Tetrahedron Letters No. 50, pp 5029 - 5030.

0040-4039/78/1208-5029$02.00/0

PHOTOINDUCED REDUCTION OF IMINES BY NADH MODELS

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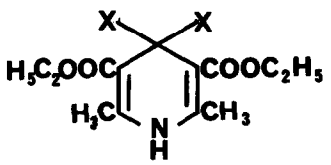
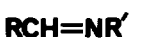
Reduction of imine bond is an important biochemical reaction catalysed by oxidoreductase enzymes dependent on pyridine nucleotide coenzymes[1]. Hydrogen transfer was shown to take place also from NADH model compounds when the imine nitrogen is chelated to metal cations[2a] or is quarternised,[2b] and an analogous reduction of a carbonyl group, catalysed by Mg^{++}, has been reported.[3]

We considered the possibility of hydrogen transfer to an imine bond by activating the NADH model. One way of achieving this objective is to photoactivate[4] the 1,4-dihydropyridine compound, thereby, inducing the hydrogen transfer. 1-4-Dihydropyridines upon irradiation normally dimerize,[5] giving linear or cage dimers. However, compound (Ia) resists[5] photodimerization possibly due to steric hinderance of the substituents, and hence is an ideal NADH model which is capable of photoactivation.

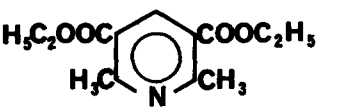


Ia;X=H
b;X=D



II

II



I

Thus, irradiation of a degassed solution of Ia (1mmole) and N-arylidineanilines (II, 1mmole) in dry benzene (500 ml) under nitrogen through a Pyrex filter for 4 hrs, evaporation of solvent, and preparative layer chromatography on silica gel gave the amines (III) in reasonable yields[6] (Table I).

Table I

Imine	IIa	IIb	IIc	IId	IIe	IIf
R	C_6H_5	p-$MeOC_6H_5$	p-HOC_6H_4	C_6H_5	p-$MeOC_6H_4$	p-$MeOC_6H_4$
R'	C_6H_5	C_6H_5	C_6H_5	2-Naphthyl	p-$MeOC_6H_4$	2-Naphthyl
Amine (III) (% yield)	60	90	60	77	92	85

The imines(II) when irradiated in benzene without the dihydropyridine under similar conditions and the dihydropyridine (Ia) itself was unchanged upon irradiation. However, the undegassed benzene solution of Ia upon irradiation, produced the pyridine compound (IV) quantitatively. Fluorescence emission from the dihydropyridine[7] (Ia) in 395-480 nm region when excited at 372 nm is quenched by the imines (II). The mechanism of photoreduction of imines, in this case, appears to be different from that observed when isopropanol[8] is the source of hydrogen. In the present case, it seems that NADH model dihydropyridine (I) absorbs energy at 372 nm and in the excited state possibly transfers one electron[9] followed by one hydrogen atom to the imine molecule. Obviously, energy is not directly absorbed by the imine due to the Pyrex filter used. That the hydrogen transfer takes place from the NADH model compound was proved by the fact that when the 4-dideutero-1,4-dihydropyridine (Ib) was used, the amines (III) thus obtained were found to contain (^{1}H n.m.r.) one deuterium atom on the benzylic carbon atom. The photoreduction was most efficient and clean with II bearing oxygen substituents on aromatic rings. No photoreduction was observed with II(R=p-$Me_2N$$C_6H_4$, R'=$C_6H_5$). Chloro and nitro substituents on the aromatic nucleus complicated the photoreduction due to simultaneous reduction of carbon-chlorine bond or the nitro group.

Although no such photochemical reductions take place in living organisms, it is possible that the NADH model (I) is photoactivated to a similar electronic state as that of NADH enzymatically activated in living systems. Similar photoinduced reductions of other functional groups are in progress.

References and Footnotes

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6. A Phillips (125w) medium pressure mercury lamp was used for irradiation. The isolated amines (III) were characterized by comparison of m.p. and spectroscopic properties of authentic samples obtained by borohydride reduction of the corresponding imines.
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(Received in UK 8 October 1978)