miscibility between the two components, two enantiomeric heterodimers will be formed besides the two homodimers upon irradiation. Along the 4 Å stack axis of one component, present in excess, each molecule of the other component will be sandwiched between two molecules of the former. The contacts to these neighbours will be nonequivalent, especially if the molecules are nonplanar. Therefore, upon irradiation, two diastereomeric transition states of the mixed dimer may be formed with an appreciable difference in rate, so that the resulting asymmetric cyclobutane may contain one enantiomer in excess. Several examples of systems corresponding to this approach have been found to adopt chiral crystal structures and, indeed one example investigated afforded an optically active photoadduct.

It was known from the earlier studies that phenyl substituted olefins (stilbenes, 1,4-diaryl butadienes) tend to adopt chiral structures. Further there were clear indications that dichloro derivatives bring about a 4 Å packing arrangement. As for the choice of the two components, thiophene and phenyl derivatives were favoured since these molecules have been found to form mixed crystals. Thus when mixed crystals of **5** and **6** were irradiated, enantiomeric heterodimers, in addition to the homodimers, were formed (Fig. 4).[58] In actual practice mixed crystals containing 85% **5** and 15% **6** were used yielding heterodimers in high percentage. When large single crystals of these were irradiated an optically active hererodimer was isolated; the optical yield of this reaction was established as ~70%. The optical yield in this reaction is seen to be a measure of the rate of reaction of the photoexcited thiophene **6** upward or downward. If there were no molecular deformation on excitation, one might anticipate that the excitation of the thienyl compound would afford equal amounts of enantiomers **7** and **8**. Since optically active dimers were obtained, the authors

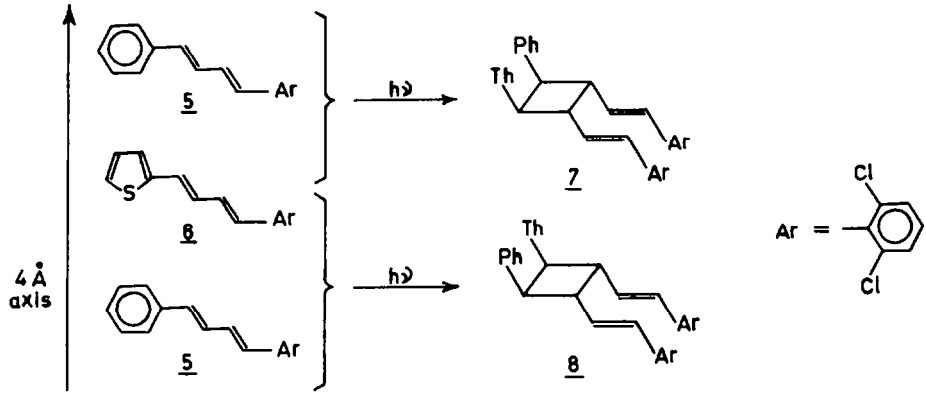


Fig. 4. Asymmetric synthesis using mixed crystals of **5** and **6**.

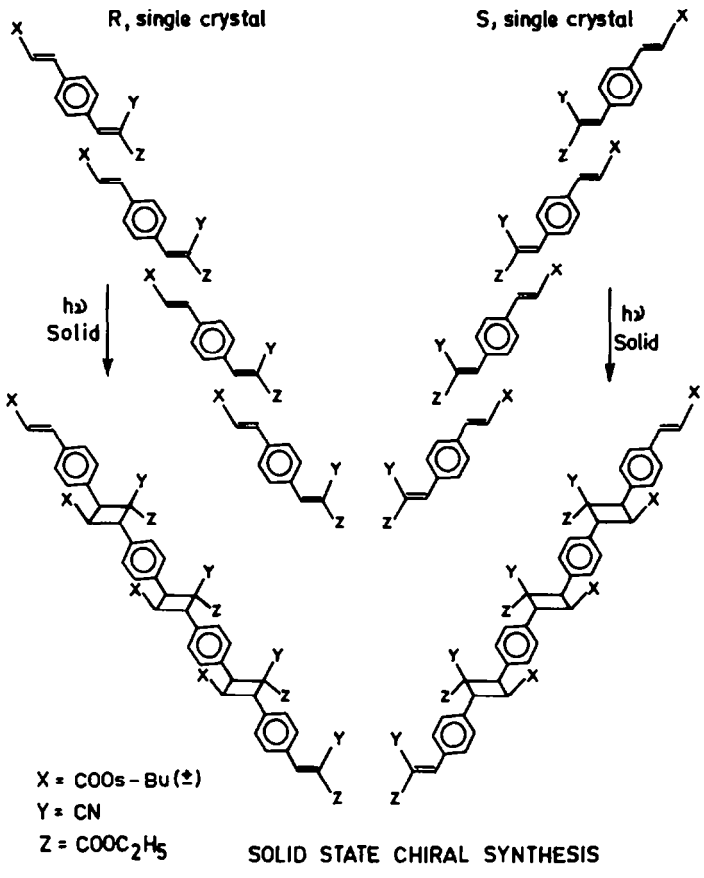


Fig. 5. Principles of solid state asymmetric synthesis.

conclude that when the thiophene moiety is excited, it is deformed and the difference in the interaction with its nearest neighbours leads to the formation of two diastereomeric transition states, giving rise to the observed asymmetric synthesis.

The strategy adopted in the second approach demanded molecules having two non-identical reactive sites pack in a chiral crystal in such a way that non-equivalent double bonds overlap. Such an arrangement would be expected to generate only one of the two possible enantiomers (Fig. 5). The actual system chosen for implementing this proposal was benzene 1,4-diacrylates.[59–64] The chiral sec-butyl group was used in order to induce the compound to crystallize in a chiral space group. When the ethyl ester (*S*)−(+)-**9** was irradiated at 5°, the chiral dimer, trimer and higher polycyclobutane oligomers were obtained in high optical yields approaching 100%.[59–63] Irradiation of the enantiomeric *R*-(−)-**9** isomer yielded products having optical rotations of the same magnitude but of opposite sign (Fig. 6). The ambiguity that the asymmetry of the products may be due to optical induction by the chiral handle instead of being due to the chiral crystal environment has been resolved through further experiments. The optically pure ester in which the ethyl group of **9** is replaced by methyl can be crystallized into a structure containing a pseudocentre of symmetry. This upon photolysis gives the optically inactive dimer after removal of the sec-butyl group. Thus it is clear that the chiral crystal environment alone controls the chirality of the product cyclobutanes and the role of the chiral handle is only to drive the monomers to a chiral space group.

There is also an interesting observation that the crystals of racemates of both ethyl ester and methyl ester of **9** are isomorphous with their respective enantiomers.[64] It has been established that in the racemate of ethyl ester crystallizing in a chiral system, the *R* and *S* sec-butyl groups are disordered. These observations suggest that starting from racemic monomer, "absolute" asymmetric synthesis with quantitative enantiomeric yield can be accomplished, provided that the compound can be crystallized as one single homochiral crystal. The preparation of such a single crystal of 50% *R* and 50% *S* composition, under equilibrium conditions demands solid solubility between the two enantiomers in all range of compositions. However, as an immisible range exists between the

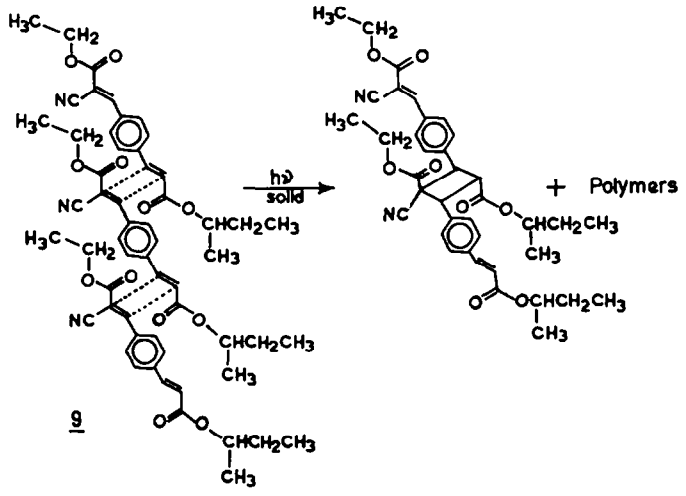


Fig. 6. Schematic representation of the asymmetric dimerization of **9**.

enantiomeric ratio of 60 : 40 and 40 : 60 of compound **9** crystals, the precipitation of equal amounts of crystals of both chiralites is not avoidable in this region by eutectic formation. Therefore, "absolute" asymmetric synthesis was carried out on the monomer crystal with low optical activity or of a racemate crystal prepared under non-thermodynamic conditions. Thus irradiation of polycrystalline **9** of 60% optical purity or above led to the formation of chiral dimers and oligomers with quantitative enantiomeric yield. Carefully crystallized samples of **9** of 22–60% optical purity led to enantiomeric excess of 90% or above.

A remarkable result was achieved when crystals of achiral monomer **10** were grown and irradiated.[65] Dimers and oligomers of either chirality with a quantitative enantiomeric yield were obtained upon irradiation of crystalline **10**. An "absolute" asymmetric synthesis with quantitative enantiomeric yield, via the process of crystallization of a non-chiral compound in a chiral crystal followed by a topochemical photoreaction is indeed a monumental success and is the result of careful planning and deep understanding of the interactions that play a role in crystals.

It is clear that the chirality in solid state asymmetric synthesis is in fact introduced in the crystallization step; the chemical reaction then transforms the chirality of the crystal into that of the product. Chiral crystals, like any other asymmetric object, exist in two enantiomorphous equienergetic forms, but careful crystallization of the material can induce the entire ensemble of molecules to aggregate into one crystal, of one handedness, presumably starting from a single nucleus. The photochemical process then transforms the conformational chirality frozen in the crystal into stable molecular chirality (Fig. 7).

It is important to realize that having a molecule in a chiral space group alone does not ensure asymmetric synthesis. A clear example is the photodimerization of 1-(2,6-dichlorophenyl)-4-phenyl *trans,trans*-1,3-butadiene (**5**). This crystallizes in a chiral space group $P2_12_12_1$, but irradiation yields a single photoproduct, the mirror-symmetric dimer.[58] Although in the crystal the reactive pairs are not related by mirror plane, they are by translation. Therefore, the photoproduct contains a mirror plane and is therefore not dissymmetric. Further, it is noteworthy that asymmetric synthesis can be achieved also from molecules crystallizing in non-chiral space groups, provided the crystal contains

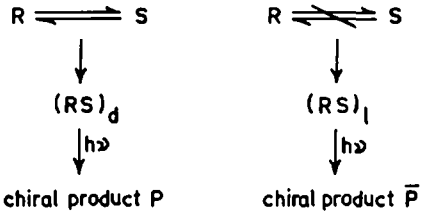


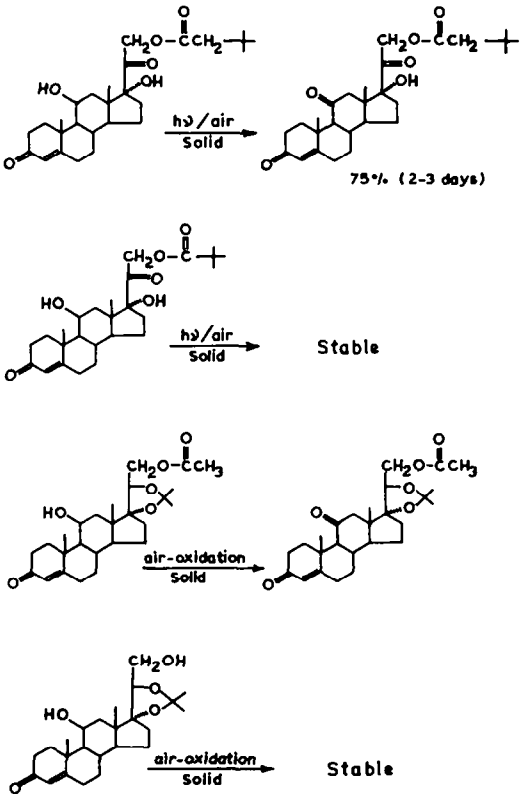
Fig. 7. Absolute asymmetric synthesis from racemic mixture.

a polar axis. No photochemical reaction has been reported from such crystals. Considering the potential use of such a technique in photochemical asymmetric induction, the recent report on the asymmetric induction achieved by a non-chiral reactant on a non-chiral crystal deserves mention. It was recognized that, it is possible, under certain conditions, to achieve stereoselectively a chiral product from non-chiral reactants by using one surface of a single crystal as the chiral template. In the experiments of Richardson and co-workers,[66,67] an aqueous solution of barium chlorate and osmium tetroxide was allowed to react on $(\bar{2}\ 1\ 0)$ and $(2\ \bar{1}\ 0)$ planes (plane group $P2$) of large single crystals of tigilic acid (space group $P\bar{1}$). The enantiomeric diol of high optical purity (~95%) was isolated.

2.5. *Permeability of crystals and gas–solid reactions*

One of the earliest photo-oxidations to be reported in the solid state was that of tetramethyl rubrene. Crystalline tetramethyl rubrene undergoes ready oxidation to a colourless transannular peroxide when illuminated in the presence of oxygen whereas oxidation of rubrene crystals was confined to the surface.[68] This difference in reactivity has been attributed to the possible differences in permeability of the two crystals to oxygen. Although this postulate has not yet been verified in rubrene and tetramethyl rubrene, the combined photochemical and X-ray studies on a few other molecules discussed below support the notion that the permeability of the crystal toward the reactive gas is essential for efficient gas–solid reaction.

The thermal and photochemical oxidation of crystalline 11-hydroxy steroids to the corresponding ketones by oxygen has been investigated in detail by Byrn and co-workers[69] recently following the initial reports by two groups.[70] It is important to note that while all of them undergo oxidation in solution, only a few are oxidizable in the crystal. Further, a small difference in structure seems to affect the reactivity (Scheme 19). Cortisol-t-butyl acetate appears to be typical of many steroids that crystallize in five polymorphs. Two of these forms are reactive toward oxygen in the presence of light. Examination of the molecular packing of one of these reactive forms (Fig. 8) shows that there is a channel running through the crystal along the 6_1-helix axis with cross-sectional area of 35 Å^2.



Scheme 19.

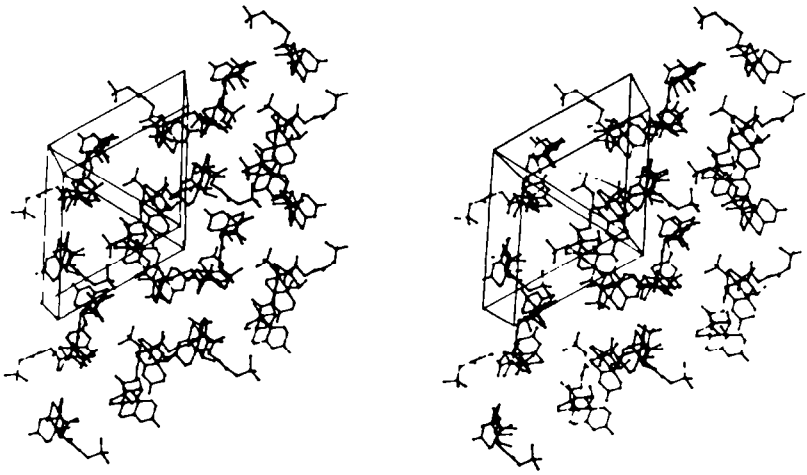


Fig. 8. Stereodrawing of the crystal packing highlighting the presence of a channel in hydrocortisone t-butyl acetate.

It has been speculated that the reactivity of this form toward oxygen is due to the unique packing which allows penetration of oxygen down the helix axis of the crystal. Oxygen thus penetrating the crystal oxidizes the C_{11} present in the channel.

Photochemical oxidation of 11-diarly thioketones in the solid state has recently been reported.[71] Quite interestingly only six were oxidized to the corresponding carbonyl compound whereas the rest were photostable. However, in solution all were readily oxidized. A comparison of the molecular packing of the above reactive and non-reactive thioketones is quite revealing in rationalizing their photoreactivity in the solid state. Typical packing arrangements for a reactive (thiobenzophenone) and an unreactive (Michler's thioketone) thione are shown in Figs. 9 and 10. For the reactive thioketones there is a channel along the shortest crystallographic axis with the reactive thiocarbonyl chromophore directed towards the channel. In the case of stable thioketones, the packing arrangement reveals that there is no channel in any direction in the unit cell. From the above examples it is clear that the permeability of the crystal toward the reacting molecule, be it a gas or a liquid, is essential for the photoreaction to take place. Crystals provide an unparalleled opportunity to control the penetration of the reactive molecule.[72] Further, in some cases it might even be possible to allow

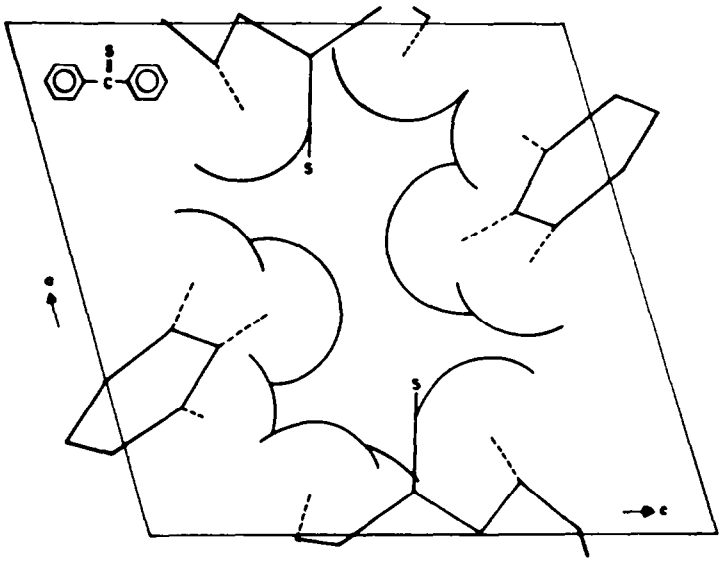


Fig. 9. Packing arrangement in thiobenzophenone. Projection of crystal packing on a plane perpendicular to the channel axis.

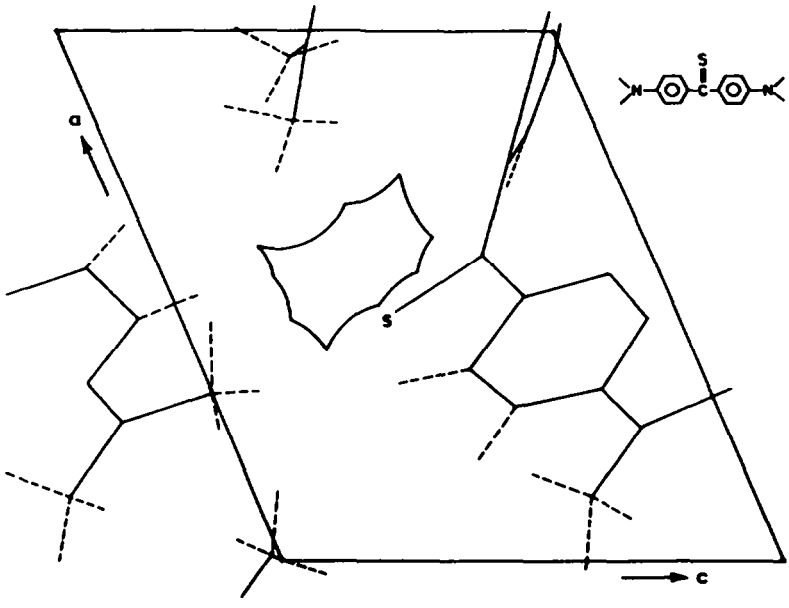


Fig. 10. Packing arrangement in Michler's thione. Projection of crystal packing on a plane perpendicular to the channel axis.

the reacting gas from a specific direction thus leading to asymmetric synthesis. An intense study is desirable in exploring gas–solid and gas–liquid reactions.

2.6. *Extent of predictability in solid state reactions—crystal engineering*

Although an understanding of the relationship between reactivity and structure enables one to explain the product formation and selectivity in many solid state reactions, these principles are not of much immediate practical value unless one can engineer a particular polymorphic form possessing the necessary topochemical attributes. There are some obvious difficulties. One of the main problems is the difficulty of achieving the desired type of crystal structure in any given case, for the factors that control crystal packing are not yet well understood. If one had complete understanding of the ways in which inter- and intramolecular forces control packing of molecules in crystals it would become feasible to design template groups of temporary attachment to functional molecules to guide photochemically reactive groups into appropriate juxtaposition in crystals. In the absence of such knowledge, it has been the usual practice to study a series of closely related compounds, so that a common structural principle can be deduced. The concept of designing molecules so as to guide their choice of crystal structure has been termed "crystal engineering" by Schmidt. The strategy to be adopted may vary from one reaction to the other. Therefore, before embarking on "crystal engineering" activity one must have a good knowledge of the crystal packing, conformation, etc. required for a particular reaction or phenomenon under consideration.

The future strength of the field will be clearly determined by increased progress in our understanding of factors controlling molecular packing. Considerable amount of effort, justifiably, is being put into the crystal engineering operation. However, at this stage *a priori* one can not predict the reactivity of a crystal.

2.7. *Role of defects and an element of uncertainty in the prediction of reactivity*

In a vast number of solid state photoreactions the crystal structure of the monomer tells directly the structure and stereochemistry of the product. The crystal structure obtained by X-ray crystallography is an averaged structure and describes largely the environment of the vast majority of molecules in the solid. However, it is known that the real crystal has surfaces, dislocations and other defects which are not readily detectable by X-ray diffraction methods. Since the normal symmetry of the sites is disrupted at these regions, molecules at these dislocations are likely to act as trapping centres for excitation and produce products whose structure may not be preditable on the basis of the crystal packing.[73,74] If the light energy can be transferred rapidly within the crystal

after absorption then the photochemistry of the ideal lattice need not be important. Instead, photoreaction would become more probable at sites of imperfection. Since the number of molecules at defect sites will be small, the reaction must be accompanied by defect multiplication to give appreciable yield of the product. Three examples provided below illustrate the serious problem posed by defects in terms of predicting the solid state reactivity.

The crystal structure of anthracene shows no molecules that are separated by <4 Å, thus the crystal structure would not appear to permit reactivity. Yet photolysis of anthracene in the crystalline state yields the dimer.[75] Thomas and Williams,[74] supported by etch-pit study, proposed that crystal defects may function as the preferred centres for reaction, it being possible that anthracene molecules have their excitation energy slightly reduced when they are displaced from regular lattice sites.

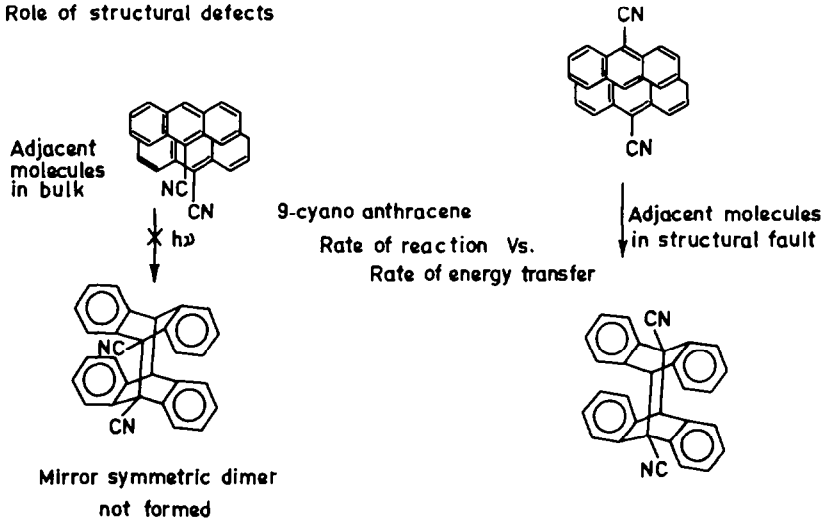
9-Cyanoanthracene molecules pack in an orthorhombic structure in which the molecules are arranged in columns with an interplanar distance of 3.5 Å. The marked overlap between molecules in the stack makes this structure ideal for head–head dimer formation. However, irradiation of 9-cyanoanthracene crystals results in a photodimer of head–tail registry (Scheme 20). This has been attributed to photoreaction at defect sites.[73] Support for this comes from optical microscopic and luminescence studies.[76,77]

Crystals of 1,8-dichloro-9-methyl anthracene belong to the space group P_{nma}. Examination of the structure shows that the molecules are too far apart (~ 7 Å) and unfavourably oriented to form the photodimer in the ordered crystal. Nevertheless, irradiation gives exclusively the head–tail dimer.[78] The efforts of Thomas and co-workers have resulted in the identification of structural imperfections, chiefly dislocations and the slip along (0 1 0) is conducive for the photoproduction of the *trans*-dimer.

From the above discussion it is evident that the presence of defects in crystals can often be a problem in predicting solid state reactivity.[79,80] Understanding the structure of molecules at the defect sites could be valuable in predicting the product structure. It seems likely that properly understanding reactions in organic crystals and fully realizing their synthetic potential will require better insight into the chemical and physical properties of solids at the molecular level both in the bulk and defect regions.

3. HOST–GUEST COMPLEXES

As discussed above, crystalline media can be used to achieve selective transformation of reactants into products. Another very exciting approach that has been the focus of several recent investigations concerns the reactivity of molecules incorporated in "host–guest complexes" also known as "inclusion compounds". The most important property of inclusion compounds is that a 'host' component can admit "guest" components into its cavity without any covalent bonds being formed.[81]

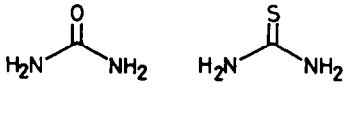


Scheme 20.

An inclusion compound is composed of two or more distinct molecules held together by non-covalent forces in a definable structural relationship. Hosts can contain cavities that are rigid or that are developed by reorganization of the hosts during the process of complexation. Monto-morrillonites, kaolinites, zeolites, graphites, etc. are a few of the well-known inorganic host components. Urea, deoxycholic acid, tri-*o*-thymotide, Dianin's compound, hydroquinones, cyclo-dextrins and perhydrotriphenylene are examples of organic host components (Scheme 21).

A fascinating aspect of the host–guest chemistry relates to the study of crystalline multimolecular inclusion compounds which may be subclassified as the true clathrate type in which the guest molecules are imprisoned in discrete closed cavities or cages; the channel type in which the guest species are accommodated in continuous canals running through the crystal and the layer type where the guest component is situated between bands of the host structure. In zeolites one has an intermediate situation where the cavities are interconnected by channels.

Most of the above-mentioned complexes offer guest sites of relatively restricted dimensions and therefore the reactivity of the guest molecules can be modified for a variety of reasons including restricted molecular motion, limited access of potential reaction partners or hydrophobic effect. We

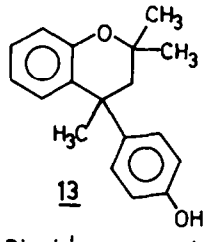


Urea

11

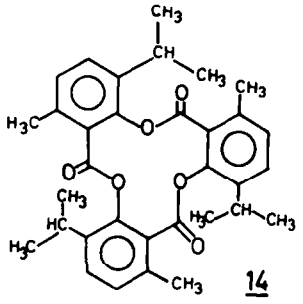
Thiourea

12



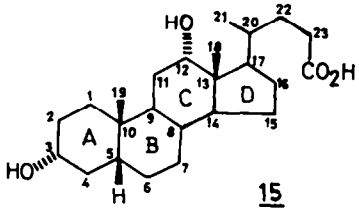
13

Dianin's compound



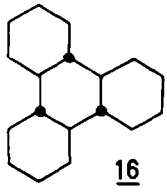
14

Tri-O-thymotide (TOT)



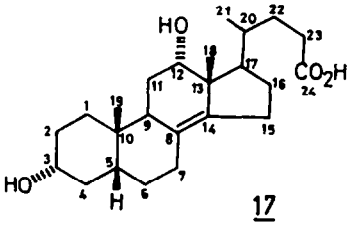
15

Deoxycholic acid (DCA)



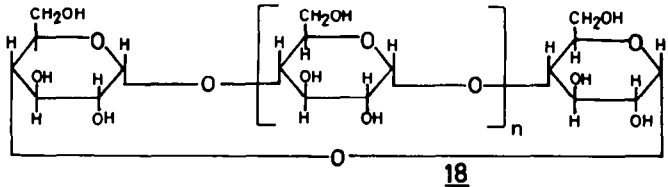
16

Perhydrotriphenylene (PHTP)



17

Apocholic acid (ACA)



18

n = 4 : α -Cyclodextrin

n = 5 : β -Cyclodextrin

n = 6 : γ -Cyclodextrin

Scheme 21.

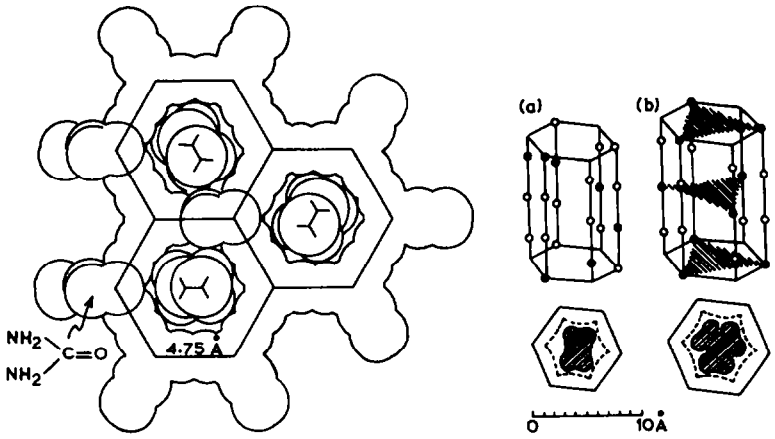


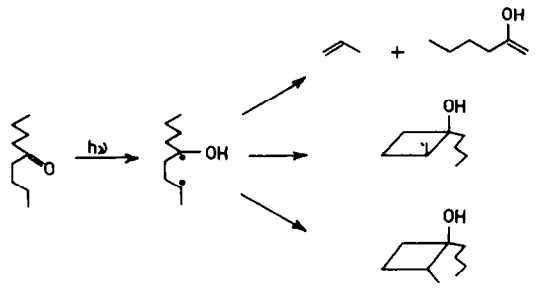
Fig. 11. (Left) End view cross-section of the urea-n-paraffin complexes. (Right) Fundamental lattice of (a) urea and (b) thiourea inclusion compounds.

present below a brief review on the structure and properties of a few of the organic inclusion complexes and an inorganic host, namely, zeolite. A brief exposition in the selective phototransformations carried out in a few host systems bring out the importance of inclusion complexes as reaction media.

3.1. *Urea and thiourea*

In 1940, Bengen discovered that urea formed crystalline addition compounds with a great variety of aliphatic straight chain molecules containing more than six carbon atoms.[82] Curiously, only unbranched parafins or their derivatives were able to form these adducts. The urea inclusion compounds generally crystallize in long hexagonal prisms or occasionally as hexagonal plates. The crystals of urea inclusion compounds can easily be distinguished from the tetragonal prisms of urea. The ability of thiourea to form crystalline inclusion complexes with a variety of organic compounds was first reported by Angla in 1947.[83] The only difference between the urea and thiourea complexes is that in the thiourea lattice the diameter of the channel is ~6.1 Å compared with 5.25 Å of that of urea. Consequently thiourea can include much larger organic molecules. Thiourea inclusion compounds are in general rhombohedral crystals. The arrangement of thiourea molecules in the crystal is similar to that of urea molecules in the urea inclusion lattice. Fig. 11 compares the urea and thiourea inclusion compound lattice.

One of the early studies in the area of reactions in inclusion complexes concerned the polymerization of unsaturated molecules in the channels of urea and thiourea.[84] A novel feature of this polymerization is that many of the monomers were found to give stereoregular polymers. de Mayo and co-workers have recently investigated the photobehaviour of 5-nonanone in urea channels.[85] 5-Nonanone in solution gives products resulting from both Type I and Type II reactions upon excitation. Surprisingly, irradiation of urea clathrate of 5-nonanone gave only Type II products and only one cyclobutanol isomer (Scheme 22). The cyclization to fragmentation ratio of Type



Scheme 22.

II diradicals for 5-nonanone in urea was 0.67, compared with 0.32 in methanol. A clear understanding of this phenomenon is presently lacking.

3.2. *Dianin's compound*

4-*p*-Hydroxyphenyl-2,2,4-trimethyl chroman, widely known as Dianin's compound, was first prepared by Dianin in 1914.[86] He reported the remarkable ability of this compound to retain tightly certain organic solvents. Subsequently it is shown to be capable of including a wide variety of guest species, for example, sulfur dioxide, iodine, ammonia and decalin.[87]

On the basis of X-ray studies, the structures of these complexes were identified as hexamer units made up of six host molecules, linked by a network of hydrogen bonds involving the hydroxyl groups.[88] Figure 12 shows a view of the cage normal to the C-axis for the unsolvated Dianin's compound. Six molecules of Dianin's compound form a cage and the cages are hour glass shaped which has been cut horizontally across the middle of each globe. The cavity has a length of aporoximately 11 Å with a central width of 4.2 Å and a maximum upper and lower widths of 6.3 Å. The ends of each cage have a width of 2.8 Å and are formed by six hydrogen bonded hydroxyl groups. Modification of Dianin's compound, like substitution in the ring or replacement of ring atoms resulted in a change in the cavity geometry and consequently modification of selective clathration properties.[89]

To date there have been two studies which report the influence of Dianin's compound on the photobehaviour of carbonyl compounds. These are: the study by de Mayo and co-workers[90] on the Norrish type I and type II reactions of arylalkyl ketones and our investigation[91] on the α-cleavage behaviour of dibenzyl ketones and benzyl phenyl acetates. The representative results of de Mayo and co-workers on the photobehaviour of twelve ketones are shown in Scheme 23. Three product ratios were determined for each compound in organic solvents and in Dianin's compound as the host: (1) F/C, the type II fragmentation to cyclization ratio, (2) t/c the *trans*-cyclobutanol to *cis*-cyclobutanol ratio and (3) type I/type II ratio in which the excited ketones partition themselves between Norrish type I and Norrish type II reactivity. The following generalizations have been made on the behaviour of ketones in the cavity of Dianin's compound: (1) type I/type II ratio is considerably enhanced in the solid complex compared to the solution media. (2) In most of the ketones, both t/c and F/C ratios are not particularly sensitive to medium effects. The relative insensitivity of F/C and t/c ratios to changes in medium probably indicates that, in general, inclusion of guest ketones in the host cavity of Dianin's compound does not greatly alter the chemical reactivity of the excited ketone and biradical intermediates produced by photolysis. A slight increase in the F/C ratio observed for a few ketones (Scheme 23) and the type I/type II ratios increase in three of the four cases investigated have been rationalized on the basis that the clathrate cavity moderately restricts the movement of the guests. Studies on α-cleavage of dibenzyl ketones described below provide support to this conclusion.

α-Cleavage reactions of dibenzyl ketones and benzyl phenyl acetates have been studied in Dianin's compound and the product distributions compared with those in organic solvents. The results are summarized in Scheme 24. The photodecarbonylation of dibenzyl ketones in a homogeneous fluid solution occurs via a free radical pathway in which coupling products (1,2-diarylethanes) are formed in quantitative yield. For an unsymmetrical dibenzyl ketone (ACOB) the coupling products AA, AB and BB are formed in the expected statistical ratio of 1 : 2 : 1. In addition to the decarbonylated products, small amounts of rearranged ketones were obtained upon photolysis

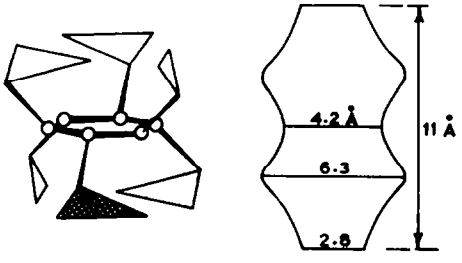
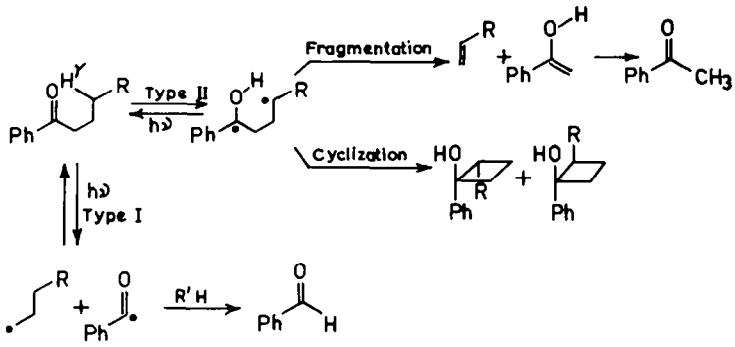
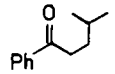
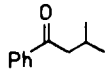
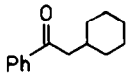
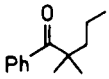
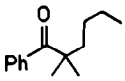


Fig. 12. The shape and size of the cavity of Dianin's compound.

