Tetrahedron Vol. 43, No. 7, pp. 1211 to 1224, 1987
Printed in Great Britain.

0040-4020/87 $3.00+.00
Pergamon Journals Ltd.

SOLID-STATE PHOTOCHEMICAL REACTIONS

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(*Received in UK* 16 *February* 1987)

INTRODUCTION

This article aims at a characterization of some of the factors which are important in reaction in crystalline solids. As background, we note, first, that molecule motion in solids is restricted, so that there are few deactivating collisions, and lifetimes of excited species may be appreciably longer than in fluids. Further, in fluids the rates of translatory and rotatory diffusions are high so that the results do not depend (except in picosecond experiments) on whether the exciting light is polarized or not, and the distribution of the product is homogeneous throughout the sample. Finally, in crystalline solids as compared to fluids and non-crystalline solids, the molecules are present in only one, or very few, conformations and there are possible only a limited number of approach pathways that could lead to intermolecular reactions.

With this background we turn to the photochemistry of crystalline solids. The subject has been reviewed;[1] a more recent review emphasizes the organo-chemical side.[2]

LATTICE CONTROL OF STEREOCHEMISTRY OF PRODUCT

This aspect of solid-state organic chemistry is relatively well known, and will be treated but briefly.

Basing themselves on results in the literature and on their studies of the (2+2) photodimerization of cinnamic acids, Cohen and Schmidt postulated[3] that "reactions in the solid state proceed with minimal atomic and molecular movement" - the topochemical postulate. In other words, the passage from the parent to the converted crystal involves only small movements, and the course of the reaction is controlled by the crystal structure. This postulate has been verified for many (2+2) cyclodimerizations.[2,4] The topochemical principle implies that a conformationally sensitive reaction will proceed in the crystal only if the molecular conformation there is one suited to reaction. This aspect has been treated extensively by Scheffer, Trotter and co-workers for reactions such as the photorearrangement of tetrahydro-1,4-naphthoquinones.[5]

The topochemical principle does not state that if the crystal has a structure suited to reaction then such reaction must occur. Just as in reactions in the fluid phase, if there are efficient competitive processes the reaction will be inhibited. Further, there are some efficient reactions, notably photoeliminations, for which the molecular movement is clearly not minimal. Therefore Cohen argued[6] that it is required only that there be minimal movement at the surface of contact of the volume containing the reactants, the reaction cavity, with the surrounding molecules. There are cases where the crystal in no way limits the movement in the interior of the cavity.[7] Finally, it should be noted that under certain circumstances extremely large strains develop during solid-state reactions, leading to deviations from topochemical behaviour.[8]

During the 1950's and '60's considerable effort was put into studies of solid-state polymerization, particularly of vinyl compounds. The expectation that such reactions would lead to highly stereoregular polymers proved, however, to be unjustified. Hirshfeld and Schmidt discussed the reasons for this and proposed that for certain types of monomers, in suitable crystal structures, reaction would lead to stereoregularity.[9] Their model is based on rigid, rod-like molecules carrying at each end functional groups which can combine intermolecularly, to generate polymer. These molecules are stacked in the crystal in such a way that in situ rotation of adjacent molecules brings their reactive groups to within combining distance. In this way the polymer chain can develop without translational displacement of the monomers.

Two realization of this model have been achieved; both can be photochemically induced. The one is the polymerization of diacetylenes, which proceeds via carbene or carbene-like intermediates.[10] The second is that of distyrylpyrazine and related compounds which proceeds by repeated (2+2) cycloadditions.[11] Lando has analysed the structures of monomer and polymer crystals and the remarkable similarity of the shapes of a polymer chain and of a stack of monomers has been illustrated.[2,12]

This similarity of external shape of product and reaction cavity has been demonstrated also for small molecules.[2,12] We would then further expect that if a reactant crystal is grown in the presence of some product from a sister crystal, this product would be incorporated into the crystal in place of the contents of some of the potential reaction cavities. This has been observed by Addadi and Lahav when a crystal which they devised for solid-state asymmetric polymerization was grown in the presence of dimer from a sister crystal.[13]

