An Unexpected Fragmentation Reaction of Tetracyanoethylene with Isobenzimidazoles

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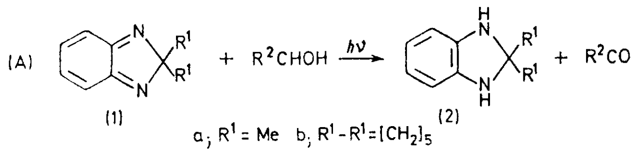
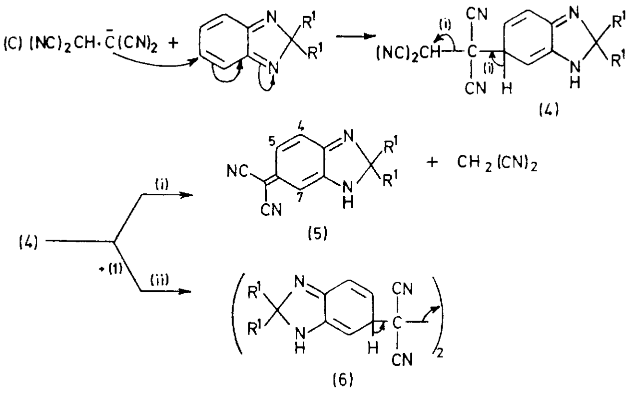
Summary Isobenzimidazoles (**1**) react with tetracyanoethylene in the cold to give novel *p*-quinonoid products (**5**) in which only half the tetracyanoethylene molecule is incorporated.

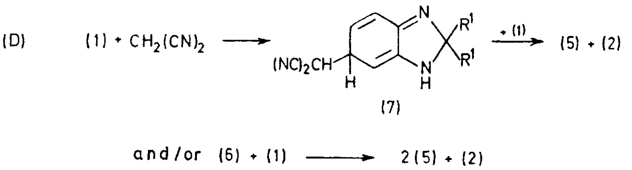
Isobenzimidazoles[1] undergo an unexpected reaction with cold, alcoholic tetracyanoethylene (TCNE) yielding the purple products (**5**) (40—50%).† The same products are formed from the mono- and di-*N*-oxides of the isobenzimidazoles but at a slower rate. This suggests that the reaction is preceded by thermal deoxygenation.[1b]



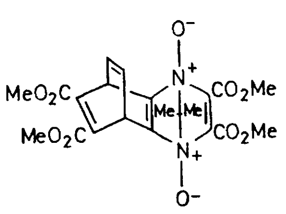
$$\text{(B)}\quad (2) + \text{TCNE} \rightleftharpoons (1) + \underset{(3)}{(NC)_2CH\cdot CH(CN)_2}$$

We believe that the reaction proceeds in at least four steps: (A) Photoreduction of the isobenzimidazoles (**1**) in alcoholic solution to the dihydro-compounds (**2**). This reaction, characteristic of quinones, occurs readily in daylight and produces acetone when Pr^iOH is used as solvent. In benzene no reaction takes place, thus supporting the suggested nature of the first step. Furthermore, the reaction of the dihydro-compound (**2**) with TCNE also gives the purple product (**5**). (B) The dihydro-isobenzimidazole (**2**) then reacts in a redox manner with TCNE to give tetracyanoethane and the isobenzimidazole in accord with the known ability of TCNE to dehydrogenate.[2] (C) Tetracyanoethane being a strong acid[3] (pK_a 3·6) then undergoes Michael addition to the isobenzimidazole giving the product (**4**) which is converted into the purple solid (**5**) by loss of malononitrile. Alternatively, treatment of (**4**) with a further mole equivalent of the isobenzimidazole would yield (**6**). As expected, both tetracyanoethane and malononitrile react with the isobenzimidazole to give the same purple product (**5**). It is of interest that the isobenzimidazole di-*N*-oxide reacts with malononitrile to give the same purple product together with its blue oxide. (D) Finally, the dimer (**6**) [or the addition product (**7**) of malononitrile to the isobenzimidazole] suffers dehydrogenation at the expense of a further mole of the isobenzimidazole.





The isobenzimidazoles (**1**) and their mono- and di-*N*-oxides show no tendency to react in a Diels–Alder manner with tetracyanoethylene or a wide variety of other dienophiles. However, with methyl acetylenedicarboxylate in cold benzene the di-*N*-oxide of (**1a**) gives a product to which we assign the structure (**8**) on the basis of elemental analysis and mass, n.m.r., and i.r. spectral data. The apparent biparticulate mode of reaction of TCNE is formally analogous to the observation of Junek and Sterk[4] that indane-1,3-dione reacts with TCNE to give 2-(dicyanomethylene)indane-1,3-dione.



(8)

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† Assignment of structure confirmed by i.r. and n.m.r. spectral data.

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