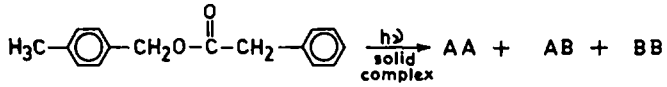


Guest Ketone	Medium	F/C	t/c	Type I/ Type II
	benzene	7.3		
	tert-butyl alcohol	15.7		
	complex	27.6		
	benzene	7.3		
	tert-butyl alcohol	9.5		
	complex	6.1		
	benzene	0.5	2.2	
	tert-butyl alcohol	0.5	1.3	
	complex	0.9	1.9	
	benzene	0.2	1.6	<0.1
	tert-butyl alcohol	0.5	1.1	0.1
	complex	0.9	1.7	0.6
	benzene	0.3	1.6	<0.1
	tert-butyl alcohol	0.7	1.1	<0.1
	complex	0.7	1.7	0.7

Scheme 23.

of dibenzyl ketones in non-homogeneous media such as micellar solution. Most interestingly, the cage effect is total for benzyl phenyl acetates and dibenzyl ketones inside Dianin's compound (Scheme 24). Small yields of rearranged products are formed in Dianin's compound. The unit cage effect observed in Dianin's compound is completely in accord with the structure of Dianin's compound. Although the cavity size is large enough to accommodate the ketones and the esters, the ends of the cavity are narrow and therefore the radical pair cannot escape from the cavity. Indeed 100% cage effect is expected. Formation of rearranged products in Dianin's cavity is probably an indication of the extent of restriction imposed by the host on the reorientational process of geminate radical pairs. The rotational process required for the rearrangement certainly will depend

β-cyclodextrin	1	86	1.5	12
DCA	1.5	97	1.5	—
Dianin's compound	—	98	—	2



β-cyclodextrin	<1	>99	<1
DCA	<1	>99	<1
Dianin's compound	<1	>99	<1

Scheme 24.

on the space available for the guest molecule in the cavity. Small amounts of rearranged products formed is in accord with the expectation that the cavities in Dianin's compound are large enough to accommodate the guest ketone and has sufficient space to allow the guest's rotation.

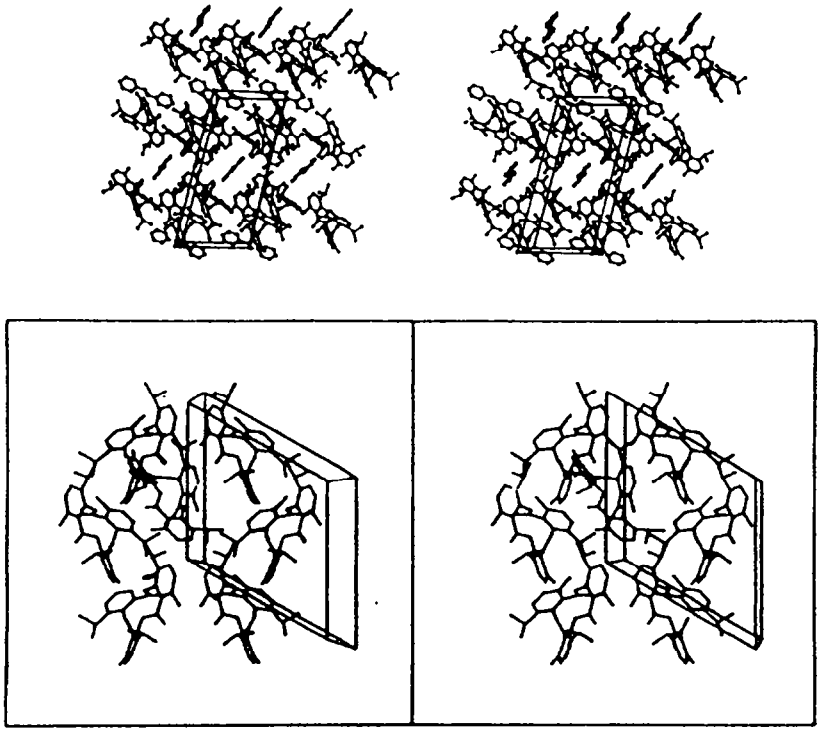
Results of the above two studies are encouraging for the reasons that they have demonstrated that organic molecules of photochemical interest can be included in Dianin's compound and the cavity imposes certain restrictions on the reactive guest molecules and on the intermediates generated upon photolysis.

3.3. *Tri-o-thymotide (TOT)*

Tri-*o*-thymotide forms crystalline inclusion compounds of both the cavity and channel types with a wide range of achiral and chiral guest species.[92] In solution, TOT exists in a chiral propeller-like conformation that undergoes rapid interconversion between P (right handed) and M (left handed) forms. In its guest-free form, TOT crystallizes in the achiral structure $Pna2_1$ containing equal amounts of the P and M forms (Fig. 13). But upon crystallization with compounds with which it forms a complex, TOT often undergoes spontaneous resolution.

The inclusion complexes of TOT present an attractive system for studying molecular and chiral recognition. Small molecules, those containing up to six non-hydrogen atoms, tend to adopt cage structures while long chain molecules generally give rise to channel complexes. An interesting study of the chiral discrimination using crystalline TOT complexes showed that the highest enantiomeric purities were observed for 2,3-dimethyl-*trans*-oxirane (47%), 2,3-dimethyl-*trans*-oxetane (38%) and 2-bromo-2-butane (37%).

Inclusion complexes of TOT provide a possible medium for reactions of included guest molecules and present an attractive system to study different thermal and photochemical reactions. In spite of such an attractive possibility only two reports have concerned the use of TOT as a host in photochemical transformations. An interesting study on the photoisomerization of *cis*- and *trans*-stilbenes and methyl cinnamates in TOT inclusion complexes has been recently reported by Green



e

Fig. 13. (Left) Stereoscopic view of the *trans*-stilbene–TOT clathrate [*J. Am. Chem. Soc.* **101**, 7529 (1979)]. (Right) Stereoview of the TOT molecules that build the walls of the cage [*J. Am. Chem. Soc.* **105**, 4561 (1983)].

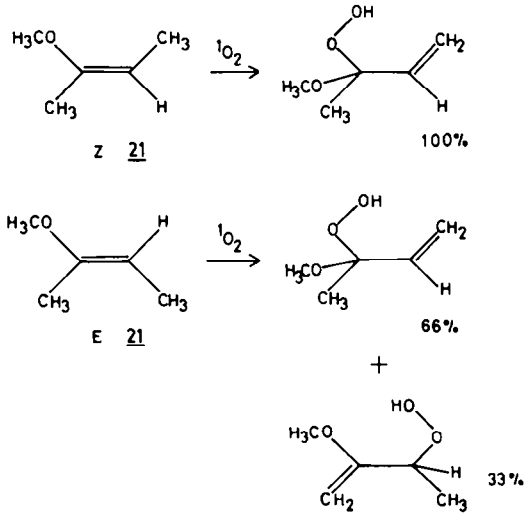
	solution	TOT-clathrate	pure guest crystal
Ph, Ph	cis ⇌ trans 80% 20%	cis → trans cis ↛ trans	cis ↛ trans cis ↛ trans
Ph, COOR	cis ⇌ trans 50% 50%	cis ⇌ trans 50% 50%	cis ↛ trans cis → trans

Scheme 25.

and co-workers.[93] In both types of guest molecules, stilbenes and cinnamates, the *cis–trans* isomerization pattern in clathrate is different from that observed in pure guest crystals. Furthermore, cinnamates, but not stilbenes, show the same behaviour in clathrates as is observed in solution (Scheme 25). Combined crystallographic and chemical studies have been utilized to understand these observations.

Both *cis*- and *trans*-stilbene inclusion compounds crystallize in the triclinic space group $P\bar{1}$ and have very similar cell constants. Each unit cell of the *trans*-stilbene–TOT clathrate contains four TOT molecules and two stilbene molecules, with the latter lying on the crystallographic centres of symmetry within two crystallographically independent sausage like channels. The *cis*-stilbene–TOT inclusion compound contains partially empty channels. On irradiation by UV light the *cis*-stilbene–TOT inclusion compound yields *trans*-stilbene and some phenanthrene, whereas the *trans*-stilbene–TOT clathrate is rather stable towards UV radiation. These observations have been rationalized stressing the importance of the coincidence or non-coincidence of molecular symmetry and cavity symmetry. In other words, a centrosymmetric cavity appears to stabilize centrosymmetric guest molecules and favour pathways from non-centrosymmetric reactants to centrosymmetric products. The *cis* and *trans* isomers of methyl cinnamate also form triclinic TOT clathrates, but in these neither the reactant nor the product can achieve the symmetry of the cavity and hence irradiation yields approximately equal amounts of *cis* and *trans* isomers starting from either pure *cis*- or *trans*-cinnamate clathrate.

The first and the most interesting example of a heterogeneous transfer of chirality from the disymmetric cavity of the TOT host to its prochiral guest has been reported very recently by Jefford and co-workers.[94] This particular example offers a great impetus to use TOT in photochemical asymmetric synthesis. Olefin **21** forms chiral clathrate with TOT. Furthermore crystals of P-(+) and M-(−) configuration could easily be separated from the clathrate by sorting the single crystals manually and by assigning their chirality from polarimetric measurements. However, the *E* isomer of **21** gave only achiral clathrates with TOT. Interestingly, photolysis of a mixture of the P-(+)-clathrate of **21** with resin bound rose bengal in an aerated medium gave the hydroperoxide which showed a residual optical activity of 0.06° (Scheme 26). Similar irradiation of M-(−)-cathrate with



Scheme 26.

rose bengal gave the product having opposite residual rotation of $-0.051°$. Although the optical purity of hydroperoxides obtained is unknown, the similarity of amplitude and complimentary sign of the rotations are significant. It is suggested that stereodifferentiation occurs during the creation of the pyramidal centre at the vinyl terminus of **21** in the chiral environment. Thus this example illustrates the possibility of conducting gas–solid reactions in a chiral environment using TOT as the host.

3.4. *Deoxycholic acid (DCA)*

3α,12α-Dihydroxy-5β-cholan-24-oic acid (deoxycholic acid) is a typical bile acid of chiral character isolated from the biles of some animals by saponification and has a perhydro-1,2-cyclopentenophenanthrene system.[95] DCA forms stable inclusion compounds of the channel type with a wide variety of organic molecules: e.g. aliphatic, aromatic and alicyclic hydrocarbons, alcohols, ketones, fatty acids, ether, nitriles, azo dyes, etc. The guest components are generally imprisoned in channels running through the host lattice composed of DCA molecules. The crystalline inclusion compounds, called "choleic acids" are often obtained by slow evaporation of a solution of DCA and guest component in ethanol or DCA in a liquid guest component and present a well-defined stoichiometry.[96] The host : guest ratio of choleic acids increases with the length of the guest molecules.

From the X-ray analyses of DCA complexes, it became clear the DCA generally crystallizes in one of the three different forms, orthorhombic, which is the most commonly observed, tetragonal and hexagonal.[97] In the orthorhombic structures one observes a two-dimensional bilayer motif with axial dimensions of $b = 13.6$, $c = 7.2$ Å. The molecules form chains by translation along the 13.6 Å axis, being interlinked front to end by O(hydroxyl)—H···O(carbonyl) hydrogen bonds. These molecules are further joined by hydrogen bonds about the 2_1-axes which are parallel to the 13.6 Å axis and spaced along the c-axis of 7 Å, so generating the bilayer. These bilayers contain grooves parallel to the c-axis which induce DCA to form channel inclusion complexes. Figure 14 shows the channel in an orthorhombic DCA complex. The orthorhombic crystals form four types of channel wall motifs depending on the nature of the occluded guest. Common to the four motifs is the host bilayer. To best fit the guest molecule, the cross-section of the channel may be varied within limits, by a change in interlayer separation along a, by an offset along the b-axis between neighbouring bilayers and by relating the bilayers about the channel c-axis by pseudo 2-fold or the 2_1 screw axis. These variations yield four channel motifs α, β, γ and δ.

Several interesting organic photoreactions have been carried out using a DCA host matrix. Most of these investigations have been sparked by the initial studies of Lahav and co-workers with a 4 : 1 molecular complex of DCA and di-t-butyl diperoxycarbonate.[98] Heating of the complex at 90° for

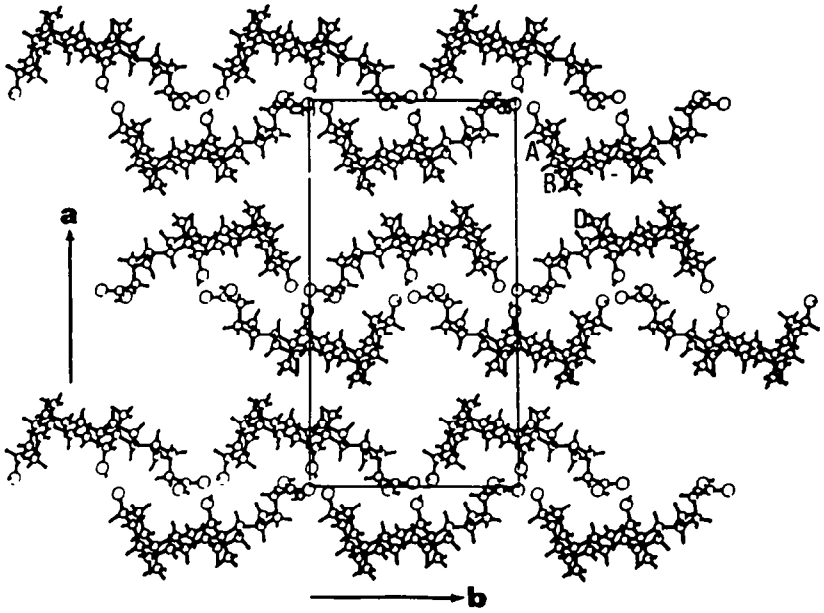
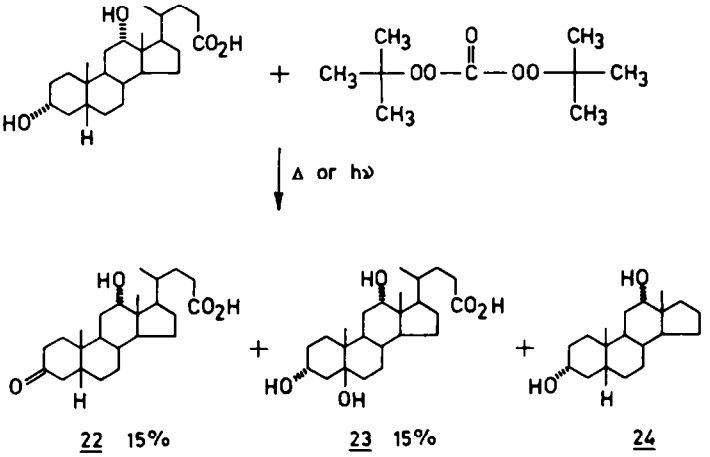


Fig. 14. Packing arrangement of DCA molecules in the α-motif viewed along the channel c-axis.

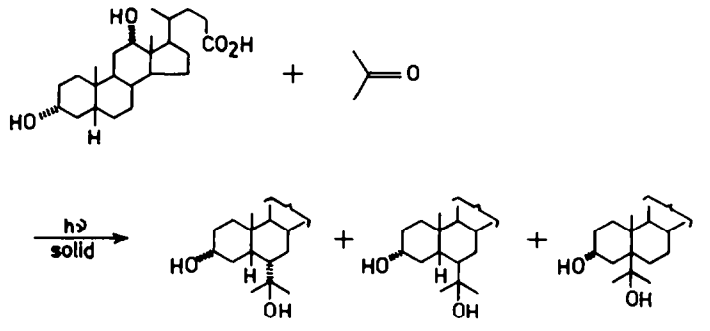


Scheme 27.

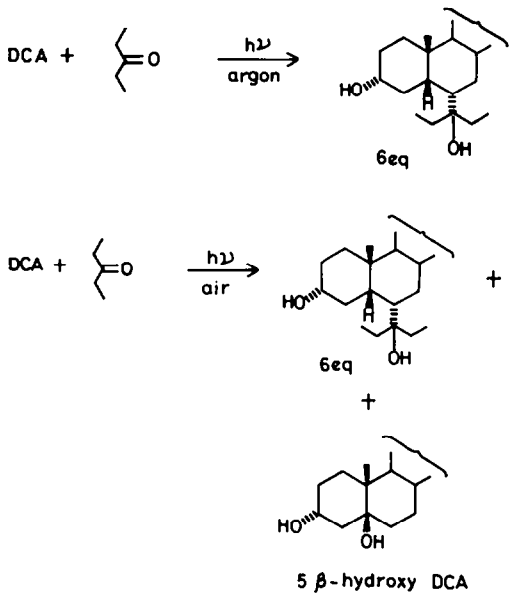
120 h or photolysis with $\lambda > 300$ nm at 25° for two weeks led to complete decomposition of the guest molecule followed by reaction with the host to give two major products **22** (15%) and **23** (15%) and traces of **24** (Scheme 27). The interesting aspect of this study is that, product **22** has been formed by a one-step regiospecific and stereospecific hydroxylation of the host lattice by the decomposition product of the guest molecule. Further, it is noteworthy that previous work in solution on similar systems has led to unselective attacks on the various positions of the steroid. Yet another early study to bring out the use of the DCA matrix especially in asymmetric synthesis was that of Andisio and Silvani. γ-Irradiation of the DCA–penta-1,3-diene complex gave optically active polypentadiene.[99]

Interesting and exhaustive studies on the solid state photochemistry of molecular complexes of DCA with ketones have been reported by Lahav, Leiserowitz and co-workers.[100–102] The photo-excited species of the ketone was expected to be capable of abstracting hydrogen from the channel wall. The stereo- and regiospecific remote functionalization of DCA obtained by this group is the result of intermolecular reaction between the excited guest and DCA.

Irradiation of the 5:3 complex of DCA with acetone in the solid state led to the formation of three major addition products as shown in Scheme 28. X-ray crystal structure analysis of the complex showed that the distances from the ketone oxygen (O^1) to the steroid hydrogens H(5), $H(6)_{eq}$ and $H(6)_{ax}$ are 3.8, 3.4 and 3.4 Å, respectively. The distance of the ketone carbon (C′) from the steroid carbons C(5) and C(6) are 3.88 and 3.87 Å, respectively, whereas the distances of the other carbons are greater than 4 Å. Thus the observed products are the result of topochemical hydrogen abstraction and a radical combination process. The topochemical nature of this solid state reaction is further evident from a comparison with the 1:1 apocholic acid (APA):acetone complex which upon photolysis under an argon atmosphere forms only traces of products. The arrangement of acetone in APA is radically different from that in the DCA complex, because the channel cross-section in the former is larger in size and different in shape. The hydrogen atom at C(20) of the steroid is at



Scheme 28.



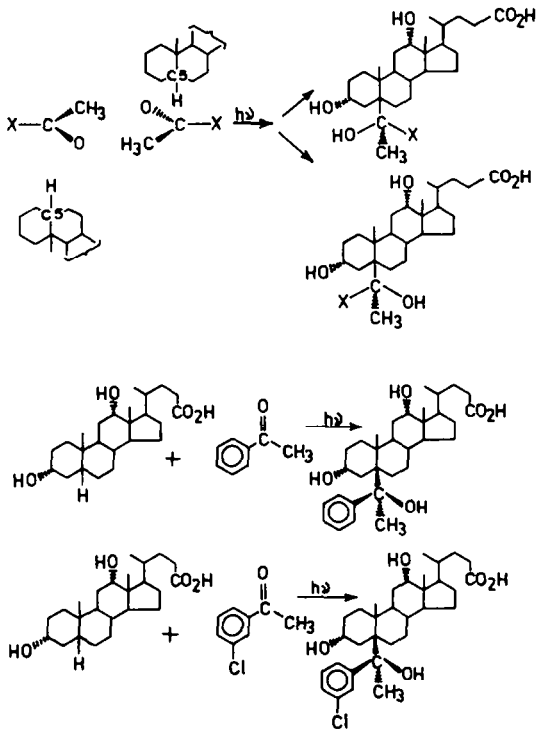
Scheme 29.

a distance of 2.9 Å from the acetone oxygen, and the C(20)···C′ distance is as long as 4.9 Å. Also, the C—H bond is parallel to the C′=O′ bond. No addition product was isolated from this complex although the O′···H contact is shorter than in the DCA complex. Therefore, it was concluded that if the neighbouring C—H and C′=O′ bonds are colinear and the distance between the carbonyl carbon and the carbon at the abstracting centre is large, no addition reaction takes place.

Several additional reactions of similar nature have been extensively investigated by Lahav, Leiserowitz and co-workers.[101,102] One such example is the photolysis of the 2 : 1 DCA–diethyl ketone complex. Photolysis of the above complex under argon for days under sunlamps yielded only one addition product (Scheme 29). The room temperature crystal structure showed that O′ is 3.3 Å away from $H(6)_{eq}$ and 3.9 Å from $H(6)_{ax}$; the C(6)—C′ distance is 3.8 Å. The H(5)—O′ contact is 3.3 Å, however no C(5) addition product was formed, presumably because of the long C(5)···C′ distance of 4.2 Å. Evidence for the H(5) abstraction is provided by the crystallization and irradiation of the complex in the presence of air which gave 5β-hydroxy DCA together with the 6 eq. addition product (Scheme 29). These studies have unequivocally demonstrated that the guest ketone molecules occupy defined crystallographic sites and orientations inside the DCA matrix and that the addition reactions are topochemically controlled.

In another study of the structure–reactivity relationship in the DCA complex with prochiral ketones as guests, diastereomeric addition products have been obtained. The crystalline host–guest channel inclusion complexes, 5 : 2 DCA–acetophenone and 3 : 1 DCA–*m*-chloroacetophenone, each yield on UV irradiation a photoproduct via addition of a guest to the steroid tertiary carbon atom C(5) with the formation of a new chiral carbon centre with *S* configuration (Scheme 30). Thus the addition is not only regiospecific (as demanded by topochemical nature) but also stereospecific. By virtue of the fact that these complexes maintained their crystalline integrity on photoconversion, the photoaddition pathway was monitored by determination of the crystal structures before and after the reaction. The results indicated that photoaddition of the guest molecule to C(5) takes place with a net rotation of 180° by the guest acetyl group prior to bond formation to the steroid. The examples thus far investigated provided only *S* isomers. Through "crystal engineering" operations Lahav and co-workers claim to have obtained addition with absolute configuration *R* at the newly generated chiral carbon. Details are awaited.

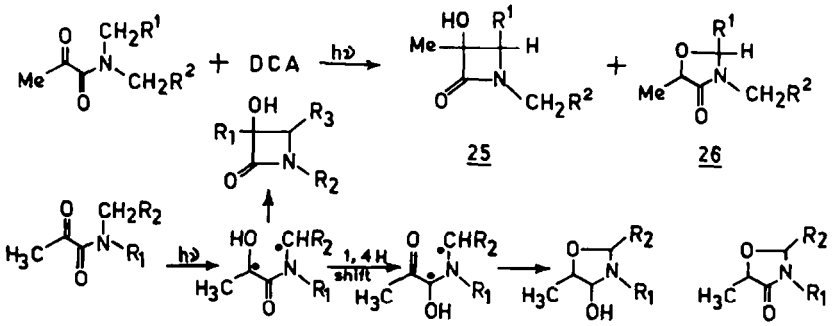
In this context attempts to utilize thiocarbonyls instead of carbonyls to functionalize the DCA matrix are noteworthy.[103] Thioketones generally undergo photooxidation and photoreduction quite readily. Therefore, it was quite surprising to observe that the photolysis of the DCA–di-t-butyl thioketone for over 50 days resulted in no change. However, X-ray structural analysis was quite revealing in understanding this photoinertness. Absence of oxidation of the guest itself has been



Scheme 30.

understood on the basis that there is no space for the molecular oxygen to diffuse into the crystal to effect photooxidation.

The above-mentioned examples deal with the intermolecular reaction between the excited guest and DCA. No doubt these are interesting, but the more exciting situation would be where the reactions of the guest can be controlled by the host without the latter participating in the reaction. Such examples are also available.[91,104] On photolysis of the complex of DCA with N,N-dialkyl pyruvamides, the guest molecule does not react with the host, but exclusively leads to the formation of β-lactams **25** by an intramolecular hydrogen abstraction process (Scheme 31). Interestingly,



			25	26
a	$R^1 = R^2 = H$	Methanol	—	24
		DCA complex	42	10
		SiO_2	—	32
b	$R^1 = R^2 = CH_3$	Methanol	—	100
		DCA complex	74	—
		SiO_2	—	26

Scheme 31.

irradiation of these pyruvamides in solution does not yield the β-lactam, instead gives the oxazolidinone **26** as the major product. This variation in product distribution has been attributed to the restraints brought on the intermediate diradical by the host matrix. Formation of **25** requires rotation of the C(OH)—CO bond as illustrated in Scheme 31. Furthermore, asymmetric induction was also observed in this reaction, though the enantiomeric excess was not high.

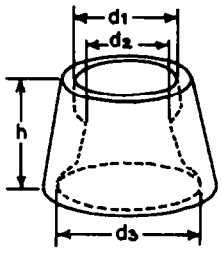
The use of the DCA matrix to generate the 'super cage' effect has recently been demonstrated by photolysing dibenzyl ketones and benzylphenyl acetates in the channels of DCA.[91] DCA generally formed an 8 : 1 complex with a large number of dibenzyl ketones and benzylphenyl acetates (Scheme 24). Photolysis of the solid complexes resulted in a single product (AB) in all cases; no rearranged products were obtained even in small amounts. The absence of rearrangement and cage escape products are possibly due to the small size of the canal.

Thus the few studies carried out so far illustrate that DCA offers a well-defined medium to carry out selective transformations of the guest molecules, and to selectively functionalize the host molecule.

3.5. *Cyclodextrins*

The recognized potential of cyclodextrin–guest interactions as models for enzyme active sites has prompted numerous investigations of these systems. Although the potential of cyclodextrins as "reaction vessels" for thermal reactions has been widely acknowledged,[105] their use in photochemical reactions is yet to be fully explored. Cyclodextrins, one of the most commonly used host systems, possess hydrophobic cavities that are able to include, in aqueous solution, a variety of organic compounds whose character may vary from hydrophobic to ionic.[105] Internal diameters and depths of cyclohexaamylose or α-cyclodextrin (4.2–8.8 and 7.8 Å), cycloheptaamylose or β-cyclodextrin (5.6–10.8 and 7.8 Å) and cyclooctaamylose or γ-cyclodextrin (6.8–12.0 and 7.8 Å) provide cavities for appropriately sized guest molecules. The oligosaccharide ring forms a torus, with the primary hydroxyl groups of the glucose residues lying on the narrow end of the torus. The secondary glucopyranose hydroxyl groups are located on the wider end (Fig. 15).

Inclusion complexes of known ratio can be precipitated from aqueous solutions of cyclodextrin when excess of guest is added. Thus precipitated α-, β- and γ-cyclodextrin complexes can have two modes of packing of cyclodextrin molecules in the crystal lattice.[106] These are described as cage or channel structures according to the overall appearance of the cavity (Fig. 16). In channel type complexes, cyclodextrin molecules are stacked on top of each other like coins in a roll, the new linearly aligned cavities producing channels in which the guest molecules are embedded. In the cage type crystals, the cavity of one cyclodextrin molecule is blocked off on both sides by adjacent cyclodextrin, thereby leading to isolated cavities. Two types of cage structures are often encountered namely brick type and herring bone type (Fig. 16). For β- and γ-cyclodextrins, a clear separation



Cyclo-dextrin	d_1 (Å)	d_2 (Å)	d_3 (Å)	h(Å)
α	5.6	4.2	8.8	7.8
β	6.8	5.6	10.8	7.8
γ	8.0	6.8	12.0	7.8

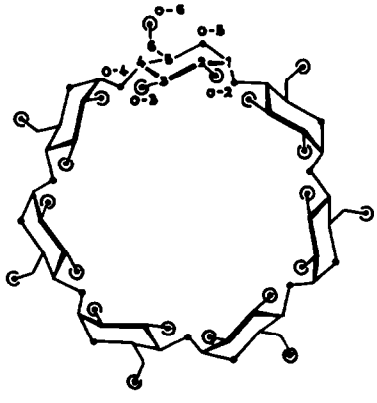


Fig. 15. Shape and structure of cyclodextrin cavity.

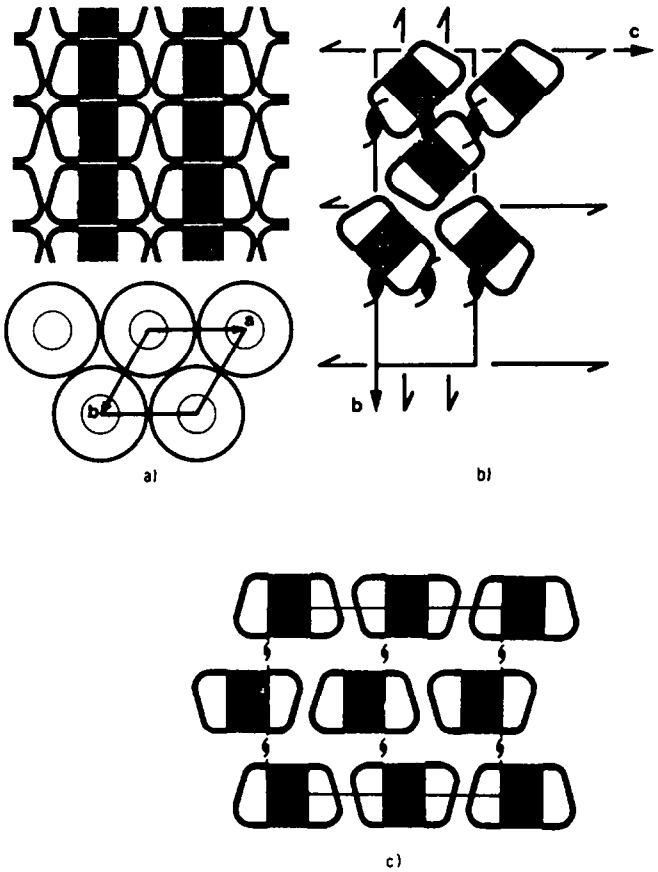


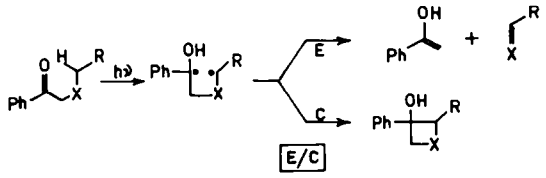
Fig. 16. Schematic representation of (a) channel type, (b) cage type and (c) brick type crystal structures formed by crystalline cyclodextrin inclusion complexes [*Carbohydr. Res.* 31, 37 (1973)].

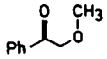
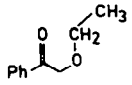
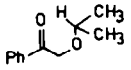
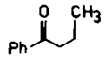
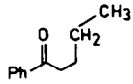
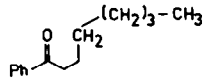
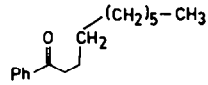
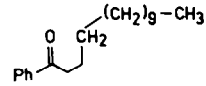
of channel and cage forming guests is not possible. Therefore one could not predict the nature of packing for a particular guest.

Photochemical reactions of cyclodextrin solid complexes alone are discussed in this section. A few interesting examples of reactions of cyclodextrin complexes in aqueous solution have been reported in the literature and these are described in Section 6. In all of the cases to be discussed below, no structural details of the complexes are available and the mechanistic rationale is solely based on circumstantial evidence from related systems.

Results of a large number of arylalkyl ketones capable of undergoing Norrish type II reaction studied in β-cyclodextrin are summarized in Scheme 32.[107] Two features are striking: (a) ratios of products derived from the 1,4-biradical (resulting from the type II process) are altered, although slightly, by cyclodextrin in comparison to organic solvents; cyclization is generally favoured in β-cyclodextrin, and (b) the effect of the cavity is more evident in ketones having larger substituents.

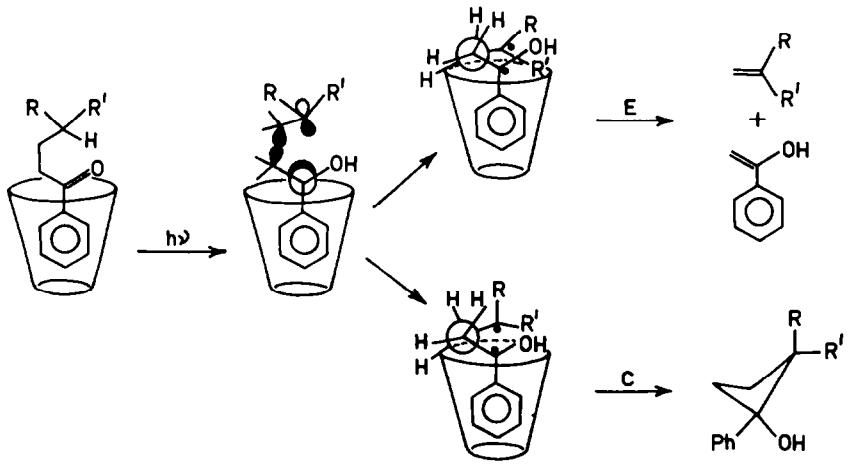
In interpreting these observations it is important to realize that the elimination reaction from 1,4-biradical requires that the four carbon atoms of the reactive sites be co-planar so that the p-orbitals of the two radicals can continuously overlap with the central σ bond undergoing cleavage. On the other hand, the transition state for cyclization requires only an overlap of the two radical centres. The initial hydrogen abstraction generates a mutually perpendicuar singularly occupied p-orbitals. To achieve a geometry suitable for cleavage an extensive bond rotation has to occur whereas cyclization can be achieved with lesser movement of atoms (Scheme 33). Increase in cyclization yield with the increase in chain length or the size of the alkyl group is consistent with this proposal. As the chain length of the ketone increases, the alkyl portion gets more strongly embedded inside the cavity thus reducing the ease of rotation of one side of the diradical. Since the side bearing the phenyl group is practically anchored into the cavity, only the alkyl side has to do all the rotations to achieve the required geometry for cleavage or cyclization. This being less probable with the longer or bulkier alkyl chain the elimination rate is reduced with respect to the cyclization.



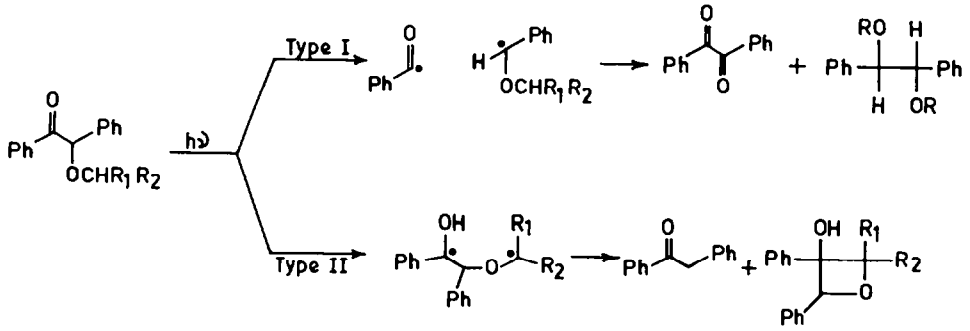
	Benzene	Acetonitrile	β-CD soln. (5 : 1)	β-CD solid
	1.92	4.67	3.58	1.67
	0.76	1.79	0.97	0.39
	3.01	2.67	2.73	1.09
	Benzene	t-Butanol	β-CD soln. (1 : 1)	β-CD solid
	6.56	8.55	3.88	3.5
	3.03	4.22	3.82	2.65
	1.2	2.55	1.76	0.79
	2.48	3.28	1.64	0.69
	1.58	2.88	1.42	0.35

Scheme 32.

Remarkable results have been obtained during the photolysis of benzoin alkyl ethers and alkyl deoxybenzoins.[108] Discussion on benzoin alkyl ethers adequately summarizes the situation. The photolysis of benzoin alkyl ethers in solution has been extensively studied and they yield products derived from the Norrish type I process. Although these molecules possess γ-hydrogen, products derived from the Norrish type II reaction were not isolated during solution phase photolysis. Most significant results were obtained upon irradiation of the solid cyclodextrin complexes of **27–29**. Under these conditions in all three cases products resulting from type I reaction were absent and type II products were obtained in near quantitative yield (Scheme 34). This is remarkable considering



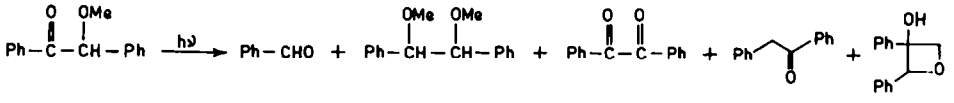
Scheme 33.