This brings us to another aspect of control by the lattice: if reaction occurs in a chiral crystal then there is no symmetry restriction on the product formed. In other words, product from reaction in a chiral crystal may be chiral, non racemic.[6,14] Several photochemical reactions have been used to achieve such "asymmetric synthesis": one is the photoheterodimerization of a mixed crystal of an aryl-phenyl butadiene with its aryl-thiophene analogue;[15] another is the (2+2) photopolymerization of unsymmetrical 1,4-divinyl-benzenes conducted by Addadi and Lahav, which yields chiral polymer with essentially quantitative enantiomeric excess.[13,16] Finally, there is the recent experiment on mixed crystals of cinnamide with cinnamic acid.[17] The cinnamide crystal is centrosymmetric: when this crystal is grown in the presence of cinnamic acid the latter is occluded into the crystal through centrically related faces, to populate enantiomerically related sites. When such a crystal is cleaved and the two halves irradiated, they yield chiral non-racemic heterodimers showing opposite signs of optical rotation.

On the whole the topochemical principle has proved very successful, but there are situations in which it is not immediately apparent whether or not the principle applies. Particularly in the (4+4) photodimerization of anthracenes there are cases of reaction occurring even though it appears that the potential reaction partners are poorly overlapped and too far apart. Amongst the 9-substituted anthracenes there are cases where the product is the head-to-tail photodimer, whereas the structure suggests that the dimer formed, if any, should be head-to-head. These "errors" have long been recognised[18] and led to the idea that photodimerization in these materials occurs not in the bulk structure but at certain structural defects at which the monomers are in the correct juxtaposition to give the observed products. This idea is based largely on the extensive and elegant studies of Jones, Thomas and Williams.[19] There are two stages in the argument:

(i) if an anthracene crystal is cleaved and one half irradiated while the other half is etched, there is found to be a one-to-one correspondene between the positions of the product crystallites and of the etch pits. This shows that the dimer crystals separate from the parent crystal preferentially at emergent dislocations.[20]

(ii) In a large number of anthracenes it was shown that certain defects (point, linear or planar) have structures which are suited to formation of the observed products;[21] in some of these cases it was found experimentally that such defects are indeed present.

In addition it has been reported that in single crystals of anthracene the initial rate of reaction varies from crystal to crystal,[22] presumably in keeping with the various defect concentrations.

All these results are in keeping with the above idea that in reactive anthracenes there are defects at which the monomers are in position to react topochemically according to the local structure. However, this question of the locus of reaction in anthracenes has not yet been unequivocally answered.

ENERGY TRANSFER

If, as seems probable, the reaction in some anthracenes occurs at specific sites, then this has important implications. The number of molecules sitting at such sites is an extremely small fraction of the total number in the crystal. Since essentially all the incident light is absorbed in the bulk crystal, for reaction to be possible the excitation energy must first be transferred from the bulk to the specific sites. Further, the overall conversions achieved are in many cases very large (50%). We must then assume that more defects are generated as a result of reaction, leading to an increase in the number of molecules suitably juxtaposed to allow photodimerization to occur. This is in keeping with the experiments which show that the kinetics are of autocatalytic type. Also, the idea that energy transfer must occur prior to reaction is supported by the fact that it is possible to inhibit the reaction by doping the crystal with small amounts of impurities of suitable excitation energies.[23] These dopants trap the mobile excitation energy and thus prevent it from reaching the sites at which reaction can occur.

This is a complex subject many details of which remain to be unravelled. Some information has been obtained by high resolution spectroscopic studies of reacting crystals.[24] For our present purpose we take a simpler approach. First, let us note that there is much evidence[25] that the path from anthracene monomer to photodimer passes by way of an excimer - a bimolecular complex carrying one quantum of excitation energy. If in the bulk crystal there is strong overlap of the π-orbitals of the monomers, absorption of light will very rapidly lead to excimer formation. [The same is apparently true of the excimer emitting diphenyl polyenes which undergo (2+2) photodimerization.[26]] However, there may be reasons, particularly steric ones, why in the bulk the excimer cannot pass on to photodimer.

