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Radical Cations from Pyridine *N*-Oxides and Lead Tetraacetate

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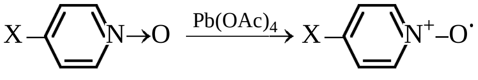
Abstract—One-electron oxidation of pyridine *N*-oxides with lead tetraacetate gives *N*-oxide radical cations. In the presence of atmospheric oxygen, the latter oxidize cyclohexane to cyclohexanone.

Catalytic decomposition of hydrogen peroxide in the presence of pyridine or one-electron electrochemical oxidation of pyridine *N*-oxide yields the radical cation of pyridine *N*-oxide [1, 2].

$$\mathrm{PyO} \xrightarrow[-\bar{e}]{} \mathrm{PyO}^{+\cdot}.$$

The same radical cation can be obtained from pyridine *N*-oxide and a photochemically generated triplet chloranil which plays the role of one-electron oxidant [3]. The radical cation of pyridine *N*-oxide exhibits a unique ability to oxidize alkanes (and some other organic compounds containing C–H bonds) in the presence of molecular oxygen to oxygen-containing derivatives (ketones and alcohols). Thus, cyclohexane reacts with the radical cation of pyridine *N*-oxide, generated in different ways, to form cyclohexanone. Such processes are quite urgent to study in connection with the problem of functionalization of alkanes. We have developed a new procedure for generating the radical cations of pyridine *N*-oxides, ivolving oxidation of the corresponding *N*-oxides with lead tetraacetate in chloroform.



Ia–**Ic** **IIa**–**IIc**

X = H (**a**), Cl (**b**), OCH_3 (**c**).

The formation of radical cations is confirmed by UV spectral data. The spectra of mixed solutions of pyridine *N*-oxides and $Pb(OAc)_4$ exhibit absorption in the range 400–460 nm. The same absorption was observed in the spectra of the radical cation of pyridine *N*-oxide, generated by photochemical oxidation of the *N*-oxide with chloranil [3]. The positions of absortion bands are almost independent of the nature of substituents in *N*-oxides **Ia**–**Ic**. Cyclohexane added to the reaction mixtures undergoes oxidation to cyclohexanone. The table lists the conditions of the reactions in the systems *N*-oxide–$Pb(OAc)_4$–cyclohexane and the yields of the reaction products.

The concentration of pyridine in the reaction mixtures (exp. nos. 1–5) was determined by GLC. The formation of cyclohexanone was proved by its reaction with 2,4-dinitrophenylhydrazine. The resulting hydrazone was identified by TLC. The concentration of cyclohexanone was determined by IR spectroscopy by the intensity of the carbonyl absorption band, after treatment of the reaction mixtures with a little aqueous sodium hydroxide for removal of acetic acid and unreacted lead tetraacetate (see Experimental).

The formation of cyclohexanone and pyridine in the systems in study can be represented by the following scheme, by analogy with the above-mentioned published data for the radical cations of *N*-oxides **IIa**–**IIc**, generated by other methods [2, 3].

Conditions of oxidation of cyclohexane with the radical cations of pyridine *N*-oxides in chloroform and yields of reaction products[a]

Exp. no.	*N*-Oxide, *c*, M	$c_{Pb(OAc)_4}$, M	Reaction time, h	Yield of cyclohexanone, %[b]	Yield of pyridine, %[b]
1	**Ia**, 0.1	0.05	5	3.4	5.5
2	**Ia**, 0.1	0.05	24	7.7	10.2
3	**Ia**, 0.1	0.05	72	11.3	20.5
4	**Ia**, 0.2	0.10	72	15.4	26.6
5	**Ia**, 0.2	0.10	168	20.5	30.7
6	**Ib**, 0.1	0.05	24	6.0	–
7	**Ic**, 0.1	0.05	24	5.4	–

[a] The concentration of cyclohexane in all the experiments was 0.25 M. [b] Per pyridine *N*-oxide.

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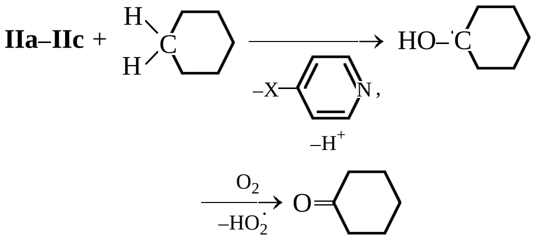

The yields of cyclohexanone (per taken *N*-oxide) in our systems involving lead tetraacetate compare with those obtained with the radical cations of *N*-oxides generated by other methods, such as electrochemical oxidation. Consequently, as would be expected, $PyO^{+\cdot}$ reacts with cyclohexane to give the same products as in systems where the formation of $PyO^{+\cdot}$ have been firmly established.

The use of lead tetraacetate in the proposed method for generation of *N*-oxide radical cations is determined by its very strong oxidative power. The normal redox potential of the system Pb^{4+}/Pb^{2+} is +1.694 V, which only slightly lower, than the potential of the system $PyO^{+\cdot}/PyO$ (+1.720 V) and much higher than the respective value for 4-methoxypyridine *N*-oxide (+1.362 V) [4]. Moreover, lead tetraacetate is readily soluble in chloroform, which allows the reaction to be performed in a homogeneous medium.

Neither pyridine *N*-oxides in the absence of $Pb(OAc)_4$, nor $Pb(OAc)_4$ in the absence of *N*-oxides oxidize cyclohexane.

EXPERIMENTAL

The IR spectra were measured on a UR-20 spectrometer, and the UV spectra were obtained on a Specord UV-Vis spectrophotometer. The quantitative analysis for pyridine was performed by GLC on an LKhM-8MD chromatograph, detector katharometer, carrier gas helium (30 ml/min), packing 5% Silicone-30 on Chromaton *N*-AW-DMCS (Chemapol) (column length 2 m), injector temperature 150°C, and oven temperature 80°C. Pyridine *N*-oxides were prepared by published procedures [5].

Reaction of pyridine *N*-oxides with cyclohexane in the presence of lead tetraacetate. Dry *N*-oxide **Ia**–**Ic** and cyclohexane were added to a solution of lead tetraacetate (dried in a vacuum dessicator over P_2O_5) in absolute chloroform (1 ml). The reagent amounts and reaction conditions are given in the table. In the postreaction mixture, the unreacted *N*-oxide was determined by IR spectroscopy (by the intensity of the characteristic N→O absorption band), and the resulting pyridine was determined by GLC (injection volume 1 μl). The chloroform solution was then treated with 0.5 ml of 1 N NaOH (to decompose the unreacted lead tetraacetate and remove acetic acid), the aqueous layer was separated, the organic layer was dried with Na_2SO_4, and the IR spectrum of the solution was measured. The concentration of the resulting cyclohexanone was determined by the intensity of the C=O absorption band at 1715 cm^{-1}.

To identify cyclohexanone, a solution of 2,4-dinitrophenylhydrazine hydrochloride in acetonitrile was added to the chloroform solution obtained after treatment of the reaction mixture with sodium hydroxide. The mixture was heated for 30 min at 50°C. The resulting 2,4-dinitrophenylhydrazone was identified by TLC on Silufol plates, eluent chloroform.

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