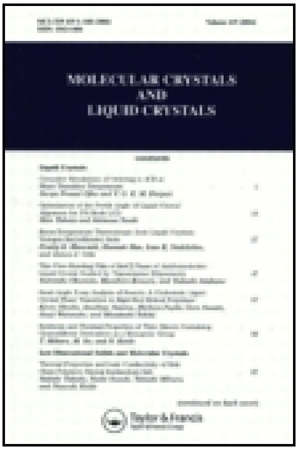

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Bimolecular Solid-state Photoreactions

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BIMOLECULAR SOLID-STATE PHOTOREACTIONS

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Abstract We have studied bimolecular photoreactions between (a) 1-methyl-2,4,5-triphenylimidazole and benzophenones, (b) indole and naphthalene or phenanthrene, and (c) 6-cyano-1,3-dimethyluracil and acenaphthylene or phenanthrene, both in the solution and solid phases. Different products (or product distributions) were obtained in the two phases and the reactions were usually more selective in the solid state than in solution.

Keywords: Solid-state Photoreactions, Bimolecular Solid-state Photoreactions, Hydrogen abstraction, Quantum yield, Porphyrin

INTRODUCTION

Among various applications of the solid state to organic photoreactions, I have been studying four aspects: (A) bimolecular solid-state photoreactions,[1-3] (B) solid-state hydrogen abstraction by excited carbonyl compounds,[4,5,10] (C) estimation of approximate solid-state quantum yields,[5-10] and (D) photocatalysis by silica gel-supported metalloporphyrins. Here I would like to describe our results concerning the first topic.

Solid-state photoreactions between two different organic compounds are little studied. In contrast, photoreactions in solution are thoroughly studied. Our purpose of studying bimolecular solid-state photoreactions is to discover novel reactions with chemo-, regio-, and stereoselectivities, which are quite different from those in solution. Solid-state photoreactions we have found are (a) oxetane formation from benzophenone and 1-methyl-2,4,5-triphenylimidazole, (b) addition of indole to naphthalene or phenanthrene, and (c) [2 + 2] cycloaddition of 6-cyanouracils with acenaphthylene or phenanthrene.

Before describing the above reactions, I will briefly describe our studies dealing with the topics (B) - (D). From the studies of our own and other workers,[4,5,7,10] I have indicated that a molecule in the crystalline state can move to a considerable degree and consequently the solid-state photoreactivity will depend on both looseness of crystal packing and reaction temperature in addition to crystal structure.[10] In this context, violation of Scheffer's criteria[12] for solid-state hydrogen abstraction by excited carbonyl groups as well as violation of Schmidt's criteria[13] for solid-state alkene photodimerization is not surprising.

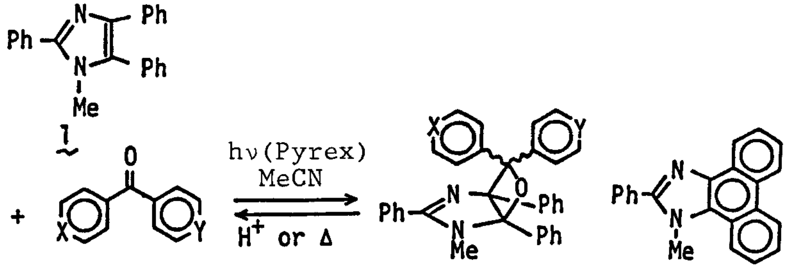
We have proposed a convenient method to estimate solid-state quantum yields.[5,8] The procedure is very simple: dissolve a sample with ether or methylene chloride in a Pyrex tube, evaporate the solvent to leave a coated crystalline film whose surface area is adjusted to be constant as precisely as possible, and then irradiate after degassing on a merry-go-round apparatus. The obtained quantum yields may not be very precise because of the problems associated with imperfect crystal structure, reflection of light from the crystal surface and variable surface area. But, we have found that the method gives results with satisfactory reproducibilities (usually ± 5 %). Furthermore, the observed quantum yield for the photodimerization of trans-cinnamic acid (0.59)[8] is not very different from the previously reported value (0.7). We have applied the present method for studying reaction mechanisms of several solid-state photoreactions.[5-10]

For example, we notice that, in the case of the homologous compounds, the lower-melting counterpart has probably looser crystal packing and thus has greater solid-state photoreactivity than the higher-melting one.[5,6,10] It is also inferred that the benzocyclobutenolization of 2,4,6-triisopropylbenzophenone in the solid state occurs through the intramolecular hydrogen abstraction from the π,π^* excited state rather than from the n,π^* excited state.[5,10]

Cationic water-soluble porphyrins, [meso-tetrakis(1-methyl-4-pyridiniumyl)porphyrinato]iron(III) and its derivatives, bind very strongly to silica gel. We have found that under the dry reaction conditions, these silica gel-immobilized iron porphyrins can very much promote autooxidation of benzhydryl ethers and photooxidation of stilbene and cyclooctene.[11]

1-METHYL-2,4,5-TRIPHENYLIMIDAZOLE AND BENZOPHENONES[1]

