

Organic Synthesis under Solvent-free Condition. An Environmentally Benign Procedure – II

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In the first part of the article, thermal solvent-free reactions were described. In this part solvent-free reactions brought about by light radiation are discussed.

Solid-state Photochemical Reactions

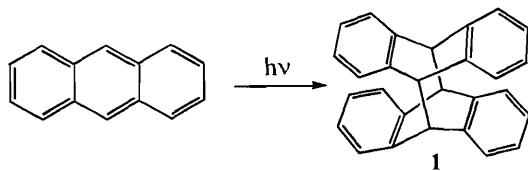
The transformation of one compound into another is a consequence of bond-breaking and bond-forming process either within the molecule (intramolecular) or between molecules (intermolecular), and is brought about thermally or photochemically. The functional group in a reactant molecule absorbs appropriate electronic energy whereby the molecule attains the excited state and forms products. The molecules that absorb light in the UV-visible range, that is, the molecules that undergo $\pi-\pi^*$ and $n-\pi^*$ electronic transitions, can in principle react when exposed to radiation of right frequency. Olefins, ketones, α,β -unsaturated carbonyl compounds, carboxylic acids and derivatives, aromatic compounds and dienes are some of the widely studied organic compound classes that undergo photochemical reactions. It should also be noted that the process vital to the occurrence and continuation of life on earth is a complex sequence of photochemical reactions called photosynthesis.

Exposing a compound to sunlight in solid state is one of the oldest reactions to be carried out in solvent-free conditions. Such reactions then were performed not with any deliberate intention to develop non-polluting or energy-saving reaction, but more out of curiosity. Photo reactions were also accidentally noticed when changes in the properties of solids exposed to sunlight were observed as in the case of anthracene by Firtsche in 1867. The correct structure (1) of the product was established in 1891.

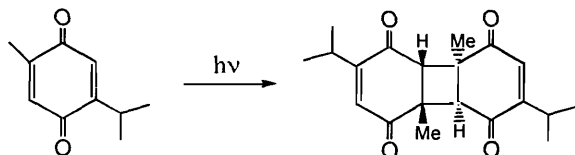
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Keywords

Sunlight, photochemistry, chiral products, inclusion complexes, stereoselective synthesis, solvent-free photoreactions.



The first solid state [2+2] cycloaddition reaction observed was of thymoquinone when it was exposed to sunlight by Liebermann in 1877.



Later on, innumerable photochemical reactions have been carried out using sunlight. Though exploiting solar energy for chemical transformations would be environmentally most benign, nevertheless practical problems have still not been overcome in most cases. Hence, in practice suitable lamps are employed for irradiating the substrates.

Photochemistry in solid state has opened up a fascinating array of possibilities to synthesize compounds with high stereoselectivity and enantioselectivity. The inclusion complexes of achiral guest and chiral host produce chiral photoproducts of the former compounds. Chiral induction can be brought about at achiral centre within a molecule if a chiral group is suitably situated in the molecule.