We can then picture two types of system. If intermolecular overlap is small there will be efficient transfer of energy in either the singlet or triplet band of the crystal. This can be considered as molecule to molecule transfer, and in typical cases an exciting quantum will visit up to several thousand molecules during its lifetime. If during the course of this journey the energy reaches a defect site at which the molecules are overlapped there is presumably formed there an excimer which decays to photodimer. For 9-substituted anthracenes only the head-to-tail dimers are formed, so the precursor excimer is probably of this same configuration. This type of energy transfer is efficient at all temperatures.

Another situation arises when the crystal structure is such that there is appreciable intermolecular overlap. In this case there is excimer formation before the energy can be transferred at the molecular level; in other words, the excitation energy rapidly becomes localized at a specific molecular pair. However, given enough thermal energy the excitation energy can be detrapped and move through the crystal by a process termed excimer-to-excimer hopping.[27] The activation energy for this process is much less than the binding energy of the excimer, and for known systems is of the order of 450 cm^{-1}. The rate of hopping is negligible below -100°C while at room temperature the energy may migrate through several hundred molecular pairs. In a crystal in which neighbouring overlapped molecules lie parallel in the bulk structure, there is presumably formed there the head-to-head excimer. For the 9-substituted anthracenes, at least, we presume that the energy migrates until it reaches a site where nearest neighbours are in trans-registry; there will be formed there the head-to-tail excimer which passes on to photodimer. Some exciting experiments based essentially on this mechanism of energy transfer are described by Ludmer and co-workers elsewhere in this issue.[28]

As regards the (2+2) photocyclodimerization of cinnamic acids and related compounds the situation is less clear. The quantum yields of fluorescence of the solid acids are low, even at the low temperatures at which the dimerization yields are negligible. Thus there must be efficient radiationless deactivation processes which compete with reaction, and this suggests that the reported quantum yield of two monomer molecules consumed per absorbed quantum must be in error.[29] For these materials there is no information as to whether or not reaction proceeds preferentially at specific sites. However, the rate of reaction appears to be independent of the quality of the crystal, suggesting that structural defects are not involved. Further, experiments on the relative yields of products from mixed crystals show that neither component traps the excitation energy, suggesting that energy is not transferred.[30] Our working hypothesis is that the radiationless deactivation and reaction are extremely fast, leading to de-excitation before the energy can be transferred.

A word should be said about sensitization. While many cases have been reported of reactions sensitized by a dopant as a result of electron or proton transfer to or from the host,[31] there are almost no verified cases of solid-state reactions initiated by direct transfer of triplet or singlet excitation energy from guest to host, processes which are well known in fluid phases.

TEXTURE

If one irradiates trans-stilbene in fluid solution there occurs partial conversion to the cis-isomer. Since reactant and product have similar solubilities, we expect the solution to remain clear throughout. On the other hand, if one irradiates anthracene in cyclohexane, dianthracene is formed and will precipitate out. Similar extremes of behaviour are observed also in solids.

In crystals the mutual solubilities of different organic materials tend to be very low. Thus, on photoreaction product is formed in parent, and in most cases there will be a tendency for the former to "precipitate out". There are various types of behaviour observed, leading to crystals having a variety of textures (sometimes referred to as morphologies).

