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PREPARATION, ESR SPECTRA AND ELECTRONIC ABSORPTION SPECTRA
OF
SUBSTITUTED PYRIDINYL RADICALS

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Recently, Kosower[1)] et al. have reported a stable organic free radical which was prepared by contacting 1-ethyl-4-carbomethoxypyridinium iodide with sodium dispersion or zinc dust in vacuo. They have proposed this free radical to be the 1-ethyl-4-carbomethoxypyridinyl radical.

The present authors[2)] have studied the electronic structures of 3- and 4-nitropyridine anion radicals by combining the experimental results of the electron spin resonance (ESR) and electronic spectra with the theoretical studies based on the molecular orbital method. In the course of the investigation, the present authors have attempted to prepare various substituted pyridinyl radicals and to measure their ESR and electronic spectra.

The 1-methyl-4-carbomethoxy-, 1-methyl-4-carboamido-, 1-methyl-4-acetyl- and 1-methyl-4-cyanopyridinyl radicals were prepared at room temperature by contacting the respective pyridinium iodide or chloride with zinc mirror in acetonitrile. The acetonitrile solution of 1-methyl-4-carbomethoxypyridinium chloride (10^{-3}- 10^{-4}mol./l) colored greenish yellow by contact with pure sublimated zinc metal in vacuo. The coloration of the solution is due to the formation of the pyridinyl radical. The acetonitrile solutions of the 1-methyl-4-carboamido- and 1-methyl-4-acetylpyridinyl radicals were colored green or yellow, and the 1-methyl-4-cyanopyridinyl radical solution colored dark blue.

FIG. 1a

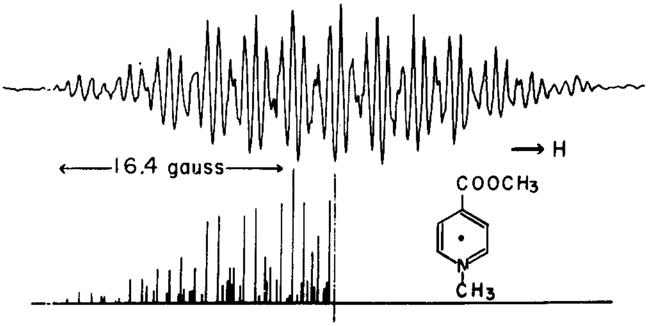
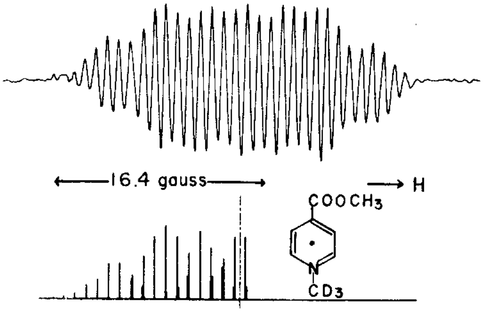


FIG. 1b



The ESR spectrum of 1-methyl-4-carbomethoxypyridinyl radical was measured to be as shown in FIG. 1a. In order to analyze exactly the ESR spectrum of this radical, the 1-deuteromethyl-4-carbomethoxypyridinyl radical was prepared and its ESR spectrum was measured with the result shown in FIG. 1b. From the hyperfine structures of the ESR spectra shown in FIG. 1a and 1b, the hyperfine splitting constants associated with the nitrogen and hydrogen (deuterium) atoms were determined to be as shown in TABLE I. Reconstructions based on these splitting constants match well with the observed spectra as shown in FIG. 1a and 1b. The other substituted pyridinyl radicals also showed strong ESR spectra with hyperfine structures from which the splitting constants associated with the nitrogen and hydrogen atoms were determined.
The results are summarized in TABLE I.

TABLE I

Hyperfine Splitting Constants due to Nitrogen and Hydrogen Atoms of Substituted Pyridinyl Radicals. (Gauss Unit)

		4-COOCH$_3$		4-CN	4-COCH$_3$
A_N	(ring)	6.25 ± 0.3	(6.2)*	7.0 ± 0.4	5.6 ± 0.4
A_H	(N-CH$_3$)	5.55 ± 0.2	(A_D= 0.9)*	5.6 ± 0.3	4.9 ± 0.4
A_H	(2,6-)	3.55 ± 0.2	(3.6)*	4.1 ± 0.3	3.1 ± 0.4
A_H	(3,5-)	0.8 ± 0.1	(0.9)*	1.3 ± 0.3	0.6 ± 0.4
A_H	(O-CH$_3$):	0.8 ± 0.1	(0.9)*	A_N(CN):1.3 ± 0.3	A_H(CCH$_3$):0.6

*) The results of the 1-deuteromethyl-4-carbomethoxypyridinyl radical.

