The Photo-Birch Reduction of Aromatic Hydrocarbons Using Sodium Borohydride and 1,4-Dicyanobenzene

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Summary The efficient photo-reduction of phenanthrene, anthracene, and naphthalene by sodium borohydride in the presence of 1,4-dicyanobenzene is reported.

THE Birch reduction is a well-known synthetic method for the reduction of aromatic rings *via* anion radicals and dianions of aromatic compounds.[1] Such anionic species can also be generated by photoreactions of some donor-acceptor pairs in polar solvents,[2,3] thus leading to a Birch-type of photoreduction.[3] Similar photoreductions of aromatic compounds have been accomplished in low yields by other reductants such as sodium borohydride[3—6] and sodium sulphite.[5] In the case of sodium borohydride, the direct attack of hydride[3] or electron-transfer from the borohydride[6] to excited aromatic rings has been suggested as the mechanism. We now report an efficient photo-Birch reduction of phenanthrene, anthracene, and naphthalene by sodium borohydride in the presence of 1,4-dicyanobenzene, possibly *via* the cation radicals of the aromatic hydrocarbons, which is different from the previous borohydride reduction.

Irradiation of a 10% aqueous acetonitrile solution (200 cm^3) containing phenanthrene (2·77 g), sodium borohydride (2·7 g) and 1,4-dicyanobenzene (A) (1·92 g) through Pyrex by a high-pressure mercury arc for 8 h gave 9,10-dihydrophenanthrene (1·7 g, 71%), phenanthrene (0·3 g) and (A, 0·3 g).†

In a similar way, the photoreduction of anthracene and naphthalene gave 9,10-dihydroanthracene m.p. 104—106 °C (70%) and 1,4-dihydronaphthalene (30%) respectively. In the case of 2-methyl-, 2,3-dimethyl- and 2,6-dimethylnaphthalenes, the photoreductions gave a mixture of dihydronaphthalenes.

The photoreduction requires the co-existence of sodium borohydride, water and (A), the absence of each leading to only low yields or lack of reduction, as in the photocyanation of aromatic hydrocarbons with cyanide anion in the presence of (A).[7] In place of (A), 1,2- and 1,3-dicyanobenzenes can also be effectively used for this photoreduction.

When the photoreduction of phenanthrene or anthracene was carried out in the presence of deuterium oxide instead of water, a monodeuteriated compound was produced

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† Percentage yields are based on unrecovered hydrocarbons. As the conversion increased, the 1,4-dicyanobenzene was consumed and benzonitrile was formed to some extent.

predominantly, ([$^2H_2$] 0%, [$^2H_1$] 70—80% and [$^2H_0$] 20—30%) demonstrating the involvement of one proton from the water in the reduction pathway.

Since the photoreaction in the absence of (A) is very slow, direct attack of hydride on the excited hydrocarbons is very unlikely. Since formation of a naphthalene–(A) exciplex is known[8] and moreover some exciplexes dissociate into ion radicals in polar media,[9] initiation by electron-transfer from the excited hydrocarbons (D) to (A) would give a possible mechanistic pathway;‡ nucleophilic attack of hydride on the cation radicals ($D^{+\cdot}$) generates the radicals (·DH) which are either reduced by electron reversal from (A) anion radicals ($A^{-\cdot}$) and subsequent protonation, or undergo bimolecular disproportionation to give the reduced compound DH_2 to a minor extent (equation 1).§

$$\begin{array}{l} A+D \xrightarrow{h\nu} A^{-\cdot}+D^{+\cdot} \xrightarrow{H^-} A^{-\cdot}+\cdot DH \rightarrow A+{}^{-}DH \xrightarrow{X_2O} A+DHX \\ \qquad\qquad\qquad\qquad\qquad\quad \mid \qquad (X = H \text{ or } {}^2H) \\ \qquad\qquad\qquad\qquad\qquad\quad \mid \cdot DH \\ \qquad\qquad\qquad\qquad\qquad\quad \llcorner\!\rightarrow D+DH_2 \end{array} \tag{1}$$

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‡ U.v. spectral measurements showed no indication of the formation of charge-transfer complexes in the ground state.

§ A referee pointed out alternative mechanistic pathways, *i.e.* electron transfer from borohydride to the exciplex or direct attack of borohydride to the exciplex, which cannot be ruled out.

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