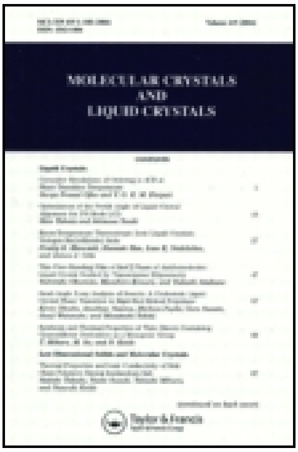

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Solid State Reactivity of Complex Compounds. The Norrish Type II Reaction in Crystalline 1,1,6,6-Tetraphenylhexa-2,4-Diyne-1,6-Diol and in Solid p-Isopropylcalix[8]Arene

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SOLID STATE REACTIVITY OF COMPLEX COMPOUNDS. THE NORRISH TYPE II REACTION IN CRYSTALLINE 1,1,6,6-TETRAPHENYLHEXA-2,4-DIYNE-1,6-DIOL AND IN SOLID p-ISOPROPYLCALIX[8]ARENE.

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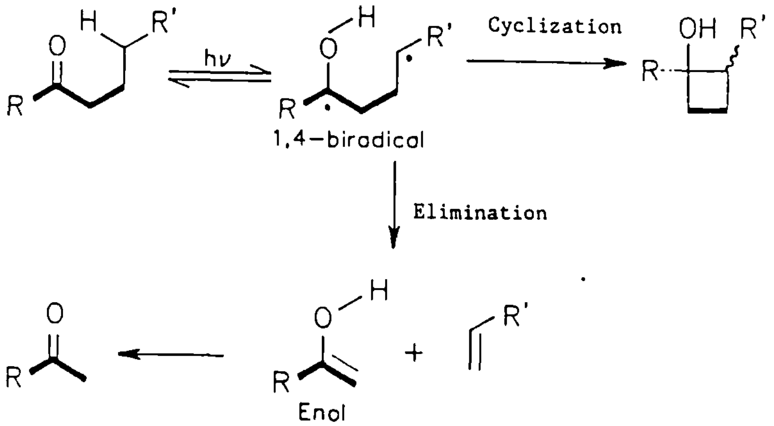
Abstract. Below are presented the Norrish Type II reaction of butyrophenone (Bph) and valerophenone (Vph) in benzene, tert-butanol and as complex compounds with 1,1,6,6-tetraphenyl-2,4-diyne-1,6-diol 1 and p-isopropylcalix[8]arene 2 in the solid state and in solution. Product distributions lead to conclusions about the factors influencing the course of the reactions in the solid state.

INTRODUCTION

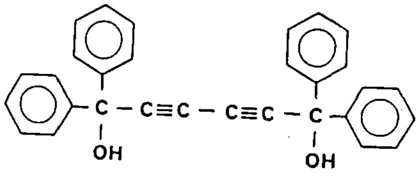
The Norrish Type II reaction has been the subject of numerous investigations and is probably one of the best understood photochemical reactions[1,2]. The light-induced Norrish Type II reaction consists of intramolecular γ-hydrogen atom abstraction by an excited oxygen atom in ketones, in the triplet n,π^* state , to produce a 1,4-biradical. This 1,4-biradical can undergo three common reactions : elimination to an alkene and an enol, cyclization to cyclobutanols and reverse hydrogen transfer to the starting ketones.



Several factors influence the photochemical process of Norrish Type II reactions. Among them two main ones can be pointed out, the <u>conformational flexibility</u> of the reacting ketones and the <u>polarity of the medium</u>. On the one hand the preference for γ-hydrogen abstraction in acyclic ketones has been attributed to the fact that the molecule is flexible enough to choose, from among various transition states, the six-membered cyclic one[3-6]. On the other hand hydrogen bonding of the hydroxyl group of the 1,4-biradical by solvent molecules stabilizes the intermediate preventing reverse hydrogen transfer and increasing the ratio of cyclization to cyclobutanols[7].

Because of their well known mechanism, Norrish Type II reactions have been used as probes in organized assemblies to provide precise information on the environment, structure and mode of interaction of reacting ketones implicated in the reaction. For instance, Norrish Type II reactions of aryl alkyl ketones have been investigated in ordered media such as micelles[7], monolayers[8], liquid crystalline solvents[9] and inclusion compounds[10-12].

In this communication we report our recent results on the photochemical reactivity in the solid state of guest butyrophenone (Bph) and valerophenone (Vph) included in 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol 1[13] p-isopropylcalix[8]arene 2[14].