In some cases the product accumulates in solution in the parent phase. If product and parent are mutually soluble in all proportions then this will lead to a single crystal to single crystal transformation, as is observed in the polymerization of some diacetylenes. Such reaction can be used to produce large single crystals of polymer, of perfection similar to that of the parent crystal.[32] Similar behaviour has been reported for some photodimerizing benzylcyclopentenones.[33]

A second type of behaviour is exhibited by the cinnamic acids: on irradiation the parent crystals are found to become opaque and to powder, and X-ray powder measurements show a loss of long range order. After 30-60% conversion the powder pattern characteristic of the dimer crystals appears. There is no indication of topotaxy, that is, the crystal axes of product and parent crystals are randomly distributed with respect to one another. Such results can be interpreted as indicating that there is appreciable solid solubility of dimer in monomer, but eventually the solubility limit is passed, and randomly oriented crystals separate out; or that the product at an early stage of reaction segregates from the parent as an amorphous powder, which subsequently crystallizes.

Finally, we turn to the photodimerizing anthracenes. Here, as we have said, it seems that reaction occurs preferentially at specific sites. Further, even at low conversions product crystallites separate out. These are markedly aligned with respect to the axes of the parent crystal.[34]

It is more or less accepted to label reactions in which there is phase separation as "heterogeneous", and those where there is no such separation as "homogeneous". A given reaction may be homogeneous up to a certain conversion, beyond which phase separation occurs. It seems that a principal factor determining the behaviour is the strain engendered during reaction,[35] that is, the extra energy stored in the crystal as a result of the mismatch between product and environment. If the monomer molecules are flexible or their crystals contain solvent of crystallization, there are ready modes for relaxation, the strain will be minimized, and the reaction tends towards the homogeneous.[36] The other extreme is provided by the dianthracenes which are rigid and tend to be rejected by the parent crystal, even at low conversions.

Not only the chemical natures of product and reactant affect the texture: several cases are known where homogeneous behaviour is "frozen in" at low temperatures, but phase separation occurs on subsequent warming, or if the irradiation is performed at a higher temperature.[37] It is very probable that the texture can be determined also by the conditions of the irradiation, via their effect on the gradient of the concentration of the product. Thus, strongly absorbed light will bring about much more conversion near the illuminated face than in the interior of the crystal. On the other hand, weakly absorbed light will yield a more-or-less uniform low concentration of product throughout the crystal. The former case is expected to be associated with phase separation, the latter with homogeneous behaviour. Experiments to test this have not been reported (but see[31]), but one can consider performing these with lights of different wavelengths and/or polarizations.

In the above, reference has been made only to the main classes of behaviour. There are systems which show interesting special properties. Thus, crystals of distyrylpyrazine and related compounds crack on irradiation giving fibrils of polymer which are, more or less, but not exactly, aligned with respect to one another.[38]

There is one large class of materials which undergoes single crystal - single crystal transformations which has not been mentioned. These are the channel or cage inclusion complexes with photoactive molecules as guests. This is too large a field to be entered here, but reference should be made to the recent work on the complexes of various ketones included in crystals of deoxycholic acid. These systems provide ways of substituting the steroid molecule with considerable regio- and stereo-specificity.[39]

The question of texture is of some significance. First, homogeneous reactions can be used to prepare single crystals of product, which may be technically important. We can think, for example, of such properties as electrical conductivity, piezoelectricity and harmonic generation. We have mentioned the possibility of preparing large single crystals of poly-diacetylenes.

Homogeneous reactions are important, from a more basic point of view, because they enable in some cases determination of the crystal and molecular structures of the species present at the start of reaction and at various degrees of conversion. This gives us the structure of the reactant and product, which was important in the development of our ideas on the poly-diacetylenes,[40] and may also give information on the mechanism of the reaction.

A further point to recall is that as long as the product is in solid solution in the parent, the conformation of the product is determined by the structure of the parent ("structural mimicry"). But once the product separates out in its own crystal phase the conformation will be determined by this new structure. For a flexible molecule the difference may be very appreciable. In some cases the only way to achieve the first conformation is by solid-state reaction. Thus, poly-diacetylene molecules will be in the planar, extended-chain conformation only as long as the system is homogeneous. Once the structure is destroyed it is not possible to re-establish this conformation.