We have found that 1-methyl-2,4,5-triphenylimidazole (1) produced stable oxetane photoadducts 3b - 3e with good efficiency upon irradiation in the presence of large excess of various benzophenone derivatives 2a - 2e in acetonitrile solution under bubbling of nitrogen (Scheme I). Dehydrocyclization into the phenanthrene ring 4a - 4d also occurred as a minor reaction. These oxetanes readily underwent cycloreversion by acid catalysis or by heating. The lack of oxetane formation from 4,4'-dimethoxybenzophenone (2a) was ascribed to efficient triplet energy transfer quenching of its triplet state by the ground state of 1. Since there is an inherent interest in thermoreversible photoreactions, which may serve as model systems for photochromic information storage and solar energy storage, solid-state irradiations of mixtures of 1 and 2a - 2e were carried out.



2	3	4
a; X = Y = MeOC	0	54 %
b; X = Y = MeC	53	9
c; X = MeC, Y = HC	59	6
d; X = Y = HC	64	3
e; X = HC, Y = N	85	0

SCHEME I Photoreaction of 1 and 2 in solution.

A mixed solid sample for the irradiation was prepared either by grinding a mixture of crystals in an agate mortar or by melting a mixture of crystals followed by resolidifying the melt. Both samples gave similar results.

Figure 1 shows the apparatus for preparative solid-state photolysis. A solid sample is spread on the inside of the face A and is pressed by means of a Pyrex plate and a cotton packing to fix it. By using this apparatus, we have carried out irradiations under inert atmosphere and at variable temperatures.

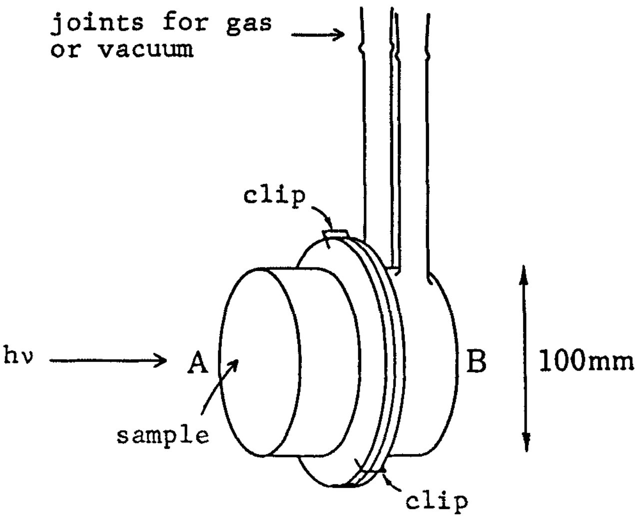
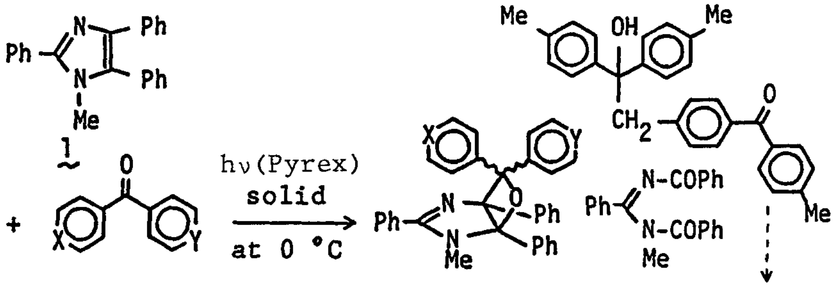


FIGURE 1 Apparatus for solid-state photolysis.

We have found that, upon photolysis of a mixed solid of **1** and **2** (1 : 6 molar ratio) under a nitrogen atmosphere, the oxetane is formed only from benzophenone (**2d**) (Scheme II). Furthermore, the dehydrocyclization product of phenanthrene type **4** was not produced and, instead, an oxidation product **5** was produced. Except for the case of 4,4'-dimethylbenzophenone (**2b**), a single photoproduct was formed. It appears that only a mixed solid of benzophenone (**2d**) and 1-methyl-2,4,5-triphenylimidazole (**1**) can take a mutual molecular geometric arrangement that is suitable for the oxetane formation to occur.



2	3	5	6
a; X = Y = MeOC	0	15	- %
b; X = Y = MeC	0	1	15
c; X = MeC, Y = HC	0	8	-
d; X = Y = HC	47(22)#	0(0)#	-
e; X = HC, Y = N	0	6	-

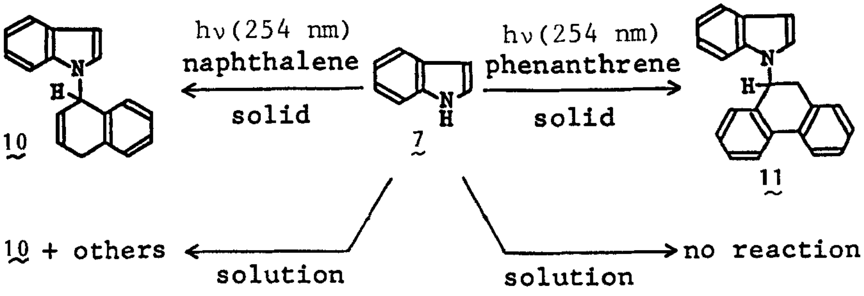
#At -20 °C in parentheses

SCHEME II Photoreaction of 1 and 2 in the solid state.

