Photoreduction of Aromatic Hydrocarbons by Lithium Aluminium Hydride and Sodium Borohydride

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Summary Aromatic hydrocarbons are photoreduced in aprotic solvents by lithium aluminium hydride and sodium borohydride to their corresponding aromatic radical anion by two distinct mechanisms: in one the hydrocarbon interacts with a photodecomposition product of the hydride, in the other the photoexcited hydrocarbon interacts with the hydride; a dark reaction between pyrene and lithium aluminium hydride is also observed.

When a degassed solution of lithium aluminium hydride ($LiAlH_4$) and an aromatic hydrocarbon [naphthalene, azulene, anthracene, or pyrene] in tetrahydrofuran/2-methyl tetrahydrofuran (THF/MTHF) was irradiated (250 watt xenon-Hg arc) with $\lambda < 340$ nm at ambient temperature, the respective hydrocarbon radical anions were produced. The presence of these anions was confirmed by both electron paramagnetic resonance (e.p.r.) and, in the case of pyrene and anthracene, by optical absorption spectroscopic techniques. Similarly aromatic hydrocarbons were also photoreduced to their radical anions in degassed solutions of sodium borohydride in hexamethylphosphoramide (HMPA).

Two possible mechanisms for such a photoreduction process are clearly possible, involving either (1) the initial photodecomposition of the hydride, or (2) the interaction of a photoexcited hydrocarbon with the unperturbed hydride. The presence of mechanism (2) was shown by the irradiation at room temp. of a pyrene–$LiAlH_4$–1,2-dimethoxyethane solution with light which was absorbed only into the singlet manifold of the hydrocarbon. (335 nm filter, 2 parts saturated $CoCl_2$ and 1 part saturated $NiSO_4$ in a 1 cm quartz cell). The disappearance of pyrene (ϕ *ca.* 0·1) was obtained indicating that the main pathway by which photoreduction occurs is that of the photoexcited hydrocarbon interacting with $LiAlH_4$.

However the presence of mechanism (1) has also been demonstrated on irradiation of hydride solvent systems at low temperature by the appearance of solvent derived radicals and, in some cases, trapped electrons. Thus irradiation of a benzene–$LiAlH_4$–THF/MTHF sample at −170° produced the benzene radical anion and radical species formed from the solvent.[1–3] When the aromatic hydrocarbon is absent the e.p.r. signal of the trapped electron[2] is seen as well as that of the solvent derived radicals. If the hydride is also absent no paramagnetic species are observed.

Similarly no radical species was observed following room temperature irradiation of a pyrene–$NaBH_4$–isopropyl alcohol (IPA) solution, but irradiation at −170° gave the $CH_3\dot{C}OHCH_3$ radical.[4] We have also used di-isobutylaluminium hydride (DIBAH) for the photoreduction of pyrene in THF/MTHF solution. Irradiation at room temp. gave no e.p.r. observable radical species (although pyrene photoreduction occurred), however at −170° solvent derived radical species were observed.[5] Irradiation of the THF/MTHF solutions of DIBAH or of $NaBH_4$ in HMPA or IPA also gave the solvent derived radical species whereas if the metal hydrides were not present, no radical species were formed.

These results pose the question whether optical excitation is a prerequisite for these reduction processes, or if an additional thermally controlled mechanism is involved. The dark reaction between pyrene–$LiAlH_4$–THF/MTHF was studied by storing two degassed solutions in the dark at −10° and 60° respectively. The low temperature sample did not show any reaction after 72 h whereas the high temperature sample turned red and was shown by e.p.r. to contain the pyrene radical anion. Irradiation of the dark low temperature sample at −10° immediately produced the radical anion. Hence, a thermally activated process is indeed present, and the reaction is, to our knowledge, the first case of a hydride reagent reducing an aromatic system in the dark and doing so by a one electron process.[6]

Our results suggesting the involvement of a one electron reduction mechanism for $NaBH_4$ are in contrast to those of Witkop[7] and Barltrop[8] who have proposed hydride attack upon the photoexcited substrate in protic media and those photoreduction experiments[9,10] using tri-n-butylstannane which are proposed to proceed by hydrogen atom abstraction.†

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† Concerning mechanism (2), the referee has suggested the possibility of the initial step being hydrogen abstraction by the excited hydrocarbon followed by deprotonation of the neutral radical so produced. We have no positive experimental evidence to distinguish between this mechanism and one involving electron transfer.

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