CHEMISTRY LETTERS, pp. 1107-1110, 1972. Published by the Chemical Society of Japan

A STABLE FREE RADICAL, 1-METHYL-2-METHOXYCARBONYLPYRIDINYL

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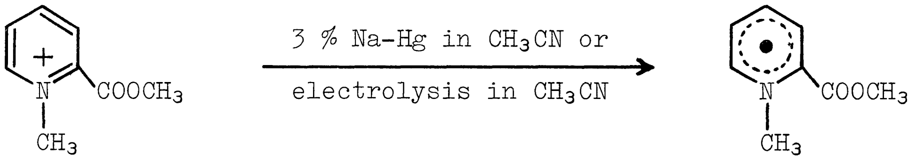
A stable free radical, 1-methyl-2-methoxycarbonylpyridinyl, has been prepared by the reduction of the corresponding pyridinium iodide with 3 % sodium amalgam. The radical can be isolated in a pure form by distillation under a vacuum. Analysis of the hyperfine structure of the ESR spectrum reasonably explained the radical structure.

It has been known that a stable radical, 1-ethyl-4-methoxycarbonylpyridinyl,$^{1)}$ and its homologs$^{2,3)}$ can be isolated in pure forms and show peculiar physical and chemical properties. Among the physical properties, the dimeric association and the complex formation with magnesium iodide and sodium iodide of the radicals have been particularly investigated.$^{4-6)}$ We are interested in the preparation of the isomeric pyridinyl radicals. The preparation and isolation by distillation of 1-methyl-2-methoxycarbonylpyridinyl(I) will be reported.

Generation of the radical I was preliminarily examined by the electrochemical reduction of the corresponding pyridinium iodide, using a cell with platinum electrodes for the electron spin resonance (ESR) study. The electrolysis of 1-methyl-2-methoxycarbonylpyridinium iodide (II) in degassed acetonitrile at ca. 1 V, in the presence of a large amount of tetra-n-propylammonium perchlorate as the supporting electrolyte, produced a green solution which exhibited a strong ESR signal. The radical was stable for a long period after the current was turned off. Hyperfine structure of the ESR spectrum was identical with that of the pure radical solution prepared by the following experiment.



II

I

Treatment of II with 3 % sodium amalgam in degassed acetonitrile at around 5°C afforded also a green solution which exhibited a strong ESR signal. After stirring for about 2 hours, acetonitrile was removed and the residue was extracted with 2-methyltetrahydrofuran (MTHF). The solvent of the extract was removed and then the radical was distilled by warming the flask containing the extraction residue to 90~100°C and cooling the condenser with liquid nitrogen. The radical condensed as a green solid was transferred with MTHF to a receiver connected with the cells for measurements of ESR and absorption spectra. The apparatus used in this preparation is similar to that used for the 4-methoxycarbonyl isomer by Kosower and Poziomek.[1)]

The ESR spectrum of the radical solution shown in Fig. 1 consists of more than 170 hyperfine splitting lines within a total extent of 44.4 gauss. In order to analyze the hyperfine structure, the deuterated compound, 1-trideuteriomethyl-2-methoxycarbonylpyridinyl (III), was prepared in the same way as I from the corresponding pyridinium iodide and the ESR spectrum was measured. A comparison between the spectra of I and III first revealed that a splitting constant 5.70 gauss, which represents the coupling with three equivalent hydrogen atoms in I, corresponded to a constant of 0.87 gauss in the spectrum of III. The latter constant represents the coupling with three deuterium atoms of the trideuteriomethyl group in III. Other splitting constants were determined by spectral simulation with a computer. The constants are listed in Table 1. The assignments for the constants were given tentatively according to the type of splitting and by comparing them with the assignments for the constants in the 4-methoxycarbonyl isomer.[2)] Thus, the radical structure of I was reasonably confirmed by the analysis of the ESR hyperfine structure. Using the observed splitting constants, we have evaluated the spin densities on the carbon atoms of this radical with the McConnell relation, $\underline{a}_i = \underline{Q}\,\rho_i$. The results are included in Table 1.

