

PHOTODIMERIZATION OF ACRYLONITRILE

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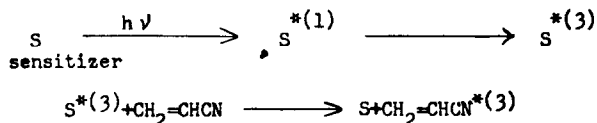
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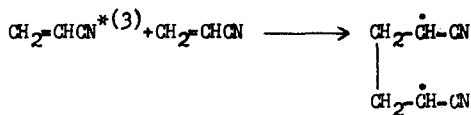
In 1949 Coyner¹⁾ and Bayer²⁾ reported that thermal dimerization of acrylonitrile produced 1,2-dicyanocyclobutane. We have found that acrylonitrile dimerizes into 1,2-dicyanocyclobutane photochemically in the presence of sensitizers³⁾. In a typical example, a solution containing 32.2g of acrylonitrile, 31.5g of acetonitrile, 1g of benzophenone and 1g of ammonia water was irradiated by a 270W high pressure mercury lamp at 20°C for 6 hours. As the result 9.58% of acrylonitrile converted into 1,2-dicyanocyclobutane and no polymer was formed. The ratio of cis and trans dimers was 58/42.*

Search for effective sensitizers has revealed that they are required to have the excitation energy of triplet more than ca. 62 kcal/mol. Namely, propiophenone (74.6), xanthone (74.2), acetophenone (73.6), benzaldehyde (71.9), carbazole (70.1), benzophenone (68.5), thioxanthone (65.5) and 4-phenylbenzophenone (62.8) are effective as sensitizers, but naphthalene (60.9), benzil (53.7), eosin (43.0) and anthracene (42.5) do not sensitize the photodimerization of acrylonitrile, where the values of the excitation energy of triplet (kcal/mol)⁴⁾⁵⁾ are parenthesized.

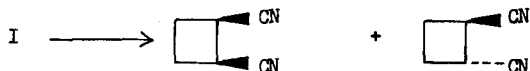
From the results we suggest a following reaction mechanism. Probably,



* Authentic samples of cis and trans 1,2-dicyanocyclobutane were prepared according to Lehn and Raymond.⁷⁾

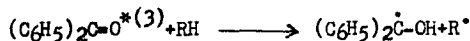


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intramolecular coupling of the biradial I proceeds so rapidly that dimerization predominates over polymerization. If the cycloaddition reaction mechanism is concerted one, the reaction must be stereospecific⁶⁾. Therefore the cis/trans ratio of the produced dimers indicates that the cyclodimerization proceeds mainly through a multistep mechanism involving the discrete biradical intermediate.

Photoreaction of acrylonitrile in ethanol or cyclohexane also gives 1,2-dicyanocyclobutane. But in those instances, linear high polymer is a main product. These results are not difficult to interpret, because the following reaction is well known⁵⁾, where RH is alcohol or saturated hydrocarbon. It seems likely



that the reactive radicals derived from the reaction of benzophenone at excited triplet state with solvents attack acrylonitrile monomer to initiate chain reaction of polymerization. Therefore selection of a solvent is important.

Details will be reported later.

References

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