INDOLE AND NAPHTHALENE OR PHENANTHRENE[2]

Irradiation of a mixed solid of indole (7) and naphthalene (8) (1 : 3 molar ratio), which was prepared by resolidifying the melt, gave an addition product, 1-(1,4-dihydro-1-naphthyl)indole (10) as a single photoproduct (Scheme III). In acetonitrile, methanol, or benzene solution, uncharacterized byproducts were also obtained. This result as well as the results for 1 and 2 (Schemes I and II) suggest that a bimolecular photoreaction may occur more selectively in the solid state than in solution, as is often observed with crystals of pure materials. This may imply the presence of certain regular patterns of intermolecular interactions in mixed solids.

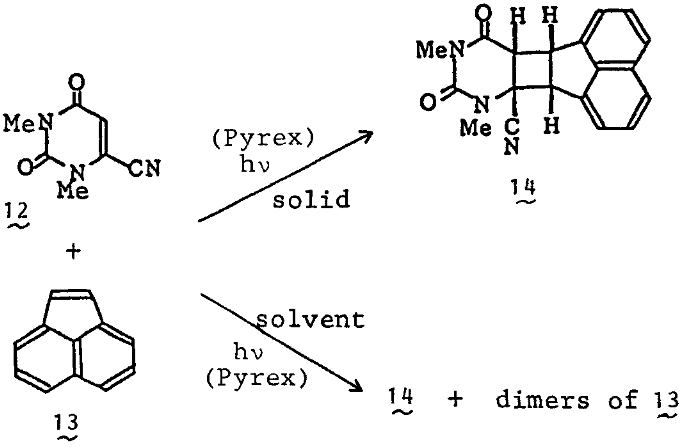
Similar irradiation of a 1 : 3 mixed solid of indole (7) and phenanthrene (9) gave also a single photoproduct, 1-(9,10-dihydro-9-phenanthryl)indole (11), whereas no reaction occurred in solvents (Scheme III). This solid-state reaction may be an example of the case that close juxtaposition of reagents in solids may promote the photoreaction.



SCHEME III Bimolecular photoreaction of indole.

6-CYANO-1,3-DIMETHYLURACIL AND ACENAPHTHYLENE OR PHENANTHRENE[3]

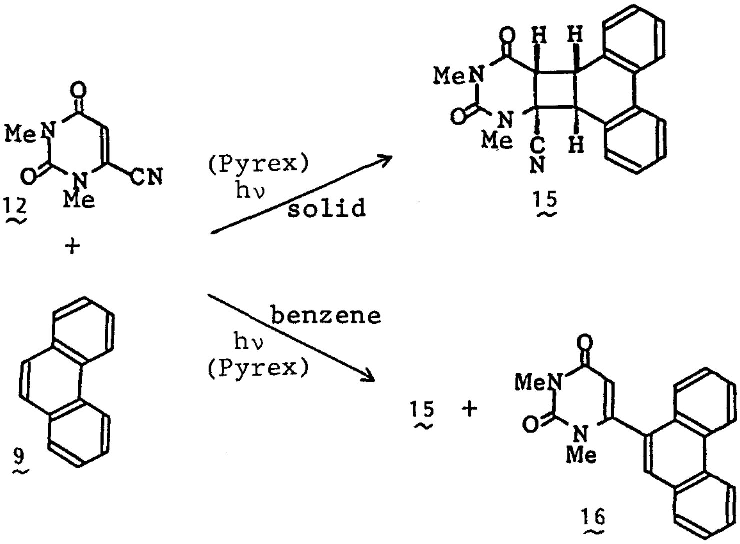
A higher selectivity in a bimolecular photoreaction attained by the solid-state (vide supra) was also observed in the following examples. Thus, irradiation of a 1 : 2 mixed solid of 6-cyano-1,3-dimethyluracil (12) and acenaphthylene (13), which was prepared by resolidifying the melt, gave a cis [2 + 2] adduct 14 as the sole product (Scheme IV). When the reaction was done in acetonitrile, methanol or benzene, the



SCHEME IV Photoreaction of 12 and acenaphthylene.

trans and cis photodimers of acenaphthylene (13) were obtained in addition of the cis [2 + 2] adduct 14.

Similar irradiation of a 1 : 2 mixed solid of 6-cyano-1,3-dimethyluracil (12) and phenanthrene (9) gave a cis [2 + 2] adduct 15 (Scheme V). When the reaction was done in benzene, the cis [2 + 2] adduct 15 and 6-(9-phenanthryl)-1,3-dimethyluracil (16) were obtained.



SCHEME V Photoreaction of 12 and phenanthrene.

CONCLUSION

Bimolecular photoreactions between two different compounds may often occur more selectively in the solid state than in solution, as is often observed with crystals of pure materials.

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