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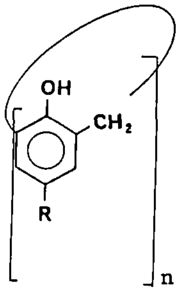


2
n = 8
R = isopropyl

RESULTS AND DISCUSSION

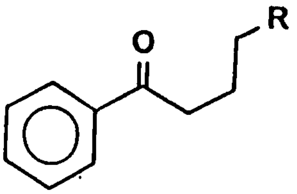
Complex compounds were prepared by dissolving compound 1 or 2 in the appropriate ketone with warming, then precipitating or crystallizing at low temperature. The molar host-guest ratio was found by ^1H nmr and elemental analysis. 1 forms 1:2 complexes with BPh and VPh. Melting points of the complexes 1-BPh and 2-VPh are 50-52°C and 39-40°C respectively. 2 was shown to form a 1:2 complex with BPh, 2-BPh, which melts at 165-180°C. 2 formed a 2:3 complex with VPh, 2-VPh, which melts at 165-190°C. Even though the solution phase photochemistry of BPh and VPh is well documented[15], for the sake of comparison under a common set of reaction conditions, each was irradiated in a non-polar solvent (benzene) and in a strong hydrogen bonding solvent (tert-butanol or t-BuOH). Photolysis of the ketones and complexes were conducted in N_2 saturated 0.1 M solutions. For solid photolysis, complexes were degassed by several evacuation-nitrogen purge cycles. The light source consisted of the output from a Molectron UV 22 pulsed nitrogen laser (wavelenght 337 nm). All product ratios were determined by gas chromatography using the appropriate internal standards[15].

Product distribution upon photolysis is listed in table I. From these data one notes that elimination products are favoured in t-BuOH solutions for pure BPh and VPh as compared to benzene. This effect is possibly explained by the presence of hydrogen-bonding between the 1,4-biradical and t-BuOH molecules. Parallely, it is observed that trans- cyclobutanol is preferred in benzene solutions. The same behaviour is observed when the solid complexes are dissolved in benzene or t-BuOH. The same values for elimination to cyclization ratios and for trans-to-cis cyclobutanol ratios for the complexes in

TABLE I Products ratios upon photolysis of ketones

Condition	Elimination to cyclization products ratio	Trans to cis cyclobutanol ratio
	Butyrophenone	
Benzene	4.7	-
tBuOH	10.4	-
1 -BPh in benzene	4.8	-
1 -BPh solid	no reaction	-
2 -BPh in benzene	5.4	-
2 -BPh in tBuOH	9.4	-
2 -BPh solid	9.6	-
	Valerophenone	
Benzene	2.3	2.9
tBuOH	4.0	1.5
1 -VPh in benzene	2.3	2.9
1 -VPh solid	2.3	2.4
2 -VPh in benzene	2.4	3.0
2 -VPh in tBuOH	3.8	1.5
2 -VPh solid	3.4	2.3

The tabulated ratios correspond to average values ranging from 2 to 60%.



Butyrophenone (BPh) R = H
Valerophenone (VPh) R = methyl

solution is explained by dissociation of the solid when dissolved. This is explained by stronger interactions with solvent molecules of the reacting BPh and VPh even in the presence of complexing agent 1 or 2 . For the solid state irradiations of complex compounds the following observations are made: 1 -BPh does not react. The lack of reactivity suggests that the diyne-diol 1 imposes a conformation on BPh that is not suitable for γ-hydrogen abstraction. One can speculate the linear aliphatic chain is in an extended conformation. This extended conformation inside the cavity of 1 prevents the excited ketone from forming the 1,4-biradical. Such prevention of a Norrish Type II reaction has already been noticed for benzoin alkyl ethers in crystalline cyclodextrin[16]. For 1 -VPh solids, both elimination of cyclization and trans-to-cis cyclobutanol ratios are similar to the ones observed for pure VPh in benzene. This suggests that VPh molecule is located in the non polar region of the 1 solid structure and/or the molecular packing of 1 determines the fate of the reaction. For 2 -Bph and 2 -Vph the elimination to cyclization ratios of the solid state reaction is similar to the ones observed in t-BuOH solutions. This effect is probably due to the presence of hydrogen-bonding between the carbonyl function of the ketones and hydroxyl groups of the calixarenes. The fact that the trans-to-cis cyclobutanol ratio in the case of 2 -Ph in the solid is similar to the ratio in benzene suggests that the that 1,4-biradical conformation, transoid or cisoid, is directed by the calixarene lattice. Such an ability to direct the conformational motion of the 1,4-biradical intermediates to product formation has been seen during irradiation of arylalkylphenones in liquid crystals[17].

CONCLUSION

In this communication we have shown that the Norrish Type II reaction during the solid state irradiations can be influenced by two factors: solvent-type effects on excited state reactivity (hydrogen bonding similar to t-BuOH solution effects and non polar effects similar to benzene) and an encapsulation effect on the formation of 1,4-biradical intermediates.

Of interest is the absence of reactivity of B-Ph when included in diyne-diol 1 crystalline structures. This observation is reminiscent of the protective effect on photolysis due to supramolecular structures[13].

Our present work is directed into two directions. X-ray crystalline structure determination of 1 -BPh and Type II photochemistry of ketones in asymetric calixarene architectures are currently under investigation[19].

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