Photoreduction of Naphthalenes by Sodium Borohydride

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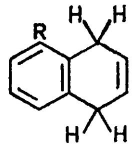
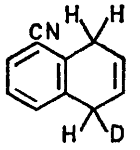
Summary U.v. irradiation of 1-cyanonaphthalene and 1- and 2-methoxycarbonylnaphthalene in the presence of sodium borohydride gives dihydronaphthalenes by a mechanism involving hydride attack upon the excited organic molecules.

Irradiation of a solution of 1-cyanonaphthalene in acetonitrile and in the presence of an aqueous alkaline solution of NaBH$_4$ with a medium pressure arc (filtered, $\lambda > 255$ nm) rapidly gave the dihydronaphthalene (I; R = CN) (24%); τ 6·48 and 6·59 (CH$_2$, m) assigned to the 8- and 5-positions respectively by comparison with *o*- and *m*-toluonitrile.

Irradiation of 1-cyanonaphthalene and sodium borodeuteride in H_2O–MeCN gave (II) and complementary irradiation with sodium borohydride in D_2O–MeCN gave (III). The position of the deuterium in the products was assigned by comparison of the intensities of the CH$_2$ n.m.r. multiplets with those for (I; R = CN).

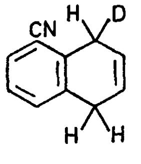
(I)

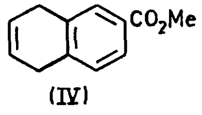




(II)

(III)

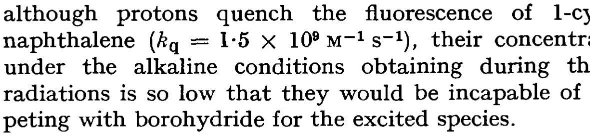




(IV)

Irradiation of 1- and 2-methoxycarbonylnaphthalene through a Pyrex filter gave (I; R = CO$_2$Me) and (IV) in 44% and 20% yields respectively.

The reduction can occur only by transfer of (i) H$^-$ followed by H$^+$; (ii) 2 H$\cdot$; (iii) 2 electrons and 2 H$^+$ irrespective of the order of transfer; (iv) H$^+$ then H$^-$. We think that for our system mechanism (i) is the most likely since: (a) NaBH$_4$ efficiently quenches the fluorescence of 1-cyanonaphthalene ($k_q = 3{\cdot}3 \times 10^9$ M^{-1} s^{-1}).[1] (b) Mechanism (ii) can be eliminated because, irrespective of the origin of the hydrogen atoms, it does not explain the difference in the labelling patterns derived from NaBH$_4$–D_2O and NaBD$_4$–H_2O. (c) If the initial step were electron transfer (mechanism (iii)) (*cf.* photochemical reduction of naphthalenes by amines which appears[2] to involve initial electron transfer)



(i)

then the products would be similar to those generated by the Birch reduction[3] which, with 1-naphthoic acid, is known to be the 1,4-dihydro-compound. (d) Initial proton transfer [mechanisms (iii) and (iv)] is most improbable because, although protons quench the fluorescence of 1-cyanonaphthalene ($k_q = 1{\cdot}5 \times 10^9$ M^{-1} s^{-1}), their concentration under the alkaline conditions obtaining during the irradiations is so low that they would be incapable of competing with borohydride for the excited species.

Naphthalene itself is photoreduced in the presence of NaBH$_4$ to 1,4-dihydronaphthalene and tetralin. The extension of these reactions to benzenoid and other systems will be reported elsewhere.

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[1] I. B. Berlman, 'Handbook of Fluorescence Spectra of Aromatic Compounds,' Academic Press, New York, 1963, p. 35 gives the lifetime of singlet excited 1-cyanonaphthalene as 26 ns.

[2] J. A. Barltrop and R. J. Owers, *Chem. Comm.*, 1970, 1462.

[3] A. J. Birch, *J. Chem. Soc.*, 1944, 430; *Quart. Rev.*, 1950, 4, 69.