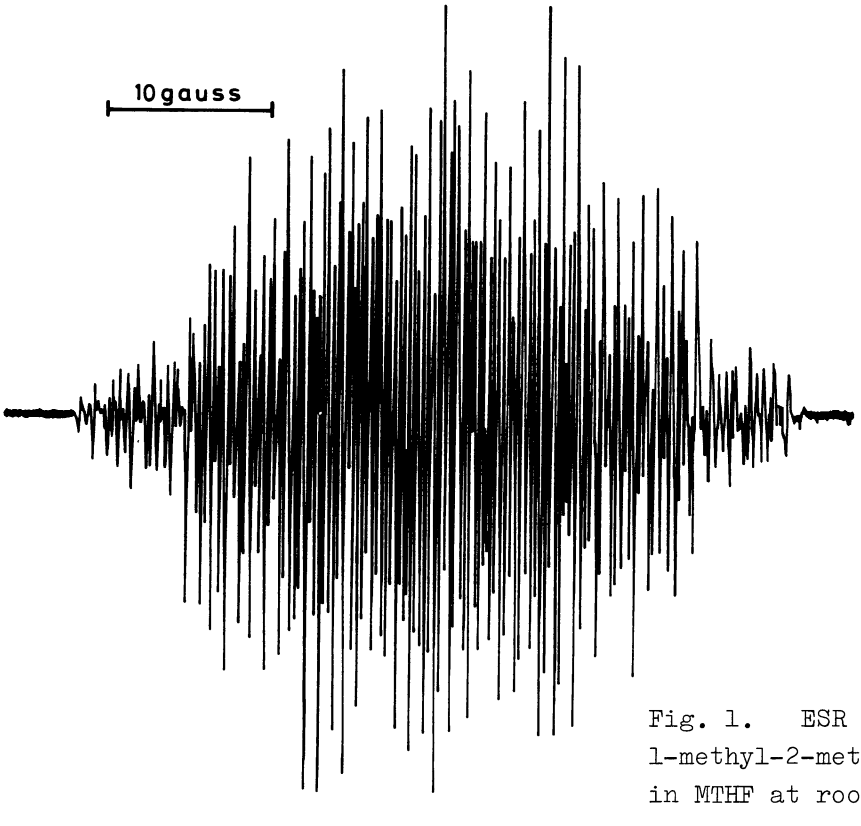


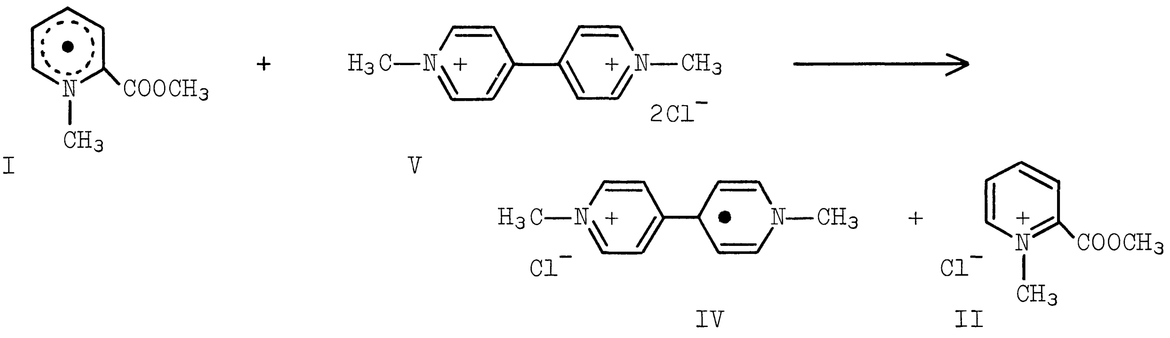
Fig. 1. ESR spectrum of 1-methyl-2-methoxycarbonylpyridinyl in MTHF at room temperature.

Table 1. Observed Splitting Constants ($\underline{a}_i$) and Spin Densities Evaluated from the Constants for 1-Methyl-2-methoxycarbonylpyridinyl

Position	$\underline{a}_i$, gauss I ($N-CH_3$)	 III ($N-CD_3$)	Spin density, ρ_i*
1	6.65	6.43	
3	1.53	1.53	0.055
4	6.36	6.24	0.230
5	1.10	1.10	0.040
6	2.46	2.46	0.089
$N-C\underline{H}(\underline{D})_3$	5.70	0.87	
$COOC\underline{H}_3$	0.89	0.89	

* Evaluated by the relation, $\underline{a}_i = \underline{Q}^H_{CH} \rho_i$, in which an average $|\underline{Q}^H_{CH}|$ value (= 27.7 gauss) for neutral cycloheptatrienyl and cyclopentadienyl radicals was adopted.