A word of caution is in place: we have used the expression "single crystal to single crystal transformation" to describe a process where a given reactant crystal transforms continuously to one product crystal. For such a process, then, the X-ray diffraction pattern of one single crystal of reactant is replaced by the pattern of one single crystal of product. However, the X-ray test alone is ambiguous, because the same result will be obtained for a sample in which the product separates out as a number of crystallites, highly aligned with respect to one another. Thus, microscopic examination of the system is also necessary.

INFORMATION ON MECHANISMS

Our ideas about the detailed mechanisms of reactions are almost always based on indirect evidence: we never "see" the atoms moving or the electrons which are involved. Nevertheless, during the years there has arisen a very successful edifice of ideas on reaction mechanisms. Central to this is the classification of electrons in molecules into various types - σ, π and n - based on both experimental and theoretical evidence. We even think that we know how such electrons are distributed in space. Thus, the distribution of σ-electrons is thought to be cylindrically symmetric about the bond; π-electrons, which are found in olefinic systems, are thought to be concentrated above and below the double bond, with the plane of the bond system being a nodal one; and n-electrons are said to occupy rather compact orbitals in the vicinity of hetero-atoms.

The relevance of this discussion to the present article is the following: in recent years careful X-ray analyses have enabled the crystallographers to obtain detailed information about the electron distribution in molecules. And it turns out that one can "see" the σ-, π- and n-electrons, and they prove to have very much the predicted spatial distributions. If one has a map of the electron distribution in the molecule of a reactive crystal, and knows, from stereochemical and structural analyses of a single crystal - single crystal transformation, what atomic movements are involved in reaction, then one can begin to feel confident that one is arriving at an extremely intimate picture of the reaction pathway. (An alternative method for using X-ray data to give information on reaction pathways has been developed by Bürgi, Dunitz and co-workers.[41] It is, however, not applicable to photochemical reactions.)

To my knowledge the "full treatment", that is studies both of the molecular electron distribution and of the stereochemical course of reaction, has been given only in one case, that of the cumulene tetraphenylbutatriene. The photodimerization of this material involves π-electron interaction. However, there has been studied also a large number of solid-state reactions which are initiated by abstraction of hydrogen from a C-H bond by photoexcited carbonyl. It has been proposed on both experimental and theoretical grounds (for a summary of the arguments see [39,42]) that this reaction involves the lone pair electron, in the $n\pi^*$ state, which is essentially in a p_y orbital of the oxygen. It is known, from other studies,[43] that in the ground state at least, there is a lone pair on oxygen concentrated in the plane of the carbonyl system and at about 100° to C=O; this is very close to theoretical predictions for the p_y orbital. Thus, if the model of participation of the p_y electron in hydrogen abstraction is correct, we would expect a preferred pre-reaction geometry in which the to-be-abstracted hydrogen is in the plane of the carbonyl system and approximately perpendicular to the C=O band.

The most detailed information available concerns tetraphenylbutatriene (Fig.1):

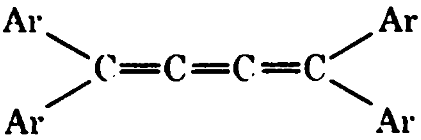

Figure 1

Tetra-aryl butatriene.

This material had been reported to photodimerize by (2+2) cycloaddition of the central, 3γ, bonds of nearest neighbour molecules. This seemed strange, since our experience has shown that (2+2) photodimerization involves neighbours for which there is appreciable π-electron overlap. But we are taught that for the $\beta\gamma$ bonds the π-electrons are distributed mainly in-plane, so that face-to-face close packing of the monomers would not lead to appreciable overlap of the π-electrons of this bond. In fact, Berkovitch-Yellin and co-workers[44] on reinvestigating the structure of the dimer found it to be the centric diallenecyclobutane (Fig.2), and it proved that in the reactant crystal there is good contact of the $\alpha\beta$ double bond of one monomer with the $\gamma\delta$ double bond of its neighbour.[45] Careful analysis of the crystal and molecular structures of the butatriene enabled determination of the molecular electron distribution[45] (Fig.3), which proved to be very similar to our expectations.