27 $R_1 = R_2 = H$ (a) $R_1 = R_2 = H$

28 $R_1 = H;\ R_2 = CH_3$ (b) $R_1 = H;\ R_2 = CH_3$

29 $R_1 = R_2 = CH_3$ (c) $R_1 = R_2 = CH_3$

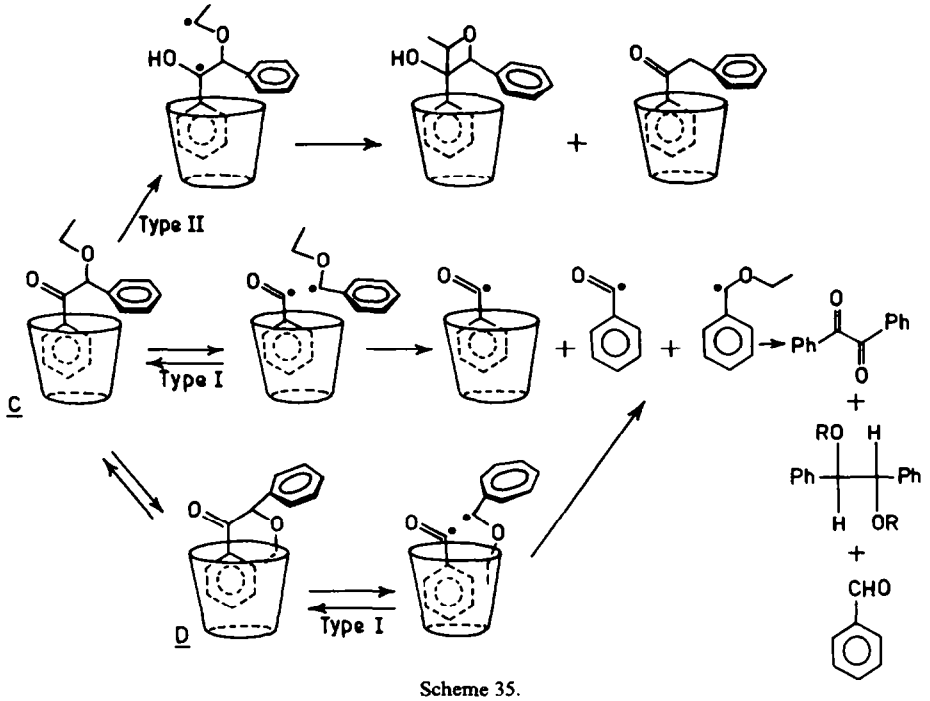


Benzene	18	58	24	—	—
Methanol	28	62	10	1	—
β-Cyclodextrin/solid (degassed)	8	—	—	69	22
β-Cyclodextrin /solid/O_2	Ph—COOH Ph—COOMe	32 40		16	11
β-Cyclodextrin (soln., 1 : 1)	23	54	7	12	4
β-Cyclodextrin (soln., 1 : 5)	14	53	14	15	4

Scheme 34.

that irradiation of crystalline benzoin ethers results in no reaction. The importance of the cyclodextrin cavity in bringing about this remarkable change in the photobehaviour of **27–29** is revealed by the following observations. When microcrystalline **27–29** under identical conditions were irradiated they were recovered unchanged. Further, irradiation of a mechanical mixture of cyclodextrin and benzoin ethers did not yield the type II products. The proposed mechanism is illustrated in Scheme 35. While complex **C** can give both the type I and type II reactions, complex **D** can undergo only the type I reaction. Interconversion between **C** and **D** both in the ground and excited states would severely be restricted in the solid state. Formation of oxetanols and deoxybenzoin under conditions wherein the motion of the atoms is restricted suggest that at least a few of the benzoin ether molecules are included by cyclodextrin in a conformation suitable for γ-hydrogen abstraction. The most surprising observation was the isolation of the type II products in yields ~60% with the rest being starting benzoin ethers. Therefore, it can be inferred that the majority and not a few of the benzoin ether molecules are trapped by cyclodextrin in the conformation suitable for the type II process. Thus the photochemistry of benzoin ethers is an example of the use of cyclodextrin in controlling the conformation of the guest molecule and thus altering the nature of the excited state chemistry.

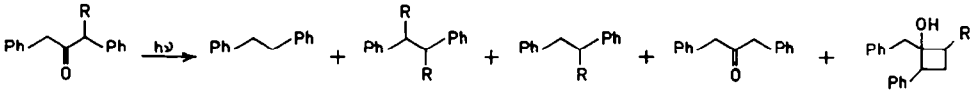
Since both the type I and type II reactions are expected from **C***, absence of type I products in the photolysis mixture was surprising. A clue to this intriguing behaviour became available when the complexes were irradiated in an aerated atmosphere. Under these conditions, oxygen trapped products of the type I benzoyl–benzyl radical pair were isolated (Scheme 34). Therefore, it is clear that the type I reaction does indeed occur in the absence of oxygen but the radical pair generated by this process undergoes geminate recombination. Thus the near quantitative formation of the type II products in the solid complexes under degassed conditions is the result of two features namely, conformational effect and super cage effect—the former facilitates the occurrence of the type II and the latter suppresses the formation of the type I products.



Scheme 35.

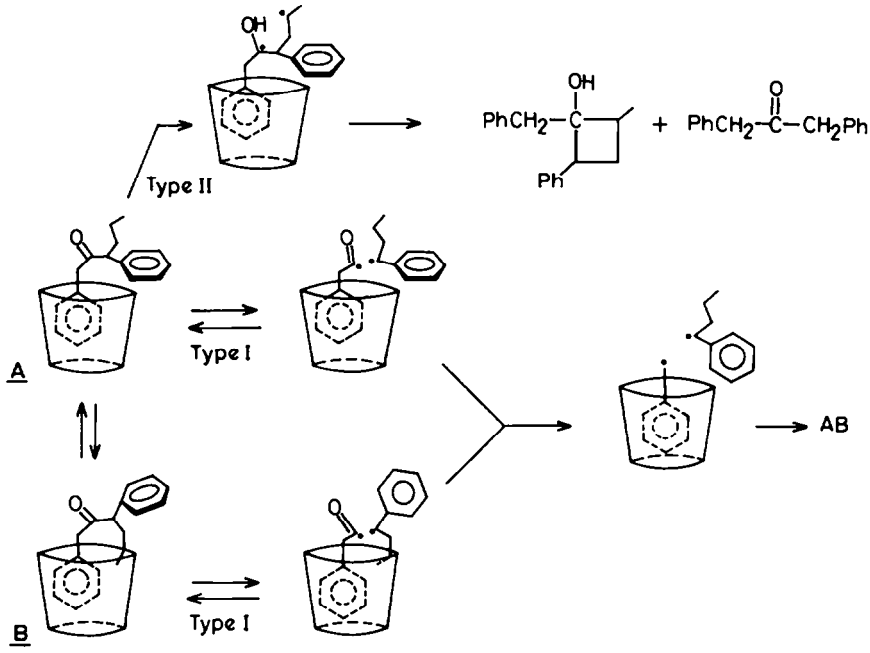
Conformational effect, i.e. preference for a particular conformational isomer by cyclodextrin is further exemplified by the results on α-alkyl dibenzyl ketones.[109] Those undergo both type I and type II reactions in solution. Interestingly, when **30–32** are included in β-cyclodextrin and photolysed in the solid state, products derived from the type I process alone are obtained (Scheme 36). Note that the product selectivity is reversed with respect to benzoin ethers discussed above. Such a selectivity has been rationalized on the basis of Scheme 37. While complex **A** can give both type I and type II products, complex **B** can give only type I products. It is suggested that probably cyclodextrin prefers to complex conformer **B** and thus no type II products result. Unlike the benzoin ethers, the cage return has to compete with the decarbonylation. The latter being efficient, products derived from α-cleavage alone are obtained in substantial yield. The two examples presented above amply illustrate that cyclodextrin can influence the course of reactions of included molecules and thus bring about selectivity in photochemical transformations.

Simulation of "super cage effect" using cyclodextrin was indirectly evident in the examples



		AA	BB	AB		
30	R = CH_2-CH_3					
	Benzene	21	21	45	13	—
	Methanol	23	21	44	13	—
	β-Cyclodextrin (solid)	<0.5	<0.5	99	—	—
31	R = $CH_2-CH_2-CH_3$					
	Benzene	23	22	45	4	7
	Methanol	21	19	39	4	8
	β-Cyclodextrin (solid)	<0.5	<0.5	99	—	—
32	R = $CH_2-CH_2-CH_2-CH_3$					
	Benzene	17	17	38	14	19
	Methanol	17	17	35	15	19
	β-Cyclodextrin (solid)	<0.5	<0.5	99	—	—

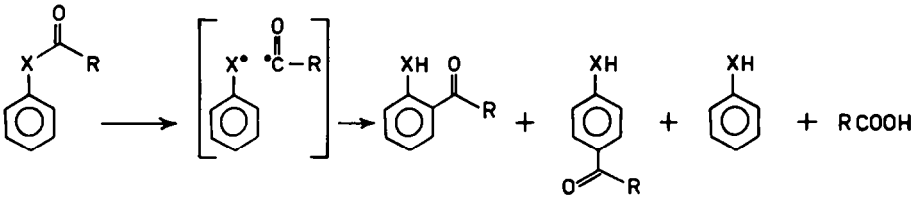
Scheme 36.



Scheme 37.

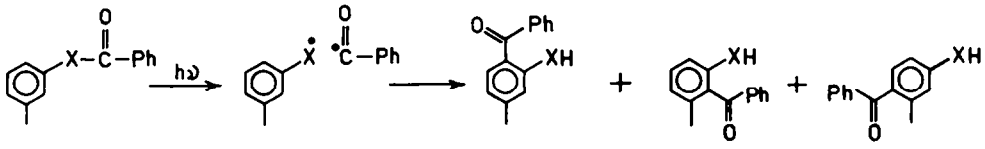
discussed above. This effect has been clearly illustrated by the photobehaviour of dibenzyl ketones and benzylphenyl acetates.[91] As discussed earlier with Dianin's compound, photolysis of these systems in solution gives rise to three radical coupling products AA, BB and AB (Scheme 24). Remarkably, in cyclodextrin medium in the solid state only one product, namely AB, was obtained in all the six compounds investigated (Scheme 24). This suggests that the radical pair generated via decarbonylation or decarboxylation is kept together by the cyclodextrin cavity and thus results in a single product.

Cyclodextrins, due to extensive usage as a host in thermal reactions, allow a certain amount of predictability regarding the structure of the complexes. Because of this, careful planning can be done in diverting reactions to particular products. This has been illustrated recently through the studies on photo-Fries reaction.[110] Photolysis of phenyl esters and anilides results in photo-Fries rearrangement to give *o*- and *p*-phenolic ketones (or anilinic ketones). Furthermore, in the case of *m*-substituted phenyl esters and anilides two *o*- and a *p*-isomer are obtained. As shown in Schemes 38 and 39 photolysis of solid cyclodextrin complexes of esters and anilides results in unique selectivity



X = O; R = Ph					
	MeOH	48	30	14	8
	C_6H_6	55	30	15	—
	β-CD-H_2O (1:10)	~99	≃1	—	—
	β-CD solid	~99	≃1	—	—
X = NH; R = Ph					
	EtOH	65	35	—	—
	β-CD-H_2O (1:10)	96	4	—	—
	β-CD solid	100	—	—	—

Scheme 38.

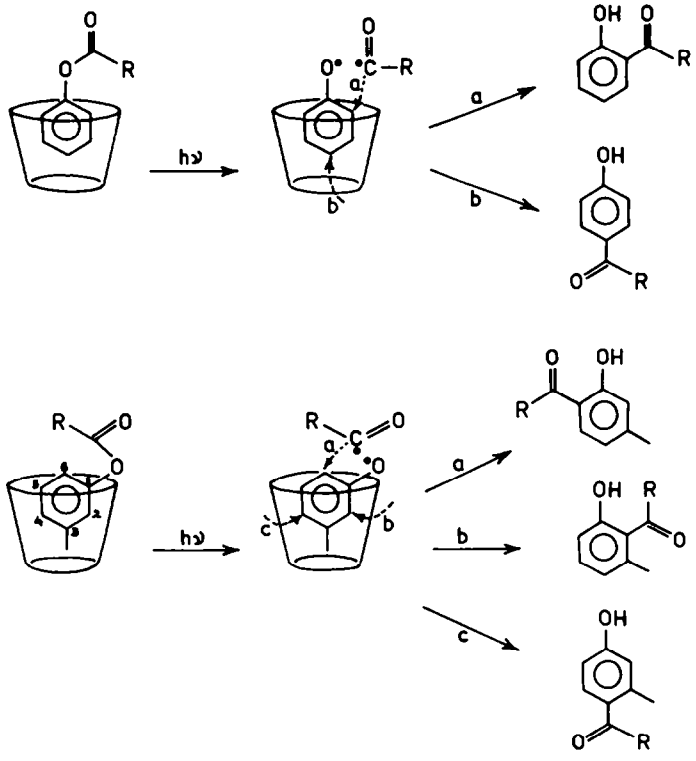


X = O	Methanol	26	21	26
	β-CD soln. (1 : 10)	66	34	—
	β-CD solid	97	3	—
X = NH	Ethanol	41.7	41.7	16.6
	β-CD soln. (1 : 10)	64	36	—
	β-CD solid	100%	—	—

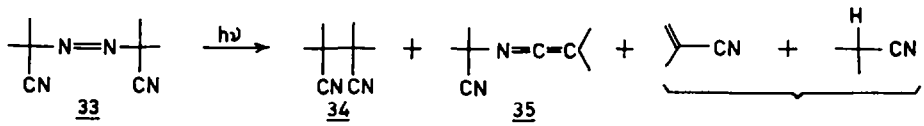
Scheme 39.

in product distribution. Although absence of the *para* product is significant, obtention of only one *o*-isomer in predominant yield from *m*-substituted esters and anilides is remarkable. Such selectivity is indeed expected on the basis of the expected structure of the complex based on extensive studies on ester hydrolysis of Breslow[111] and Griffiths and Bender.[112] This is illustrated in Scheme 40.

Powerful control of cyclodextrin on the guest reactivity is further evident from the photo and thermal behaviour of azo compounds.[113] Behaviour of azobisisobutyronitrile (AIBN) included in cyclodextrin along with its behaviour in solution, solid state and glassy medium are given in Scheme 41. AIBN undergoes thermal or photochemical homolysis to yield a nitrogen molecule and a pair of cyanoisopropyl radicals. The products resulting from this pair are dependent on the medium. While in solution coupling products **34** and **35** are predominant (>95%), in the solid state disproportionation products dominate (>95%). This difference in behaviour is attributed to crystal lattice effects. Further, in a glassy medium disproportionation competes with the radical coupling process and this is attributed to the high viscosity of the medium. It is surprising to note that the

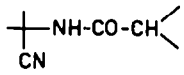


Scheme 40.



	33	34	35	
Benzene		50	45	5
Crystal		16	—	84%
β-CD solid		68	32*	—
β-CD soln.	(1 : 5)	60	40*	<2

* Identified as hydrolysed product



Scheme 41.

products obtained in cyclodextrin complexes in the solid state resemble very much those in solution. This clearly suggests that the radical motion within the cavity is not restricted to a large extent. Further studies on the behaviour of reactive intermediates in the cyclodextrin cavity is expected to yield useful information.

3.6. *Zeolites*

Zeolites are microporous, crystalline aluminosilicates of general formula $M_{x/n}[(AlO_2)_x(SiO_2)_y]\cdot mH_2O$.[114] They may be regarded as open structures of silica, SiO_2, in which aluminium has been substituted in a fraction $x/x+y$ of the tetrahedral sites. The framework thus obtained contains pores, channels and cages or interconnected voids. As the trivalent aluminium ions replace, to a given extent, tetravalent silicium ions at lattice positions, the network bears a net negative charge which must be compensated by counterions. The latter are mobile and may occupy various exchange sites depending on their radius, charge or degree of hydration, for example. They can be replaced, to various degrees, by exchange with other cations. If the zeolitic water is removed, many other molecular entities may be accommodated in the intracrystalline cavities including hydrocarbons, alkanols and a wide range of other organic and inorganic species. The characteristic parameters of a few common zeolites are given in Table 5. Figure 17 illustrates the framework of a few important zeolites. These could be of considerable use in selecting the proper host zeolite for achieving selective phototransformations. Of importance to the organic chemist is that channel or pore diameters of $\geqslant 6$ Å can allow the adsorption of benzene and other molecules of similar molecular size.

The remarkable adsorptive properties of zeolites have long been recognized, as has been their ion-exchange capacity. They are capable of ionic and molecular sieving, the size and shape of the admitted species being determined by the dimensions of the aperture openings in zeolite. Thus it is

Table 5. Characteristics of a few zeolites

Type	Si/Al	Nature of channel/cage	Pore size (dia Å)	Cavity size free dimension (dia Å)
NaA	1.0	3D channel α and β cages	4.1	β = 6.6 α = 11.4
NaX	1.23	3D channel α and β cages	7.4	β = 6.6 α = 11.8
NaY	2.43	3D channel α and β cages	7.4	β = 6.6 α = 11.8
Mordenite (LZ–M5)	5	Interconnected unidimensional channels (two)	Small channel 2.9 × 5.7 Large channel 6.7 × 7.0	—
LZ–105 (ZSM–5)	25	3D channel straight plus zig-zag	6	—
Silicalite	100	3D channel straight plus zig-zag	6	—

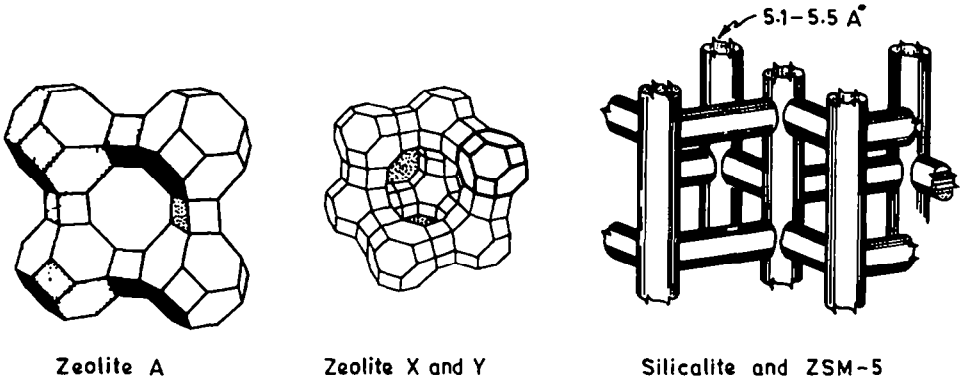
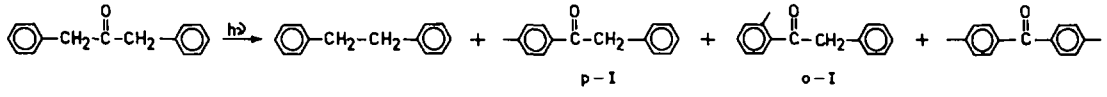


Fig. 17. Pictorial representation of cavities, channels and cages in a few zeolites.

well known that zeolites display shape selective catalytic and adsorptive properties in important industrial chemical processes. However, the possibility that the internal spaces or cavities of zeolites can exert topological control on organic photochemical reactions has been recognized only recently. Results of photochemical behaviour of dibenzyl ketones[115] and arylalkyl ketones[116] adsorbed on a number of zeolites investigated by Turro and co-workers are striking and thus opens the way for employing these substances as a medium for organic photochemical studies.

Photolyses of dibenzylketone (DBK) and *p*-methyl dibenzylketone (*p*-Me DBK) were conducted on NaA, NaX, NaY and pentasil zeolites. The observed results using NaA as the host are analogous to those observed in homogeneous solution. These results contrast sharply with those found for DBK and *p*-Me DBK on NaX and NaY (Scheme 42). These differences are readily understood on the basis of the pore openings of NaA (4 Å), NaX and NaY (8 Å). The pore openings of NaX and NaY are large enough to allow ready access to the internal zeolite voids by the ketones whereas the pore opening of NaA is too small to allow entrance. Thus the chemical behaviour of molecules adsorbed on the outer and inner surfaces of the zeolite could be considerably different. More surprisingly, the product distributions formed on NaX and NaY were found to be strikingly sensitive to additives admitted into the zeolite framework. In the case of NaX, the yield of diphenyl ethane (DPE) drops from 60 to 6% when either benzene, cyclohexane or n-hexane vapour is added to the system. For NaY, under similar conditions, the yield of DPE drops from 85 to 37%. Simultaneously, isomers of DBK become the major products. This remarkable observation has been rationalized on the basis of the internal structure of the zeolite shown in Fig. 18. The additives are postulated to fill up the remaining void space in the super cage cavities and the additive molecules tend to serve as a thin-walled molecular cage within the zeolite cages. The inclusion of additives in the same super cage as ketone will cause congestion of the available void space and will seriously restrict the diffusional and less so, rotational motion of the radical pairs produced by photolysis of DBK. As a result, isomerization becomes competitive or favoured relative to diffusional separation or decarbonylation.

Results obtained using pentasil zeolites such as LZ-105, Na-ZSM-5 and Na-ZSM-11 are truly



Zeolite				
NaA				
NaX	60%		40% (p-I + o-I)	—
NaX + ⬡	6%	~40%	52%	—
NaY	85%		15% (p-I + o-I)	—
NaY + ⬡	37%		30% (p-I + o-I)	33%
LZ-105	90%		10% (p-I + o-I)	—
LZ-105 + ⬡	90%		10% (p-I + o-I)	—

Scheme 42.

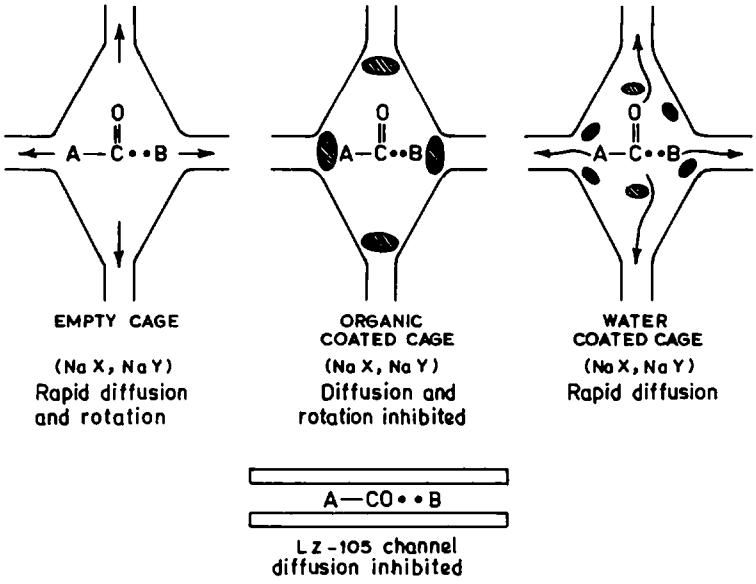


Fig. 18. Schematic representations for primary radical pair in zeolite cages [*J. Am. Chem. Soc.* **107**, 3739 (1985)].

striking.[117] Product selectivity obtained in the case of *p*-methylbenzyl benzyl ketone and *o*-methylbenzyl benzyl ketone (*o*-Me DBK) are encouraging indeed for further investigation of other photoreactions in this media. Table 6 summarizes the results obtained for these two ketones in LZ-105 which represents the other two zeolite systems. The cage effect is close to unity for *p*-Me DBK in LZ-105. The reaction in this case is established to occur inside the zeolite cavity or channel by the following two ingeneous experiments (a) isooctane fails to extract any products from the photolysed mixture present inside the zeolite as its size is too large to enter the pores and (b) the free radical scavenger 2,2,6,6-tetramethylpiperidin-1-oxyl (TMPO) which is adsorbed on the outer surface of the zeolite fails to quench the reaction. Photolyses of *o*-Me DBK in the presence of pentasil zeolites follow strikingly different pathways due to the shape selectivity and molecular diffusional characteristics of radicals on the zeolite surfaces. As seen in Table 6, both isooctane and TMPO influence the products isolated indicating that the *o*-Me DBK is adsorbed only on the exterior surface of the zeolite. Selective formation of AA and BB over AB results from the selective sieving of B

Table 6. Relative yields of products from photolysis of *p*-methyl-benzyl benzyl ketone and *p*-methyl benzyl benzyl ketone on pentazil zeolites[a,b]

Zeolite	Condition[c]	*p*-ACOB			*o*-ACOB		
		p-A-*p*-A	*p*-AB	BB	*o*-A-*o*-A	*o*-AB	BB
LZ-105	isooctane	0	0	0	270	100	0
	benzene	3	100	3	270	100	220
	benzene (svg)	0	80	3	0	1	0
Na-ZSM-5	isooctane	0	0	0	65	100	0
	benzene	4	100	3	65	100	55
	benzene (svg)	0	89	0	0	1	0
Na-ZSM-11	isooctane	0	0	0	25	100	0
	benzene	1	100	1	25	100	25
	benzene (svg)	0	72	0	0	1	0

[a] Yields of *p*-AB and *o*-AB normalized to 100%.

[b] Taken from: N. J. Turro, X. Lei, C. C. Cheng, D. R. Corbin and L. Abrams, *J. Am. Chem. Soc.* **107**, 5824 (1985).

[c] Isooctane: after irradiation, the sample was washed with isooctane and then analysed for products by vapour-phase chromatography (VPC). Benzene: after irradiation, the sample was first washed with isooctane and then with benzene. The two washes were combined and analysed for products by VPC. Benzene (svg): samples irradiated in the presence of the radical scavenger TMPO, then washed with benzene, and analysed for products by VPC. Ratio ketone: TMPO = 1:6.

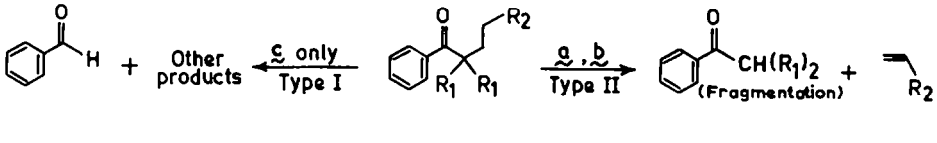
radicals into the zeolite interior. The sieved B radicals are inhibited from coupling with A radicals which must remain on the external surface. As a result AA and BB coupling becomes dominant over AB coupling. It is important to realize that in other constrained media such as micelles, silica gel surfaces and liquid crystals only the cage effect can be achieved and thus enhance the yield of AB at the expense of AA and BB. Zeolites present unique surroundings in which the reversal in product selectivity is possible.

Small selectivity has been achieved in Norrish type I and type II reactions of aryl alkyl ketones in commonly available zeolites[116] (Scheme 43). The zeolites conduce the formation of cyclobutanol (with respect to organic solvent) over fragmentation products from the type II diradical. However, silicalite presents a different situation. Similarly, type I reactivity is enhanced in silicalite over the type II. These differences are attributed to the zeolite structures into which the reactive molecules are adsorbed. The variations observed in zeolite as well as in other constrained media such as crystalline state, micelle, cyclodextrin and Dianin's compound inclusion complexes are closely similar and can be understood in terms of the moderate restriction imposed by the cavity on the reacting molecule or the diradical intermediate.

3.7. *Miscellaneous host systems*

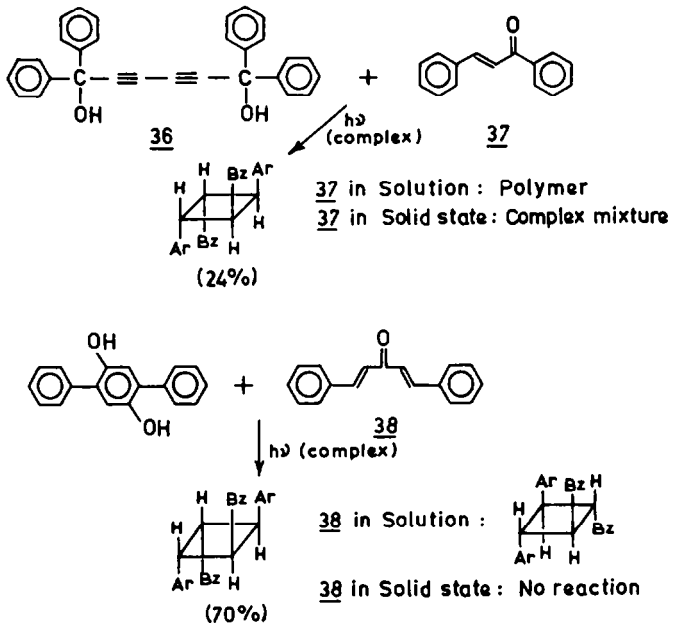
Toda and Akagi reported[118] in 1968 that diacetylene diol **36** forms crystalline stoichiometric inclusion complexes with a variety of small molecules. The features that contribute to complex formation are hydrogen bonding with the OH groups, the linear nature of the acetylenic bond and π interactions with the aryl ring. The large end groups at the end of the linear chain act as spacers preventing the hosts from packing closely. Such a loose packing creates voids in the crystal and these voids are occupied by the guest molecules. Several structural analogues of the parent diacetylene diol **36** have recently been synthesized and reported to form channel inclusion complexes.[119] A point of interest to this review is the remarkable use of this host in photochemical reactions. Since **36** forms inclusion complexes with a wide range of organic molecules, its potential use in controlling chemical reactions needs no emphasis.

Irradiation of powdered complexes of benzylidene acetophenones **37** and **38** gave a single photoproduct (>80% yield) which has been characterized to be a *syn* head–tail dimer (Scheme 44).[120] It is important to note that irradiation of **37** gives in solution a mixture of *cis* and *trans* isomers of **37** and polymer and in the solid state (pure crystals) a complex of stereoisomeric photodimers in low yields. X-ray crystal structure of the complex of **37** with benzylidene acetophenone has recently been reported and the packing is reproduced in Fig. 19. Benzylidene acetophenone in the absence of host matrix crystallizes in two polymorphic modifications and the distances between the centres of double bonds are 5.2 and 4.8 Å in polymorphs I and II. A remarkable effect of **36** is to bring the two reactive molecules closer in the inclusion complex. The molecules of the guest are packed in parallel pairs related by an inversion centre (Fig. 19). As a result, the planes



Zeolite	a	b		c	
	F/C	F/C	t/c	Type I/Type II	F/C
Na^+–A (4A)	2.7	2.3	2.2	0.30	0.50
Na^+–Y (LZ-Y52)	0.82	0.83	0.72	0.38	0.47
Na^+–X (13X)	3.2	3.8	—	—	—
Na^+–Mordenite (LZ-M5) (large-port)	2.5	2.2	2.3	—	—
Silicalite (S-115)	>50	>50	N.A.	>50	N.A.

Scheme 43.



Scheme 44.

of the double bonds are parallel and the centre to centre distance is 3.862 Å. The arrangement enables the photodimerization to give the *syn* head–tail dimer (Scheme 44). Thus it is clear that **36** may be used as a backbone for various guest molecules which are potentially photochemically active. In this context, yet another host molecule which has been successfully utilized by Todar and Kaftory is 2,5-diphenyl hydroquinone.[119] Dibenzylidene acetone when included in the latter yields the *syn* head–tail dimer in good yields (Scheme 44). Use of the host in this dimerization reaction becomes evident when one realizes that the guest dibenzylidene acetone yields the all *trans* dimer in solution and is light stable in the solid state.

Formation of channel inclusion complexes by perhydrotriphenylene was reported by Fariana in 1963.[121] Of the organic compounds capable of acting as guests in this host media mention may be made of linear and branched hydrocarbons, mono- and dicarboxylic acids, alicyclic and aromatic molecules and ethers. In general, perhydrotriphenylene (PHTP) forms channel like inclusion compounds (in analogy to urea and thiourea) both with low molecular weight substances and with linear macromolecules. A solid inclusion complex of resolved +(PHTP) and *trans*-1,3-butadiene was used in the first solid state asymmetric synthesis.[122] After exposure to γ-rays, a solid polymer of high chemical, steric and optical purity was obtained. This study revealed for the first time that optical activity may be induced in simple chemical systems under rather primitive and scarcely selective conditions, like the use of ionizing radiations and in the absence of complex reagents.

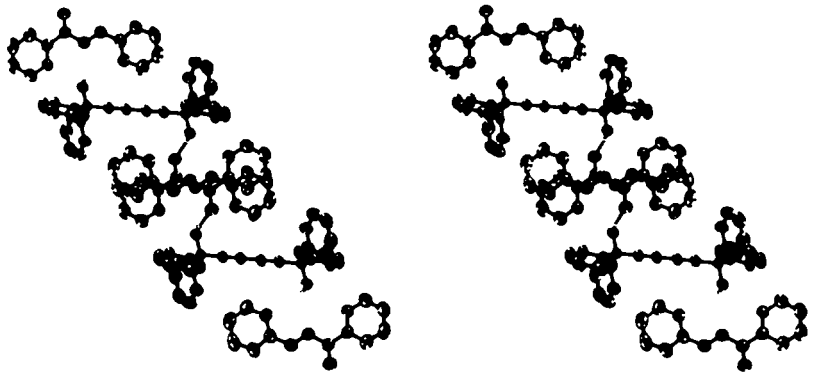


Fig. 19. Stereoscopic view of the two reacting molecules of the host and guest complex (**36** and **37**) [*J. Org. Chem.* **50**, 2154 (1985)].

4. PHOTOCHEMICAL REACTIONS ON NON-REACTIVE SURFACES: SILICA GEL

In recent years, the photochemistry of organic molecules bound to the surfaces of microporous solids such as silica gel are being investigated extensively. Silica gel, an amorphous form of silica, is a three-dimensional network of SiO_4 tetrahedra linked via siloxane bonds. The particles of silica gel or porous silica are characterized by their specific surface area, pore volume and diameter.[123] The size, porosity and surface area of the silica gel can be controlled by adjusting the pH and the ionic strength of the medium in which the polymerization of silicic acid is effected.

The surface of silica gel generally consists of two types of functions, namely, siloxane and silanol groups. Three types of silanol groups, namely, isolated, vicinal and geminal silanol groups, exist on the surface (Fig. 20).[124] These silanol functions are responsible for the affinity of the silica gel surface towards water. The lesser the physiosorbed water,the more active is the surface. Specific interactions of the adsorbate with the active hydroxyls of silica gel as well as non-specific interactions with the whole of the adsorbant contribute to the physisorption.[125] The most important interactions of the substrate with the surface are hydrogen bonding, static charge–dipole, dipole–dipole and van der Waals or dispersion (dipole–induced dipole and induced dipole–induced dipole) interactions.[126] The basic effects of surface binding on organic molecules are dependent on steric and electronic interactions and the photochemical fate will be controlled by the specific orientations while adsorbed on the surface.[125] In other words, photoreactivity will depend on which parts of the molecules are experiencing the adsorbtive effects, namely, inhibitions to rotation and migration, decreased probability of making contact with other reagents, etc.

A major impedence to the study of photochemical reactions of substrates adsorbed on silica gel is the opaqueness of the medium. This can be circumvented by several means, one of them being the tumbling of the reaction vessel during photolysis such that the surface gets replenished continuously. The opaqueness can be reduced by immersion in an inert solvent with a refractive index close to that of the solid. Only non-polar solvents such as cyclohexane, benzene and carbon tetrachloride can be used in these slurries since solvents of greater polarity will compete with the intended adsorbates for the available binding sites and will result in incomplete substrate adsorption. Some of the reports discussed here present the results from the investigations of substrates adsorbed on silica gel in the solid state while others describe the reactions conducted in silica gel (either wet or dry)/solvent matrix and, in general, the solvent is either cyclohexane or benzene.

4.1. *Alteration of the electronic properties*

Electronic absorption spectra are very sensitive to the environment of the molecules since any interaction between a molecule and its neighbour affects the energies of both the ground and the excited states, the extent of perturbation being proportional to the interaction. Silica gel is known to exert a profound influence over the absorption spectra of some of the adsorbates. These spectral changes can be characterized by one of the following variations: (i) displacement of the absorption spectra as a whole to higher or lower frequencies, (ii) changes in the extinction coefficients of the absorption bands, (iii) broadening of the absorption bands, (iv) appearance of new absorption bands. Any of these variations might alter the photochemical reactivity of the substrate since photochemical reactions are, to a large extent, dependent on the excited state properties.

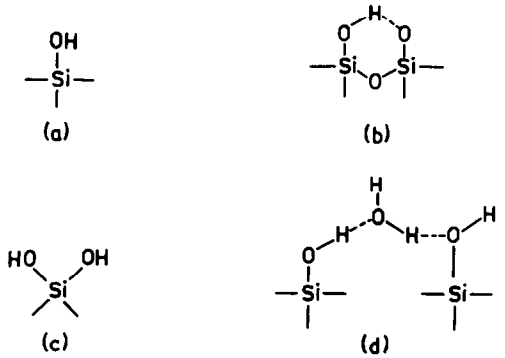


Fig. 20. Surface functionalities of silica gel [*Pure Appl. Chem.* **54**, 1623 (1982)].

