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PHOTOCHEMICAL REDUCTION OF PYRIDINIUM AND PYRIDINE COMPOUNDS IN THE PRESENCE OF DIETHYLAMINE[1)]

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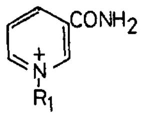
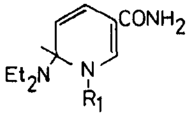
Some aromatic compounds, such as naphthalene, phenanthrene, anthracene, and biphenyl, are known to be reduced to the corresponding dihydro (or tetrahydro) derivatives upon irradiation in the presence of aliphatic tertiary amines in polar solvents.[2)] The photolysis of benzene under similar conditions leads to the 1,4-photoadducts of amines (primary, secondary, and/or tertiary) and minor amounts of reduced products (cyclohexa-1,4-diene and tetrahydrobiphenyl).[3-5)] Unlike the case of carbocyclic compounds, no study has been made on the photoreduction of heterocyclic system in the presence of aliphatic amines. In this communication, we wish to report the photochemical reduction of heterocyclic compounds in the presence of diethylamine (DEA). A study of photoreduction of heteroaromatic rings is also important in relation to the biological system, where photon is transformed into chemical energy and stored through the reduction of NAD^+ to NADH.

In the system containing I and DEA, thermal reactions took place. As soon as DEA (10%(v/v)) was added into an aqueous solution of I (0.2 M), the solution turned yellow and lemon yellow crystals were isolated from this solution, mp $\geq$ 130°C (decomp.). On the basis of the mass spectroscopic data, this crystalline material was suggested to be a 1:1 adduct between DEA and I, as shown by II, the yield of the adduct based on the initial concentration of I being 9 %. An absorption maximum at 395 nm was observed of the adduct, which was unstable and decomposed

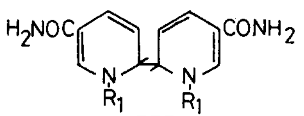


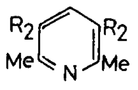
I



II

into the original pyridinium compound on standing in dilute solution. At the lower concentration of I ($[I]_0$ = 2.5 x 10^{-4} M, [DEA] = 10%(v/v)), on the other hand, growth of absorptions with λ_{max} at 262 and 357 nm was observed. The spectrum was not that of II but was in good agreement with that of 1,6-dihydro derivative prepared by the $NaBH_4$-reduction of I.[6]


III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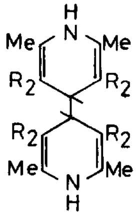
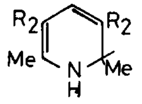

V


VI

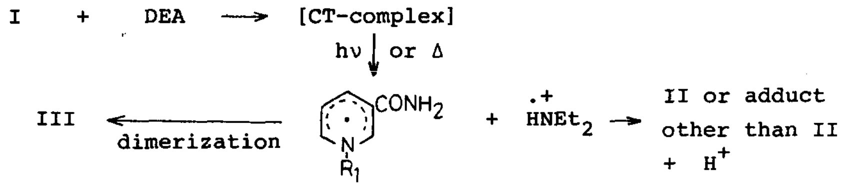
R_1 = CH_2Ph
R_2 = CO_2Et

The reaction of I with DEA was greatly enhanced upon irradiation. Irradiation (100W high-pressure mercury arc; N_2, 4 hr) of an aqueous solution of I (0.053 M, 150 ml) containing 6.7%(v/v) DEA gave the 6,6'-dimeric reduced nicotineamide (III) (19 %) accompanied with a small amount of impurities. Other than the recovery of unreacted I (61 %), water-soluble tarry materials were also obtained. A part of the crude product III was recrystallized from methanol, mp 162.5-164.5°C (decomp.). UV λ_{max} (MeCN) 280 and 358 nm. Identification of III was made by comparing the UV, NMR, and mass spectra with those of the authentic sample.[7,8] Other reduced compounds, such as 1,2-, 1,4-, and 1,6-dihydronicotineamides, were not detected in this reaction.

The formation of III proceeded upon irradiation of light >360 nm where no absorption was expected of I itself. Pyridinium compounds are good electron acceptor, as indicated by Kosowar,[9] and form charge-transfer complexes with many electron donors such as phenol, imidazole, benzene, and thiomethyl ether.[10,11] Then, it may be suggested that not only III but also the adduct between DEA and I are produced *via* a CT-complex (Scheme 1).