The electronic spectrum of the 1-methyl-4-carbomethoxypyridinyl radical in acetonitrile was measured in parallel with the ESR spectrum. The result is shown in FIG. 2. The three absorption bands appeared at 307, 396 and 650-690 mμ. These bands disappeared when the solution was exposed to air. The electronic spectra of the other substituted pyridinyl radicals were also measured. It was found that all these pyridinyl radicals showed three absorption bands in the visible region except for the 1-methyl-4-carboamidopyridinyl radical. The observed maximum wavelengths (λ_{max}'s) are summarized in TABLE II.

FIG. 2

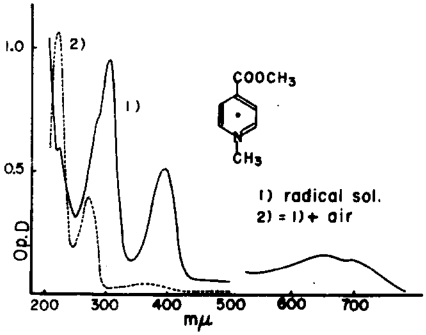


TABLE II

Electronic Absorption Bands of Substituted Pyridinyl Radicals.

Substituent	λ_{max}		
4-$COOCH_3$	307 mμ	396 mμ	650 (690)** mμ
4-$COCH_3$	326	432	(600)*
4-$CONH_2$	300**	403	-
4-CN	313	395	605 (550,670)**

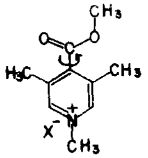
*) very weak band. **) shoulder.

The preparation of 1,2,6- or 1,3,5-trimethyl 4-substituted pyridinyl radicals has been attempted. The 1,2,6-trimethyl 4-substituted pyridinyl and 1,3,5-trimethyl-4-cyanopyridinyl radicals could be obtained from the corresponding pyridinium iodides. However, the 1,3,5-trimethyl-4-carbomethoxy- and 1,3,5-trimethyl-4-carboamidopyridinyl radicals could not be obtained despite careful and repeated experiments.

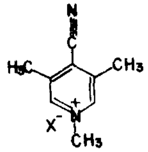
TABLE III

Stability of Substituted Pyridinyl Radicals at Room Temperature.

	$4-COOCH_3$	$4-CONH_2$	4-CN
no alkyl	2-3 days	1-2 hrs.	ca. a week
3,5-dimethyl	no radical	no radical	ca. 2 days
2,6-dimethyl	10-20 min.	ca. 10 min.	1-2 hrs.



large steric hindrance



small steric hindrance

The stability of these substituted pyridinyl radicals in acetonitrile was shown in TABLE III. The results given in TABLE III seem to be explained by considering the steric hindrance of the methyl groups at 3 and 5 positions. The $COOCH_3$ and $CONH_2$ groups at 4 position are probably prohibited by the steric hindrance from the coplanarity with the pyridinium ring. This discrepancy from the coplanarity causes the decrement in the resonance stabilization due to the $COOCH_3$ and $CONH_2$ groups. This seems to be the reason why the electron affinities of the 1,3,5-trimethyl-4-carbomethoxy- and 1,3,5-trimethyl-4-carboamidopyridinium ring are so small that the corresponding pyridinyl radicals could not be obtained.

From the hyperfine splitting constants of the ESR spectra of the pyridinyl radicals summarized in TABLE I, it is inferred that an odd electron is not localized on the ring nitrogen atom but distributed over the pyridinyl radicals. This shows that the pyridinyl radicals are of π-type as usual aromatic anion radicals. The substituted pyridinyl radicals may have electronic structures similar to those of substituted pyridine anion radicals. These points will be discussed with details in the full paper.

REFERANCE

1) E.M. Kosower and E.J. Poziomek, J. Am. Chem. Soc., 85, 2035 (1963).

2) M. Itoh, T. Okamoto and S. Nagakura, Bull. Chem. Soc. Japan, 36, 1665 (1963); M. Itoh and S. Nagakura, ibid., 38, (1965) in press.