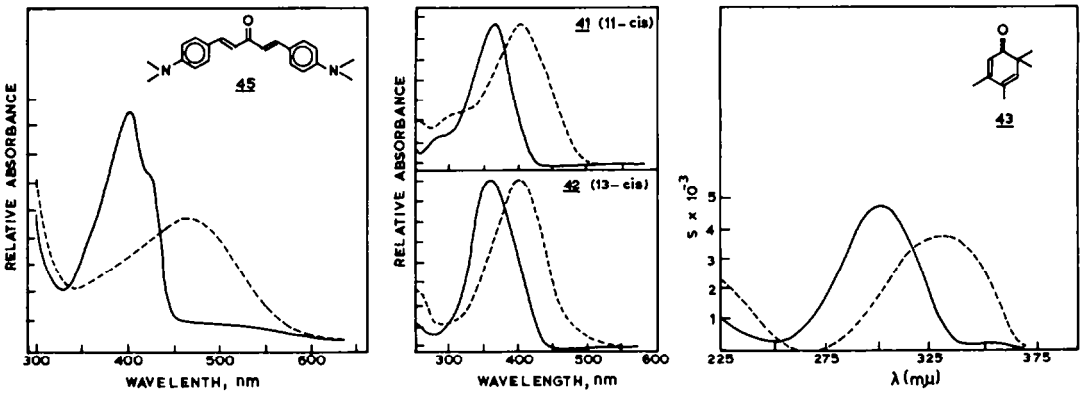
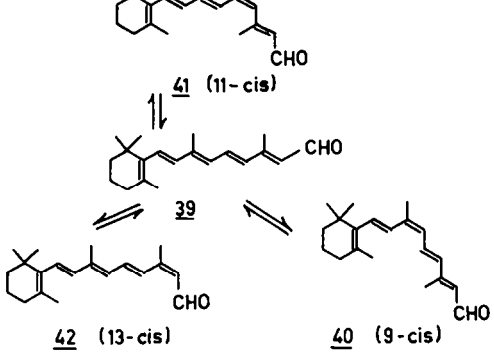


Fig. 21. Electronic absorption spectra of **45**, **41**, **42** and **43** in cyclohexane (solid curve) and cyclohexane–silica gel slurry (dashed curve).

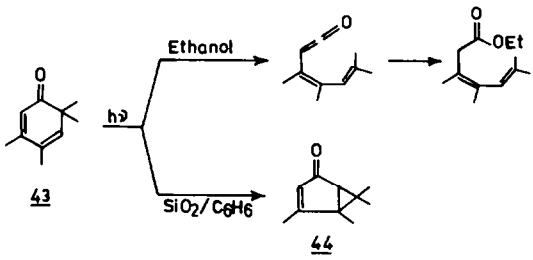
The adsorption of retinal isomers **39**–**42** onto silica gel is accompanied by a substantial red shift of the $\pi\pi^*$ band (Fig. 21(a)).[127] Hence the photoisomerization of these substrates proceeded upon irradiation at 514.5 nm in the adsorbed state while in solvents they were inert even to prolonged irradiations at this wavelength. A novel pattern of photoreactivity was observed in silica gel/cyclohexane slurry and this could not be attributed to the polarity effects. The photostationary state was a mixture consisting of 29% all-*trans* (**39**), 22% 9-*cis* (**40**), 36% 11-*cis* (**41**) and 12% 13-*cis* (**42**) isomers (Scheme 45). A comparison of the quantum efficiencies of disappearance (Φ_d) and appearance (Φ_a) of the photoproducts demonstrated the effect of silica gel/cyclohexane matrix. For example, the Φ_d value for all-*trans* retinal resembles that found in non-polar solvents and yet the photoproducts include the 11-*cis* isomer that is characteristically obtained in polar solvents. However, despite the similarity in the obtention of the 11-*cis* isomer the effect of silica gel is unique as seen by the vast differences in the absolute and relative Φ_a value in silica gel and methanol. The reactivities of other



	Photostationary state composition			
Medium	39	40	41	42
Hexane	70	5	0	24%
Ethanol	52.5	7	19.5	24.5
$SiO_2 - C_6H_{12}$	29	22	36	12

	Quantum yield data		
Medium	39→40	39→41	39→42
3-methylpentane	0.015	—	0.105
Methanol	0·0006	0·0018	0·0036
$SiO_2 - C_6H_{12}$	0·018	0.11	0·001

Scheme 45.



Scheme 46.

isomers also afford interesting comparisons. All these effects imposed by the silica gel matrix were attributed to an interplay of electronic and steric factors.

An interesting influence of the silica gel matrix is the reversal in the ordering of the $n\pi^*$ and $\pi\pi^*$ levels in some dienones and its consequence on the reactivity.[128] The 2,4-cyclohexadienone **43** undergoes photochemical reaction from the $n\pi^*$ single state yielding the solvent adduct derived via ketene. However, a new isomeric product (**44**) was isolated in silica gel/cyclohexane slurry (Scheme 46). The UV absorption spectra of the dienone **43** reproduced in Fig. 21, shows that the $n\pi^*$ band is completely obscured by the $\pi\pi^*$ band due to a bathochromic shift of the latter. Thus, it is seen that the silica gel medium perturbs the electronic spectra of cyclohexadienones in such a way that their photoreactivity is completely modified.

No [2+2] cycloaddition product was observed on irradiation of *trans,trans*-1,5-bis(4-(dimethylamino)phenyl)-1,4-pentadien-3-one (**45**) adsorbed onto silica gel[129] while the reaction occurred smoothly in solution. Silica gel produces a red shift of $\sim 3500\ cm^{-1}$ in the electronic spectrum of **45** (Fig. 21). Though the authors were unable to assign the low energy band to the $\pi\pi^*$ absorption unequivocally, they suspected a reordering of the absorption bands. In such a case, the loss of reactivity could be due to a change in the excited state configuration. It is to be noted that the forces that are responsible for the adsorption of 45 on silica gel are probably hydrogen bonding and electrostatic interactions. This might lead to the expectation that silica gel would restrict the mobility of the substrate.

The consequences of alteration of the triplet energies of some ketones, used as sensitizers, by silica gel surface is illustrated in the *cis–trans* isomerization of piperylene.[130] The composition of the photostationary state of piperylene is well known to be sensitive to the triplet energies of the sensitizers. The *trans*-piperylene concentration was brought down from 80 to 73% due to the increase in the triplet energy of the sensitizer biacetyl from 55 to 58 kcal mol^{-1} as a result of adsorption on silica gel. Thus, this reaction exemplifies an indirect influence of environment induced change in excitation energy on reactivity.

4.2. *Restriction on translational motion*

One of the ways in which adsorption could influence a photochemical process is by imposing constraints on molecular transportation. The basic question in this regard is whether the migration of excited species or its closed shell ground state could occur within the lifetime of the photochemically excited species.

The cage effect, a consequence of translational restriction, was studied in detail by de Mayo, Turro and co-workers using the Norrish type I reactions of dibenzyl ketones, benzyl esters and the photoextrusion reaction of sulfones.[131–135] They investigated the influence of various factors such as temperature, coverage, pore dimensions, hydration of the surface, magnetic field and spin multiplicity of the geminate radical pair in order to obtain a comprehensive account of the effect of physisorption on silica gel over the translational motion of the radical pairs. Silica gel was shown to restrict the diffusion of the geminate radical pairs away from each other in all the cases studied. Temperature, porosity and spin multiplicity had considerable influence over cage effect while hydration had a negligible effect.

The profile of percent cage as a function of coverage, obtained by Turro *et al.*,[131] for *p*-methyldibenzyl ketone were qualitatively similar on silica gel surfaces of various pore dimensions (Fig. 22). The percent cage was substantial at low coverages and decreased with increasing coverage, reaching a limiting value. It was also observed that the limiting percent cage was higher when the

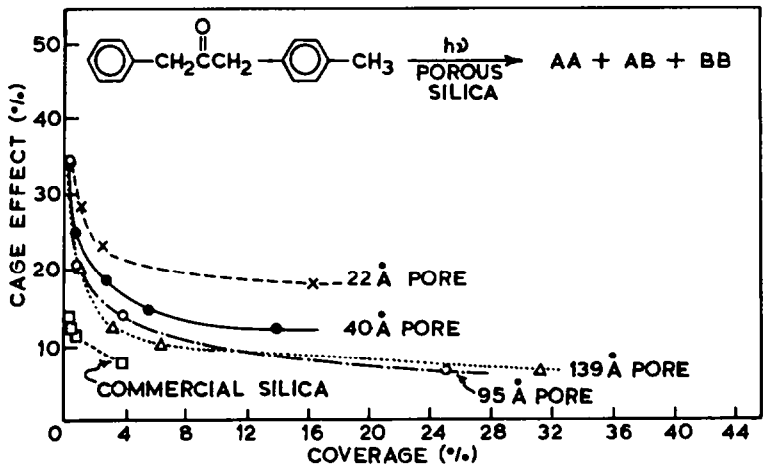


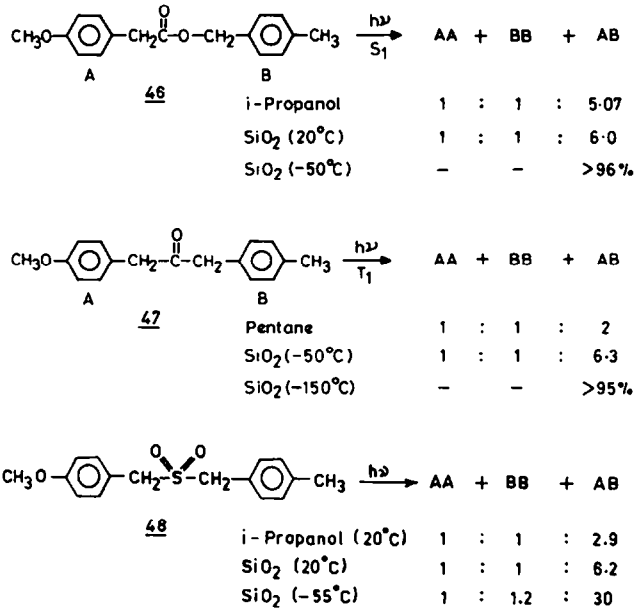
Fig. 22. Cage effect as a function of coverage for the photolysis of dibenzyl ketone on porous silica of various pore sizes [*J. Am. Chem. Soc.* **106**, 5023 (1984)].

median pore size was smaller. The authors interpreted these results by assuming an analogy between the properties of the reaction space provided by silica pores and the restricted space provided by micelles. With this analogy they suggested that larger the pore size, lower is the efficiency of return of the geminate radical pairs to a common space in which efficient recombination could occur, and more efficient is the escape from an initial pore. Magnetic field effect was reported to be significant only in the low coverage region for silica gel of smaller pores. Johnston and Wong[132] attempted to examine the cage effect imposed on the geminate radical pairs of DBK by silica gel matrix as reflected in the ^{13}C enrichment efficiencies during photolysis. Substantial enrichment was observed for the cage products namely, the recovered dibenzyl ketone and the rearranged product (Scheme 24) obtained after partial photolysis of dibenzyl ketone on silica gel, the enrichment parameter ranging from 1.12 to 1.18. The ^{13}C contents of the rearranged product and the recovered DBK were 30.4 and 35.6%, respectively, while that of DBK before photolysis was only 25%. In addition, these authors observed that lowering of the photolysis temperature and a variation in water content of silica gel did not affect the enrichment parameter significantly. In this regard, the comments of Turro *et al.* are noteworthy.[133]

The water content of the silica gel surface as well as the presence of coadsorbates were shown to exert a negligible influence on the cage effect.[134] However, temperature as well as spin multiplicity of the radical pairs were reported to have considerable control over the cage effect.[134,135] The cage product AB was found to be the greatest contributor (>96%) at $-50°$ in the case of **46** whereas at this temperature the contribution of AB obtained from both ketone **47** and sulfone **48** was only ~75% though the cage product contributed ~95% at $-165°$ in both these cases (Scheme 47). These differences were attributed to the difference in the spin multiplicities, a short-lived singlet radical pair in the former case while longer-lived triplets in the latter two cases. An increase in temperature resulted in a decreased cage effect in all three cases.

An inhibitive influence on the translational motion of radical pairs, probably singlets, by silica gel was also noticed in the photo-Fries rearrangement of phenyl benzoates[136] and anilides.[137] In both the cases unidentified by-products and phenol or aniline were less for most of the compounds examined on silica gel in comparison with other solvents. However, no variation in the *ortho/para* product ratios was observed for esters **49a** and **b** in silica gel/pentane slurry while the *para* product was more for the anilides **50a–c** and for ester **49a** in silica gel with respect to organic solvents (Scheme 48). Both these reactions were shown to be intramolecular reactions. It can be seen that though the silica gel matrix provides sufficient translational freedom for *para* recombination, a restriction for the diffusion of the geminate radical pairs is imposed by the surface thus exhibiting a quasi-cage effect.

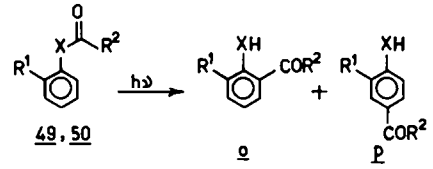
Having examined the restriction to the movement and diffusion of geminate radical pairs on the silica gel surface, it is interesting to examine the effects imposed by this matrix on the translational motion of the closed shell molecules in the ground and in the excited state. In this regard the work



Scheme 47.

on acenaphthylene dimerization is worth mention.[138–140] The *cis/trans* dimer ratio varied linearly up to 15% and at about 40% the curve flattened to an asymptote, the value of the *cis/trans* ratio being 21 at this point (Fig. 23), corresponding to ~95–97% of the reaction occurring from the singlet state. Coadsorption of acenaphthene along with acenaphthylene onto silica gel lowered the *cis/trans* ratio with respect to that at the same coverage in the absence of acenaphthene, suggesting a decrease in the nearest neighbour pairs of acenaphthylene which increases the triplet state reaction. A comprehensive analysis of all these results led the authors to conclude that there exists an inhomogeneous distribution of acenaphthylene on the silica gel surface, even at low coverages, thus increasing the nearest neighbour concentration.

The photodimerization of 9-cyanophenanthrene occurred to a greater extent on the degassed



49 a X = O; R^1 = H; R^2 = Ph
b X = O; R^1 = H; R^2 = Mesityl

50 a X = NH; R^1 = H; R^2 = Me
b X = NH; R^1 = Me; R^2 = Me
c X = NH; R^1 = H; R^2 = Ph

Compound	Medium	o/p	Compound	Medium	o/p
49 a	A	1.08	50 a	D	1.58
	B	1.20		C	1.12
	C	0.79	50 b	D	0.86
49 b	A	0.77		C	0.65
	B	0.76	50 c	D	2.00
				C	1.07

A = Pentane B = SiO_2/Pentane
C = SiO_2 dry D = Methanol

Scheme 48.

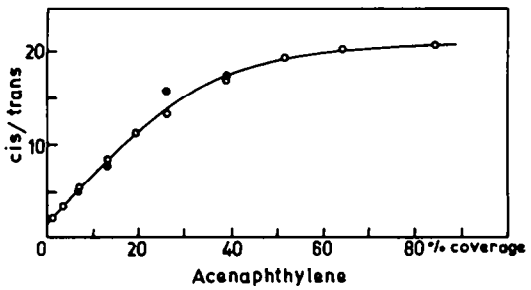


Fig. 23. Plot of *cis/trans* dimer against acenaphthylene concentration on silica gel [*Pure Appl. Chem.* **54**, 1623 (1982)].

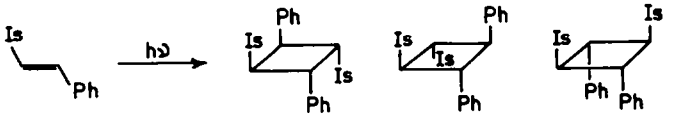
silica gel surface at higher temperatures.[139] The authors attributed this to a greater mobility of the more strongly adsorbed 9-cyanophenanthrene accompanying an increase in temperature.

A dimerization reaction wherein only one dimer was formed in the solid state while four dimers were obtained in solution along with an unidentified product was chosen by Donati *et al.* to study the effects imposed by the silica gel matrix.[141] The results reported by these authors for the dimerization of 3-methyl-4-nitro-5-styrylisoxazole in various media are assembled in Scheme 49. Though the photoproducts observed on dry silica gel are the same as those obtained in benzene, the relative yields are different. This may probably be due to the restriction imposed on the translational movement with reaction occurring between the nearest neighbours as in the case of acenaphthylene or due to a directionality in the molecular motion imposed by the silica gel matrix.

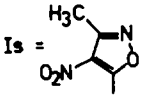
4.3. *Restriction on rotational motion*

Depending on the nature of adsorption and on which part of the adsorbate is involved in the process of adsorption, it can be expected that the steric constraints for the rotational movement of various portions of the adsorbate, imposed by the silica gel surface, would be different. For example, if a reaction requires drastic geometrical changes either on going from the reactant to the product or to the transition state, especially in the portions of the substrate involved in adsorption, then certain modifications can be anticipated to be imposed on the reactivity by the silica gel matrix since the potential barriers for rotation about reactive bonds would be altered.

The role of steric constraints in geometrical reorganizations is exemplified in the *cis–trans* isomerization of stilbenes.[142] It was observed that the time required for the establishment of the photostationary state was significantly increased and that the composition of the photostationary state changed from 93% *cis* isomer in cyclohexane solution to 60% *cis* isomer in silica gel/cyclohexane slurry. The authors suggested that adsorption modified the quantum efficiencies of intersystem crossing from singlet to triplet and thereby affected the efficiencies of *cis–trans* conversions. Steric influence on the potential barrier to rotation was also encountered in the *E–Z* isomerization of 1-(9-anthryl)-4,4-diphenyl-2,3-diazabutadiene.[143] The quantum yield for the pho-



Benzene	35	44	16%
Crystal	>99	—	—
SiO_2 (dry)	89	3.6	6.5
SiO_2–C_6H_{12}	84	6.7	8.6

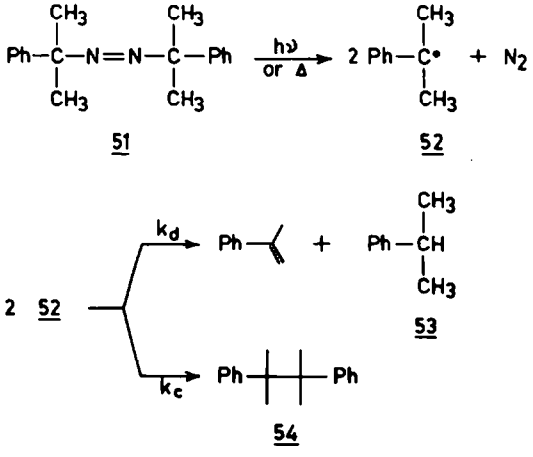


Scheme 49.

toreaction of the *E*-isomer (Φ_E) was reported to be greater by a factor of 3–10 in silica gel/cyclohexane matrix in comparison with the solution results. These two examples illustrate that silica gel is not very efficient in arresting the rotational motion though it restricts the same.

Irradiation of azobisisobutyronitrile (AIBN) in silica gel/benzene matrix was claimed to give rise to **34** (Scheme 41) as the sole product.[144] This was interpreted to be due to the loss of rotational freedom imposed by the silica gel/benzene matrix on the cyanopropyl radicals formed as a consequence of nitrogen elimination. The authors argued that if rotation of the cyanopropyl radicals had been permissible, the unsymmetrical coupling product **35** would have formed (Scheme 41). Prompted by such a remarkable observation, Lefler, de Mayo and co-workers[145,146] investigated in detail the decomposition of some azo compounds on the silica gel surface. Reinvestigation of the photolysis of AIBN by de Mayo and co-workers[145] revealed the formation of the unsymmetrical coupling product **35** along with its hydrolysis product, N-cyanopropyl isobutyramide, making together 50% of the products. Moreover, irradiation of a mixture of deuterated and undeuterated AIBN ([$^2H_{12}$]AIBN + [$^2H_0$]AIBN) resulted in a significant amount of the scrambled product ([$^2H_6$]N-cyanopropyl isobutyramide) suggesting that the cyanopropyl radicals diffuse away from the initial cage before recombination. These results indicate that the silica gel surface offers very little restriction to rotational and translational movement of the cyanopropyl radicals formed by nitrogen extrusion. Lefler and Zupancic[146] investigated the decomposition of azocumene and their comments on the restriction imposed by the silica gel matrix to translational and rotational mobilities of substrates are noteworthy. The authors, by EPR studies, have shown that the cumyl radicals **52** produced by photolysis of azocumene **51** are rotationally mobile at $-153°$ though their translation is inhibited by the silica gel surface at this temperature and they become both translationally and rotationally mobile at $-129°$. However, for the bulkier molecule, 1,1,3,3-bisdiphenylene-2-phenyl allyl, a radical scavenger, even rotational freedom was not attained completely at temperatures as high as 185°. This led the authors to bring out the role played by the radical size in the restriction of their translational and rotational mobilities by the silica gel surface. It was also noted that the ratio of cumene **53** to α,α-dicumyl **54** (Scheme 50) was five times greater in silica gel than in solvents. This was interpreted as due to the number of orientations favouring disproportionation being more than those favourable for coupling. This would lead to an increased yield of the disproportionation product **53** relative to the coupling product **54** as a consequence of the constraints to rotational and translational mobilities.

In this context, the photochemical reaction of α-oxoamides, in which oxazolidinones **26** and β-lactams **25** (Scheme 31) are the main products is noteworthy.[147] Though the reaction seems to resemble the Norrish type II process apparently, the reaction mechanism is different. In this reaction, the ratio of the products **25/26** was shown to have a remarkable dependence on the medium (protic or aprotic and acidic or basic). From the results obtained for the α-oxoamides (Scheme 31) adsorbed on silica gel the authors concluded that the restriction of molecular flexibility or motion is not very severe and that the observed effect can very easily be explained on the basis of the acidic environment



Scheme 50.

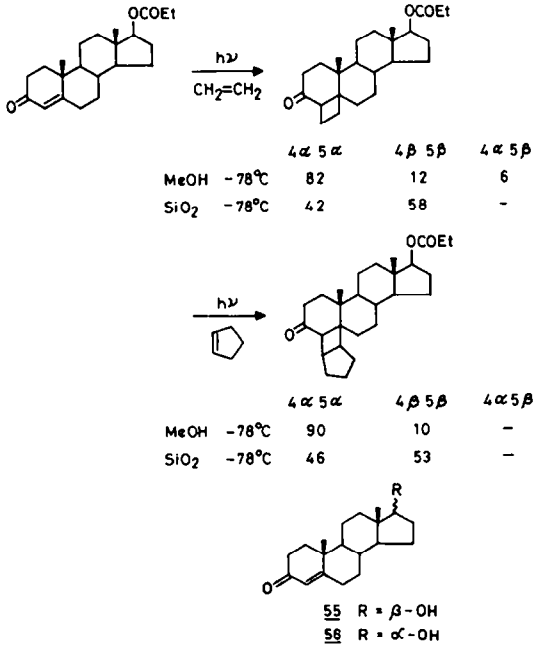
provided by the silanol functions. Thus it can be inferred that silica gel does not hamper the rotational motion in the case of medium sized adsorbates.

4.4. *Consequences of preferred modes of adsorption*

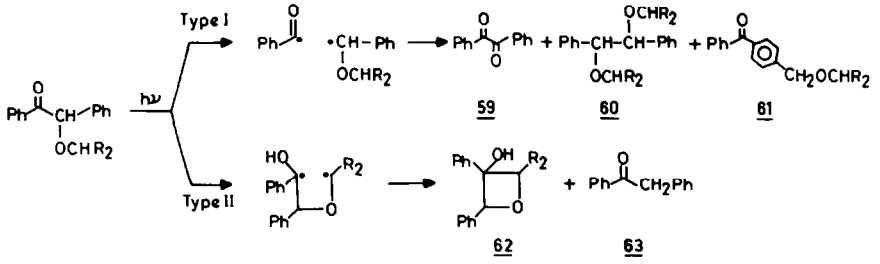
The process of physisorption involves stabilizing interactions between the adsorbate and adsorbant. Hence, among the different possible orientations of the adsorbate on silica gel, the orientations that interact more strongly with the surface would be preferred. This preference in the orientation of the substrate might lead to a modification in the reactivity.

Steroidal enones are suitable substrates for investigating the orientational effect on the silica gel since they can be adsorbed on the silica gel surface either from the more hindered or from the less hindered side of the almost planar molecule or the molecule will take a perpendicular orientation. de Mayo and co-workers utilized the photocycloaddition reactions of steroidal enones with alkenes and allenes to probe into the orientational influence of silica gel.[148] Silica gel not only reduced the attack from the less hindered α side but also increased the barrier to inversion of the 1,4-biradical required for the formation of the *trans*-fused $4\alpha,5\beta$ adduct (Scheme 51). The preference for the reaction from the more hindered side can be understood on the basis of adsorption involving the less hindered side. The most effective binding site in the enone chromophore is the carbonyl oxygen. However, if the binding occurs only at the enone oxygen, then the molecule can take up even an upright position. It is only due to the secondary forces that the molecule takes up a flat disposition on the silica gel surface. This orientation would prevent the attack at the adsorbed face. In order to investigate the secondary forces, the authors chose the steroidal enones **55** and **56** with the 17-hydroxy group in the α- and β-sides, respectively. Both these compounds did not show any great difference in selectivity in silica gel in comparison with the 17β-propionate. These results led the authors to conclude that irrespective of the 17-substituent the molecule was lying, at least partly, flat on the silica gel surface and that cumulative secondary forces were already operative. However, it is to be noted that the adsorptive effect was not strong enough to prevent the attack from the α-side entirely.

Yet another novel example, wherein an organic molecule prefers to be adsorbed on the surface with a conformation different from that in solution, has been reported by de Mayo *et al.*[149] A consequence of this is the opening of another reaction pathway that is not observed in solution. Silica gel adsorption has been illustrated to modify the conformer populations and to impose constraints for diffusion of the geminate radical pairs derived from benzoin ethers as a result of



Scheme 51.



			Type I			Type II		I : II	
			60	59	61	63	62		
57	R_2=H	MeOH(−78°C)	29·9	14·2	3·6	0	0·3	47·7	0·3
		SiO_2(−78°C)	10·8	2·5	39·6	6·2	6·0	52·9	12·2
58	R_2=CH_3								
		MeOH(−78°C)	44·7	25·2	18·3	0	0	88·2	0·0
		SiO_2(−78°C)	6·8	6·4	58·3	13·4	20·2	71·5	33·6

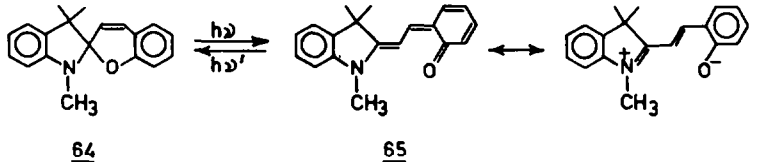
Scheme 52.

which the type II/type I ratio would be altered. For both **57** and **58** the type II products were more in silica gel in comparison to methanol and among the type I products, yield of the rearranged product **61** increased in silica gel at the expense of others (Scheme 52), the effect being more pronounced at lower temperatures. The results are interpreted to be the combined consequence of two separate functions of the silica gel on the substrate, namely, conformational control and restricted movement.

It is of interest to find out how the conformational control imposed by silica gel would influence the reactivity. For this purpose the photolysis of arylalkyl ketones is suitable for study.[150] Laser induced photolysis of valerophenone and diphenylbutyrophenone gave rise to both elimination and cyclization products. However, the ratio of elimination to cyclization in silica gel, which is highly polar, was similar to that obtained in non-polar solvents, though the *cis/trans* cyclobutanol proportion resembled that reported in polar solvents. These results cannot be explained on the basis of polarity effects and a unique influence of silica gel has to be responsible for the observed trends.

An example wherein the stabilities of potentially interconvertible species is greatly dependent on the medium is encountered with the spiropyran–merocyanine equilibrium.[142,151] Spiropyrans and merocyanines are photochemically interconvertible species with entirely different steric and electrostatic demands. From polarity considerations, the spiropyran form having two perpendicular ring systems would be stabilized in non-polar solvents whereas the planar merocyanine form would be stabilized by polar solvents. Silica gel stabilizes the merocyanine form and this is anticipated due to polarity considerations. However, it is to be noted that on silica gel or silicic acid **65** to **64** interconversion (Scheme 53) occurred even without initiation by light while it is not so facile in methanol, a solvent of comparable polarity. It is, indeed, worthwhile to mention that the contact area of the merocyanine with the silica gel surface would be more because of the planarity of the substrate and this would result in greater stability of the merocyanine. Thus an interplay of steric and electronic factors acting favourably affects this equilibrium reaction very greatly.

Thus a variety of reactions have been studied on the silica gel surface and it is indeed interesting to find out that the influence of silica gel is manifold. Examples are encountered wherein reactivities are modified by varying factors such as electronic excitation energies, reordering of electronic energy levels, limitations imposed on the translational and rotational mobilities and preference in



Scheme 53.

orientations accompanying adsorption. These reveal the potential application of silica gel in modifying chemical reactions.

5. LIQUID CRYSTALS AS REACTION MEDIA

Though liquid crystals are known and their physical properties are well examined and utilized over a long period of time,[152] only since the last two decades has their influence on the physical properties of dissolved solute molecules been investigated. After the first report on the influence of liquid crystals on chemical reactions by Svedberg[153] in 1916, this area of research had been dormant for at least 50 years. Since liquid crystals possess properties intermediate to liquids and solids, the reactivity of a molecule incorporated in a liquid crystal is expected to be different from that in isotropic solvents. The rigidity present in a solid matrix is absent in liquid crystals and hence permits molecular motion as well as conformational flexibility. At the same time, due to the order in the liquid crystalline phase, the randomness in motion and flexibility of the dissolved solute, prevalent in solutions, is restricted.

Liquid crystals do not melt sharply at a particular temperature as normal crystals do. The crystal lattice is broken partly at a particular temperature leading to a turbid liquid which on further heating gives rise to a clear liquid at a different temperature and this phenomenon is reversible. The intermediate state, having some unique optical and magnetic properties in addition to those inherited from the solid and liquid phases, is termed as the liquid crystalline state.

Liquid crystals can be classified broadly into two categories, namely, lyotropic and thermotropic, depending on the principal way in which the order in the parent solid state is destroyed. Lyotropic liquid crystals are formed by addition of controlled amounts of water or other polar solvents to certain amphiphilic compounds. Thermotropic liquid crystals obtained by temperature variations can be further subdivided into various categories such as nematic (thread-like), smectic (soap-like) and cholesteric (with a macroscopic twist) liquid crystals. These mesophases are interconvertible in some cases. The structures adopted by thermotropic liquid crystals, often used as reaction media, are shown in Fig. 24. Most of the liquid crystalline compounds have polarizable aromatic nuclei held in a planar skeleton. There are some liquid crystals that are formed from chiral molecules such as cholesteryl esters. These generally possess macroscopic twist and are called cholesteric liquid crystals.

The following considerations lead one to think positively about the use of liquid crystalline media in bringing about selective organic transformations. If the structures of the solute and solvent molecules are compatible, then solute molecules can be incorporated into the liquid crystalline

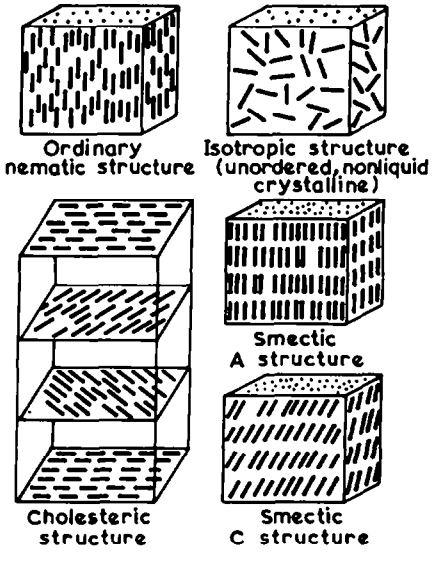
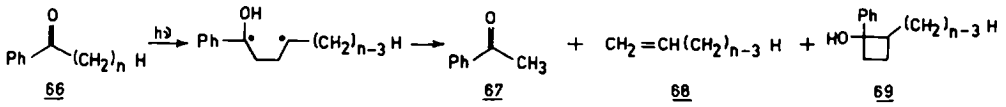


Fig. 24. Schematic representation of the arrangement of molecules in liquid crystals.



66
a: n = 4 d: n = 19
b: n = 10 e: n = 21
c: n = 17

67 68 69

Ratio of 67/69

	n-heptane	n-heptadecane	n-butyl stearate
a: (20°C)	2.8	2.9	3.3
b: (20°C)	0.9	1.9	2.0
c: (20°C)	1.1	1.2	21
d: (20°C)	1.5	0.7	15

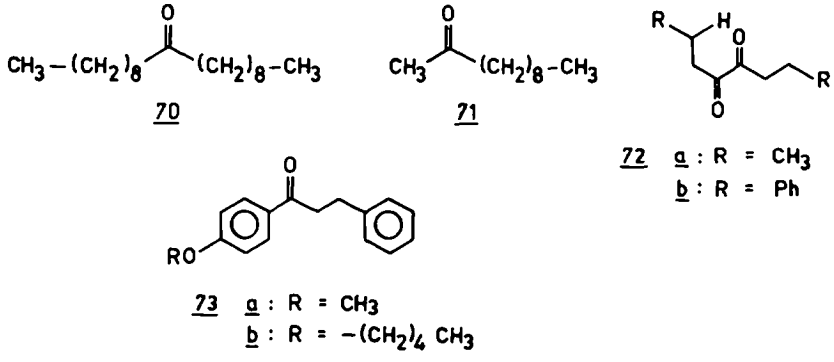
Scheme 54.

matrix without disrupting the solvent order. With such molecules the reactions leading to a product with steric demands that would disturb the microscopic solvent order would be unfavourable. In some cases, the rigidity of the solvent molecules might prevent a bimolecular and/or a unimolecular reaction which would otherwise be feasible. Alternatively solvent order could be a driving force in product formation. Examples of the latter type can be encountered in reactions wherein the product fits in the mesophase better than the reactants. Thus, depending upon the microenvironment of the solute molecules and the changes that would be imposed on this environment due to reaction, the reactivity of a solute would be modified. Recently, a few reports have appeared regarding the influences of liquid crystalline solvents on the rates, efficiencies and stereochemistry of a variety of chemical reactions. A brief survey of these reports, which provide valuable information about the influence of solvent order on chemical reactions, is presented in the following paragraphs.

5.1. *Consequences of structural compatibility of solute and solvent*

As a consequence of alignment and depending on the degree of alignment, molecular movements of solutes in different mesophases could be different from those which are accessible in crystalline solids, monolayers and other ordered media and in isotropic liquids. This has been illustrated most elegantly by the recent studies of Wiess, Turro and co-workers[154] on the Norrish type II reactions of phenyl alkyl ketones **66a–e** and dialkyl ketones **70** and **71** (Scheme 54 and 55) with varying alkyl chain length in the smectic, isotropic and solid phases of n-butyl stearate. The flexibility of the alkyl chain was expected to vary depending on the compatibility of its structure with that of the solvent. If the lengths of the solute and solvent are comparable, then the solute fits in the solvent matrix more rigidly and doing least damage to the solvent order. Whereas, if a solute is of different length in comparison with the solvent, either coiling or translational motion of the solute, permissible inside the layer of the smectic phase, would disrupt the microscopic order thereby reducing the anisotropy of the environment.

The ratio of elimination to cyclization for ketones **66c–e** and **70** was shown to exhibit a strong phase dependence with a 7–8 fold increase in the smectic phase relative to the isotropic phase (Fig. 25, Scheme 54). The observed variation was rationalized as follows: the attainment of transition



70 71 72 a: R = CH_3
b: R = Ph

73 a: R = CH_3
b: R = $-(CH_2)_4\,CH_3$

Scheme 55.