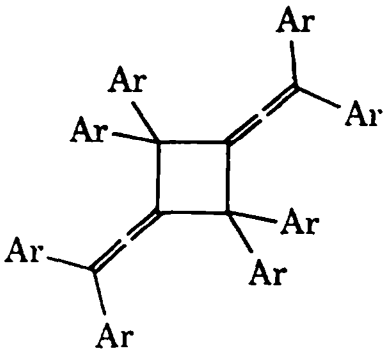

Figure 2

The dimerization product from tetra-arylbutatriene.

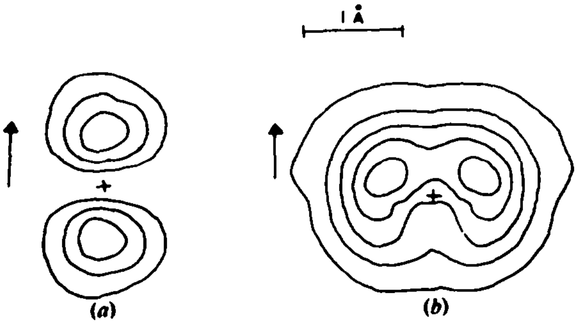

Figure 3

π-Density diagrams in the section perpendicular to (a) the 'outer' bond, and (b) the 'inner' bond of the butatriene chains through their center. Contour intervals 0.1 eÅ^{-3} The arrows indicate the direction perpendicular to the butatriene plane.

Turning now to hydrogen abstraction by ketones: an extensive series of studies has been made by Scheffer, Trotter and co-workers[5,46] on this reaction both in solution and in the solid state. The following discussion is confined to the tetrahydro-1,4-naphthoquinones (Fig.4). X-ray structure analyses of this series of compounds show that all have similar "twist" conformation with the bridgehead substituents staggered; the cyclohexene ring adopts a half-chair conformation and is cis-fused to the more-nearly planar ene-dione ring. A major product on irradiation in the solid state is the 1,4-ketoalcohol, whose formation can be interpreted as resulting from 1,6-bonding of the diradical resulting from extraction of H_β by the adjacent carbonyl (Fig.4). In fact, the geometry of the molecule seems just right for the abstraction: the H.....O distance is of the order of 2.5Å, shorter than the van der Waals distance of 2.72Å, the C-H bond is almost in the plane of the carbonyl system, and the C=O...H angle is about 82°. The occurrence of this reaction can thus be taken as evidence for p_y-electron participation. An important aspect of the reaction is that the overall change in molecular shape is small, the crystal allowing the 1,6-bonding of the diradical to complete the process. It should be stressed that there may be competitive reactions such as abstraction of H_γ by C(3), followed by 3,5 bonding and leading to a diketone, and even intermolecular cyclodimerization.

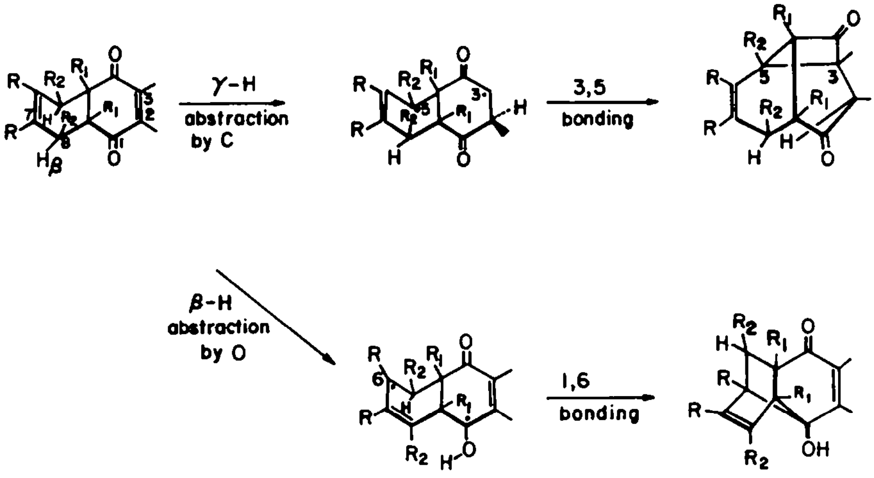

Figure 4

Hydrogen abstraction in tetrahydro-1,4-naphthoquinones.