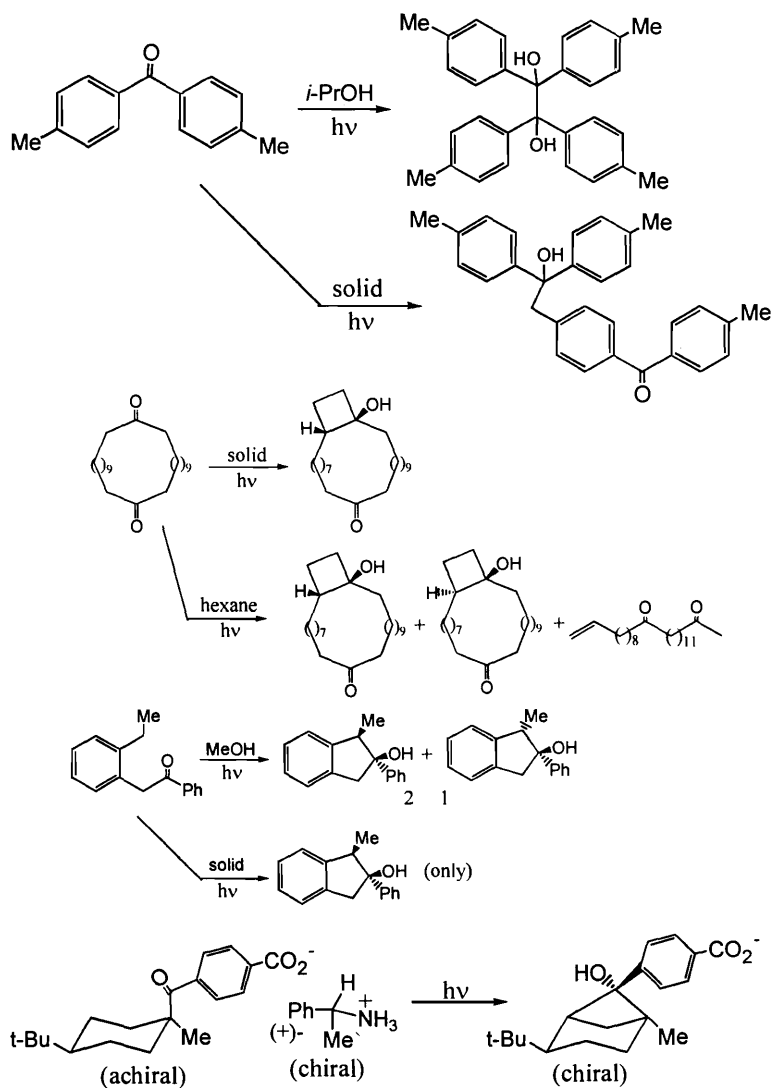
Some randomly selected solid-state photo reactions are given below for illustration. The results of irradiation in solution in a few cases are also mentioned to highlight the fascinating differences.

Hydrogen Abstractions

Photoreductions of ketones either by intramolecular hydrogen abstraction-cyclization (Norrish type II reaction) or by intermolecular process is well known. It has been observed that photo-

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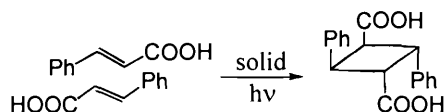
Enantioselectivity is achieved by solid-state photoreaction of the salt of a prochiral keto acid and optically active amine.

Cycloadditions

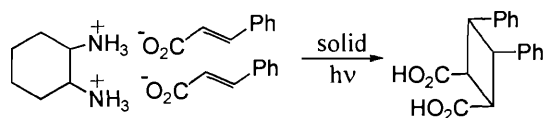
[2+2] cycloaddition is one of the most exploited photochemical reactions in organic synthesis for the construction of cyclobutane ring system. Dimerization of α,β -unsaturated ketones, alde-

hydres or carboxylic acids, etc. occurs easily in solid state or in solution.

Crystals of cinnamic acid dimerize to truxillic acid on irradiation. (This experiment can be given to MSc students. Just spread out cinnamic acid, crystallised from ethanol, on a tray and keep it in the bright sunlight for a few days. The reaction may be monitored by TLC or melting point).

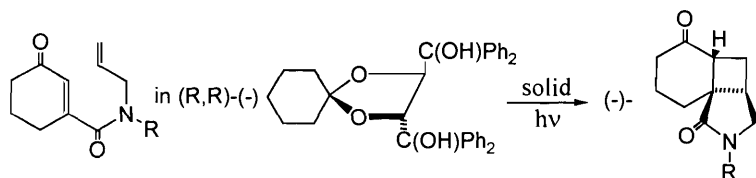


The orientation of the neighbouring cinnamic acid molecules in the solid state can be changed by cocrystallizing the acid with a 1,2-diamine and the stereo-isomeric dimer β -truxinic acid can be obtained.



The study of photodimerization of cinnamic acid and its derivatives is a popular subject and much information is available.