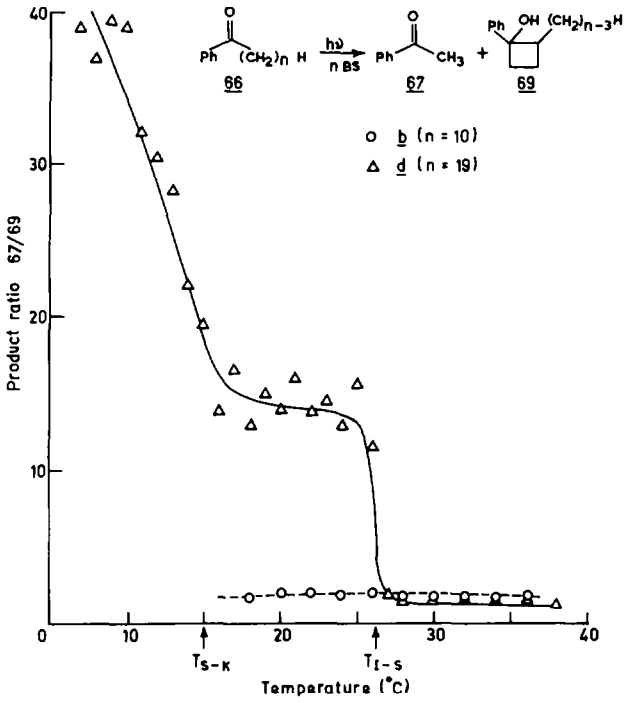


Fig. 25. Temperature dependence on the ratio of elimination to cyclization products for photolysis of **66** in n-butyl stearate [*J. Am. Chem. Soc.* **106**, 7033 (1984)].

state geometry for cyclobutanol formation requires the rotation of the phenyl substituted radical centre away from its equilibrium position. The phenyl group would be placed in a direction perpendicular to the long axes of the ketone and the surrounding n-butyl stearate in the transition state for cyclobutanol formation. This would cause a disruption of the smectic structure and as a consequence, geometries leading to cyclobutanol formation would be unfavourable. Alternatively, rotation of the unsubstituted radical centre would also produce intra- and intermolecular disturbances for several methylene groups along the alkyl chain. However, the motions required for the elimination reaction to proceed would cause only a little disruption of the smectic order. Similar arguments were extended to account for the preferential formation of *trans*-cyclobutanol with respect to the *cis* isomer in the case of **70** in the smectic phase.

The observation that for molecules **66a, b** and **71** with alkyl chains very much shorter than that of n-butyl stearate elimination to cyclization ratio is virtually unaltered (Scheme 54) was taken as a support to the above arguments, since the lack of rigidity when ketones **66a, b** and **71** are incorporated in the liquid crystalline matrix is expected to reduce the anisotropy of the micro-environment, thereby providing greater lability for conformational reorganizations. Supportive results were also obtained in the case of α-diketones **72a** and **b** (Scheme 55) on photolysis in the smectic phase of n-butyl stearate and in some other nematic and cholesteric solvents.[155] Due to the poor fit of these ketones in the mesophases no dependence was observed for the preferential formation of one of the diastereomeric cyclobutanols. Though the authors have observed some phase dependent variations in the quantum efficiencies for the disappearance of the starting diketones, the origin of these differences are unclear.

Leigh's work[156] on the triplet lifetimes of β-phenyl-4-alkoxypropiophenones **73a** and **b** (Scheme 55) emphasizes that the ability of smectic phases to inhibit the cyclization of even a highly oriented solute may depend critically on the structural features defining the fit of the solute into the smectic array. He observed striking differences in the Arrhenius parameters for the triplet decay of **73a** in the smectic phase of BCCN (*trans,trans*-4,4′-butylbicyclohexyl-4-carbonitrile), E_a being 10 kcal mol^{-1} higher and $\Delta S^{\neq}$ *ca* 30 eu more positive in highly ordered smectic phase relative to the values in the more fluid nematic phase. The large increase in the triplet lifetime of **73a** in smectic BCCN (370 ns) with respect to the nematic phase (122 ns) suggests that the probe is solvated tightly in the former phase. In its *trans* conformation **73a** is one carbon atom shorter than BCCN and hence

might reside comfortably within the solvent layers with only minor disruption of the local order. This is further evidenced by the observation that for **73a** in ECCN, the ethyl analogue of BCCN, and for **73b** in both ECCN and BCCN, no such effect of smectic order was observed. This was indeed anticipated since the longer chain lengths of **73a** with respect to ECCN and that of **73b** with respect to both BCCN and ECCN would cause local disruption in the solvent order so that bond rotations leading to intramolecular quenching would be unimpeded.

It is evident from the above examples that the compatibility of solute structure with that of the solvent and minimum disruption of solvent order by the solute as well as the transition state are essential for obtaining favourable influence in the liquid crystalline state.

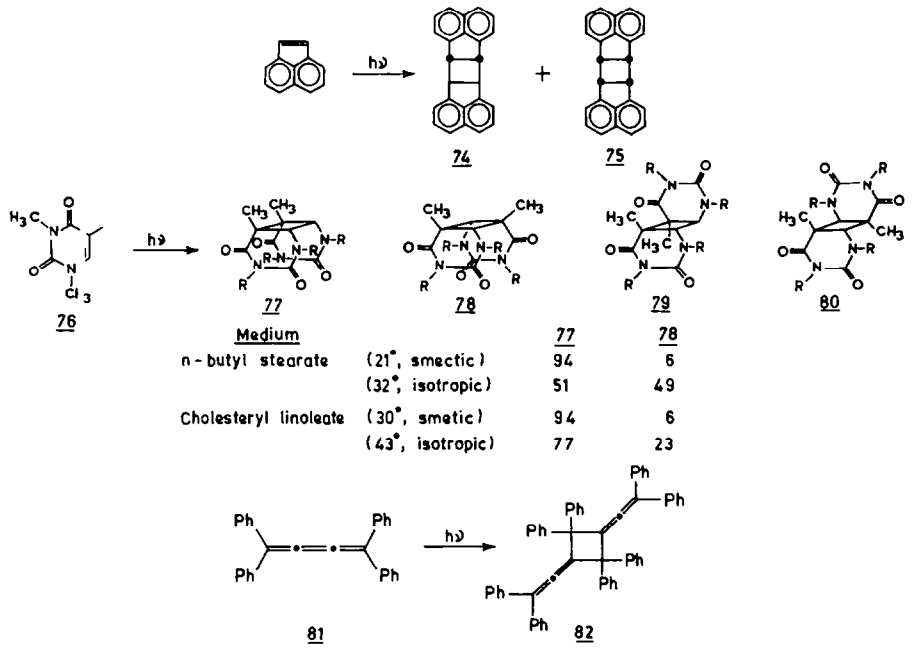
5.2. *Orientational restrictions and effect of order on bimolecular reactions*

There are examples of mesomorphic order exerting stereochemical control over dimerization reactions. One such case is the dimerization of acenaphthylene (Scheme 56). A remarkable increase in the production of *trans* dimer **74** was reported in cholesteric liquid crystals with the ratio of *trans/cis* depending on the concentration of acenaphthylene.[157] In solutions, *cis* product **75** was obtained almost exclusively from singlet excitation while a mixture of *cis* and *trans* products was obtained on triplet excitation. Lowering of *cis* dimer production in the mesophase was attributed to the enhanced efficiency of the triplet reaction in comparison with the singlet as shown by quantum yield measurements.[158,159] In general, it is known that triplet state reactions are promoted by an increase in the viscosity of the medium. Natural extension of this theory to the observations in the cholesteric phase would point to viscosity as the influencing factor. However, neither the smectic phase of n-butyl stearate nor the nematic phase of phenyl benzoyloxybenzoate, both having viscosities comparable to the cholesteric phase of the 1/1 mixture of 5α-cholestan-3β-yl acetate and 5α-cholestan-3β-yl nonanoate, did not influence the yield of the *trans* dimer significantly. This led the authors to conclude that the observed effect was due to specific orientation and motional anisotropy of the substrate in the cholesteric mesophase.[159]

The authors[158,159] ascribed the increase in triplet efficiencies in the cholesteric mesophase to the increase in the fraction of acenaphthylene–acenaphthylene collisions which have coplanar or parallel planar orientations and not to the increase in the total number of collisions per unit time. Nerbonne and Weiss[159] explained the observations based on the differences in mobilities of solute molecules in different directions in various phases. They argued that a planar solute in a nematic or smectic phase is equally free to diffuse in any direction perpendicular to the long axes of the solvent molecules with the same rate while the diffusional rate would be different in a direction parallel to the long axes. This anisotropy in motion, however, would have no appreciable control over the fraction of collisions with parallel plane orientations whereas, the layered structure of cholesteric phase controls the diffusion in different directions in a different way from the nematic and smectic phases. The macro-structure of the cholesteric phases might be responsible in forcing the acenaphthylene molecules to remain parallel during their diffusion and this might be the factor effecting the increase in efficiency. However, it is to be noted that these arguments are only tentative and yet to gain direct evidence.

Another report on the favourable solute orientations during bimolecular collision is the photodimerization of 1,3-dimethylthymine **76** in the anisotropic solvents cholesteryl oleyl carbonate, cholesteryl linoleate both forming smectic as well as cholesteric phases and in n-butyl stearate, which is a smectogen.[160] In isotropic solvents including water all the four *cis* fused dimers **77–80** were formed (Scheme 56) while dimers **77** and **78** were the sole products in frozen solutions of isotropic solvents. In contrast, highly selective dimerization was observed upon irradiation in liquid crystalline matrices at temperatures suitable for preserving the anisotropy. Thus, the *cis-syn* dimer **77** was formed almost exclusively in either of the mesomorphic states while the selectivity reduced sharply when the solvent anisotropy was disrupted. Increased quantum efficiency was noted for this triplet reaction in the mesophases. These effects were attributed, in general, to the long and short range orders of the liquid crystalline phases, though no specific reasoning was put forth for the preferences in the orientations during solute–solute collisions.

Similar preference in intersolute orientations is reported for the photodimerization of tetraphenylbutatriene **81** (Scheme 56).[161] The only dimer formed in the nematic liquid crystalline phase and in stretched and unstretched polyethylene films was the same dimer as that obtained on solid state photolysis, namely, **82**. Here again the observation was rationalized by the influence of the



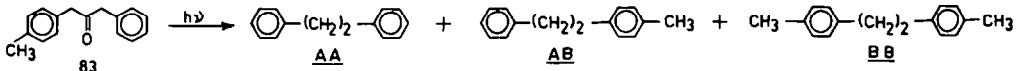
Scheme 56.

matrix on the relative orientations of the solute molecules and on the basis of increased lifetime of the excited state providing enough time for collision of the excited monomer with another substrate molecule.

A reaction in which the liquid crystalline order modifies the reactivity of solvent molecules is encountered in cholesteryl *trans*-cinnamate.[162] In hexane solution *cis*-cinnamate formation is greater on photolysis in comparison with dimer production. The rate of dimerization is higher in the mesomorphic state than in the others. Though the mesomorphic order influenced the rate of dimerization, it did not exert great control over the stereochemical course of the reaction.

5.3. *Consequence of restriction of solute diffusion*

It is evident from the above examples that liquid crystals do not inhibit the diffusion of substrates though it facilitates differential movement. An exploration of the effectiveness of liquid crystals in providing solvent containment barrier for the diffusion of radical pairs was made by Turro and co-workers.[163] On the basis of the fraction in cage combination (F_c) of the radical pairs produced by the photolysis of 1-(4-methylphenyl)-3-phenylpropane-2-one **83** (Scheme 57), conducted in solid, liquid crystalline and isotropic phases of 35/65 (w/w) mixture of cholesteryl chloride/cholesteryl nonanoate (CCl/CN), *trans,trans*-4′-n-butylbicyclohexane-4-carbonitrile (BCCN) and n-butyl stearate (BS), the authors attempted to understand the efficiencies of mesomorphic phases in imposing cage constraints.



Medium	Temp. and Nature	F_c^*
Cholesteryl chloride/ Cholesteryl nonanate	51° (cholesteric)	0.196
	86° (isotropic)	0.133
trans, trans -4′-n-butyl bicyclohexane -4- Carbonitrile	46° (smectic)	0.088
	61° (nematic)	0.080
	82° (isotropic)	0.106
n-butyl stearate	17° (smectic)	0.192
	28° (isotropic)	0.021

$$F_c^* = \frac{AB-(AA+AB)}{AA+AB+BB}$$

Scheme 57.

The effect of phase type on F_c (cage effect) in the three liquid crystalline solvents at a fixed (1 wt %) initial concentration of **83** is reproduced in Scheme 57. The BCCN and CCl/CN samples were only slightly sensitive to phase changes and temperature though the absolute values of F_c are inexplicable by viscosity considerations alone. Only in the case of BS a significant drop in F_c was observed both by a temperature increase and by a phase change from smectic to isotropic. Essential in the interpretation of the observed results in the mesophases is the determination of diffusional coefficients along specific solvent axes. Another point of extreme importance in this study is the probability that a benzyl radical fragment would traverse the layer barriers in the smectic phases of BS and BCCN. In the absence of these data no definite predictions could be made as to the efficiency of liquid crystalline media in imposing cage constraints.

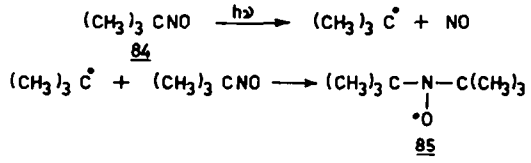
In this context, the photolysis of 2-nitroso-2-methylpropane **84** is noteworthy.[164] Before going into the results of photolysis in mesophases, it is important to take note of the fact that the nitroso compound **84**, which normally exists in equilibrium with its dimer, stays in the nematic phase of 4-methoxybenzilidene-4-butylaniline (MBBA) preferentially in the dimeric form, the equilibrium constant for dimer formation being 100 fold higher in the nematic phase with respect to that in benzene. This is in accord with the expectation that the dimer being longer would fit in the mesophase with lesser damage to the order in comparison with the monomer.

The photolysis of **84** yields the di-t-butylnitroxyl radical **85** (Scheme 58) and the initial rate of photolysis was followed by the observation of this radical by the EPR technique. Drastic reduction in the formation of di-t-butyl-nitroxyl radicals in the isotropic phase was proved to be due to the consumption of the t-butyl radicals, produced in the first step, by the solvent molecules. The increased production of nitroxyl radicals accompanying the change from the isotropic to the liquid crystalline phase at temperatures below 40° was primarily associated with the emergence of ordered structure in the solvent. The probabilities of formation of primary radicals and of their interaction with the molecules of the nitroso compound and solvent should depend on the structure of the solvent matrix and on the mutual orientation of the interacting molecules which might be critically phase dependent. From the observed results it can be concluded that the degree of orientation effects increase in the interaction between the nitroso compound and t-butyl radicals while the steric hindrance for the interaction between t-butyl radicals and oriented solvent molecules also increases. The effect of viscosity in directing the observed variations is ruled out since the nematic phase of 4-methoxy-3-hexyloxyphenyl benzoate (MHOPB) having similar viscosity variations leads to a smooth temperature dependence (a positive temperature coefficient) irrespective of the phase (whether liquid crystalline or isotropic). Thus, it is very clearly seen from this example the influence of the structure of the solvent cell in modifying the reactivity of the trapped reactants.

5.4. *Asymmetric induction by liquid crystals*

Organic chemists in their endeavour to mimic nature have explored various possibilities to bring in optical selectivity in chemical reactions. One such attempt was to place the reactant molecules in an asymmetric environment. Cholesteric liquid crystals, due to their macroscopic twist (Fig. 24), are expected to induce specificity in chirality in chemical reactions. However, several controversial reports have been made regarding the asymmetric induction by cholesteric mesophases in thermal reactions.[165,166] It is relevant to take note of the conclusions from a careful analysis made by Dondoni *et al.*[165] and Kagan and co-workers[166] on asymmetric induction in thermal reactions using liquid crystalline media before proceeding with a survey of induced asymmetry in photochemical reactions.

Dondoni *et al.*[165] discourage any hope of obtaining significant asymmetric induction by conducting the reactions in cholesteric mesophases due to the following reasons. (i) The pitch of the cholesteric helices is very large (normally greater than 4000 Å) with respect to the molecular



Scheme 58.

Table 7. Photoasymmetric synthesis of hexahelicine in a mixture of cholesteryl chloride and cholesteryl myristate[a]

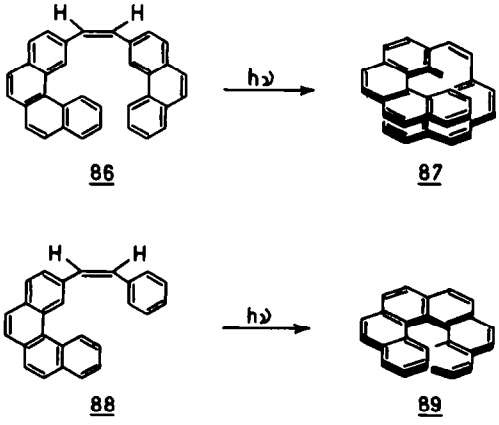
Temp. (°)	Hexlix handedness	Percentage enantiomeric excess (%)
31 ± 1	left handed	0.05
41 ± 1	nematic	0.19
51 ± 1	right handed	0.29
61 ± 1	right handed	0.43
70 ± 1	isotropic	0.03

[a] Adopted from: H. Hibert and G. Solladie, *J. Org. Chem.* **45**, 5393 (1980).

dimensions and practically, the solute molecules (having dimensions not greater than 50 Å) see in their neighbourhood a nematic achiral microstructure. (ii) The orientation of the molecules such as rod shaped ones with their long axes parallel to the local magnetic director is defined only with respect to their direction and two orientations rotated by 180° are equally possible. (iii) There is considerable free rotation along the long molecular axis due to which the enantiotopic cross-section of the liquid crystalline matrix as seen by each guest molecule would be different.

Taking note of these arguments, Hibert and Solladie[167] reported the photoasymmetric synthesis of hexahelicene **89** in cholesteric liquid crystals. They conducted the photoconversion of 2-styryl-benzo[*c*]phenanthrene **88** in the cholesteric system containing a mixture of cholesteryl chloride and cholesteryl myristate with a weight ratio of 1.75/1.00. This system is unique since it offers four different phases at various temperature ranges. The enantiomeric excess observed in various phases at different temperatures are summarized in Table 7. Though the asymmetric induction is small, the observed trends are indeed promising. The salient observations of these authors are: (i) enantiomeric excess which is very low in the isotropic phase is increased in the compensated nematic phase suggesting that the solute–solvent interactions controlling the stereochemistry of cyclization is increased by the local ordering of the mesophase. (ii) the results in the cholesteric phases reveal the added effect imposed by the helical structure, the right-handed helix affording an additive effect while an opposing effect is induced by the left-handed helix (iii) pitch and enantiomeric excess have an inverse relationship.

Similar results were also reported for the photoasymmetric induction in hexahelicene **89** and octahelicene **87** formation (Scheme 59) in a mechanically twisted nematic mesophase of a 1/1 (wt %) mixture of *p*-cyanophenyl *p*-butylbenzoate and *p*-cyanophenyl *p*-heptylbenzoate.[168] Nakazaki *et al.* have also noted in both the cases that a right-handed mechanical twist of the mesophase results in the production of helicenes with positive chirality. However, the maximum optical induction observed by these authors was only 0.2%.



Scheme 59.

Maximum asymmetric induction reported sofar in the photoasymmetric synthesis was again in the case of hexahelicene in the cholesteric phase of 3:2 weight mixture of cholesteryl nonanoate and cholesteryl chloride.[169] The right-handed helix gives rise to about 1% enantiomeric excess and, interestingly, with positive chirality.

These reports make one a little more hopeful about inducing optical selectivity by incorporating the solute molecules in a liquid crystalline matrix provided one is capable of exerting control over the pitch and handedness of the liquid crystalline helix.

6. PHOTOREACTIONS IN AQUEOUS MEDIA—CONSEQUENCES OF HYDROPHOBIC INTERACTIONS

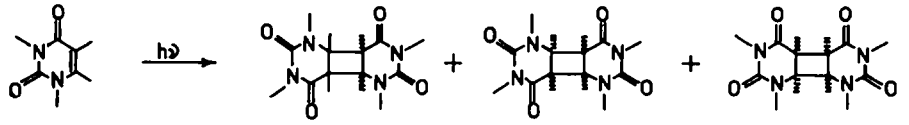
The peculiar features exhibited by aqueous solutions of some very simple organic molecules have been studied over the last several decades. Solute association in water is now an accepted phenomenon, although the origin of such a behaviour is yet to be fully understood. This unique property of water can bring about unexpected alterations in the course of reactions. In addition to preassembling reactants, a certain degree of organization at the molecular level can provide advantages. In this context, the interface between two phases is important mainly because of the specialized physical properties imparted to the system by the interface. Reactant organization in water can be achieved in various ways including in assemblies such as micelles, microemulsions, vesicles and in specialized host systems. In micellar solution, hydrophobic molecules may be solubilized in the hydrocarbon core. Microemulsions also provide a microheterogeneity that resemble that of micelles. More rigid hosts such as cyclodextrin, amylose, etc. offer a wide variety of locations and interactions that are not present in micelles or microemulsions. All these microheterogeneous systems share the following common features: (a) provide a hydrophobic pocket into which organic molecules can be assembled and (b) offer an interface between the aqueous exterior and a hydrocarbon-like interior wherein the reactants can be aligned. The driving force behind the selectivity observed in such systems is the hydrophobic interactions which force the reactants to seek the hydrocarbon-like hosts for their residence during their stay in water. In this section, we highlight with several examples the various features of the above microheterogeneous media and point out how one could use them to achieve selectivity.

6.1. *Photochemical reactions in water: aggregation of organic reactants*

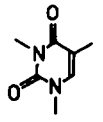
Most of the organic molecules due to their hydrophobicity are expected to associate in water and this has been established to be so in many cases.[170] This will result in non-uniform dispersion of the solute in water and in microenvironments having high local concentrations. In these microheterogeneous environments with high local concentrations addition reactions involving bimolecular collisions will be accelerated. Striking rate enhancement were reported in thermal Diels–Alder reactions.[171] Moreover, in some cases, pre-associations in specific orientations were induced by the hydrophobic effect in water leading to significant product selectivities.[172] Pre-associations may also be expected to influence photochemical cycloaddition reactions since the pre-associated species do not require diffusional motion prior to reaction and hence addition could compete favourably with other pathways deactivating the excited state.

The role of aggregates in photochemical dimerization of thymine, uracil and their derivatives, all having considerable solubility in water has been investigated by Morrison and others.[173–176] Osmometric determination of apparent molecular weights as a function of concentration in aqueous medium has established the ground state aggregation of these substrates. As a consequence of pre-association, dimerization quantum efficiencies for these substrates increased considerably in water in comparison with other organic solvents. It was shown that dimerization occurred via the singlet state in dimethyl thymine,[174] dimethyl uracil[175] and tetramethyl uracil[176] in an aqueous medium. The authors suggested that the singlet state dimerization contributing almost entirely in aqueous medium was due to ground state aggregates. There was no specificity in the product distribution due to pre-association and, in general, the product proportions are in line with the expectations based on polarity considerations (Scheme 60).

The effect of association on photochemical reactivities of stilbenes[177] and alkyl cinnamates,[178] having poor solubilities in water has been recently demonstrated in our laboratory. In organic solvents, the dimerization reactions are not efficient while in an aqueous medium they successfully compete with the geometric isomerization. Deviation from Beer's law was observed for *cis*-stilbene



Water	27·8%	63·1%	9·1%	ø = 0·015
CH_3CN	24·9	68·2	6·7	ø = 0·0047
CH_3OH	31·4	68·6	—	ø = 0·004



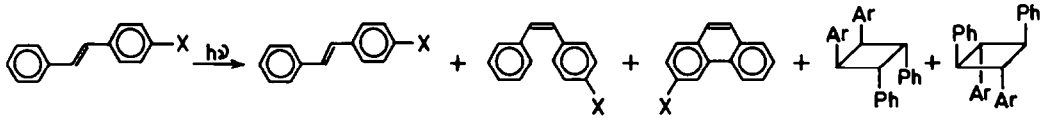
	syn h-t	+ syn h-h	+ anti h-t	+ anti h-h	(dimers)
Water	38	39	18	6	ø = 0·014
CH_3CN	37	49	11	4	ø = 0·0015
CH_3OH	42	37	18	3	ø = 0·002

Scheme 60.

and *trans*-ethyl cinnamate giving an evidence for ground state association. Even at concentrations as low as 10^{-6} M of *trans*-stilbene in water, dimerization occurred efficiently within 24 h of irradiation while in benzene it was observed only at concentrations as high as 0.1 M. Two dimers were obtained upon irradiation of stilbenes **90–93** in water in competition with the isomerization and cyclization products. The ratios of dimers **94** to **95** were similar to those obtained in benzene at high concentrations (Scheme 61). Similar observations were obtained with alkyl cinnamates. Dimerization did compete with isomerization and the *syn* head–head dimer was the major isomer. In both stilbenes and cinnamates dimerization efficiency was reduced by addition of guanidinium chloride which decreases the hydrophobicity in water and was enhanced by addition of lithium chloride, which increases the hydrophobicity in aqueous solutions. These results are consistent with the proposal that the hydrophobic association is the cause for dimerization in aqueous medium.

Coumarin underwent dimerization in water with increased efficiency even at low concentrations (0.001 M) when compared to organic solvents (Scheme 62).[179] Ground state association could be the cause for the enhancement in the quantum efficiency of dimerization. It was observed that coumarin exhibited moderate fluorescence in aqueous solution while none was detected in benzene. This led to the proposal that singlet state life-time of coumarin increased considerably in water and this might be one of the factors responsible for the enhanced dimerization efficiency. The contribution of pre-association cannot be ruled out on the basis of absence of deviation from Beer's law alone since even in the case of uracil derivatives, wherein aggregation was shown to occur by osmometric measurements, no deviation from Beer's law was observed. The dimer that crystallized out of water during irradiation was shown to be the *syn* head–head dimer. In addition, *syn* head–tail was also formed in low yields but it was soluble in aqueous medium.[180]

The importance of interactions of the substrate with water in controlling the reactivities of the



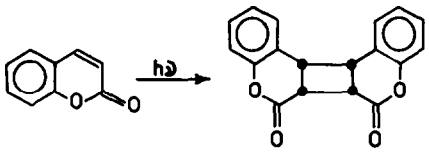
90 X = H
91 X = CH_3
92 X = F
93 X = CN

94 **95**

Product distribution after 24 hrs of Photolysis

X = H	Benzene	12	84	4	—	—
	Water	33	11	33	12	10
	Water + LiCl	27	7	25	25	17
	Water + Guanidinium chloride	21	11	53	8	6

Scheme 61.



(0.02 M) Syn-HH Anti-HH

Solvent	Product	Quantum yield
Methanol	Anti-HH	$< 10^{-5}$
Benzene	Anti-HH	$< 10^{-5}$
Water	Syn-HH	2×10^{-3}
SDS	Syn-HH	2×10^{-3}
CTAB	Syn-HH	0.3×10^{-3}
Triton X 100	Syn-HH	1×10^{-3}

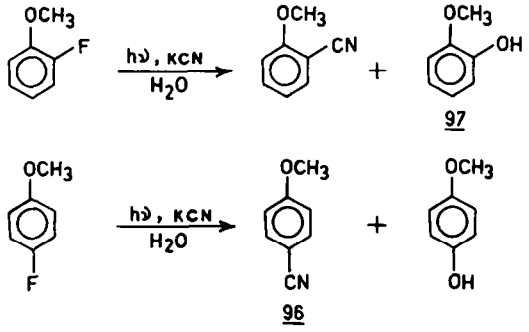
Scheme 62.

solute is very nicely exemplified in the photochemical aromatic nucleophilic substitution reactions of fluoroanisoles.[181] Substitution of fluorine by cyano group is effected by the reaction of the cation radical with cyanide ions. In water the photocyanation product **96** was the predominant one for 4-fluroanisole while the photohydroxylation product **97** was formed in large excess in the case of α-fluoroanisole (Scheme 63). Based on these, the authors hypothesized that the hydrogen bonding of water with the methoxy group might allow photohydroxylation to occur preferentially in 2-fluoroanisole while such hydrogen bonding would have negligible influence in accelerating photohydroxylation in 4-fluoroanisole due to distance criterion. The authors also investigated the modifications in solvent order and its influence on the photoreactivities of the two anisoles.

Thus, it is clear that, apart from polarity effects, water provides a microheterogeneous environment and modifies the reactivities in a unique way. It is important to realize that so little is known about the association structure or kinetics of organic molecules in water implying that there is much more to understand regarding the role of water as the solvent for reactions in general.

6.2. *Photochemical reactions in micellar media*

The term micelle denotes an assembly formed by aggregation of surfactant molecules in water. Surfactant molecules are characterized by two distinct functionalities,[182] namely, hydrophobic and hydrophilic groups. The hydrophobic group is generally a long hydrocarbon chain and the hydrophilic group is either ionic or nonionic. When these amphiphatic molecules are dispersed in water, the hydrophilic part would very easily be solvated whereas the hydrophobic part would resist solvation. The hydrophobic repulsion between the hydrocarbon chain and water is responsible for the aggregation of surfactant molecules in water in such a way that the hydrophobic moieties form an oil-like pool from which the hydrophilic head groups stick out and are solvated by water. Depending on the van der Waals interaction between the hydrocarbon chains, electrostatic repulsion



Scheme 63.

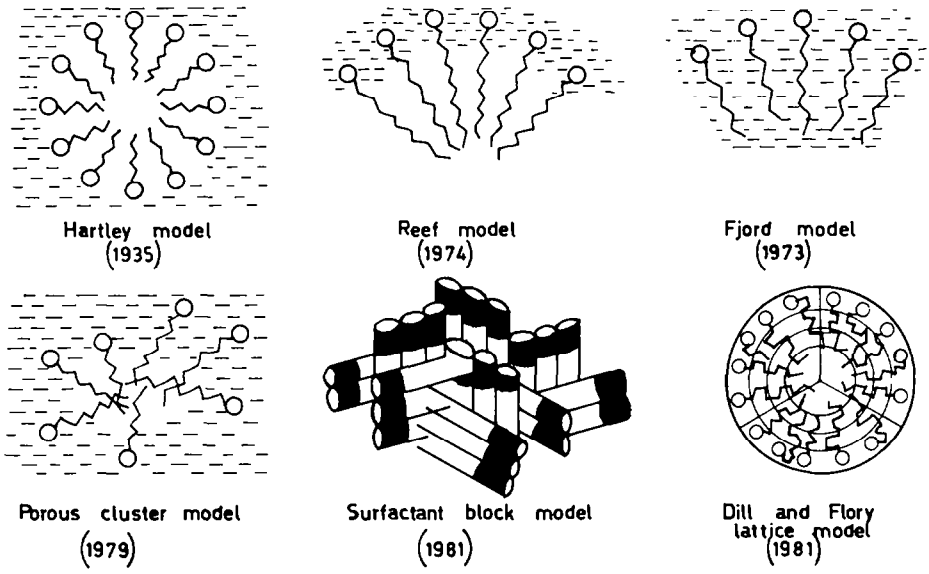


Fig. 26. Various structural models for micelle.

between the charged head groups, the extent of water penetration into the micelles and other variable experimental parameters, micelles of various structures would be formed. The exact structure of a micelle is unknown, although several intelligent guesses have been put forth. Figure 26 depicts some of these models. A conventional representation of a micelle is that by Hartley (Fig. 27) and is more useful for visualization.

Micelles do not exist at all concentrations and temperatures. There is a very small concentration range below which aggregation to micelles is absent and above which association leads to micelle formation. This concentration range is called critical micelle concentration (CMC). The number of molecules that aggregate to form micelles is called the aggregation number. The structure, aggregation number and critical micelle concentration are all dependent on the nature of the hydrocarbon chain, counterions, electrostatic interactions, temperature and added electrolytes.

Though micelles provide a microscopically heterogeneous environment, they are generally small enough for the macroscopic properties to approximate to those of truly homogeneous solutions. Moreover, the surfactant molecules are in dynamic equilibrium either between two micelles or between a micelle and bulk water. The hydrophobic interior of a micelle provides a restricted volume of hydrophobic space in an aqueous environment. Organic substrates, due to their hydrophobicity, would tend to get solubilized inside the micelles. The site of solubilization may either be the micellar core or the interface or the substrate may penetrate to a particular depth into the surface layer. An amphiphilic solute may be oriented with its polar portion in the surface layer and its non-polar

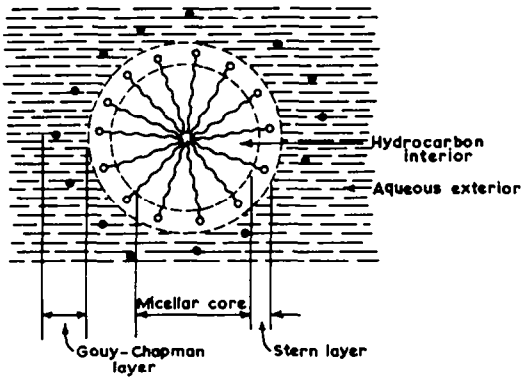


Fig. 27. Hartley model of a spherical micelle.

portion in the hydrophobic region of the micelle. Depending on the site of solubilization and the nature of permissible interactions, the reactivity of the substrate will be modified. The effects that are generally imposed by solubilization can be categorized as cage, preorientational, localization, microviscosity, polarity and counterion effects.[183]

6.2.1. *Cage effect.* The solubilization of organic molecules in micelles would modify the dynamics of the substrate in a unique way that is not feasible in homogeneous solutions. Since hydrophobicity of the solute is the driving force for the solubilization inside the micelles, the substrate should overcome the hydrophobic barrier in order to diffuse out of the micelle and this would impose a restriction on the exit of the substrate from the micelle. Hence, the time spent by the solute (reactants or intermediates derived from them) inside the restricted volume of the micelle would be higher. In other words, micelles have the capacity to hold two reactive species together for a longer period of time in comparison with homogeneous solutions. Due to the increase in the time spent by the reactive species or intermediates together inside the restricted space of the micelle, the probability of reaction between the reactive species is increased. The ability of micelles to hold two reactive intermediates together long enough for reaction to occur between them is termed the "cage effects". Micellar aggregates are very effective in imposing cage constraints on a reaction such as photofragmentation reaction and this might alter the reactivities of the substrate. However, this effect cannot be attributed to the higher microviscosity of the micellar aggregates since some reactions which do not lead to an increase in cage products even in highly viscous homogeneous media experience a marked cage effect in micellar microenvironments.

A pronounced cage effect was observed in the photodecarbonylation reaction of dibenzyl ketones.[184] The observed increase in the cage product AB during the photolysis of 3-(4-methylphenyl)-1-phenyl acetone (4-Me DBK) in hexadecyltrimethylammonium chloride (HDTCl) was attributed to the reaction occurring in micellar aggregates. The effect of microviscosity being responsible for the observed cage effect was ruled out because photolyses in media with varying viscosities covering the microviscosity range of micelles is reported to produce no cage effect. The profile of percent cage plotted against surfactant concentration (Fig. 28) flattens to constancy above CMC. It is to be noted that cage effect would be pronounced only if the micellar aggregate is not crowded with the substrate molecules. If the occupancy number, i.e. the number of molecules of the substrate per micelle is high, the probability of reaction between the radicals produced by cleavage of two substrate molecules present in the same micelle would be higher and would lead to a decrease in the cage product.[185] This is illustrated by the analysis of the cage effect observed during the photolysis of 4-methyl-4′-methoxydibenzyl ketone and 4-methylbenzyl-4′-methoxyphenyl acetate,

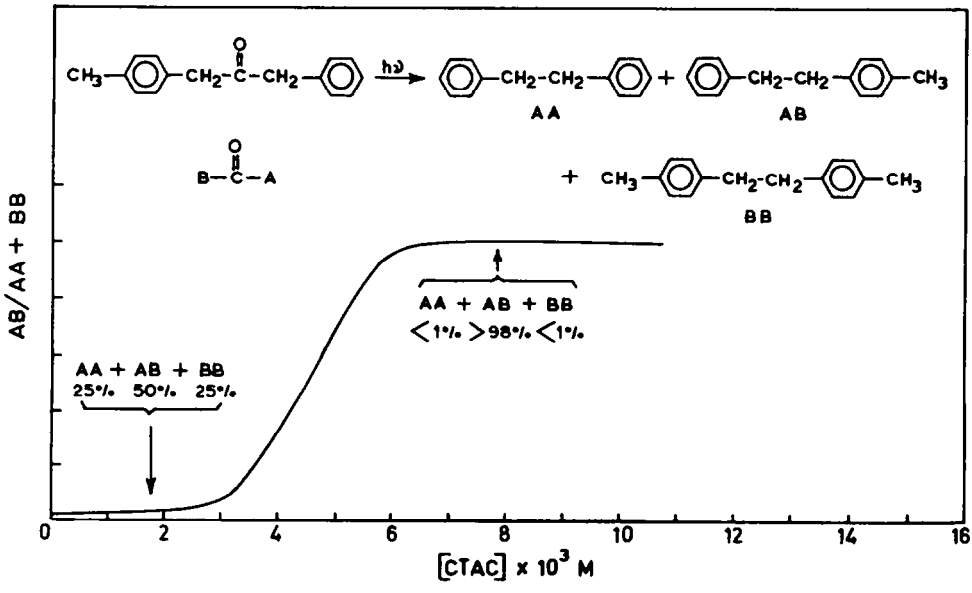


Fig. 28. Variation on the ratio of AB to the sum of AA+BB as a function of detergent concentration [*J. Am. Chem. Soc.* **100**, 7431 (1978)].

