

PHOTOCHEMICAL REDUCTION OF 4-NITROPYRIDINE 1-OXIDE
AND ITS METHYL-SUBSTITUTED DERIVATIVES IN ETHANOL

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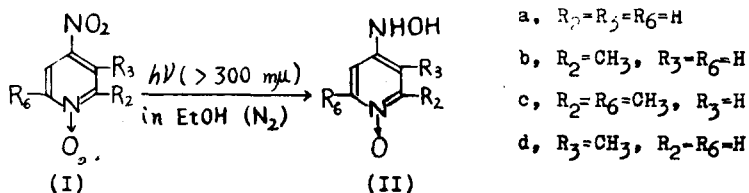
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We have extended our studies on the photochemical reaction^{1,2} of pyridine, quinoline, and isoquinoline N-oxides to 4-nitropyridine 1-oxide and its methyl-substituted derivatives (I) and we now report novel photochemical reduction of these N-oxides to the corresponding 4-hydroxyaminopyridine 1-oxides (II) in a quantitative yield.



In a typical experiment, 1.0 g. of 4-nitropyridine 1-oxide (Ia) in 600 ml. of absolute ethanol was irradiated by 450 W Hanovia high-pressure mercury immersion lamp (Pyrex filter was used to avoid the light of wavelength shorter than 300 $m\mu$) in nitrogen atmosphere and the irradiation mixture was checked

periodically by UV spectroscopy. Changes in the spectra of a diluted solution of the mixture are shown in Figure 1. The presence of the two isosbestic points at 254 and 308 μ in these spectra indicate that the transformation of the N-oxide to one product proceeded during the irradiation.

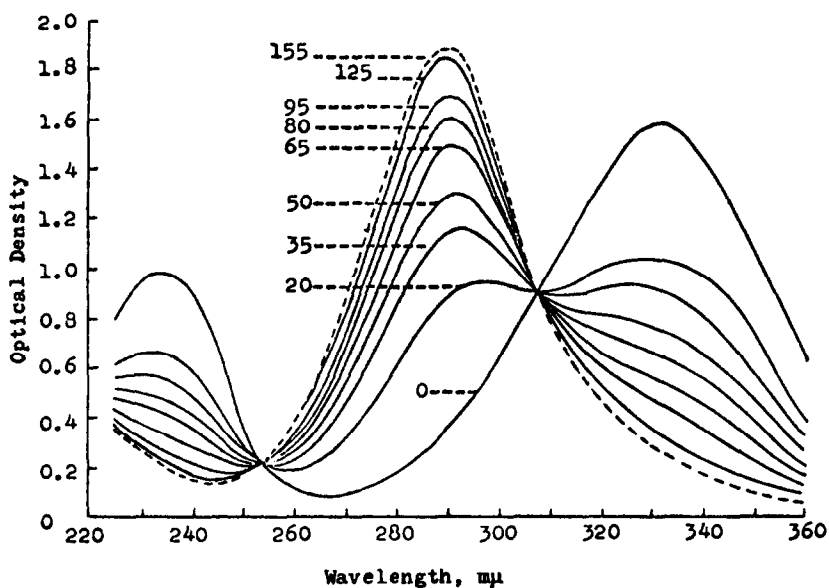


Figure 1. The progressive change of the spectrum of 4-nitropyridine 1-oxide on 3130 Å. irradiation in absolute ethanol solution. Numbers refer to irradiation time in minutes, and the dotted line denotes a spectrum of the product at room temperature.

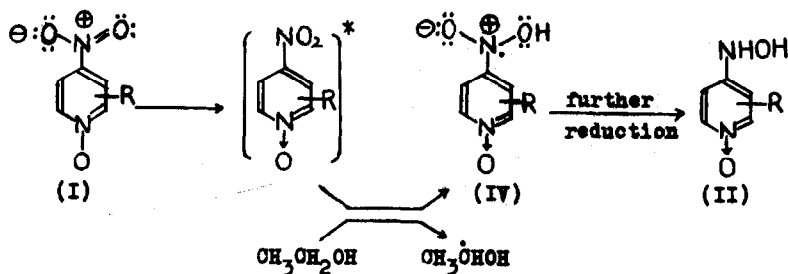
After all of the N-oxide was consumed (under this condition, about 160 minutes of irradiation was necessary), the irradiated mixture was concentrated under a reduced pressure in nitrogen atmosphere to afford a crystalline mass, mp 219° dec, $\lambda_{\text{max}}^{\text{EtOH}}$ 290 μ ($\log \epsilon$ 4.31). The UV and IR spectra of this product