Another example of hydrogen abstraction followed by formation of a new C-C bond is provided by the recent studies of Lahav, Leiserowitz, Popovitz-Biro and co-workers on the regiospecific and stereospecific photoaddition of guest ketones to host deoxycholic acid in the channels of solid bile acids.[39,42] We treat the prochiral guests acetophenone and its p-F and m-Cl derivatives, which give similar and unexpected results. All these guests attach themselves to C(5) of the steroid A-ring (Fig.5a). The reaction goes in two steps: first there is abstraction of the hydrogen of C(5)-H, to give a pair of radicals centered on the prochiral ketyl radical and on (C5); there follows a coupling of the two radicals with formation of a new C-C bond. It was found that in all these systems the C-H bond is approximately perpendicular to the plane of the carbonyl systems, which does not seem to be in keeping with participation of the p_y electron. However, the matter is not simple: the new chiral carbon centre generated during reaction has an absolute configuration S, opposite to that expected from the initial structure at the reaction site (Fig.5a). Thus, there apparently occurs an 180° rotation about the (O=C)-Ar bond prior to addition. This is interpreted as follows: there is first a partial rotation which brings the oxygen p_y orbital more or less colinear with the C(5)-H bond; now the p_y orbital does point towards the hydrogen and abstraction occurs (Fig.5b). It is not clear what is the driving force for this rotation; its occurrence suggests that there must be some attractive interaction between the p_y electron and the [C(5)]-H in the configuration achieved in the excited state. The second step of the reaction utilizes the π^* electron for formation of the C-C bond. It appears (Fig.5b) that, although the β-lobe of the π^* orbital on carbonyl atom C is initially closer to the steroid than is the α-lobe, the latter is closer after the rotation and it is this, α, lobe which participates in the formation of the new bond. While some aspects of this proposal are still obscure, the rotation is a real effect and some such mechanism must be operative.

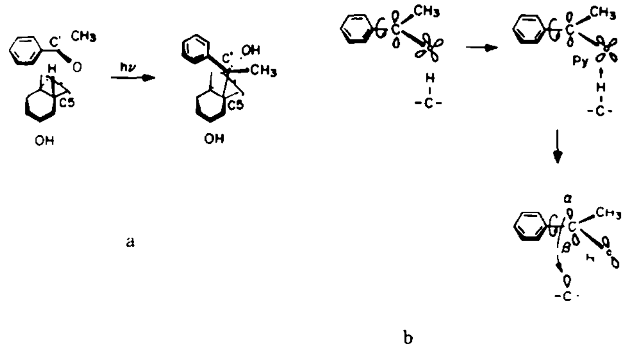

Figure 5

(a) Stereochemistry of the addition of acetophenone to C(5) of the steroid (only ring A shown);

(b) Orbital involvement in the reaction.

SUMMARY

The solid-state provides some unique possibilities of determining reaction parameters. Thus, studies of reactions associated with single crystal - single crystal transformations, and highly refined X-ray diffraction analyses of electron distribution in the parent molecules, provide information on the reaction's driving force and the atomic movement involved. The stereochemical course of the reaction is controlled by the interactions of the reactant molecules with their environment, and therefore by the local structure at the reaction site. This control by structure shows that at least up to the transition state the reactant molecule feels the ground state enviroment; thus we can consider the product-forming step as taking place in solid solution. Depending on the rigidities of the product molecule and of the parent crystal structure there may or may not occur, subsequently, crystallization of the product in its own structure. This corresponds to heterogeneous or homogeneous reaction, respectively. The texture of the resultant solid may be of technical significance.

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