Photoinduced Reactions of Polycyanoaromatic Compounds with Aliphatic Nitriles

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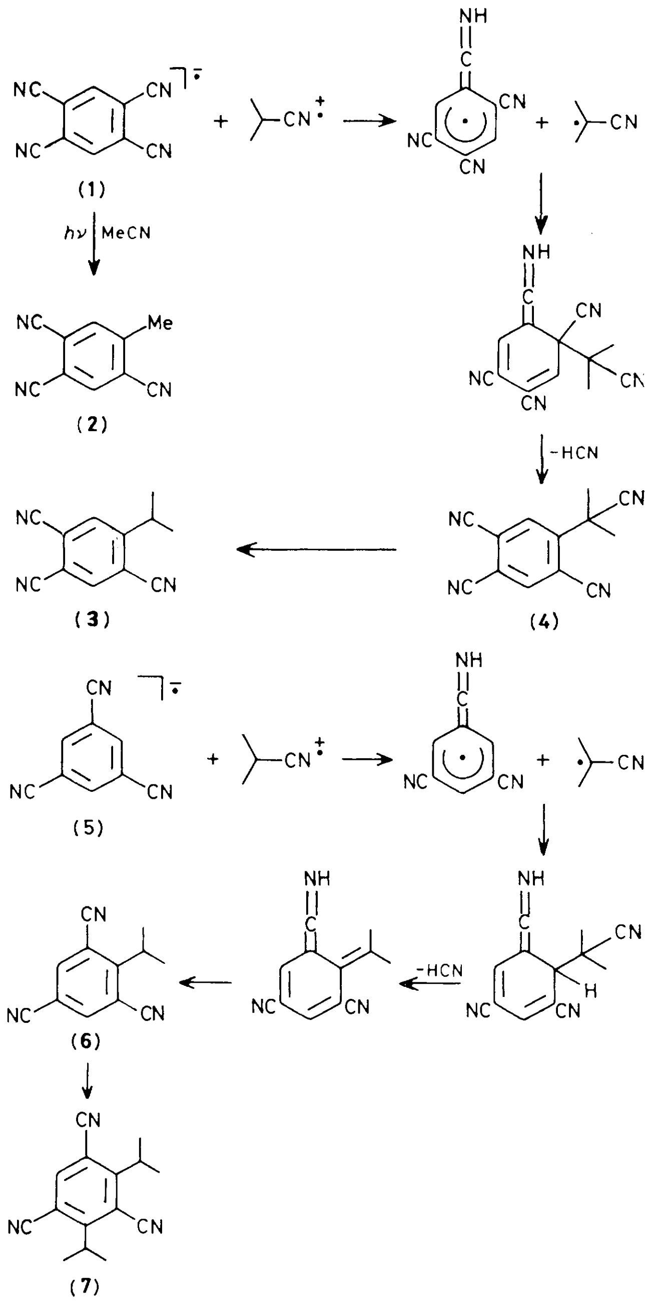
Upon irradiation of 1,3,5-tricyanobenzene in isobutyronitrile one or two ring hydrogens were replaced with isopropyl groups, while in the case of 1,2,4,5-tetracyanobenzene one of the cyano groups was replaced.

In 1965 Sofue and Nagakura reported that irradiation of 1,2,4,5-tetracyanobenzene (TCNB), (**1**) in acetonitrile gave a TCNB radical anion which was detected through flash photolysis.[1] We report here that in accord with this result irradiation of this system gave substitution products as in the case of TCNB–toluene[2] or TCNB–ether systems.[3]

Irradiation of (**1**) (26 mg) in acetonitrile (20 ml) with a 12 W low pressure mercury arc under nitrogen for 24 h gave 2,4,5-tricyanotoluene (**2**), m.p. 140—142 °C, in 16% yield. A similar irradiation of (**1**) (24 mg) in isobutyronitrile (20 ml) for 20 h gave 2,4,5-tricyanocumene (**3**), m.p. 105—108 °C, and the cyanopropyl derivative (**4**), m.p. 137—141 °C, in 39 and 12% yields respectively.

While 1,3,5-tricyanobenzene (**5**) was stable in acetonitrile upon irradiation under similar conditions, it reacted with isobutyronitrile to give 2,4,6-tricyanocumene (**6**), m.p. 97—99 °C, an isomer of (**3**), and the disubstituted product (**7**), m.p. 184—185 °C, in 31 and 5% yields respectively.

Dicyanobenzene (DCNB) did not react with isobutyronitrile under similar irradiation conditions, while we have already reported that 9,10-dicyanoanthracene (DCNA) reacted with isobutyronitrile upon irradiation in the presence of triethylamine to give 9-isopropyl-10-cyanoanthracene.[4] Since tricyanobenzene did not thermally react with 2,2-azoisobutyronitrile, the substitution mentioned here is not a typical radical reaction. Referring to Nagakura's flash photolytic results and considering the dependency of reactivity on the electron affinities of the cyanoaromatic compounds [(**1**) 0.4, (**5**) 0.1, and DCNB 0 eV],[5] we suggest that the reaction proceeds through charge-transfer from the aliphatic nitrile to the polycyanoaromatic compounds. The reaction possibly proceeds as general photoinduced electron transfer reactions proceed.[2,3,6]



Scheme 1

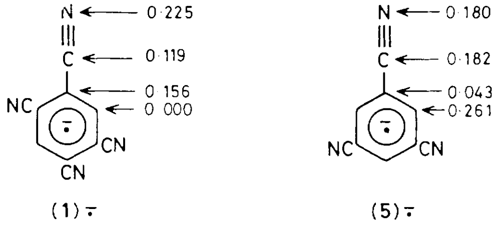


Figure 1

To account for the difference in the position of substitution in (**1**) (1-CN group) and (**5**) (2-H atom) we assume that the proton-transfer from the radical cation to the radical anion occurs onto the nitrogen instead of the ring carbon of the acceptor. Succeeding radical coupling, elimination of HCN, and rearrangement would produce (**4**) or (**6**) as shown in Scheme 1.

Another conceivable mechanism is direct attack of the cyanoisopropyl radical onto the ring carbon having higher frontier electron densities in the acceptor, since the positions of substitution in (**1**) and (**5**) aforementioned are in accord with those having higher frontier electron densities[7] in the radical anions. The densities $f_r^{(E)}$ of $(\mathbf{1})^{\cdot-}$ and $(\mathbf{5})^{\cdot-}$ calculated by the simple Hückel method are shown in Figure 1.

Although the reaction mechanism of the secondary processes is not yet clear, this reaction provides the first example of aliphatic nitriles reacting as electron donors upon irradiation. This is another example of DCNA–acetonitrile type reactions[4] where the solvent aliphatic nitrile can participate in the photochemical reactions of donor–acceptor systems.

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