Table 8. Dependence of cage effect on occupancy number in micelles: photolysis of 4-methyl, 4′-methoxy dibenzyl ketone and 4-methylbenzyl-4′-methoxy phenyl acetate in potassium dodecanoate micelles (0.08 M)[a]

Substrate	Conc. (mM)	Ratio of AA	AB	BB
(1) 4-Methylbenzyl-4′-methoxy phenyl acetate	0.76	1	72	1.1
	1.21	1.4	44	1.0
	2.02	1.2	26	1.0
	3.00	1.1	15	1.0
(2) 4-Methyl,4′-methoxy dibenzyl ketone	0.60	1.4	14	1.0
	0.83	1.2	7.5	1.0
	1.01	1.0	6.4	1.2

[a] Adopted from: D. Avnir, L. J. Johnston, P. de Mayo and S. K. Wong, *J. Chem. Soc. Chem. Commun.* 958 (1981).

at various concentrations of the substrates corresponding to different occupancy numbers (Table 8).

The influence of detergent chainlength and charge on the cage effect was investigated by Turro and Weed.[186] Based on the results obtained for the photodecarbonylation of 4-Me DBK in sulfate detergents of chainlengths 6–14 methylene units they inferred that the radical escape is inversely proportional to the hydrophobic size of the micelles. In this reaction, the charge on the detergent was found to play a minor role since the cage effect was observed to be the same in two micelles of almost the same size, namely, cationic dodecyl trimethylammonium chloride and anionic sodium dodecyl sulfate (SDS).

The hydrophobicity of the substrate is one of the determining factors in the average solubilization site of substrates in micelles. A variation in the hydrophobicity of the substrate would be expected to alter the rate of escape of the geminate radical pairs from micelles since the radical pairs generated at the interior of the micelles would have to traverse a longer distance or should have to overcome a greater barrier in order to escape from the micellar cage. The increase in percent cage experienced by the secondary radical pairs produced by the photolyses of various substituted dibenzyl ketones in micellar HDTCl correlated very well with the hydrophobicity of the dibenzyl ketones (Table 9).[187]

The role of radical pair lifetimes in controlling the cage reactions is exemplified in the comparative studies of the photoextrusion reactions of dibenzyl ketones, esters and sulfones. Due to solubilization the cage product AB is formed preferentially in micelles and the percent cage effect is a measure of the ability of micelles to hold the geminate radical pairs together. During the photolyses of dibenzyl ketones (DBK), sulfones (DBS) and esters (DBE) the secondary radical pairs produced after extrusion of either carbonmonoxide, sulfur dioxide or carbon dioxide would be the same and hence any difference in the observed cage effect should be due to the differences in the reactivities of the primary radical pairs. The percent cage effect for 4-Me DBK in micellar SDS was only 35% while that for 4-Me DBS was $\simeq 82\%$.[188] One probable reason for this variation could be the difference in CO and SO_2 extrusion rates. The rate constant for CO extrusion is $6 \times 10^6\ s^{-1}$ whereas that for SO_2 elimination is $\simeq 10^8\ s^{-1}$. A comparison of these rate constants with the rate constant for exit from

Table 9. Dependence of cage effect[a] on the hydrophobicity of the dibenzyl ketone in HDTCl micelle[b]

Ketone	Cage effect (%)
DBK	33
4-Methyl DBK	59
4-Cl DBK	52
4-Br DBK	70
4,4′-di-t-butyl DBK	95

[a] Cage effect refer to the efficiency of combination of geminate benzyl radical pairs.

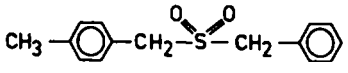
[b] Adopted from: N. J. Turro and G. C. Weed, *J. Am. Chem. Soc.* **105**, 1861 (1983).

micelles ($\simeq 10^6\ s^{-1}$) reveals that the secondary radical pairs produced by SO_2 extrusion would be closer to each other than those produced by CO extrusion. Hence intramolecular cage reaction would occur to a greater extent in DBS derived radicals. The variation in the observed cage effects in these two reactions can also be attributed to the existence of singlet state reactivity in DBS. At this juncture it is to be noted that the cage products obtained by CO_2 extrusion from 4-methylbenzyl-4′-methoxy phenyl acetate in sodium dodecanoate was $\simeq 97\%$ when the occupancy number was 0.64 while that for the corresponding ketone in the same micellar solutions at a comparable occupancy (0.61) was only 77%.[185] Thus the importance of spin multiplicities and the lifetimes of the radical pairs is demonstrated.

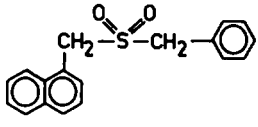
The chemistry of benzylic radical pairs in micellar media is expected to be dependent on the spin multiplicity of the radical pairs.[189] The applied magnetic field would split the triplet energy levels and would lift the degeneracy of the three triplet states. This would result in a decrease in the intersystem crossing efficiency from the triplet radical pair to the singlet radical pair prior to extrusion. The decreased efficiency of intersystem crossing would increase the lifetime of the triplet radical pair and hence would allow more time for the escape of the radicals from micelles. This is reflected on the decreased cage effect during the photoextrusion of CO and SO_2 from several dibenzyl ketones and dibenzyl sulfones in micellar HDTCl solutions in the presence of an external magnetic field (Table 10).[188,189]

An interesting consequence of the cage effect in micelles is the ^{13}C enrichment in reactants in radical pair reactions.[190] For example, the photolysis of DBK proceeds via an initial triplet pair ^3D. Intersystem crossing of the triplet radical pair would be facilitated by nuclear hyperfine interactions which is feasible when the carbonyl carbon is ^{13}C. Hence hyperfine radicals with ^{13}C would undergo efficient intersystem crossing giving rise to the singlet radical pair that could undergo recombination to either the starting ketone or the rearranged ketone whereas geminate pairs with ^{12}C nuclei would have a longer lifetime and would escape as free radicals in a facile manner (Scheme 64). As a result, during the photoreaction the starting ketone would be enriched in ^{13}C and the extent of enrichment is a measure of cage effect and hyperfine coupling constant. This was indeed observed and the enrichment parameter for DBK was as high as 1.68 in HDTCl, the cage constraints imposed by micelles being much greater than those in silica gel and liquid crystals.

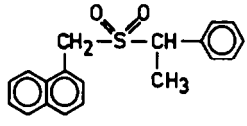
Chart 2. (For Table 10.)



Sulfone 1



Sulfone 2



Sulfone 3

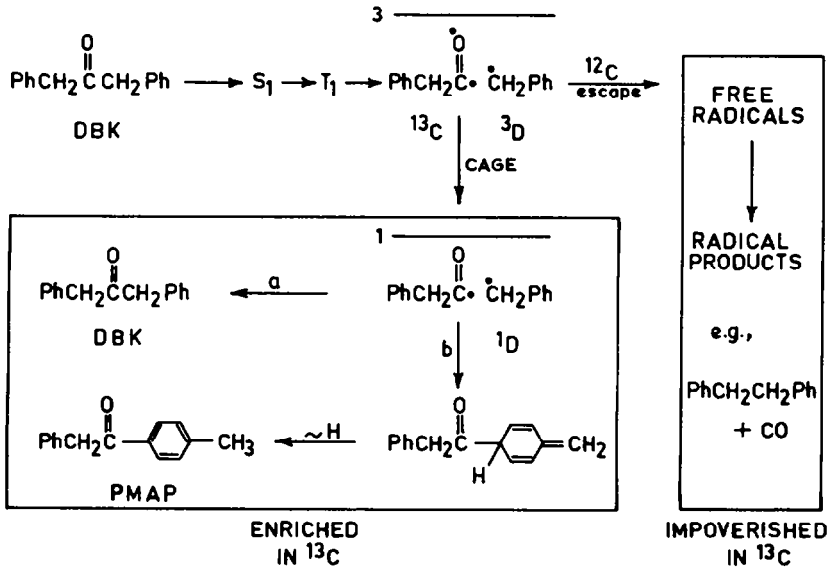
Table 10. Effect of external magnetic field on the cage effects in SDS micelles[a]

Compound	Cage effect 0 Field (%)	Cage effect External field[b] (%)
Sulfone 1[c]	82	40
Sulfone 2	82	45
Sulfone 3	82	45
DBK	31	16
4-Me-DBK	52	31
4,4′-di Me-DBK	59	31

[a] Adopted from: I. R. Gould, C. H. Tung, N. J. Turro, R. S. Givens and B. Matuszewski, *J. Am. Chem. Soc.* **106**, 1789 (1984); N. J. Turro and G. C. Weed, *Ibid.* **105**, 1861 (1983).

[b] External magnetic field for sulfones 3 KG; for ketones: 13 KG.

[c] For structures see Chart 2.



Scheme 64.

The study of benzoquinone and naphthaquinone photolyses[191] in micellar aggregates revealed that the escape of quinone radicals from the micellar core is competing with the intersystem crossing of the triplet radical pair $\overline{QH^{\circ}\ {}^{\circ}S}$ produced by hydrogen abstraction from the micelle by the excited quinone triplet. The product formed by intersystem crossing within the micellar super cage is the semiquinone–surfactant adduct. A similar adduct was also reported in benzophenone photolysis.[191] Efficient intersystem crossing in the micelle sequestered $\overline{BPH^{\circ}\ S^{\circ}}$ radical pairs resulted in products in which the benzophenone is attached to the detergent backbone.

Another consequence of cage effect is reflected in the photoreactivity of benzoin ethers.[192] In organic solvents benzoin ethers undergo facile Norrish type I reaction leading to benzil, pinacol ether and benzaldehyde as discussed in Section 3.5. The conformations suitable for Norrish type II hydrogen abstraction are not attainable in organic solvents whereas in micelles as in β-cyclodextrin and in silica gel type II reaction does occur. The contributing factors for this would be the reduction in the efficiency of the type I process and a variation in conformer populations. The efficiency of the type I process would be reduced because of the cage constraints holding the geminate radical pairs together. This is indeed demonstrated by the reduction in type I products with an increase in the hydrophobic size of the micelles (Table 11). Moreover, the solubilization inside the micelles

Table 11. Micellar effect on Norrish type I and type II reactions of benzoin methyl ether[a-c]

Medium	Occupancy number	60	59	63	62	61
Benzene	—	65	1	—	—	—
Methanol	—	35	1	—	—	—
SDS	0.5	33	—	12	7	—
	1	24	—	12	6	—
	2	35	—	14	7	—
DTAB	1.0	37	—	6	6	—
DTAC	1.0	30	—	5	5	—
CTAB	0.5	6	—	3	47	6
	1.0	12	—	3	42	5
	4.0	24	—	4	18	—
CTAC	0.5	7	1	1	61	7
	1.0	8	7	4	51	4
	4.0	27	—	4	27	2

[a] Unpublished results of S. Devanathan.

[b] Yields of benzaldehyde and benzoic acid derived from benzoyl radical are not included as accurate determination was not possible under our condition.

[c] For structure of products see Scheme 52.

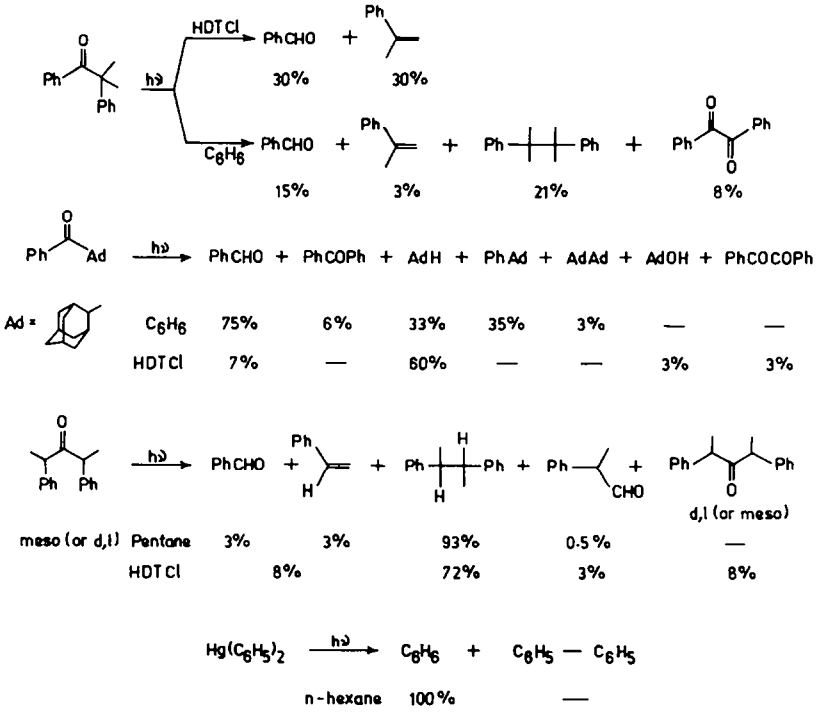
might demand the two oxygens, i.e. the carbonyl oxygen and alkoxy oxygen, to point towards the interface and hence might populate the conformers favourable for type II hydrogen abstraction. These effects are very clearly illustrated by the data presented in Table 11.

Yet another reaction wherein radical pairs are generated and the micellar cage effect is observed is the photo-Fries rearrangement of aryl esters.[193] The reaction that is sluggish in organic solvents with unidentifiable by-products and phenol contributing considerably is modified into a clean reaction that proceeds at a greater rate in micelles. Several other examples wherein cage constraints imposed by micelles modify the reactivities of the solubilized substrates are assembled in Scheme 65.[194]

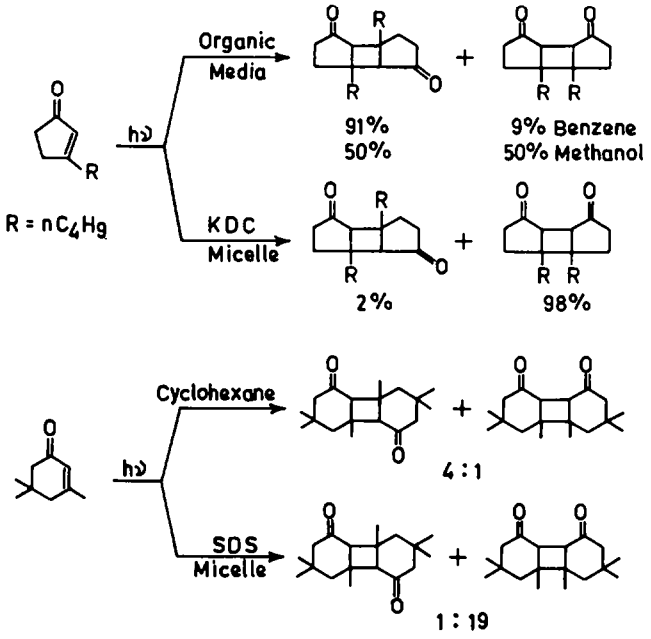
6.2.2. *Pre-orientational effect.* There are a number of evidences for site specific solubilization. For example, alkyl substituted benzenes and naphthalenes with longer alkyl chains are shown to have greater tendency to reside in the micellar core and aromatic compounds with polar substituents have a tendency to reside at the micelle–water interface with the polar substituent pointing towards the interface.[195] Thus, depending on the hydrophobicity of the substrate and other interactions of the substrate with micelles, the substrates occupy, on average, a specific site with a specific orientation. The capability of micelles to solubilize substrates in a specific orientation is called the "pre-orientational effect". The alignment of substrates in the micellar aggregates might restrict the randomnesss in the approach of reactants in bimolecular reactions and hence might lead to regioselectivities.

Micellar pre-orientation has been shown to have a profound influence over the photochemical dimerization of 3-alkylcyclopentenones.[196] Efficient dimerization in potassium dodecanoate micelles was observed for 3-n-butyl- and 3-n-decylcyclopentenones with a reversal in regiochemistry in comparison with that in organic solvents (Scheme 66). Almost exclusive formation of head–head dimers was attributed to the favourable orientation of cyclopentenone with the carbonyl oxygen at the interface while the remaining hydrophobic portion is oriented away from the interface penetrating the micellar structure. Similar orientation of isophorone[197] and coumarins[179] resulted in high regioselectivities (Schemes 62 and 66).

The *syn* head–head dimer of coumarin was the exclusive product in micellar sodium dodecyl sulfate (SDS). The formation of the *syn* head–head dimer and the absence of triplet state reactivity



Scheme 65.



Scheme 66.

was well accounted on the basis of orientations at the interface. However, it is to be noted that in all the above-mentioned cases, an increase in polarity would also induce similar trends in the variation in product distributions though not to such an extent.

The preferential orientation effect of micellar aggregates is also reflected in the photodimerization of 2-substituted naphthalenes such as 2-methoxynaphthalene.[198] The methoxy oxygen would be present at the interface (Fig. 29) and this would prevent the *trans* orientation of two naphthalene units that is thermodynamically favourable during dimerization. Hence, the *cis* adducts or products derived from them are exclusively formed in micellar aggregates while the *trans* dimer is the major product in organic solvents and this effect is independent of the charge on the micelle (Scheme 67). Favourable head–head dimerization was also encountered in 9-substituted anthracenes in micellar solutions of CTAB, CTAC and SDS when the 9-substituent is a polar one such as hydroxymethyl (Scheme 68).[199] This was attributed to the pre-orientation of the substrate in such a way that the polar group would be predominantly directed towards the micelle–water interface and the electrostatic repulsion between the *syn*-oriented monomers would be partially compensated by the interface.

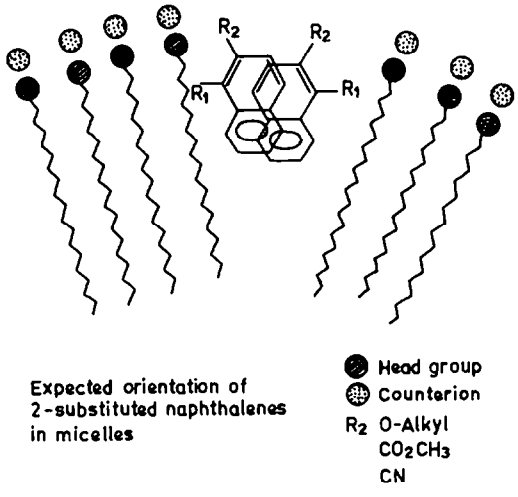
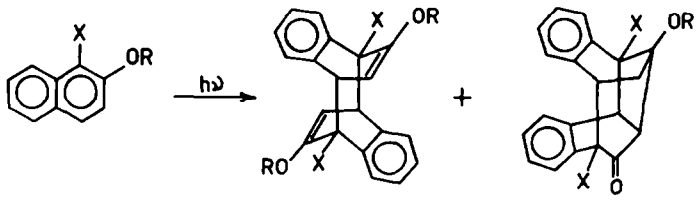
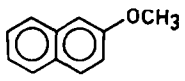
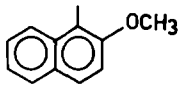


Fig. 29. Suggested arrangement of 2-substituted naphthalenes in micelles.





Benzene	80	—
SDS	—	60
CTAB	—	30
CTAC	—	71
DTAC	—	67

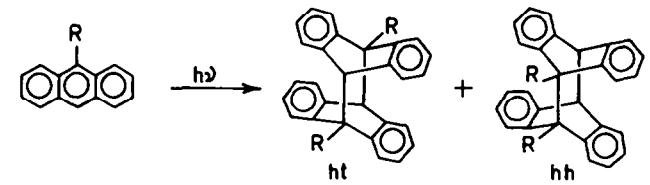


Cyclohexane	50	45
SDS	—	45
CTAB	—	12
CTAC	—	61
DTAC	—	65

Scheme 67.

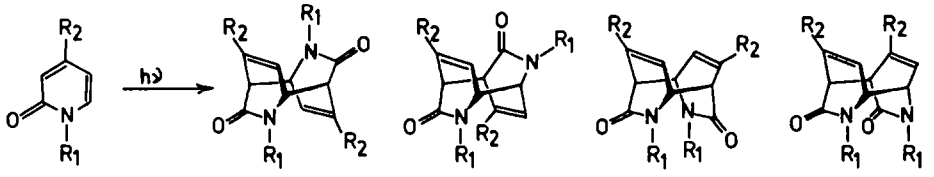
Micellar pre-orientation is responsible for the reversal in regiochemistry in the [4+4] photocycloaddition of 2-pyridones also.[200] In homogeneous solutions 2-pyridones give *trans* dimers as the major product and no dependence on the substituent chainlength was noticed in the *cis/trans* ratio. Whereas in hexadecyl trimethylammonium bromide (HDTBr) depending on the chainlengths of R^1 and R^2 a variation in the *cis/trans* ratio was noticed. In cases where the substituent chainlengths favoured the monomer localization and orientation, complete reversal in regioselectivity was reported (Scheme 69).

Regioselectivity was induced not only in photodimerization reactions but also in photocycloaddition reactions of olefins to 3-alkyl cyclopentenones.[201] Photocycloaddition of 3-n-butylcyclopentenone in the presence of an excess of 1-hexane and 1-octene in organic solvents gave two adducts **99** and **100**. The ratio, which was slightly solvent dependent was roughly 1 : 1 (Scheme 70). However, irradiation in KDC micelle gave preferentially **99**. These results are consistent with the simplified model shown in Fig. 30 in which the cyclopentenone is oriented in the micelle with the polar carbonyl function in the interface and the hydrophobic butyl chain in the micelle interior. Similarly, the hydrophobic alkene is mainly incorporated into the relatively non-polar micelle interior. The orientation of the olefin was further fixed by the introduction of acetoxy group. Under these conditions, a more pronounced effect of the micellar environment upon cycloaddition



Medium	R = CH_2OH	R = CH_2CH_2COOH	R = COOH	R = CH_3
	Φ ht/hh			
Diethyl ether	1.2	3·5	4.9	1.5
Methanol	3·2	8·9	4·8	2.0
CTAC	0·76	1·9	—	1·7
CTAB	0·76	1·4	—	1·5
SDS	0·67	0·91	1·4	1·7

Scheme 68.

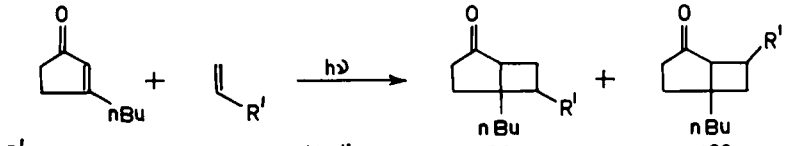


		trans-anti	trans-syn	cis-anti	cis-syn
$R_1 = (CH_2)_2COOH$, $R_2 = H$	EtOH	85%	0%	15%	0%
	H_2O	79	0	8	13
	CTAB	51	0	23	26
$R_1 = (CH_2)_{10}COOH$, $R_2 = H$	EtOH	81	0	19	0
	H_2O	66	0	18	16
	CTAB	70	0	15	15
$R_1 = (CH_2)_2COOH$, $R = C_3H_7$	EtOH	100	—	—	—
	H_2O	48	24	14	14
	CTAB	0	0	65	35

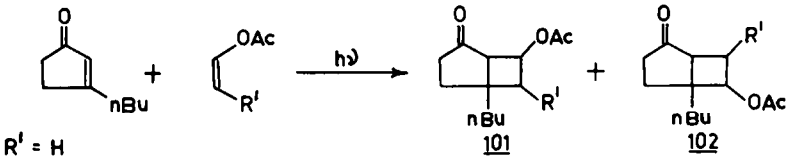
Scheme 69.

regiochemistry was observed. For example, 1-heptenyl acetate in organic solvents gave **102** exclusively, whereas in micelles **101** was obtained as the sole product (Scheme 70). This example convincingly illustrates that by careful manipulation and choice, it is possible to direct photocycloadditions to yield products of desired regiochemistry.

In order to obtain reversal in regiochemistry by the pre-orientational effect of micellar aggregates it is essential that the forces that control regiochemistry should be weaker than the orientational effect. In the cases of dimerization reactions discussed above polarity effects and pre-orientational



	Medium	99	100
$R' = C_4H_9$ 1-Hexene (97)	cyclohexane	51	49
	diethyl ether	57	43
	KDC micelle	78	22
$R' = C_6H_{13}$ 1-Octene (98)	cyclohexane	53	47
	diethyl ether	47	53
	KDC micelle	88	12



		101	102
$R' = H$ Vinylacetate	cyclohexane	25	75
	diethyl ether	26	74
	KDC micelle	51	49
$R' = C_5H_{11}$ 1-Heptenyl acetate	Methanol	0	100
	cyclohexane	0	100
	KDC micelle	70	30

Scheme 70.

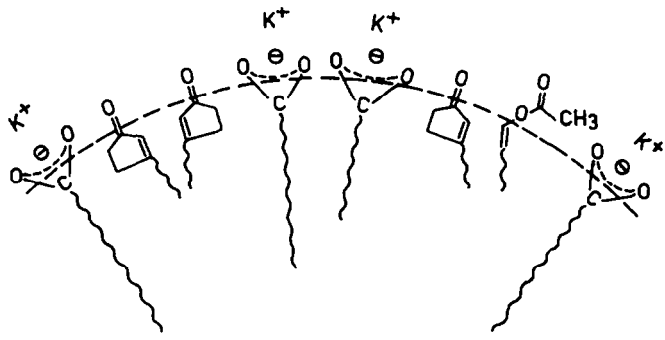


Fig. 30. Possible arrangements of enones and olefins in micelles.

effects acted in an additive fashion and hence no controversial results were obtained. In order to establish the pre-orientational effect unequivocally the photochemical dimerization of 7-alkoxy-coumarins, a reaction that is insensitive to polarity effects was studied.[202] Expected reversal in product distribution giving rise to the *syn* head–head dimer was not observed for any of the coumarins investigated. If the forces that control the regiochemistry of additions are stronger than the hydrophobic association energies, realignment of molecules overcoming the hydrophobic barrier may be feasible (Fig. 31). Another plausible explanation may be that the preference for alkoxy oxygen to remain closer to the Stern layer while the alkyl chain still coils into the micellar interior may create a competition between the carbonyl oxygen and alkoxy oxygen to occupy the interface due to which the orientations favouring both *syn* head–head and *syn* head–tail may be feasible and thermodynamically more stable *syn* head–tail may be formed in higher yields. Regiochemistry of dimerization could not be predicted correctly for 9-methyl anthracene also.[199] While *cis* fused adducts were formed for some 4-substituted anthracenes, 9-methyl anthracene gave rise to the head–tail dimer in greater yield (Scheme 68) in micellar solutions of potassium dodecanoate. This might probably be because of the absence of a polar group in the substrate to orient it at the interface. This along with the greater ease of reversal of the head–head dimer was expected to be responsible for the observed effect.

6.2.3. *Effect of microviscosity.* Due to the hydrophobic association of surfactants in water, the micelles would contain closely packed surfactant molecules. Hence the viscosity inside the micelles would be very much higher in comparison with the surrounding aqueous medium. Because of the

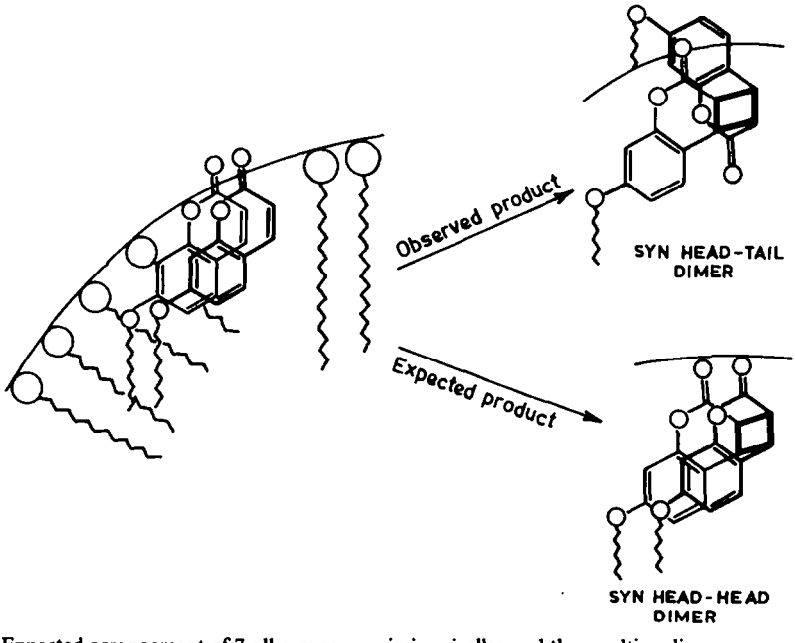
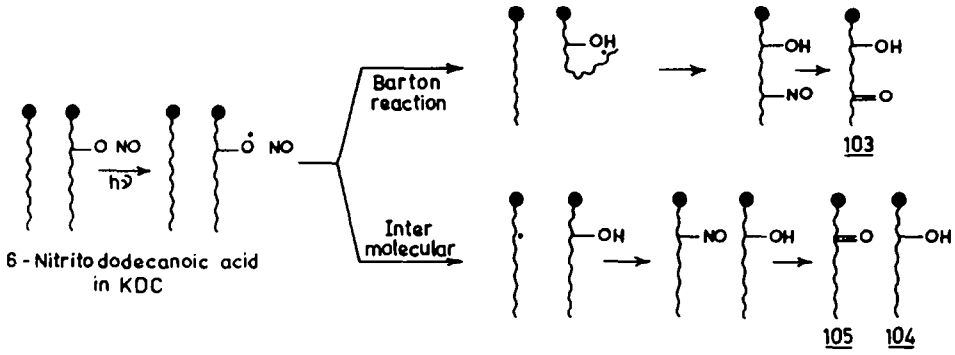


Fig. 31. Expected arrangement of 7-alkoxy coumarin in micelles and the resulting dimers upon photolysis.



Medium	103	104	105	103/105
n-hexane	40%	4.8%	12%	8.3
hexadecane	13	17	15	0.87
KDC micelle	5.4	16	39	0.14

Scheme 71.

unusually high microviscosity of the micellar medium a substrate molecule incorporated in micelles would have lesser translational and rotational freedom and this might be reflected in the chemical reactivity of the substrate.

Law and de Mayo investigated the photolysis of alkyl nitrites in micellar potassium dodecanoate.[203] The Barton product **103** (Scheme 71) is a consequence of intramolecular hydrogen abstraction from the δ-position while products **104** and **105** are due to intermolecular hydrogen abstraction (Scheme 71). It was reported that in micelles the proportion of Barton's product decreased. A similar effect was observed in homogeneous organic solvents accompanying a viscosity increase. Hence a decrease in Barton's product was attributed to the microviscosity of the micellar medium preventing the conformational flexibility of the alkyl chain in order to achieve the required geometry for intramolecular hydrogen abstraction.

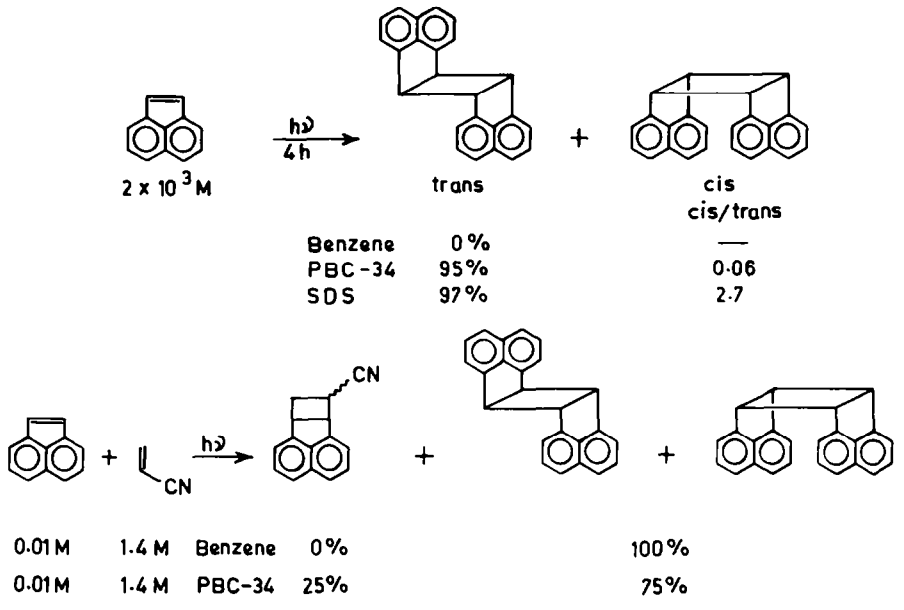
The microviscosity effect is also expected to influence the *trans–cis* isomerization rates of surfactant stilbenes.[204] It was observed that the quantum yield of *trans–cis* isomerization decreased from 0.5 in CH_2Cl_2 to 0.39 in HDTBr while the fluorescence quantum yield increased from 0.04 in CH_2Cl_2 to 0.18 in HDTBr. These effects are similar to the viscosity effects observed for stilbene and hence were attributed to the microviscosity of the micellar aggregates. An increase in the fluorescence quantum yield, due to microviscosity, was also noticed in cyanine dyes in SDS micelles.[205]

6.2.4. *Local concentration effect.* The tendency of organic substrates to get solubilized in micelles due to their hydrophobicity would result in partitioning the substrate between micelles and water. Most of the organic molecules would occupy the small volume of the micellar aggregates. This would increase the concentration of the substrate per unit volume of the micelle enormously and would promote the probability of encounters between two molecules. Due to this effect up to 1000 fold rate enhancements can be anticipated and there are indeed several examples where this effect is exploited successfully. Most of the bimolecular reactions which are not feasible in organic solvents at low concentrations can be performed at such concentrations in micellar solutions.

Photodimerization of acenaphthylene is an illustration of this effect. At acenaphthylene concentrations as low as 2×10^{-3} M, facile dimerization ($\sim$95%) takes place in micellar aggregates of anionic SDS or nonionic PBC-34 whereas at this concentration no dimerization occurs in organic solvents (Scheme 72).[206] Similarly, photocycloadditions of acrylonitrile and methyl acrylate to acenaphthylene were effected in nonionic PBC-34 in competition with dimerization while no cycloaddition was observed under the same conditions in organic solvents (Scheme 72).[207]

It is interesting to note that photodimerization of cinnamates competes with isomerization only in micellar and aqueous media.[178] Rate enhancements are also observed in many other photodimerization reactions such as coumarin dimerization.[179]

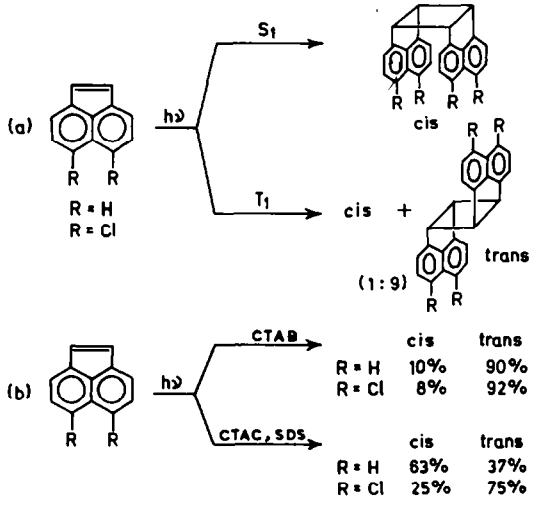
6.2.5. *Miscellaneous effects.* The Stern layer of an ionic micelle would consist of the counterions in addition to the charged head groups and the reactivities of substrates at the interface, if dependent on counterions, would be modified. For example, heavy atoms, if present as counterions, are known



Scheme 72.

to modify singlet–triplet intersystem crossing efficiencies resulting in changes in reactivities. This effect is exemplified in the photodimerization of acenaphthylenes.[208] As discussed earlier (Sections 4 and 5), the singlet state reaction leads exclusively to *cis* dimer formation while the triplet reaction gives rise to a mixture of *cis* and *trans* dimers. It was reported that the *cis/trans* ratio of acenaphthylene dimers was reduced considerably in micellar HDTBr when compared to that in micellar HDTCl under identical conditions (Scheme 73) and this was attributed to the promotion of the triplet state reactivity by the bromide counterions. Bromide ions are known to increase singlet–triplet intersystem crossing efficiencies via intermolecular spin–orbit coupling. A similar increase in the triplet state reaction was observed in micellar HDTBr for the dimerization of 5,6-dichloroacenaphthylene. However, it is to be noted that not all reactions with competing singlet and triplet reactivities would be modified in a similar fashion. Note must be taken of the modifications in the relative intersystem crossing efficiencies between $S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$.

The Stern layer of ionic micelles would be richer in the charge of the surfactant molecules due to equilibration of counterions between the Stern layer and the bulk solvent. The electrically charged interface can alter the reactivities of micelle solubilized substrates with an ionic reagent in the



Scheme 73.

aqueous exterior. For instance, an anionic detergent would enhance the reactivity of the substrate with a cationic species while a cationic surfactant would have an opposite effect.

