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# Chemistry

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Fig. 1. EPR spectra of radicals. a —4-pyridyl-2'-thiazolylcarbinol; b —2-pyridyl-2'-thiazolylcarbinol; c —3-pyridyl-2'-thiazolylcarbinol; d —p-nitrophenyl-2-thiazolylcarbinol

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## Abstract

## Full Text

## Chemistry

M. N. Shchukina, V. G. Ermolaeva, A. E. Kalmanson

# On Free Radicals—Intermediate Products in the Oxidation of Pyridylthiazolylcarbinols and Certain Other Secondary Carbinols

(Presented by Academician I. L. Knunyants, 9 IV 1964)

In studying the chemical properties of the 2-, 3-, and 4-pyridyl-2'-thiazolylcarbinols synthesized by us (I, II, and III, respectively), it was noted that these substances are unstable in the presence of air and, on storage, gradually darken and are partially converted into ketones (<sup>1-3</sup>). In alcohol or acetone, in the presence of caustic alkalis or sodium, potassium, or lithium alcoholates, pyridylthiazolylcarbinols form intensely colored solutions. On shaking with air the solutions become decolorized; on standing, the color reappears. This is repeated up to 20-25 times for III and up to

**Fig. 1.** EPR spectra of radicals. *a* —4-pyridyl-2'-thiazolylcarbinol; *b* —2-pyridyl-2'-thiazolylcarbinol; *c* —3-pyridyl-2'-thiazolylcarbinol; *d* —*p*-nitrophenyl-2-thiazolylcarbinol

40 times for I. From the decolorized solutions pyridylthiazolyl ketones were isolated, and the presence of peroxide in the solution was determined by iodometric titration. The colored solutions of pyridylthiazolylcarbinols show EPR spectra with hyperfine structure which, for the free radicals formed from I and II, consists of seven components (Fig. 1, *b*, *c*). This indicates that the unpaired electron in these radicals is delocalized and interacts with six protons. For the formation of radicals from carbinols I and II and their subsequent oxidation to ketones, the following scheme may be proposed:



Fig. 3. Change in the maximum EPR signal during successive oxidation cycles of 4-pyridyl-2'-thiazolylcarbinol

Figure 3: Fig. 3. Change in the maximum EPR signal during successive oxidation cycles of 4-pyridyl-2'-thiazolylcarbinol

- a) the absolute concentration of free radicals upon establishment of equilibrium in the system gradually decreases as oxygen is absorbed;
- b) the induction period for the appearance of radicals increases exponentially, while the rate at which equilibrium is established slows down.

These data also confirm that the oxidation reaction of 4-pyridyl-2'-thiazolylcarbinol proceeds through two consecutive stages: carbinol  $\rightarrow$  radical  $\rightarrow$  ketone, the first proceeding at a higher rate than the second.

**Fig. 3.** Change in the maximum EPR signal during successive oxidation cycles of 4-pyridyl-2'-thiazolylcarbinol

The ability to form free radicals of the carbinols studied depends on the electron-acceptor character of the substituents bound to the secondary alcohol group. An EPR study of alcoholic-alkaline solutions of a series of secondary carbinols showed that phenyl-, *p*-hydroxyphenyl-, *p*-methoxyphenyl-, and *p*-dimethylaminophenyl-2-thiazolylcarbinols do not form free anion radicals, whereas *p*-nitrophenyl- and *p*-nitrostyryl-2-thiazolylcarbinols form anion radicals giving EPR spectra (Figs. 1, 2) <sup>(6)</sup>. Intensive formation of free radicals was also observed for iodomethylates of pyridylthiazolylcarbinols and for 4-pyridyl-2'-benzthiazolylcarbinol, and to a lesser extent for 2,4'-dipyridylcarbinol and *p*-aminophenyl-2-thiazolylcarbinol.

Free radicals of carbinol anions are formed in the presence of alkali only in polar solvents (alcohol, acetone, pyridine, dimethylformamide) and are not formed under the action of metallic sodium on an ethereal or benzene solution of 4-pyridyl-2'-thiazolyl ketone, in which they differ substantially from metal ketyls. This permits the assumption that the free radicals we have detected and metal ketyls have different chemical natures. Free radicals are also formed upon reduction of 4-pyridyl-2'-thiazolyl ketone with sodium hydrosulfite in an alcoholic-alkaline solution.

The influence of electron-acceptor substituents, leading to greater mobility of the hydrogen at the central carbon atom in 4-pyridyl-2'-thiazolylcarbinol, is manifested in a number of reactions. Under the action of thionyl chloride or phosphorus halide compounds (phosphorus trichloride or phosphorus oxychloride) on III, 4-pyridyl-2'-thiazolylketone hydrochloride is formed. In the reaction with benzyl chloride and sodium alcoholate, upon heating with acrylonitrile in the presence of sodium alcoholate, upon interaction...

(V)      (VI)      (VII)      (VIII)

upon reaction with maleic anhydride in acetone, the substances (V–VIII), respectively, were obtained. The structures of these compounds were proved by analytical data and by IR and UV spectra.

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*Note: Figure translations are in progress. See original paper for figures.*

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