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THE PHOTOCYCLOADDITION OF ACENAPHTHYLENE WITH TETRACYANOETHYLENE

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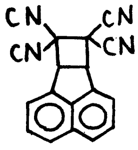
Summary. Irradiation of a solution of acenaphthylene and tetracyanoethylene yielded the cycloadduct. The excited singlet acenaphthylene is suggested to be the reactive species.

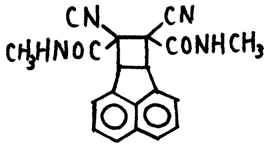
The ready photodimerization of acenaphthylene to form the cis- and trans-dimer is a well-known process and has been studied extensively from the mechanistic viewpoint.1) It has recently been concluded that the trans-dimer is formed from an acenaphthylene triplet state, while the cis-dimer is formed both from the acenaphthylene triplet state and from an acenaphthylene singlet excimer. However, very few reports have appeared on the photoaddition of acenaphthylene to other olefines. Cycloadditions to acrylonitrile,2) to maleic anhydride,3) and to cyclopentadiene4) are the only examples. In these reactions significant heavy-atom solvent effects have been observed and the acenaphthylene triplet state has been suggested to be the reactive species.

We wish to report the photocycloaddition of acenaphthylene with tetracyanoethylene in which the excited singlet acenaphthylene is suggested to be the reactive species.

In a typical experiment, the outgassed solution (blackish purple-colored) of acenaphthylene (0.05 M) and tetracyanoethylene (0.05 M) in dichloroethane was irradiated in a glass tube for 30 hr with a 500 w high-pressure mercury lamp (λ>310 nm). From the resulting solution the cycloadduct, 1,1,2,2-tetracyano-2a,8b-dihydroacenaphtho-cyclobutane (**1**), was isolated in a 18.4 % yield based on the reacted acenaphthylene, together with small amounts of unidentified products after treatment by silica column chromatography. Noticeably, the formation of acenaphthylene dimer was almost undetectable. The identification of **1**, decomp. 186°C (recryst. from dichloroethane, white columnar crystals), was made on the basis of its IR, UV, NMR, and Mass spectra, and the elemental analysis. The IR spectrum shows a weak C≡N absorption at 2250 cm^{-1}. The UV spectrum is very similar to that of acenaphthene, showing λ_{max} at 279, 290, and 300 nm. Mass: M^+ 280 (calc. M.W. 280). NMR(in deuterio DMSO): τ 1.75-2.25 (multiplet, 6H, aromatic protons), τ 4.47 (singlet, 2H, methine protons). Found: C, 76.87; H, 2.61; N, 20.32 %. Calc. for $C_{18}H_8N_4$: C, 77.15; H, 2.85; N, 20.00 %. The product **1** decomposed in refluxing methanol to give **II**, which was identified by its spectral evidences and by the elemental analysis.



(1)



(II)

Irradiation with light of wavelength longer than 330 nm, the absorption of which by tetracyanoethylene is negligibly small, gave essentially the same result, which shows that the excited acenaphthylene is a reactive species. Irradiation of an oxygen-saturated solution or in the presence of ferrocene which acts as a triplet quencher[1] (E_T 43 kcal/mole for ferrocene; E_T 43-45 kcal/mole for acenaphthylene) resulted in almost the same results (yields of **1** ; 17.2 % and 16 % respectively). Although quenching effect of acenaphthylene fluorescence is unable to be examined because of its non-fluorescent character, the absence of quenching effect by triplet quenchers strongly suggests a singlet reaction of acenaphthylene.

The mechanism of charge-transfer excitation is also possible, since acenaphthylene forms a charge-transfer complex with tetracyanoethylene in the ground state, showing a charge-transfer band at λ_{CT}max 505 nm (in CH_2Cl_2)(5). However, selective excitation in the charge-transfer band using a combined filter solution of $CuCl_2$ and $CaCl_2$ in water (500< λ <600 nm) or with a 500 w Xenone lamp through a colored-glass filter (Toshiba VY-500, λ>500 nm) for a prolonged time did not yield the cycloadduct, the reagents being recovered almost quantitatively. It may be suggested that the concentration of the charge-transfer complex is very small, or that the geometry of the charge-transfer complex is not favorable for the cycloaddition reaction between the olefinic double bond of acenaphthylene and tetracyanoethylene. The absence of acenaphthylene dimer suggests that the acenaphthylene triplet state which might be produced through a radiationless transition from the excited singlet state may not be enough populated to produce the trans-dimer. This may be interpreted as that the excited acenaphthylene may possibly be deactivated through the charge-transfer interaction with tetracyanoethylene, in addition to the singlet reaction to give the cycloadduct **1** . Further studies are in progress with respect to these points.

References

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