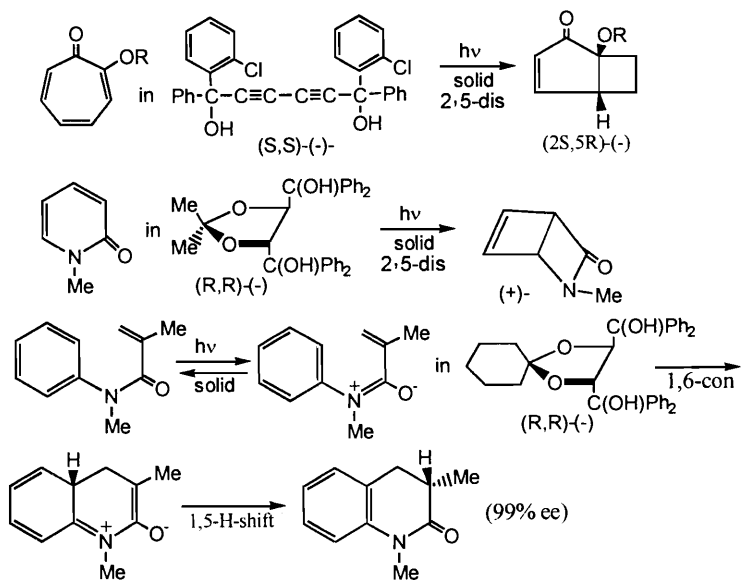
Configuration of the product can be controlled to get pure enantiomers by starting with proper crystal modifications of the substrates or using inclusion complexes of achiral substrates in optically active host molecules.



Electrocyclic Reactions

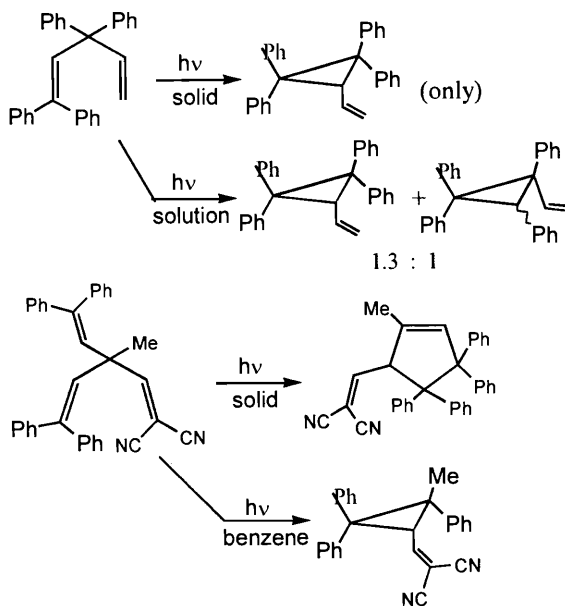
Photochemical electrocyclic reactions are found to occur in solid state. By employing inclusion compounds of prochiral

substrates in optically active hosts, optically active photo-cyclization products can be obtained.



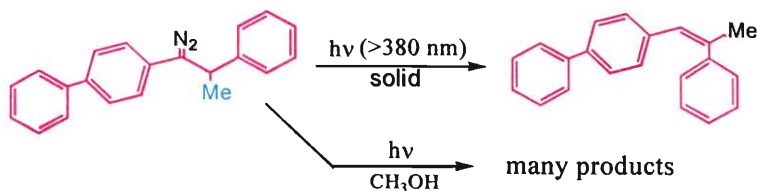
Di- π -Methane Rearrangement

1,4-Dienes undergo rearrangement to isomeric products when photolysed (irradiated).

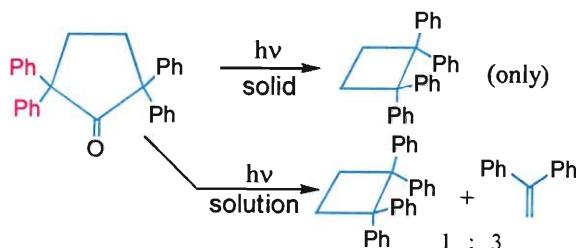


Expulsion of Small Molecules

Diazoalkanes lose nitrogen to form carbenes, which isomerize to olefins or insertion products.



Ketones undergo photodecarbonylation either in solid state or in solution and the products could be different in the two media.



Conclusion

The examples of various thermal and photochemical reactions under solvent-free conditions shown above are only a glimpse of the immense possibilities of such reactions in organic synthesis. We may not be able to totally avoid organic solvents, but continuous attempts have to be made to devise and explore synthetic methods in this direction. It is the need of the hour to save the environment and cut costs of production. One way of achieving this is to keep the solvents away whenever it is possible. It is also academically rewarding to study how the solid state structure influences the outcome of a reaction. It would be fascinating also to look into solid-gas, liquid-liquid or solid-liquid reactions in the total absence of solvents. It is gratifying to note that several Indian scientists are working in this area now. Shun the solvent to save the surroundings.

Suggested Reading

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