The electronic spectrum of the radical solution in acetonitrile is shown in Fig. 2. This spectrum is comparable with that obtained by generating 1-methyl-2-carbamoylpyridinyl radical by pulse radiolysis.[7)] Three absorption bands at 335, 408, and 550 nm of the spectrum all disappeared when the solution was exposed to air. The concentration of the solution was determined spectroscopically by the following relatively slow formation of methylviologen (paraquat) radical cation (IV) from methylviologen dichloride (V) in acetonitrile.



The intensity of the absorption band at 408 nm decreases with the increase of the radical concentration, while the intensity of the shorter band at 335 nm increases. This implies that the radical associates to form the dimer at high concentrations in a similar manner to the association of the 4-methoxycarbonyl isomer.

The stability of the radical I is comparable with, but looks less than, that of 1-methyl-4-methoxycarbonylpyridinyl. Although I is highly reactive to oxygen, water, alcohols, and carbon tetrachloride, it is stable in a number of solvents such as isopentane, benzene, acetonitrile, and ethers. Pure radical or the solution of high concentration is less stable. Although samples of I appear unchanged at room temperature for few hours, the characteristic green color changes markedly after a day at room temperature, being accompanied by the decrease

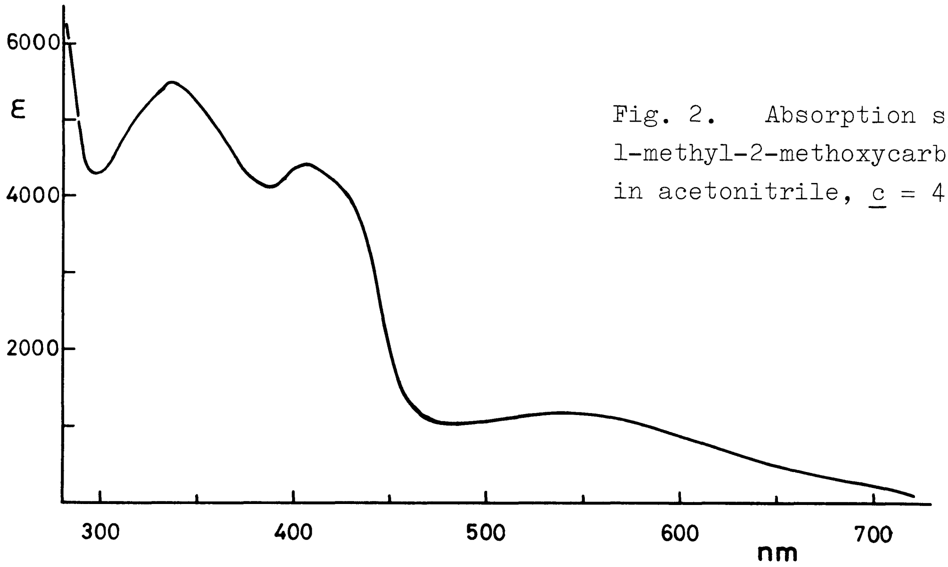


Fig. 2. Absorption spectrum of 1-methyl-2-methoxycarbonylpyridinyl in acetonitrile, $\underline{c}$ = 4.8 x 10^{-3}M/l.

of the ESR signal intensity. Distillation of I also brings about the collapse of a considerable amount of the radical, leading to a low yield in the preparation, while the preparation of the 4-methoxycarbonyl isomer shows a yield over 70 %.

Such a comparison of the stabilities of I and the 4-methoxycarbonyl isomer is comprehensible in terms of the relative reduction potentials for the corresponding analogous pyridinium ions; 1-methyl-2-ethoxycarbonylpyridinium iodide, -0.83 V, and 1-methyl-4-ethoxycarbonylpyridinium iodide, -0.77 V (in acetonitrile), both with respect to the aqueous saturated calomel electrode.8)

The radical I associates to form the dimer, as seen in the concentration dependence of the absorption spectrum. The dimerization is remarkable at low temperature and the ESR signal intensity of I in MTHF decreases with lowering the temperature, implying the formation of the diamagnetic dimer. Appearance of the associated triplet state6) by light irradiation of the radical in MTHF glass at 77°K was also observed in the ESR spectrum. The study on the association is in progress.

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(Received September 1, 1972)