were superimposable with those of 4-hydroxyaminopyridine 1-oxide (IIa).^{4,5} Further confirmation of the structure (IIa) was provided by its facile conversion to 4,4'-azoxy pyridine 1,1'-dioxide (IIIa), mp 235° dec, either by exposure of the aqueous solution of IIa to air⁴ or by the action of FeCl₃ on IIa.⁵ Under exactly the same condition, 4-nitro derivatives of 2-picoline and 2,6-lutidine 1-oxides (Ib and Ic) gave rise to the corresponding 4-hydroxyamino compounds, IIb, mp 226° dec, $\lambda_{\text{max}}^{\text{EtOH}}$ 285 m μ (log ϵ 4.32), and IIc, ^{4,5} mp 220° dec, $\lambda_{\text{max}}^{\text{EtOH}}$ 282 m μ (log ϵ 4.26). Similarly to IIa, these hydroxyamino compounds were quite unstable in air, and were auto-oxidized to the corresponding azoxy compounds,^{4,5} IIIb, mp 218° dec, and IIIc, mp 236° dec. Similarly, irradiation of 4-nitro-3-picoline 1-oxide (Id) gave rise to the corresponding 4-hydroxyamino-3-picoline 1-oxide (IIId),⁵ mp 218° dec, $\lambda_{\text{max}}^{\text{EtOH}}$ 289 m μ (log ϵ 4.24).

On the contrary, if the irradiation of the above N-oxides was carried out in oxygen atmosphere,⁶ entirely different reaction was found to take place. The spectra of Ia under this condition changed gradually with three isosbestic points at 224, 249, and 290 m μ , and finally showed a single absorption maximum at 268 m μ . The results of irradiation reaction on these N-oxides under this condition will be reported in the near future.

Since the irradiation of I in nitrogen atmosphere gives rise to the corresponding hydroxyamino compounds (II) in a quantitative yield with no exception, this method could be applied for synthetic means.

While details concerning the mechanism of this novel photochemical reduction are still lacking, it seems reasonable to assume that the key step is the abstraction of hydrogen from ethanol by the photoexcited species of I indicated in brackets to form the intermediate radical (IV) which is responsible for the formation of II. Therefore, the reaction may be represented schematically as depicted.⁷



The oxygen probably destroys this radical (IV) to the starting N-oxide (I), thus preventing the formation of II. Similar process is known to take place in the formation of pinacels from aldehydes and ketones by irradiation in alcoholic solution.⁸

In support of this mechanism, irradiation of Ia in water did not produce IIa but resulted in complete recovery of the starting N-oxide, and the change of solvent from ethanol to isopropanol⁹ enhanced the rate of the reduction as expected.

Confirmation of this mechanism and scope of this novel photochemical reduction to the variety of other related compound are now under investigation

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3. Satisfactory analyses were obtained for all the compounds described and all melting points were uncorrected.
4. F. Parisi, P. Bovina and A. Quillico (Gazz. Chim. Ital., **90**, 903(1960), ibid., **92**, 1138(1962)) synthesized IIa and IIc by the reaction of hydroxylamine with corresponding pyrones and pointed out their facile transformation to the corresponding azoxy compounds by air.
5. E. Ochiai and H. Mitarashi (Ann. Rept. ITSUU Lab., **14**, 17 (1965), ibid., **13**, 19(1963)) prepared IIa to IIc by phenylhydrazine-reduction of the corresponding 4-nitropyridine 1-oxides and obtained the corresponding azoxy compounds in a quantitative yield from the former compounds by FeCl_3 -oxidation.
6. It was confirmed that the spectral changes of I in presence or absence of oxygen were independent of their concentrations between the range of 10^{-3} ~ 10^{-5} mole/L.
7. There has appeared a communication on the reduction of excited nitroso group by ethanol; M. Shamma, J.K. Whitesell and P. L. Warner, Jr, Tetrahedron Letters, **1965**, 3869.
8. P. De Mayo, "Advance in Organic Chemistry: Methods and Results", Vol. 2, 372(1960) and references cited therein.
9. Z. Zanker and P. Schmid, Z. Physik. Chem. N. F., **17**, 11 (1958).