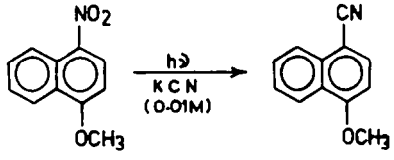
The effect of micellar charge is manifested in the photochemical aromatic substitution reaction of 4-methoxy-1-nitronaphthalene[209] and in the photorearrangement of 4-nitrophenylnitromethane.[210] The substitution of the nitro group by a cyano function was enhanced drastically by 6800 fold in the cationic surfactant HDTCl while it was decreased by the anionic micelles of SDS (Scheme 74). The electrostatic attractive interaction between the cationic HDTCl and the cyanide anion is responsible for the tremendous increase in the quantum yield. Similarly, the anionic intermediate in the photorearrangement of 4-nitrophenylnitromethane would be stabilized by the cationic micelles in addition to the increased probability of attack by OH^- on the substrate (Scheme 74) thus accounting for the observed 20 fold increase in reaction rate in micellar HDTBr relative to water.

In this context, *cis–trans* isomerization of N-methyl-4-(β-styryl)pyridinium halides by electron-transfer sensitization using $Ru(bpy)_3^{2+}$ in micellar SDS is worthy of mention.[211] The charged substrate, because of the electrostatic attraction would be present at the interface of the anionic SDS and due to the same favourable interaction$Ru(bpy)_3^{2+}$ would populate the Stern layer. This would decrease the barrier for reaction between the two positively charged species and increase the probability of the electron-transfer reaction. The establishment of facile equilibrium increases the efficiency of the relay mechanism in electron-transfer and thus explains not only the increase in quantum efficiency but also the quantum yield which has a value greater than unity in the formation of the *trans* stilbazole salt. The quantum chain process facilitated by this micelle is illustrated in Scheme 75.

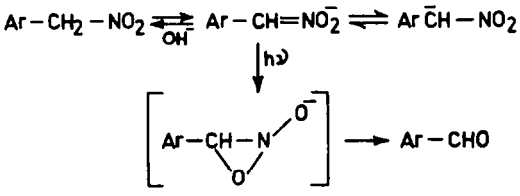
Thus, the heterogeneous micellar environment can influence a variety of chemical reactions by modifying the reaction conditions in a manner that is not feasible in homogeneous solutions.

6.3. *Studies in microemulsions*

Microemulsions are true dispersions of one liquid within another. They are considered to be stable, optically transparent, monodisperse droplets of oil in water or of water in hydrocarbon, having diameters in the range of 50–1000 Å. Microemulsions have not been as well characterized as have micelles. Nevertheless, they are slowly finding use as a medium for photochemical reactions. A common feature between micelles and microemulsions that allow for selectivity in photoreactions is that these two provide an interfacial region between an aqueous and a non-aqueous phase wherein reactive molecules can be aligned. This interfacial alignment has been used by Lattes and co-workers to achieve regiochemical selectivity during photodimerization of isophorone[197] and

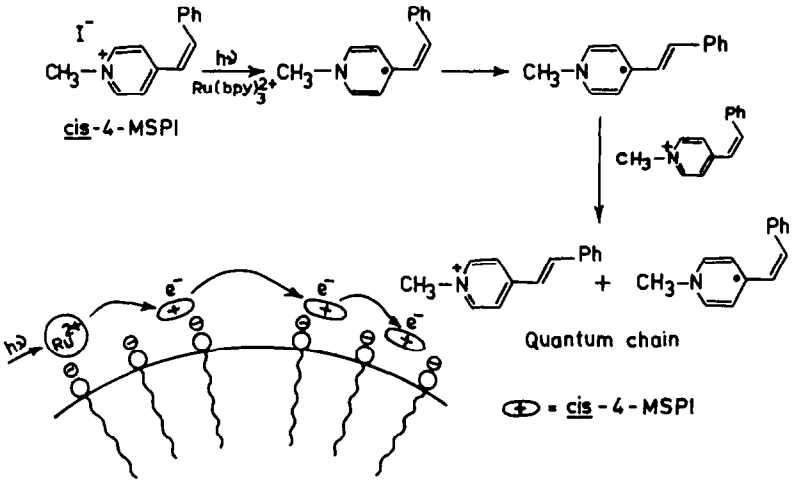


Φ (H_2O) = 1.9×10^{-5}
Φ (HDTCl) = 0.13
Φ (SDS) = 0



Φ_{CTAB}/Φ_{H_2O} = 20

Scheme 74.



Micelle	$\Phi_{c \rightarrow t}$
SDS	64
STS	86
DTAB	0.73
Water	0.58

Scheme 75.

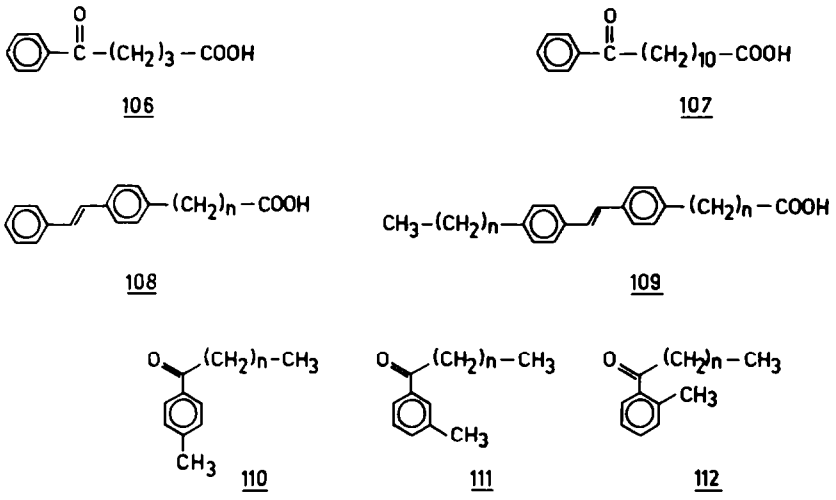
coumarin.[212] Microemulsions formed by a combination of water, cyclohexane, SDS and 1-butanol have been used as the medium for the above reactions. Isophorone which photodimerizes preferentially to the head–tail isomer in cyclohexane (HH/HT: 1/9) gives the head–head isomer in microemulsions (HH/HT: 19/1). A similar observation has been made with coumarin. The head–head dimer is the only one formed in microemulsions. This dramatic reversal in selectivity has been attributed to the orientation and concentration of molecules in the interfacial region. Geometric isomerization of the *o*-methyl ether of the oxime of 2-acetylnaphthalene has also been reported to be influenced by microemulsions.[213]

An improved understanding of the characteristics of microemulsions is needed before they can find extensive use as the reaction medium. Examples reported so far establish that they bring about similar selectivity as micelles in cycloaddition reactions. However, micelles are much easier to make and are better characterized.

6.4. *Cyclodextrin as the hydrophobic reaction cavity in water*

In contrast to the clathrates, which exist only in the solid state (Section 3) and in which the guest molecules are included in cavities or cages provided by the crystalline structure of the host, both amylose and cyclodextrins form inclusion compounds that are stable in solution as well as in the solid form. In solution, a single molecule provides the cavity in which the guest molecules are bound. The helical configuration of the high polymeric amylose molecule which gives rise to the cavity structure is stabilized only by hydrogen bonds as contrasted to the primary bonded cyclic structure of the cyclodextrins. For this reason amylose complexes may be expected to be less stable in solution than the cyclodextrin complexes. It is important to note that the reactions which involve molecular complexes in solution can be complicated by the fact that the complex is in equilibrium with the free species. Therefore to realize the total effect it is essential to use excess host to fully complex the guests.

Whitten and co-workers[214] have recently investigated the photobehaviour of amphiphilic ketones **106** and **107** and surfactant stilbenes **108** and **109** (Scheme 76) using amylose and carboxy methyl amylose as hosts in water. These studies have established that these host systems reduce the conformational mobility of the guest ketones and stilbenes in the ground and excited states. The type II quantum yield of ketones **106** and **107** is reduced to 0.14 from 1.0 upon 100% complexation with carboxymethyl amylose. Similarly, the quantum yield of *trans* to *cis* isomerization of **108** and **109** is reduced with a concomitant increase in the fluorescence yield.



Scheme 76.

Figure 32 illustrates how the *o*-, *m*- and *p*-isomers of aromatic compounds are believed to bind to cyclodextrin. This variation in the geometry of the complex, also responsible for the difference in the binding strength, can be expected to bring about a remarkable difference in selectivity in product distribution and reactivity of the bound substrates. A good example of this is the classic work by Bender and co-workers[215] on the hydrolysis reactions of *m*- and *p*-alkyl phenyl acetates. This naive approach has enabled us to achieve product selectivity during photo-Fries and photo-Claisen rearrangements. Photo-Fries rearrangement has been discussed in detail in Section 3 (Schemes 38–40) Selectivity similar to solid complexes could be achieved with high concentrations of β-cyclodextrin also in aqueous media. Although earlier studies, which used less than a molar equivalent of cyclodextrin reported *para* selectivity[216] complete complexation of the substrate with excess β-cyclodextrin resulted in the expected *o*-isomers in near quantitative yields.[110] Interesting observations were made during the photolysis of *m*-alkoxy phenyl allyl ethers in β- and α-cyclodextrin (Scheme 77).[217] The ratio of the two *ortho* products was dependent both on the size of the substrate and that of the host cavity suggesting that, subtle and rationale engineering manipulation is required to achieve the goal, namely, the exclusive obtention of one *o*-isomer. A preliminary and less refined model at this stage is that the α-cyclodextrin provides a "tight fit" while β-cyclodextrin offers a "loose fit". This tightness of binding is probably responsible for the selectivity among the *o*-isomers with α-cyclodextrin as the host. It is interesting to note that the "loose cavity" can be tightened by incorporating a "molecular spacer" such as a long hydrocarbon chain as an intramolecular appendix. The remarkable selectivity observed with long chain alkoxy phenyl allyl ethers in β-cyclodextrin is attributed to this phenomenon.

An observation which looks anamalous in the light of the above rearrangements is the formation of *p*-methyl α-phenyl acetophenones as the major product during the photolysis of dibenzyl ketones complexed to β-cyclodextrin in aqueous media. It is important to note that while irradiation of solid complexes (Schemes 36 and 37) yields AB as the main product, photolysis of dissolved complexes results mostly in rearrangement.[218] It is surprising that only the *p*-isomer is obtained although in principle both *o*- and *p*-isomers could be formed and have been isolated, during irradiation on silica

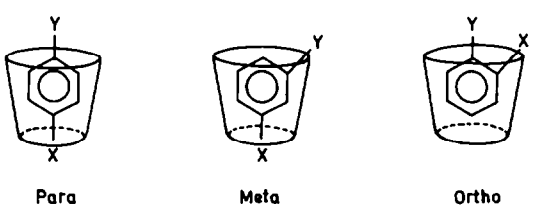
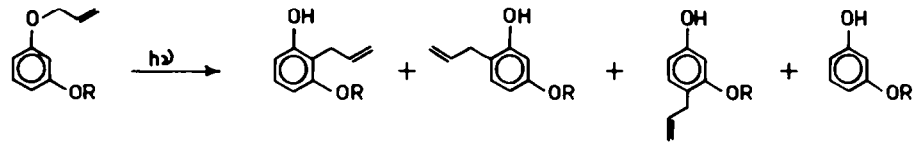


Fig. 32. A simplified comparison of how *o*-, *m*-, and *p*-disubstituted benzenes occupy the cyclodextrin cavity.

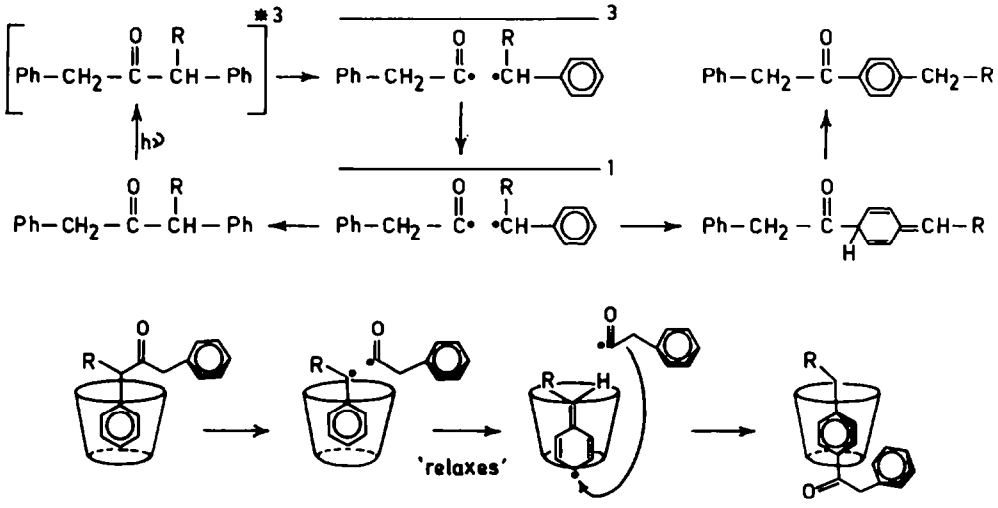


R = CH_3	Ethanol	22	28	31	19%
	Water	41	41	14	4
	α-cyclodextrin (1:10, aqueous)	23	69	8	—
	α-cyclodextrin (solid)	—	100	—	—
	β-cyclodextrin (solid)	62	30	8	—
R = $CH_2CH_2CH_3$	Ethanol	38	42	14	6
	Water	36	44	9	11
	α-cyclodextrin (1:10, aqueous)	18	72	5	5
	α-cyclodextrin (solid)	5	95	—	—
	β-cyclodextrin (solid)	51	49	—	—

Scheme 77.

gel and zeolite surfaces (Scheme 42). Based on the earlier observations with the photo-Fries and photo-Claisen rearrangements wherein the *o*-isomers were obtained in preference to the *p*-isomers, the above result is surprising. Could this be due to the differences in hydrophobicity of the aryl radicals (captured inside cyclodextrin)? The tolyl radicals generated by α-cleavage of dibenzyl ketones being more hydrophobic than the phenoxy and related radicals generated in the other two cases, probably relaxes deeper in the cavity thus exposing the backside (*p*-position) for the attack and protecting the *o*-position from the recombination with the acyl radical (Scheme 78). Although this explanation follows logic requires further support.

In the context of the geometry of the complex controlling the reactivity of the substrate, the recent reports by Liu and Weiss on the photosubstitution reactions of fluoroanisoles is worthy of mention.[219] Photohydroxylation and photocyanation of 2- and 4-fluoroanisole have been investigated in the presence of α- and β-cyclodextrin. Their results can be summarized as follows: complexation of 4-fluoroanisole by either α- or β-cyclodextrin results in an almost total loss of photoproduct formation. However, β-cyclodextrin complexation of 2-fluoroanisole inhibits photo-



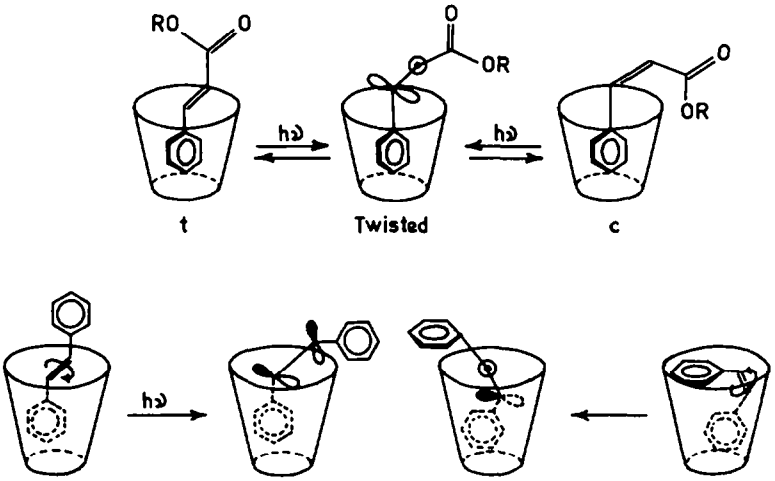
Scheme 78.

hydroxylation more than photocyanation while both are inhibited by α-cyclodextrin. These results have been rationalized on the basis of the difference in water structure near the site of attack in these two cases when present inside the α- or β-cyclodextrin. It is to be noted that the first step of the reaction involves an electron transfer between an excited and a ground state fluoroanisole. A decrease in reactivity would indeed be expected since such a bimolecular process between complexed fluoroanisoles would have poor efficiency.

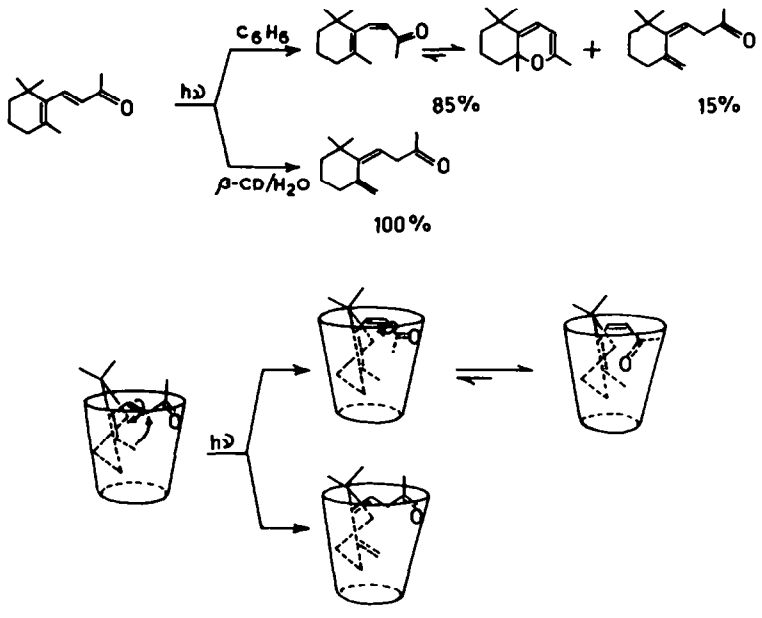
The examples discussed above illustrate that selective positions of the aromatic ring (complexed to cyclodextrin) could be protected from external attack and exclusively one isomer could be obtained as the product. The selective catalyses by cyclodextrin in these cases involve the control of orientation in the attack of one molecule (or fragment) on the other, that is bound to cyclodextrin. Cyclodextrin can also be expected to influence unimolecular reactions through restriction on rotational and translational motions of the substrates or the intermediates derived from them. A few examples of this effect are briefly mentioned below.

Norrish type II reactions of arylalkyl ketones, benzoin ethers and α-alkyl deoxy benzoins discussed earlier (Section 3, Schemes 32–37) fall under this category. In all of these cases, cyclodextrin controls the rotational motion of the diradical resulting from the hydrogen abstraction process. Results obtained in aqueous solution are similar to those in the solid state and therefore no further elaboration is needed. Preliminary results with ketones **110–112** suggest that the structure of the complex could enforce varying restrictions on the partitioning of the diradical intermediate.[220] The geometric isomerization of stilbenes was modified by β-cyclodextrin.[221] While in benzene, upon direct excitation the photostationary state of stilbenes **90–93** (Scheme 61) is heavily favoured with the *cis* isomer (~85%), excitation of cyclodextrin complexes of either *cis*- or *trans*-stilbene in aqueous medium resulted in a photostationary state enriched in the *trans*-isomer. Furthermore, the cyclization product of *cis*-stilbene, namely phenanthrene which is formed in detectable amounts in benzene solution was found to be absent during aqueous β-cyclodextrin irradiation. However, in the case of cinnamate esters the behaviour in solution and cyclodextrin were identical. The above results have been rationalized on the basis of the influence of the cyclodextrin cavity on the decay ratio of the twisted olefins (Scheme 79). Based on CPK molecular models one can visualize the structure of the cyclodextrin complexes of *cis*- and *trans*-stilbenes as shown in Scheme 79. It is inferred from this model that the decay of the twisted stilbene to *cis*-geometry will be restricted by the cavity. This effect arises due to the interaction between the phenyl ring and the rim of the cyclodextrin cavity. Indeed when the phenyl ring is replaced by a smaller group such as the ester group in the case of the cinnamate esters the behaviour in solution and in cyclodextrin is identical.

An impressive difference in the behaviour of β-ionone was observed between solution and cyclodextrin complexes (Scheme 80).[222] While in organic solvents β-ionone gives rise to products arising from geometric isomerization and 1,5-hydrogen migration, in aqueous cyclodextrin only 1,5-hydrogen migration occurs. This is partly due to the restriction imposed by the cavity on the rotation



Scheme 79.



Scheme 80.

of the double bond. This effect is augmented by the alteration of the $n\pi^*$–$\pi\pi^*$ character of the excited state of β-ionone by cyclodextrin. In addition to these studies discussed above, photoisomerization of norbornadiene, photodechlorination of chlorpromazine and photo-oxidation of 1,2-diphenyl dioxene[223] have also been investigated using cyclodextrin as the host in aqueous media. Significant alterations in the reactivity of the guests have been noticed.

The above examples assume the formation of a 1 : 1 complex between the substrate and cyclodextrin. The two guest–one host (2 : 1) inclusion complex has attracted increasing attention in recent years. The cavity size of γ-cyclodextrin is large enough to include two homo-guest molecules or two hetero-guest molecules. β-Cyclodextrin is also known to form 2 : 1 inclusion complexes. Further, a two guest–two host (2 : 2) complex generated by the association of two 1 : 1 inclusion complexes is also known. Proposed structures for a few illustrative examples are provided in Fig. 33. Studies of

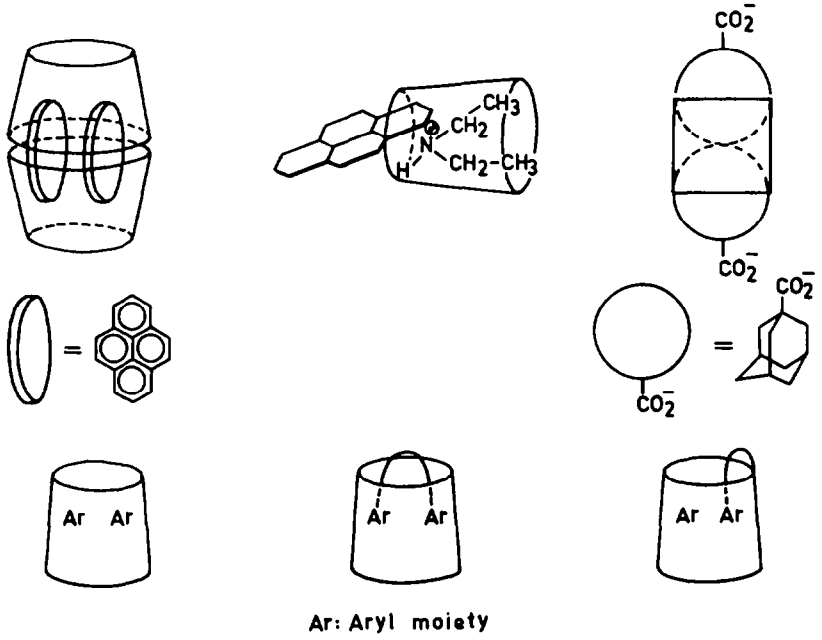


Fig. 33. Pictorial representation of a few multi-molecular complexes of cyclodextrin.

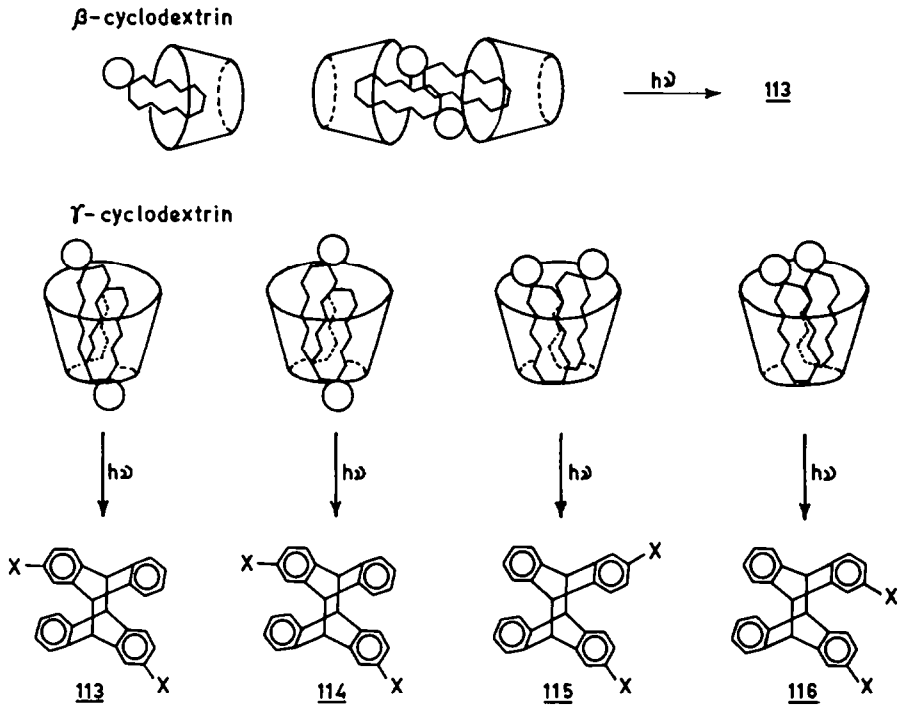


Fig. 34. The model of the inclusion complexes of β- and γ-cyclodextrin with 2-anthracene sulfonate.

such multimolecular complexes is expected to yield fascinating results as these allow for manipulation of bimolecular reactions. If a bimolecular reaction occurs between two guest molecules trapped in the cyclodextrin cavity, the reaction behaviour is expected to differ from that in the solution with respect to the reaction rate and selectivity. A report by Tamaki and Kokubu[224] on the photodimerization of water soluble anthracenes in cyclodextrin amply illustrates the potential of investigating multimolecular complexes of cyclodextrin.

Photodimerization of 2-anthracene sulfonate in water yields four dimers in the ratio 1:0.8:0.4:0.05 (Fig. 34). However, in the presence of β-cyclodextrin a single dimer was obtained. This prominent selectivity indicates that 2-anthracene sulfonate molecules trapped in β-cyclodextrin are forced to take a specific configuration mainly giving rise to dimer **113**. In the presence of γ-cyclodextrin, the quantum yield of the photodimerization was an order of magnitude greater than in the absence of it. However, the relative yields of isomers were quite similar to those in water. Existance of 2:2 and 2:1 complexes in β- and γ-cyclodextrins, respectively, have been established through optical and ^{1}H-NMR studies. The proposed mechanism involves the formation of a specifically oriented complex in the case of β-cyclodextrin and non-specific complexes with γ-cyclodextrin as illustrated in Fig. 34.

7. CONCLUSIONS

In terms of the reporting of accomplished chemistry this review can do no more than give an indication of the rapid progress in the branch of photoreactions in organized media. From the material accumulated in this review one can draw the conclusion that organized or constrained media offer special advantages in obtaining selectivity. In the opinion of the author "photochemistry" has passed its prime and along with it its youthful glamour. The brighter side of this event is that it allows for detailed special studies under a relaxed atmosphere. Under these circumstances an interdisciplinary approach utilizing "organized media" should be profitable and fascinating. Diverting competitive processes along a desired path with high specificity and stereoselectivity should be the aim.

It should be clear from this report that solid state and micellar media have attracted wider attention than any other media. Although crystals offer well-aligned reactive sites, predictability is

still poor. The future strength of the utility of the solid state as reaction media will be clearly determined by an increased progress in our understanding of the factors controlling molecular packing. Micelles, on the contrary, allow for certain predictability and the interface offered by these structures are certainly useful to align molecules. Surfaces and liquid crystals have often produced less than desirable selectivity. In both of these media flexibility is the enemy. Although host–guest chemistry is still in its infancy, the results of the investigations show that this field of research offers a valuable and versatile approach to selectivity in chemical reactions. Most of the work with molecular complexes have involved the use of cyclodextrin and only recently has attention begun to focus on other host systems. The molecular encapsulation of reagents for the sake of change of reactivities/selectivities should be an attractive aim. With specific and judicious choice of the media, photochemical transformations can be carried out more swiftly, under milder conditions with higher yields and fewer by-products and if necessary with good stereo- and regiochemical control.

Acknowledgements–It is indeed a pleasure to thank Dr G. Usha for extensive assistance during the preparation of this report. Prof. K. Venkatesan provided inspiration and stimulating and useful discussions at hours of need. These contributed to the success of organizing the material in a readable format. The author thanks Profs J. R. Scheffer, R. G. Weiss, P. de Mayo, M. D. Cohen, W. J. Leigh and N. J. Turro and Drs D. F. Eaton, A. Ueno, H. Nakanishi and R. A. Yellin for providing reprints and preprints. The work reported from our laboratory has been carried out by hard working, talented and enthusiastic individuals whose names appear in the reference section. Special thanks are due to G. Dasaratha Reddy, M. S. Syamala, S. Devanathan and B. Nageswara Rao for their constructive suggestions and skillful assistance.

REFERENCES

[1] M. A. Fox (Editor), *Organic Phototransformations in Non-homogeneous Media*, American Chemical Society, Washington, D.C. (1985). S. L. Holt (Editor), *Inorganic Reactions in Organized Media*. American Chemical Society, Washington, D.C. (1982). D. Dolphin, C. McKenna, Y. Murakami and I. Tabushi (Editors), *Biomimetic Chemistry*. American Chemical Society, Washington, D.C. (1980). M. D. Cohen, M. Lahav and A. Shanzer, *Israel J. Chem.* **25** (1985). J. R. Scheffer, V. Ramamurthy and N. J. Turro (Editors), *Tetrahedron Symposia in Print*, in preparation.
[2] J. H. Fendler, *Membrane Mimetic Chemistry*. Wiley, New York (1982). J. K. Thomas, *The Chemistry of Excitation at Interfaces*. American Chemical Society, Washington, D.C. (1984).
[3] R. Breslow, *Chemy Br.* 126 (1983). J. H. Fendler, *Chem. Engng News* 25 (2 *Jan.* 1984). M. D. Cohen and B. S. Green, *Chemy Br.* 4900 (1973). J. M. Thomas, *Ibid.* 60 (1970); 175 (1977).
[4] H. Stobbe and F. K. Steinberger, *Chem. Ber.* **55**, 2225 (1922). I. Ribber, *Ibid.* **35**, 2411 (1902). G. Ciamician and P. Silber, *Ibid.* **35**, 4128 (1902). W. Marckwald, *Z. Phys. Chem.* **30**, 140 (1899).
[5] G. M. J. Schmidt *et al.*, *Solid State Photochemistry* (Edited by D. Ginsburg). Verlag Chemie, New York (1976). L. Addadi, S. Ariel, M. Lahav, L. Leiserowitz, R. Popovitz-Biro and C. P. Tang, Chemical physics of solids and their surfaces, Specialist Periodical Reports, Vol. 8. p. 202. Royal Society, London (1979). J. M. Thomas, *Phil. Trans. R. Soc. London* **277**, 251 (1974). J. M. Thomas, S. E. Morsi and J. P. Desvergne, *Adv. Phys. Org. Chem.* **15**, 63 (1977). J. M. Thomas, *Pure Appl. Chem.* **51**, 1065 (1979). M. Hasegawa, *Chem. Rev.* **83**, 507 (1983).
[6] V. Ramamurthy and K. Venkatesan, *Chem. Rev.* (1986), in press. B. S. Green, R. A. Yellin and M. D. Cohen, *Top. Stereochem.* (1986), in press.
[7] T. Matsuura, Y. Sata and K. Ogura, *Tetrahedron Lett.* **4627** (1968). W. K. Appel, Z. Q. Jiang, J. R. Scheffer and L. Walsh, *J. Am. Chem. Soc.* **105**, 5354 (1983).
[8] A. C. Hazell, R. M. Pagni, G. Persy, E. Rommel and J. Wirz, *Helv. Chim. Acta* **64**, 2830 (1981). H. Aoyama, T. Hasegawa and Y. Omote, *J. Am. Chem. Soc.* **101**, 5343 (1979). G. Kaupp, E. Jostkleigrewe and H. J. Hermann, *Agnew. Chem. Int. Ed. Engl.* **21**, 435 (1982).
[9] H. W. Kohlshutter, *Z. Anorg. Allg. Chem.* **105**, 121 (1918).
[10] G. M. J. Schmidt, *Pure Appl. Chem.* **27**, 647 (1971). M. D. Cohen and B. S. Green, *Chemy. Br.* **9**, 490 (1973). G. M. J. Schmidt, *Reactivity of the Photoexcited Organic Molecules*, pp. 227–288. Interscience, New York (1967). M. D. Cohen and G. M. J. Schmidt, *Reactivity of Solids*, (Edited by C. de Boer), p. 556. Elsevier, Amsterdam (1961).
[11] M. D. Cohen, *Angew. Chem. Int. Ed. Engl.* **14**, 386 (1975). M. D. Cohen, *Mol. Cryst. Lig. Cryst.* **50**, 1 (1979).
[12] M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.* 1996 (1964).
[13] M. D. Cohen, G. M. J. Schmidt and F. I. Sonntag, *J. Chem. Soc.* 2000 (1964).
[14] G. M. J. Schmidt, *J. Chem. Soc.* 2014 (1964).
[15] K. Gnanaguru, N. Ramasubbu, K. Venkatesan and V. Ramamurthy, *J. Org. Chem.* **50**, 2337 (1985).
[16] N. Ramasubbu, K. Gnanaguru, K. Venkatesen and V. Ramamurthy, *Can. J. Chem.* **60**, 2159 (1982).
[17] M. M. Bhadbhade, G. S. Murthy, K. Venkatesan and V. Ramamurthy, *Chem. Phys. Lett.* **109**, 259 (1984).
[18] K. Gnanaguru, G. S. Murthy, K. Venkatesan and V. Ramamurthy, *Chem. Phys. Lett.* **109**, 255 (1984).
[19] K. Gnanaguru, N. Ramasubbu, K. Venkatesan and V. Ramamurthy, *J. Photochem.* **27**, 355 (1984).
[20] N. Ramasubbu, T. N. Guru Row, K. Venkatesan, V. Ramamurthy and C. N. R. Rao, *J. Chem. Soc. Chem. Commun.* 178 (1982).
[21] H. Nakanishi, W. Jones and J. M. Thomas, *Chem. Phys. Lett.* **71**, 44 (1980).
[22] H. Nakanishi, W. Jones, J. M. Thomas, M. B. Hursthouse and M. Motevalli, *J. Chem. Soc. Chem. Commun.* 611 (1980).
[23] W. Jones, H. Nakanishi, C. R. Theocharis and J. M. Thomas, *J. Chem. Soc. Chem. Commun.* 610 (1980).
[24] J. M. Thomas, *Nature (London)* **289**, 633 (1981).
[25] H. Nakanishi, W. Jones, J. M. Thomas, M. B. Hursthouse and M. Motevalli, *J. Phys. Chem.* **85**, 3636 (1981).
[26] W. Jones, S. Ramdas, C. R. Theocharis, J. M. Thomas and N. W. Thomas, *J. Phys. Chem.* **85**, 2594 (1981).
[27] K. H. Pfoertner, G. Englert and P. Schoenholzer, Abstracts of papers, 12th International Conference on Photochemistry,

Tokyo, Japan, p. 487 (1985). F. Nakanishi, H. Nakanishi, M. Tsuchiya and M. Hasegawa, *Bull. Chem. Soc. Japan* **49**, 3096 (1976). H. Nakanishi, M. Hasegawa and T. Mori, *Acta Crystallogr., Sect C* **41**, 70 (1985). H. Nakanishi, G. M. Parkinson, W. Jones, J. M. Thomas and M. Hasegawa, *Israel J. Chem.* **18**, 261 (1979). S. Ariel, S. Askari, J. R. Scheffer, J. Trotter and L. Walsh, *J. Am. Chem. Soc.* **106**, 5726 (1984). A. W. Hanson, *Acta Crystallogr., Sect. B* **31**, 1963 (1975). H. Mez and G. Rihs, *Helv. Chim. Acta* **56**, 2766 (1973). J. Sinnreich and H. Batzer, *Ibid.* **56**, 2760 (1973). C. R. Theocharis, W. Jones, J. M. Thomas, M. Motevalli and M. B. Hursthouse, *J. Chem. Soc. Perkin Trans.* 2 71 (1984).

[28] J. K. Frank and I. C. Paul, *J. Am. Chem. Soc.* **95**, 2324 (1973). N. J. Leonard, R. S. McCredie, M. W. Logue and R. L. Cundall, *Ibid.* **95**, 2320 (1973). H. Irngartinger, R. D. Aeker, W. Rebafka and H. A. Stabb, *Angew. Chem. Int. Ed. Engl.* **13**, 674 (1974). M. Hasegawa, M. Nohara, K. Saigo, T. Mori and H. Nakanishi, *Tetrahedron Lett.* **25**, 561 (1984). M. Hasegawa, K. Saigo, T. Mori, H. Uno, M. Nohara and H. Nakanishi, *J. Am. Chem. Soc.* **107**, 2788 (1985).