The electron affinity of the pyridines should be weaker than that of the pyridinium compounds. Corresponding to the expectation, IV did not react with DEA in the dark. Upon irradiation (30W low-pressure mercury arc; N_2, 6 hr) of a solution of IV (0.018 M, 220 ml) in 50%(v/v) aqueous acetonitrile containing DEA (10%(v/v)), however, a reaction was induced. Column chromatographic separation (silica gel, MeCN) and recrystallization from acetonitrile afforded

Scheme 1



two products: (1) 4,4'-dimeric reduced pyridine (V) (19 %) [mp > 200°C (sublim.); UV λ_{max}(MeCN) 270 and 354 nm; fluorescence F_{max}(MeCN) 450 nm; mass (m/e) 252 (1/2 $V^{\cdot+}$); NMR (DMSO-d_6) δ 8.35 (broad, NH), 3.97 (s, 4,4'-H), 3.97 (q, J 7.0 Hz, OCH_2Me), 2.05 (s, Me), and 1.18 (t, OCH_2Me)] and (2) 1,2-dihydro compound (VI) (13 %), mp 149-153°C; UV λ_{max}(MeOH) 212, 283, and 373.5 nm; fluorescence F_{max} (MeOH) 490 nm; M^+ 253; NMR ($CDCl_3$) δ 7.70 (s, 4-H), 6.93 (broad, NH), 4.52 (q, $J_{2,Me}$ 6.5 Hz, 2-H), 4.18 (q, J 7.0 Hz, OCH_2Me), 2.39 (s, 6-Me), 1.30 (t, OCH_2Me), and 1.18 (d, 2-Me).

The effects of the irradiation time on the formation of V and VI are summarized in Table 1. Prolonged irradiation (14 hr) increased the yield of VI (27 %) and reduced that of V (3 %). Electronic absorption indicated that V (λ_{max} 360 nm) was almost quantitatively converted to VI (λ_{max} 373 nm) upon irradiation in aqueous acetonitrile containing DEA. In the absence of DEA, a rapid photolysis of V took place but VI was not produced at all. Together with V and VI, 2,6-dimethyl-3,5-pyridinedicarboxylic acid (from ethyl acetate) was isolated (8 %) in Run. No. 1. Although the amine adducts are always produced in the carbocyclic compound-aliphatic amine systems,[2-5] no photoadduct between DEA and IV was isolated in the present photolysis.

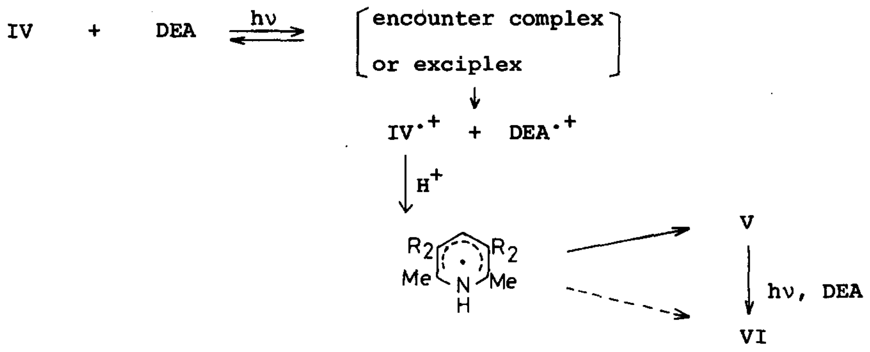
Table 1. Yields of V and VI varing with irradiation time[a)]

Run No.	Irradiation time, hr	V, %	VI, %
1	3	14	12
2	6	19	13
3	6.25	19	17
4	14	3	27

a) The yields of V and VI were calculated on the basis of the initial concentration of IV.

The photoreduction of IV with DEA was greatly affected by the concentration of water in acetonitrile. The optimum concentration was 50%(v/v). In acetonitrile, the formation of V and VI was markedly depressed and a photoproduct with λ_{max} at 315 nm was obtained. At higher water concentrations (90-95%(v/v)), V and VI were produced, but the rate of formation was reduced in comparison with that in 50%(v/v) aqueous acetonitrile. Then, the photoreduction of IV in the presence of DEA is suggested to proceed *via* an ionic transient as expected in the reaction where either encounter complex or exciplex is involved (Scheme 2). The electron-transfer from DEA to photoexcited IV should be enhanced in the presence of strongly polar solvents like water. Deactivation of the encounter complex or exciplex, however, will be also accelerated under the same condition. A net result of the effects on these competing processes is expected to give the observed water concentration dependence of the reaction yield.

Scheme 2



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