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THE PHOTOCHEMICAL ADDITION OF HYDROXYLIC SOLVENTS TO PHENAZINE

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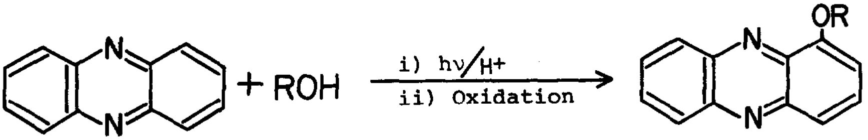
Phenazine(I) is reduced to 5,10-dihydrophenazine(II) upon irradiation in hydrogen-donating solvents.1) Recently, Bailey, Roe and Hercules2) have studied the photochemistry of I in acidic methanol and postulated on the basis of spectroscopic evidence that in strongly acidic methanol(HCl in methanol) the reaction product is the green phenazinium cation radical, which is produced by the reaction of II with phenazinium cation, without isolation of the product.

We now wish to report on the contrary to the above result2) that irradiation of I in hydroxylic solvents in the presence of strong acids gives the solvent-addition products.

A solution of I in 2M aqueous H_3PO_4 was irradiated with a 100W high pressure Hg lamp under N_2 at room temperature. The resulting green solution containing green precipitate was oxidized with air, neutralized with Na_2CO_3 and then extracted with ether. Work up of the ether extract gave a mixture of unchanged I and 1-hydroxyphenazine(IIIa). A solution of I in alcohol containing p-toluene sulfonic acid(TsOH) was also irradiated similarly and oxidized with an aqueous potassium ferricyanide. After evaporation of the solvent, the mixture was neutralized with Na_2CO_3 and then extracted with ether. Chromatography of the ether extract on alumina gave I and 1-alkoxyphenazine(IIIb and IIIc).

Irradiation of I in AcOH containing TsOH and work up of the resulting mixture afforded I and 1-acetoxyphenazine(IIId). The results are summarized in Table 1. These photochemical addition reactions did not take place in the absence of the acids.



I

III a,R=H b,R=CH_3
c,R=C_2H_5 d,R=CH_3CO

Table 1. Photochemical Addition of Solvents[a]

Solvent, ml	Irradiation Time, hr	Conversion, %	Product Compd.	Yield,%	Ratio[c]
2M H_3PO_4, 200	7	48	IIIa	94	0.9
2M H_3PO_4, 200	48	47	IIIa	100	0.9
MeOH, 50 TsOH, 1.0[b]	7	35	IIIb	74	0.4
EtOH, 50 TsOH, 1.0[b]	7	30	IIIc	54	0.2
AcOH, 50 TsOH, 1.0[b]	7	25	IIId	74[d]	0.2

a) A 100mg of phenazine was irradiated. b) The weight(g) of TsOH added.
c) The molar ratio of the product to phenazine found in the reaction mixture.
d) The yield of IIId was estimated as that of IIIa obtained by hydrolysis.

The structure of IIIa and IIIb was confirmed by the comparison with the respective authentic sample prepared by the method of Surrey,[3] which was identical in every respect. The structure of IIIc was established by the physical properties and elemental analysis[m.p. 126-127° (lit.[4] 130°): C,75.10; H,5.32; N,12.57. $C_{14}H_{12}N_2O$ requires C,74.99; H,5.38; N,12.49%: picrate,m.p.188-190°(lit.[4] 195°)]. The ir spectral pattern of IIIc was similar to that of IIIb. The structure of IIId was determined by the spectroscopic data[nmr($CDCl_3$),δ 2.56(S,CH_3), 7.65-8.30 (m,aromatic)]. The ir spectrum(KBr) was identical with that[5] of the authentic sample. Further proof about the structure of IIId was secured by conversion into IIIa upon treatment with an aqueous NaOH.