[29] J. R. Scheffer, *Accts Chem. Res.* **13**, 283 (1980).

[30] H. Aoyama, T. Hasegawa and Y. Omote, *J. Am. Chem. Soc.* **101**, 5343 (1979). S. Ariel, V. Ramamurthy, J. R. Scheffer and J. Trotter, *Ibid.* **105**, 6959 (1983). P. J. Wagner, B. P. Giri, J. C. Scaiano, D. L. Ward, E. Gabe and F. L. Lee, *Ibid.* **107**, 5483 (1985). S. Evans, N. Omkaram, J. R. Scheffer and J. Trotter, *Tetrahedron Lett.* **26**, 5903 (1985).

[31] K. Padmanabhan, D. Döpp, K. Venkatesan and V. Ramamurthy, *J. Chem. Soc. Perkin Trans 2*, 897 (1986); K. Padmanabhan, R. Schmidt, D. Döpp, V. Ramamurthy and K. Venkatesan, *Ibid.* (1986), in press.

[32] A. A. Dzakpasu, S. E. V. Phillips, J. R. Scheffer and J. Trotter, *J. Am. Chem. Soc.* **98**, 6049 (1976).

[33] J. R. Scheffer and A. A. Dzakpasu, *J. Am. Chem. Soc.* **100**, 2163 (1979).

[34] W. K. Appel, T. J. Greenhough, J. R. Scheffer and J. Trotter, *J. Am. Chem. Soc.* **101**, 213 (1979).

[35] G. Quinkert, T. Tabata, E. A. J. Hickmann and W. Dobrat, *Angew. Chem. Int. Ed. Engl.* **10**, 199 (1971).

[36] G. Quinkert, K. Opitz, W. W. Wiersdorff and J. Weinlich, *Tetrahedron Lett.* 1863 (1963).

[37] H. Tomioka and Y. Izawa, *J. Chem. Soc. Chem. Commun.* 445 (1980).

[38] J. M. McBride, *J. Am. Chem. Soc.* **93**, 6302 (1971).

[39] K. J. Skinner, R. J. Blaskiewicz and J. M. McBride, *Israel J. Chem.* **10**, 457 (1972).

[40] A. B. Jaffe, K. J. Skinner and J. M. McBride, *J. Am. Chem. Soc.* **94**, 8510 (1972).

[41] N. J. Karch, E. T. Koh, B. L. Whitsel and J. M. McBride, *J. Am. Chem. Soc.* **97**, 6729 (1975).

[42] J. M. McBride and M. R. Gisler, *Mol. Cryst. Lig. Cryst.* **52**, 121 (1979).

[43] M. W. Vary and J. M. McBride, *Mol. Cryst. Liq. Cryst.* **52**, 133 (1979).

[44] D. M. Walter and J. M. McBride, *J. Am. Chem. Soc.* **103**, 7069 (1981).

[45] D. W. Walter and J. M. McBride, *J. Am. Chem. Soc.* **103**, 7064 (1981).

[46] J. M. McBride and M. W. Vary, *Tetrahedron* **38**, 765 (1982).

[47] J. M. McBride, *Accts Chem. Res.* **16**, 304 (1983).

[48] M. D. Cohen, G. M. J. Schmidt and S. Flavian, *J. Chem. Soc.* 2041 (1964).

[49] M. D. Cohen, Y. Hirshberg and G. M. J. Schmidt, *J. Chem. Soc.* 2051 (1964).

[50] M. D. Cohen, Y. Hirshberg and G. M. J. Schmidt, *J. Chem. Soc.* 2060 (1964).

[51] J. Bergman, L. Leiserowitz and G. M. J. Schmidt, *J. Chem. Soc.* 2068 (1964).

[52] J. R. Canon, V. A. Patrick, C. L. Raston and A. H. White, *Aust. J. Chem.* **31**, 1265 (1978).

[53] S. E. Evans, N. Omkaram, J. R. Scheffer and J. Trotter, *Tetrahedron Lett.* **27**, 1419 (1986).

[54] J. van Mil, L. Addadi, M. Lahav and L. Leiserowitz, *J. Chem. Soc. Chem. Commun.* 584 (1982).

[55] B. S. Green, M. Lahav and D. Rabinovich, *Accts Chem. Res.* **12**, 191 (1979).

[56] L. Addadi and M. Lahav, *Pure Appl. Chem.* **51**, 1269 (1979).

[57] V. K. Blsky and P. M. Zorkii, *Acta Cryst.* **33A**, 1004 (1977).

[58] A. Elgavi, B. S. Green and G. M. J. Schmidt, *J. Am. Chem. Soc.* **95**, 2058 (1973).

[59] B. S. Green, M. Lahav and G. M. J. Schmidt, *Mol. Cryst. Liq. Cryst.* **29**, 187 (1975).

[60] L. Addadi, M. D. Cohen and M. Lahav, *J. Chem. Soc. Chem. Commun.* 471 (1975).

[61] L. Addadi, M. D. Cohen and M. Lahav, *Mol. Cryst. Liq. Cryst.* **32**, 137 (1976).

[62] L. Addadi and M. Lahav, *J. Am. Chem. Soc.* **100**, 2838 (1978).

[63] L. Addadi, E. Gavi, M. Lahav and L. Leiserowitz, *Israel J. Chem.* **15**, 116 (1976–77).

[64] L. Addadi and M. Lahav, *J. Am. Chem. Soc.* **101**, 2152 (1979).

[65] L. Addadi, J. van Mil and M. Lahav, *J. Am. Chem. Soc.* **104**, 3422 (1982).

[66] H. L. Holland and M. F. Richardson, *Mol. Cryst. Liq. Cryst.* **58**, 311 (1980).

[67] P. C. Chenchaiah, H. L. Holland and M. F. Richardson, *J. Chem. Soc. Chem. Commun.* 436 (1982).

[68] R. M. Hochstrasser, *Can. J. Chem.* **37**, 1123 (1959).

[69] C. T. Lin, P. Perrier, G. G. Clay, P. A. Sutton and S. R. Byrn, *J. Org. Chem.* **47**, 2978 (1982).

[70] G. Brenner, F. E. Roberts, A. Hoinowski, J. Budavari, B. Powell, D. Hinkley and E. Schoenewaldt, *Angew. Chem. Int. Ed. Engl.* **8**, 975 (1969). M. L. Lewbart, *Nature* **222**, 663 (1969).

[71] P. Arjunan, V. Ramamurthy and K. Venkatesan, *J. Org. Chem.* **49**, 1765 (1984).

[72] I. C. Paul and D. Y. Curtin, *Accts Chem. Res.* **6**, 217 (1973). I. C. Paul and D. Y. Curtin, *Science* **187**, 19 (1975).

[73] D. P. Craig and P. Sarti-Fantoni, *Chem. Commun.* 742 (1966).

[74] J. M. Thomas and J. O. Williams, *Chem. Commun.* 432 (1967).

[75] B. Stevens, T. Dickinson and R. R. Sharpe, *Nature (London)* **204**, 876 (1964).

[76] M. D. Cohen, Z. Ludmer, J. M. Thomas and J. O. Williams, *Chem. Commun.* 1172 (1969).

[77] M. D. Cohen, Z. Ludmer, J. M. Thomas and J. O. Williams, *Proc. R. Soc. London, Ser. A* **324**, 459 (1971).

[78] M. D. Cohen, I. Ron, G. M. J. Schmidt and J. M. Thomas, *Nature (London)* **224**, 167 (1969).

[79] J. M. Thomas and J. O. Williams, Surface and defects properties of solids, Specialist Periodical Reports, Vol. 1, p. 129. Chemical Society, London (1972).

[80] J. M. Thomas and J. O. Williams, *Prog. Solid State Chem.* **6**, 119 (1971).

[81] J. L. Atwood, J. E. D. Davies and D. D. MacNicol, *Inclusion Compounds*, Vols 1–3, Academic Press, London (1984).

[82] M. F. Bengen, German Patent Appl. OZ 123438 (18 Mar. 1940).

[83] B. Angla, *Compt. Rend.* **224**(402), 116 (1947).

[84] D. W. White, *J. Am. Chem. Soc.* **82**, 5678 (1960). J. F. Brown and D. W. White, *Ibid.* **82**, 5671 (1960).

[85] H. L. Casal, P. de Mayo, J. F. Miranda and J. C. Scaiano, *J. Am. Chem. Soc.* **105**, 155 (1983).

[86] A. P. Dianin, *J. Russ. Phys. Chem. Soc.* **46**, 1310 (1914).

[87] W. Baker, A. J. Floyd, J. F. W. McOmie, G. Pope, A. S. Weaving and J. H. Wild, *J. Chem. Soc.* 2010 (1956).

[88] W. Baker and J. F. W. McOmie, *Chem. Ind.* (*London*) 256 (1955). J. L. Flippen and I. L. Karle, *J. Am. Chem. Soc.* **92**, 3749 (1970).
[89] D. D. MacNicol, J. J. McKendrick and D. R. Wilson, *Chem. Soc. Rev.* **7**, 65 (1978).
[90] P. G. Goswami, P. de Mayo, N. Ramnath, G. Bernard, N. Omkaram, J. R. Scheffer and Y. F. Wong, *Can. J. Chem.* **63**, 2719 (1986).
[91] B. Nageswara Rao, N. J. Turro and V. Ramamurthy, *J. Org. Chem.* **51**, 460 (1986).
[92] W. Baker, B. Gilbert and W. D. Ollis, *J. Chem. Soc.* 1443 (1952). A. C. D. Newman and H. M. Powell, *Ibid.* 3747 (1952). D. Lawton and H. M. Powell, *Ibid.* 2339 (1958).
[93] R. Arad-Yellin, B. S. Green, M. Knossow and G. Tsoucaris, *J. Am. Chem. Soc.* **105**, 4561 (1983). R. Arad-Yellin, B. S. Green, M. Knossow, N. Rysanek and G. Tsoucaris, *J. Incln. Phenomena* **3**, 317 (1985).
[94] R. Gerdil, G. Barchietto and C. W. Jefford, *J. Am. Chem. Soc.* **106**, 8004 (1984).
[95] L. Fieser and M. Fieser, *Steroids*, Chap. 3, pp. 53 and 56. Reinhold, New York (1959).
[96] W. C. Herndon, *J. Chem. Ed.* **44**, 724 (1967). E. Giglio, *J. Mol. Str.* **75**, 39 (1981).
[97] S. C. DeSanctis, V. M. Coiro, E. Giglio, S. Pagliuca, N. V. Pavel and C. Quagliata, *Acta Cryst.* **B34**, 1928 (1978). S. C. DeSanctis, E. Giglio, F. Petri and C. Quagliata, *Ibid.* **B35**, 226 (1979).
[98] N. Friedman, M. Lahav, L. Leiserowitz, R. Popovitz-Biro, C. P. Tang and Z. Zaretskii, *J. Chem. Soc. Chem. Commun.* 864 (1975).
[99] G. Audisio and A. Silvani, *J. Chem. Soc. Chem. Commun.* 481 (1976). M. Miyata and K. Takemoto, *Polym. J.* **9**, 111 (1977).
[100] M. Lahav, L. Leiserowitz, R. Popovitz-Biro and C. P. Tang, *J. Am. Chem. Soc.* **100**, 2542 (1978). R. Popovitz-Biro, C. P. Tang, H. C. Chang, M. Lahav and L. Leiserowitz, *Ibid.* **107**, 4043 (1985).
[101] H. C. Chang, C. P. Tang, R. Popovitz-Biro, M. Lahav and L. Leiserowitz, *Nouv. J. Chim.* **5**, 475 (1981). H. C. Chang, R. Popovitz-Biro, M. Lahav and L. Leiserowitz, *J. Am. Chem. Soc.* **104**, 614 (1982). R. Popovitz-Biro, H. C. Chang, C. P. Tang, N. R. Shochet, M. Lahav and L. Leiserowitz, *Pure Appl. Chem.* **52**, 2693 (1980). R. Popovitz-Biro, C. P. Tang, H. C. Chang, N. R. Shochet, M. Lahav and L. Leiserowitz, *Nouv. J. Chim.* **6**, 75 (1982).
[102] C. P. Tang, H. C. Chang, R. Popovitz-Biro, F. Frolow, M. Lahav, L. Leiserowitz and R. K. McMullen, *J. Am. Chem. Soc.* **107**, 4058 (1985).
[103] K. Padmanabhan, K. Venkatesan and V. Ramamurthy, *Can. J. Chem.* **62**, 2025 (1984).
[104] H. Aoyama, K. Miyazaki, M. Sakamoto and Y. Omote, *J. Chem. Soc. Chem. Commun.* 333 (1983).
[105] M. L. Bender and M. Komiyama, *Cyclodextrin Chemistry*, Springer, Berlin (1978). I. Tabushi and Y. Kuroda, *Adv. Catalysis* **32**, 417 (1983).
[106] W. Saenger, *Angew. Chem. Int. Ed. Engl.* **19**, 344 (1980).
[107] S. Sharat, G. Usha, C. H. Tung, N. J. Turro and V. Ramamurthy, *J. Org. Chem.* **51**, 941 (1986). G. Dasaratha Reddy, B. Jeyasree and V. Ramamurthy, *J. Org. Chem.* (1986), in press.
[108] G. Dasaratha Reddy, G. Usha, K. V. Ramanathan and V. Ramamurthy, *J. Org. Chem.* **51**, 3085 (1986). G. Dasaratha Reddy and V. Ramamurthy, Unpublished results.
[109] G. Dasaratha Reddy, B. Nageswara Rao and V. Ramamurthy, Unpublished results.
[110] B. Nageswara Rao, M. S. Syamala and V. Ramamurthy, Unpublished results.
[111] R. Breslow, *Science* (*Washington, D.C.*) **218**, 532 (1982). R. Breslow, *Accts Chem. Res.* **13**, 170 (1980).
[112] D. W. Griffiths and M. L. Bender, *Adv. Catalysis* **23**, 209 (1973).
[113] G. Desaratha Reddy and V. Ramamurthy, Unpublished results.
[114] E. G. Derouane, *Intercalation Chemistry* (Edited by M. S. Wittingham and A. J. Jacobson), p. 101. Academic Press, New York (1982).
[115] N. J. Turro and P. Wan, *J. Am. Chem. Soc.* **107**, 678 (1985). N. J. Turro, C. C. Cheng, X. G. Lei and E. M. Flanigen, *Ibid.* **107**, 3739 (1985).
[116] N. J. Turro and P. Wan, *Tetrahedron Lett.* **25**, 3655 (1984).
[117] N. J. Turro, X. G. Lei, C. C. Cheng, D. R. Corbin and L. Abrams, *J. Am. Chem. Soc.* **107**, 5824 (1985).
[118] F. Toda and K. Akagi, *Tetrahedron Lett.* 3695 (1968).
[119] H. Hart, L. T. W. Liu and D. L. Ward, *J. Am. Chem. Soc.* **106**, 4043 (1984).
[120] K. Tanaka and F. Toda, *J. Chem. Soc. Chem. Commun.* 593 (1983). M. Kafatory, K. Tanaka and F. Toda, *J. Org. Chem.* **50**, 2154 (1985).
[121] M. Farina, *Tetrahedron Lett.* 2097 (1963).
[122] M. Farina, G. Audisio and G. Natta, *J. Am. Chem. Soc.* **89**, 5071 (1967).
[123] K. K. Unger, *Porous Silica*. Elsevier Scientific, Amsterdam (1979).
[124] C. G. Armistead, A. J. Tylor, F. H. Hambleton, S. A. Mitchell and J. A. Hockey, *J. Phys. Chem.* **73**, 3947 (1969).
[125] C. H. Nicholls and P. A. Leermakers, *Adv. Photochem.* **8**, 315 (1971).
[126] A. Terenin, *Adv. Catalyt.* **15**, 227 (1964).
[127] M. E. Zawadzki and A. B. Ellis, *J. Org. Chem.* **48**, 3156 (1983).
[128] J. Griffith and H. Hart, *J. Am. Chem. Soc.* **90**, 5296 (1968).
[129] J. M. Eisenhart and A. B. Ellis, *J. Org. Chem.* **50**, 4108 (1985).
[130] L. D. Weis, B. W. Bowen and P. A. Leermakers, *J. Am. Chem. Soc.* **88**, 3176 (1966).
[131] N. J. Turro, C. C. Cheng and W. Mahler, *J. Am. Chem. Soc.* **106**, 5022 (1984).
[132] L. J. Johnston and S. K. Wong, *Can. J. Chem.* **62**, 1999 (1984).
[133] N. J. Turro, C. C. Cheng, P. Wan and C. J. Chung, *J. Phys. Chem.* **89**, 1567 (1985).
[134] B. Frederick, L. J. Johnston, P. de Mayo and S. K. Wong, *Can. J. Chem.* **62**, 403 (1984).
[135] D. Avnir, L. J. Johnston, P. de Mayo and S. K. Wong, *J. Chem. Soc. Chem. Commun.* 958 (1981).
[136] D. Avnir, P. de Mayo and I. Ono, *J. Chem. Soc. Chem. Commun.* 1109 (1978).
[137] M. M. A. Malik and P. de Mayo, *Can. J. Chem.* **62**, 1275 (1984).
[138] P. De Mayo, K. Okada, M. Rafalska, A. C. Weedon and G. S. K. Wong, *J. Chem. Soc. Chem. Commun.* 820 (1981).
[139] R. K. Bauer, R. Borenstein, P. de Mayo, K. Okada, M. Rafalska, W. R. Ware and K. C. Wu, *J. Am. Chem. Soc.* **104**, 4635 (1982).
[140] P. de Mayo, *Pure Appl. Chem.* **54**, 1623 (1982).
[141] D. Donati, M. Fiorenza and P. S. Fantoni, *J. Heterocyclic Chem.* **16**, 253 (1979).
[142] L. D. Weis, T. R. Evans and P. A. Leermakers, *J. Am. Chem. Soc.* **90**, 6109 (1968).

[143] D. Fassler, R. Gade and W. Guenther, *J. Photochem.* **13**, 49 (1980).
[144] P. A. Leermakers, L. D. Weis and H. T. Thomas, *J. Am. Chem. Soc.* **87**, 4403 (1965). P. A. Leermakers, H. T. Thomas, L. D. Weis and F. C. Jones, *Ibid.* **88**, 5075 (1966).
[145] L. J. Johnston, P. de Mayo and S. K. Wong, *J. Chem. Soc. Chem. Commun.* 1106 (1982). L. J. Johnston, P. de Mayo and S. K. Wong, *J. Org. Chem.* **49**, 20 (1984).
[146] J. E. Leffler and J. J. Zupancic, *J. Am. Chem. Soc.* **102**, 259 (1980).
[147] H. Aoyama, K. Miyazaki, M. Sakamoto and Y. Omote, *Chem. Lett.* 1583 (1983).
[148] R. Farwaha, P. de Mayo, J. H. Schauble and Y. C. Toong, *J. Org. Chem.* **50**, 245 (1985). V. Dave, R. Farwaha, P. de Mayo and J. B. Stothers, *Can. J. Chem.* **63**, 2401 (1985).
[149] P. de Mayo, A. Nakamura, P. W. K. Tsang and S. K. Wong, *J. Am. Chem. Soc.* **104**, 6824 (1982).
[150] N. J. Turro, I. R. Gould, M. B. Zimmt and C. C. Cheng, *Chem. Phys. Lett.* **119**, 484 (1985).
[151] T. R. Evans, A. F. Toth and P. A. Leermakers, *J. Am. Chem. Soc.* **89**, 5060 (1967).
[152] S. Chandrasekhar, *Liquid Crystals*. Cambridge University Press, London (1977). W. G. Shaw and G. H. Brown, *Chem. Rev.* **57**, 1049 (1957). J. J. Wolken and G. H. Brown, *Liquid Crystals and Biological Systems*. Academic Press, New York (1980).
[153] T. Svedberg, *Kolloid Z.*, **18**, 54, 101 (1916).
[154] D. A. Hrovat, J. H. Liu, N. J. Turro and R. G. Weiss, *J. Am. Chem. Soc.* **106**, 7033 (1984).
[155] J. M. Nerbonne and R. G. Weiss, *Israel J. Chem.* **18**, 266 (1979).
[156] W. J. Leigh, *J. Am. Chem. Soc.* **107**, 6114 (1985).
[157] T. Nakano and H. Hirata, *Bul. Chem. Soc. Japan* **55**, 947 (1982).
[158] J. M. Nerbonne and R. G. Weiss, *J. Am. Chem. Soc.* **100**, 2571 (1978).
[159] J. M. Nerbonne and R. G. Weiss, *J. Am. Chem. Soc.* **101**, 402 (1979).
[160] T. Kuneida, T. Takahashi and M. Hirobe, *Tetrahedron Lett.* **24**, 5107 (1983).
[161] G. Aviv, J. Sagiv and A. Yogev, *Mol. Cryst. Liq. Cryst.* **36**, 349 (1976).
[162] Y. Tanaka, H. Tsuchiya, M. Suzuki and K. Tsuda, *Mol. Cryst. Liq. Cryst.* **68**, 113 (1981).
[163] D. A. Hrovat, J. H. Liu, N. J. Turro and R. G. Weiss, *J. Am. Chem. Soc.* **106**, 5291 (1984).
[164] G. B. Sergeev, V. A. Batyuk, M. B. Stepanov and T. I. Shabatine, *Dokl. Akad. Nauk USSR* **246**, 552 (1979).
[165] A. Dondoni, A. Medici, S. Colonna, G. Gottarelli and B. Samori, *Mol. Cryst. Liq. Cryst.* **55**, 47 (1979).
[166] C. Eskenazi, J. F. Nicoud and H. B. Kagan, *J. Org. Chem.* **44**, 995 (1979).
[167] M. Hibert and G. Solladie, *J. Org. Chem.* **45**, 5393 (1980).
[168] M. Nakazaki, K. Yamatoto, K. Fujiwara and M. Maeda, *J. Chem. Soc. Chem. Commun.* 1086 (1979).
[169] M. Nakazaki, K. Yamatoto and K. Fujiwara, *Chem. Lett.* 863 (1978).
[170] D. G. Duff and C. H. Giles, *Water—a comprehensive treatise* (Edited by F. Franks), Vol. 4, p. 175. Plenum, New York (1975). D. Eagland, *Water—a comprehensive treatise* (Edited by F. Franks), Vol. 4, p. 305. Plenum, New York (1975).
[171] D. C. Rideout and R. Breslow, *J. Am. Chem. Soc.* **102**, 7816 (1980).
[172] P. A. Grieco, P. Garner and Z. M. Ho, *Tetrahedron Lett.* **24**, 1897 (1983). P. A. Grieco, P. Garner, K. Yoshida and J. C. Huffman, *Ibid.* **24**, 3807 (1983). P. A. Grieco, K. Yoshida and P. Garner, *J. Org. Chem.* **48**, 3137 (1983). R. Breslow, U. Maitra and D. Rideout, *Tetrahedron Lett.* **24**, 1901 (1983). R. Breslow and U. Maitra, *Ibid.* **25**, 1239 (1984).
[173] G. J. Fisher and H. E. Johns, *Photochem. Photobiol.* **11**, 429 (1970).
[174] H. Morrison, R. Kleopfer and A. Feeley, *J. Chem. Soc. Chem. Commun.* 358 (1968). R. Kleopfer and H. Morrison, *J. Am. Chem. Soc.* **94**, 255 (1972). R. Lisewski and K. L. Wierzchowski, *J. Chem. Soc. Chem. Commun.* 348 (1968). K. L. Wierzchowski and R. Lisewski, *Mol. Photochem.* **3**, 231 (1971).
[175] E. Stepien, R. Lisewski and K. L. Wierzchowski, *Acta Biochim. Pol.* **20**, 313 (1973).
[176] J. G. Otten, C. S. Yeh, S. Byrn and H. Morrison, *J. Am. Chem. Soc.* **90**, 6353 (1977).
[177] M. S. Syamala and V. Ramamurthy, *J. Org. Chem* (1986), in press.
[178] S. Devanathan and V. Ramamurthy, *J. Photochem.* (1986), in press.
[179] K. Muthuramu and V. Ramamurthy, *J. Org. Chem.* **47**, 3976 (1982).
[180] G. Usha and V. Ramamurthy, Unpublished results.
[181] J. H. Liu and R. G. Weiss, *J. Org. Chem.* **50**, 3685 (1985).
[182] J. H. Fendler and E. J. Fendler, *Catalysis in Micellar and Macromolecular Systems*. Academic Press, New York (1975). J. H. Fendler, *Membrane Mimetic Chemistry*. Wiley, New York (1982). J. K. Thomas, *The Chemistry of Excitation at Interfaces*. American Chemical Society, Washington, D.C. (1984).
[183] J. K. Thomas, *Chem. Rev.* **80**, 283 (1980). N. J. Turro, M. Gratzel and A. M. Braun, *Angew, Chem. Int. Ed. Engl.* **19**, 675 (1980). D. G. Whitten, J. C. Russell and R. H. Schmehl, *Tetrahedron* **38**, 2455 (1982). N. Ramnath, V. Ramesh and V. Ramamurthy, *J. Photochem.* **31**, 75 (1985). N. J. Turro, G. S. Cox and M. A. Paczkowski, *Top. Curr. Chem.* **129**, 57 (1985).
[184] N. J. Turro and W. R. Cherry, *J. Am. Chem. Soc.* **100**, 7431 (1978).
[185] D. Avnir, L. J. Johnston, P. de Mayo and S. K. Wong, *J. Chem. Soc. Chem. Commun.* 958 (1981).
[186] N. J. Turro and G. C. Weed, *J. Am. Chem. Soc.* **105**, 1861 (1983).
[187] I. R. Gould, M. B. Zimmt, N. J. Turro, B. H. Baretz and G. F. Lehr, *J. Am. Chem. Soc.* **107**, 4607 (1985).
[188] I. R. Gould, C. H. Tung, N. J. Turro, R. S. Givens and B. Matuszewski, *J. Am. Chem. Soc.* **106**, 1789 (1984).
[189] N. J. Turro, *Proc. Natn. Acac. Sci. U.S.A.* **80**, 609 (1983). N. J. Turro and B. Kraeutler, *Accts Chem. Res.* **13**, 369 (1980).
[190] N. J. Turro and B. Kraeutler, *J. Am. Chem. Soc.* **100**, 7432 (1978). N. J. Turro, B. Kreutler and D. R. Anderson, *Ibid.* **101**, 7435 (1979). R. S. Hutton, H. D. Roth, B. Kraeutler, W. R. Cherry and N. J. Turro, *Ibid.* **101**, 2227 (1979). N. J. Turro, M. F. Chow, C. J. Chung, G. C. Weed and B. Kraeutler, *Ibid.* **102**, 4843 (1980). N. J. Turro, M. F. Chow and B. Kraeutler, *Chem. Phys. Lett.* **73**, 545 (1980). B. Kraeutler and N. J. Turro, *Ibid.* **70**, 266 (1980). N. J. Turro, D. R. Anderson, M. F. Chow, C. J. Chung and B. Kraeutler, *J. Am. Chem. Soc.* **103**, 3892 (1981). N. J. Turro, M. F. Chow, C. J. Chung and B. Kraeutler, *Ibid.* **103**, 3886 (1981). N. J. Turro, M. F. Chow, C. J. Chung, Y. Tanimoto and G. C. Weed, *Ibid.* **103**, 4574 (1981). G. F. Lehr and N. J. Turro, *Tetrahedron* **37**, 3411 (1981). N. J. Turro, C. J. Chung, G. Jones and W. G. Becker, *J. Phys. Chem.* **86**, 3677 (1982). N. J. Turro, C. J. Chung, R. G. Lawler and W. J. Smith, *Tetrahedron Lett.* **23**, 3223 (1982).
[191] Y. Sakaguchi, H. Hayashi, H. Murai and Y. J. I'haya, *Chem. Phys. Lett.* **110**, 275 (1984). Y. Sakaguchi and H. Hayashi, *Ibid.* **106**, 420 (1984). Y. Sakaguchi and H. Hayashi, *J. Phys. Chem.* **88**, 1437 (1984). Y. Tanimoto, H. Udagawa, Y. Katsuda and M. Itoh, *Ibid.* **87**, 3976 (1983). Y. Tanimoto, H. Udagawa and M. Itoh, *Ibid.* **87**, 724 (1983). Y. Tanimoto,

K. Shimizu and M. Itoh, *Photochem. Photobiol.* **39**, 511 (1984). J. C. Scaiano and E. B. Abuin, *Chem. Phys. Lett.* **81**, 209 (1981). D. J. Longnot, P. Jacques and J. P. Fouassier, *J. Photochem.* **17**, 75 (1981); **19**, 59 (1982). A. M. Braun, M. Kreig, N. J. Turro, M. Aikawa, I. R. Gould, G. A. Graf and P. C. C. Lee, *J. Am. Chem. Soc.* **103**, 7312 (1981). J. C. Scaiano, E. B. Abuin and L. C. Stewart, *Ibid.* **104**, 5673 (1982). Y. Sakaguchi, S. Nagakura and H. Hayashi, *Chem. Phys. Lett.* **72**, 420 (1980). Y. Sakaguchi, S. Nagakura and H. Hayashi, *Ibid.* **82**, 213 (1981).

[192] S. Devanathan, M. S. Syamala and V. Ramamurthy, *J. Org. Chem.* (1986), in press.

[193] A. K. Singh and T. S. Raghuraman, *Tetrahedron Lett.* **26**, 4125 (1985).

[194] T. Wolff, *J. Photochem.* **18**, 269 (1982). B. Baretz and N. J. Turro, *J. Am. Chem. Soc.* **105**, 1309 (1093). N. J. Turro and J. Mattay, *Ibid.* **103**, 4200 (1981). N. J. Turro, D. R. Anderson and B. Kraeutler, *Tetrahedron Lett.* **21**, 3 (1980). N. J. Turro and C. H. Tung, *Ibid.* **21**, 4321 (1980).

[195] P. Mukerjee and J. Cardinal, *J. Phys. Chem.* **82**, 1620 (1978). J. G. Erickson and G. Gilberg, *Acta Chem. Scand.* **20**, 2019 (1966). E. J. Fendler, C. L. Day and J. H. Fendler, *J. Phys. Chem.* **76**, 1460 (1972). M. Almgren, F. Grieser and J. K. Thomas, *J. Am. Chem. Soc.* **101**, 279 (1979). K. Kalyanasundaram and J. K. Thomas, *J. Phys. Chem.* **81**, 2176 (1977). J. H. Fendler, E. J. Fendler, G. A. Intanze, P. S. Shih and L. K. Patterson, *J. Am. Chem. Soc.* **97**, 89 (1975). K. N. Ganesh, P. Mitra and D. Balasubramanian, *J. Phys. Chem.* **86**, 4291 (1982). J. K. Thomas and M. Almgren, *Solution Chemistry of Surfactants* (Edited by K. L. Mittal) Vol. 2, p. 559. Plenum, New York (1979).

[196] K. H. Lee and P. de Mayo, *Photochem. Photobiol.* **31**, 311 (1980). K. H. Lee and P. de Mayo, *J. Chem. Soc. Chem. Commun.* 493 (1979).

[197] R. Fargues, M. T. Maurette, E. Oliveros, M. Riviere and A. Lattes, *Nouv. J. Chim.* **3**, 487 (1979). R. Fargues, M. T. Maurette, E. Oliveros, M. Riviere and A. Lattes, *J. Photochem.* **18**, 101 (1982).

[198] V. Ramesh and V. Ramamurthy, *J. Org. Chem.* **49**, 536 (1984).

[199] T. Wolff, *J. Photochem.* **16**, 343 (1981). T. Wolff and N. Muller, *Ibid.* **23**, 131 (1983). T. Wolff, N. Muller and G. van Buanu, *Ibid.* **22**, 61 (1983).

[200] Y. Nakamura, T. Kato and Y. Morita, *Tetrahedron Lett.* **22**, 1025 (1981).

[201] P. de Mayo and L. K. Sydnes, *J. Chem. Soc. Chem. Commun.* 994 (1980). N. Berenjian, P. de Mayo, M. Sturgeon, L. K. Sydnes and A. C. Weedon, *Can. J. Chem.* **60**, 425 (1982).

[202] K. Muthuramu, N. Ramnath and V. Ramamurthy, *J. Org. Chem.* **48**, 1872 (1983). N. Ramnath and V. Ramamurthy, *Ibid.* **49**, 2827 (1984). K. Muthuramu and V. Ramamurthy, *Ind. J. Chem. Sect. B* **23**, 502 (1984).

[203] K. Y. Law and P. de Mayo, *J. Chem. Soc. Chem. Commun.* 1110 (1978).

[204] B. R. Suddaby, P. E. Brown, J. C. Russell and D. G. Whitten, *J. Am. Chem. Soc.* **107**, 5609 (1985). J. C. Russell, S. B. Costa, R. P. Seiders and D. G. Whitten, *Ibid.* **102**, 5678 (1980). J. C. Russell, D. G. Whitten and A. M. Braun, *Ibid.* **103**, 3219 (1981). F. H. Quinna and D. G. Whitten, *Ibid.* **99**, 877 (1977).

[205] R. H. Baker, M. Grätzel and R. Steiger, *J. Am. Chem. Soc.* **102**, 847 (1980).

[206] Y. Nakamura, Y. Imakura, T. Kato and Y. Morita, *J. Chem. Soc. Chem. Commun.* 887 (1977).

[207] Y. Nakamura, Y. Imakura and Y. Morita, *Chem. Lett.* 965 (1978).

[208] V. Ramesh and V. Ramamurthy, *J. Photochem.* **24**, 395 (1984). H. Mayer and J. Sauer, *Tetrahedron Lett.* **24**, 4091 (1983). R. Braun, F. Schuster and J. Sauer, *Ibid.* **27**, 1285 (1986).

[209] R. R. Hautala and R. L. Letsinger, *J. Org. Chem.* **36**, 3762 (1971).

[210] K. Yamada, K. Shigehiro, T. Kujezuka and H. Iida, *Bull. Chem. Soc. Japan* **51**, 2447 (1978).

[211] K. Takagi, K. Aoshima, Y. Sawaki and H. Iwamura, *J. Am. Chem. Soc.* **107**, 47 (1985).

[212] R. S. Fargues, M. T. Maurette, E. Oliveros, M. Riviere and A. Lattes, *Tetrahedron* **40**, 2381 (1984).

[213] I. Rico, M. T. Maurette, E. Oliveros, M. Riviere and A. Lattes, *Tetrahedron* **36**, 1779 (1980). I. Rico, M. T. Maurette, E. Oliveros, M. Riviere and A. Lattes, *Tetrahedron Lett.* 4795 (1978).

[214] Y. Hui, J. C. Russell and D. G. Whitten, *J. Am. Chem. Soc.* **105**, 1374 (1983). Y. Hui, J. R. Winkle and D. G. Whitten, *J. Phys. Chem.* **87**, 23 (1983). B. R. Suddaby, R. N. Dominey, Y. Hui and D. G. Whitten, *Can. J. Chem.* **63**, 1315 (1985).

[215] R. L. Van Etten, J. F. Sebastian, G. A. Clowes and M. L. Bender, *J. Am. Chem. Soc.* **89**, 3242 (1967). R. L. Van Etten, G. A. Clowes, J. F. Sebastian and M. L. Bender, *Ibid.* **89**, 3253 (1967).

[216] M. Odhara and M. Watanabe, *Angew. Chem. Int. Ed. Engl.* **14**, 820 (1975). R. Chenevert and N. Voyer, *Tetrahedron Lett.* **25**, 5007 (1984). R. Chenevert and R. Plante, *Can. J. Chem.* **61**, 1092 (1983).

[217] M. S. Syamala and V. Ramamurthy, Unpublished results.

[218] B. Nageswara Rao and V. Ramamurthy, Unpublished results.

[219] J. H. Liu and R. G. Weiss, *J. Photochem.* **30**, 303 (1985). J. H. Liu and R. G. Weiss, *Israel J. Chem.* **25**, 228 (1985).

[220] G. Dasaratha Reddy and V. Ramamurthy, Unpublished results.

[221] M. S. Syamala, S. Devanathan and V. Ramamurthy, *J. Photochem.* **34**, 219 (1986).

[222] P. Arjunan and V. Ramamurthy, *J. Photochem.* **33**, 123 (1986).

[223] D. C. Neckers and J. Paczkowski, *J. Am. Chem. Soc.* **108**, 291 (1986). T. Yumoto, K. Hayakawa, K. Kawase, H. Yamakita and H. Taoda, *Chem. Lett.* 1021 (1985). K. Uekama, T. Irie and F. Hirayama, *Ibid.* 1109 (1978).

[224] T. Tamaki and T. Kokubu, *J. Incln. Phenomena* **2**, 815 (1984). T. Tamaki, *Chem. Lett.* 53 (1984).