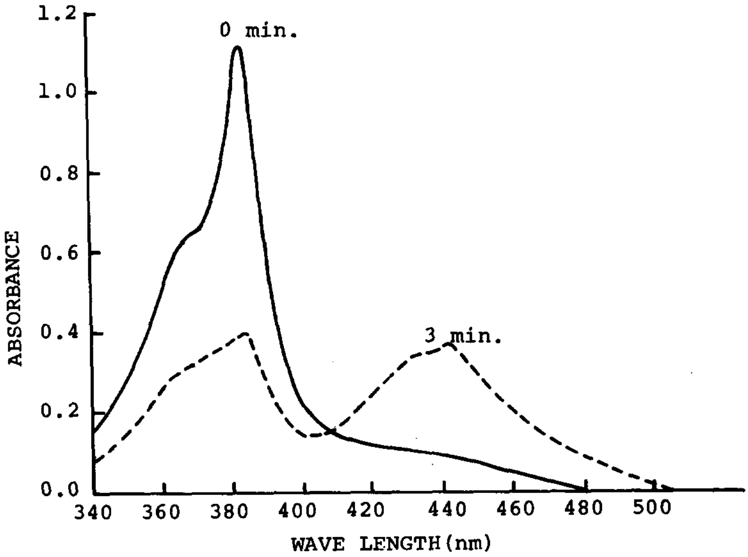
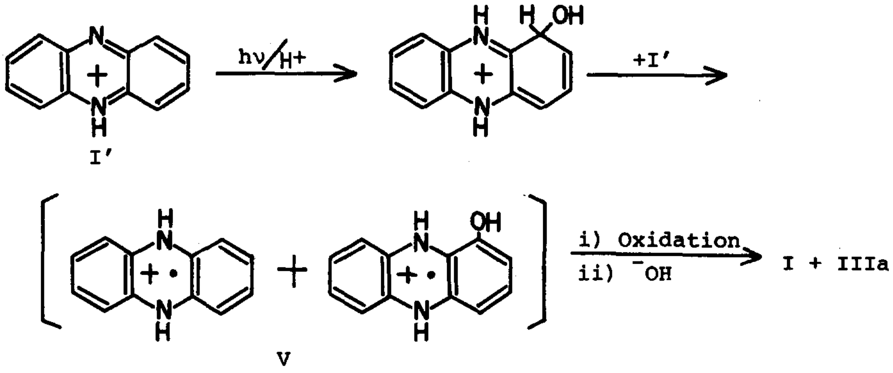


Fig.1. Spectral change during irradiation of phenazine in 2M H_3PO_4 soln. Initial concentration; 4.9 x 10^{-5}M.

Preliminary mechanistic study of these photochemical reactions was carried out for the photohydration reaction to give IIIa. A solution of I in 2M H_3PO_4 in a cell was photolyzed after degassing by a freeze-pump-thaw cycle method. The uv spectral change during the photolysis was shown in Fig 1. The uv spectrum obtained after irradiation for 3 min was same in shape as that of phenazinium cation radical(IV) prepared by the similar method to that of Fellion and Uebersfeld.[6] The esr spectrum of the green precipitate obtained by the photolysis showed the same g-value(2.003) as that of the known esr spectrum of IV previously reported.[7] These results would indicate that the associate complex(V) of the cation radicals is produced by the photolysis. The product analysis also showed that the molar ratio of IIIa to I in the reaction mixture reaches a plateau, which is very close to unity, upon extensive irradiation(Table 1). IIIa was unreactive under reaction conditions and recovered unchanged after irradiation in 2M H_3PO_4 for 7 hr.

On the basis of these observations we propose the following mechanism for the photohydration reaction. (I exists in the cation form(I') under the reaction conditions). Similar mechanism would hold for other reactions. The photochemical reactions reported in this communication would provide a useful synthetic method for the compounds listed in Table 1.[8,9]



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8. Irradiation of a solution of I in 2M H_3PO_4 with bubbling air increased the conversion of I and the yield of IIIa up to 86 and 94%, respectively.
9. This work was supported in part by a grant from the Ministry of Education.