

Mass Spectra of Styrylpyridinecarboxylates

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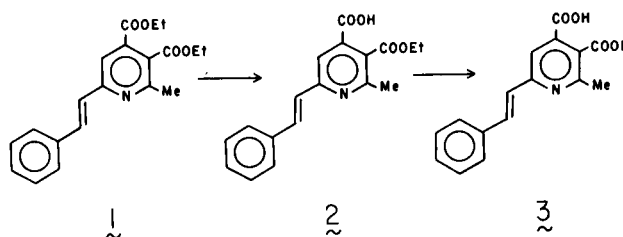
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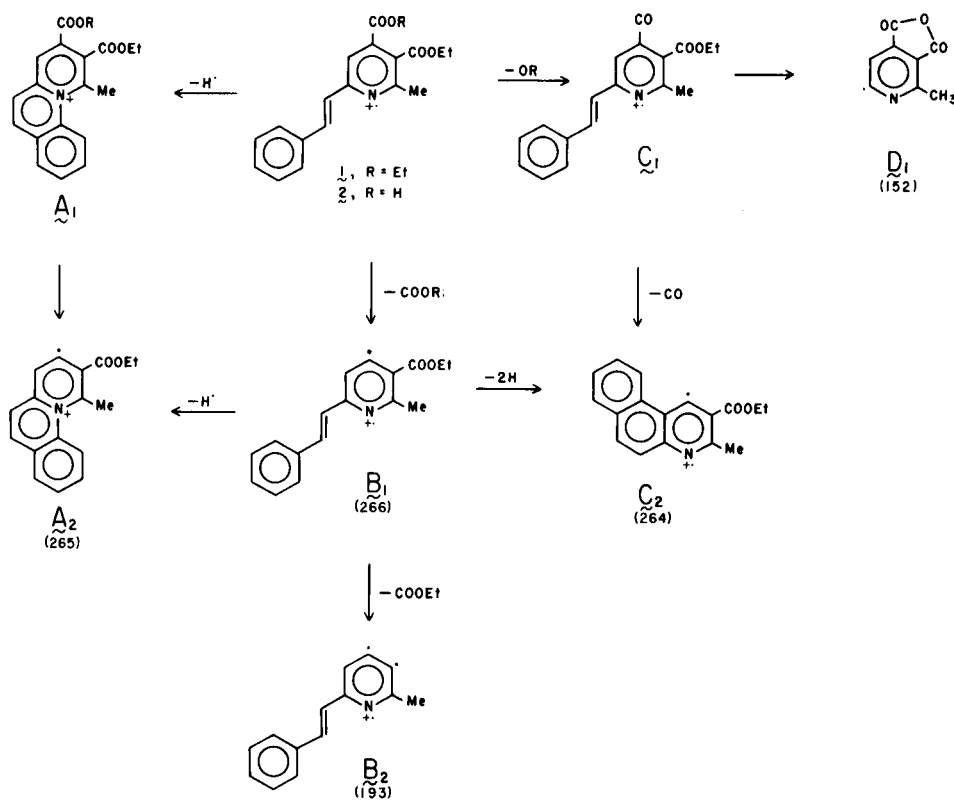
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The mass spectra of styrylarenes, such as stilbene, show that during electron bombardment these compounds undergo cyclization to give phenanthrene type cations (1). We have recently observed similar cyclizations in the mass spectra of 5-styrylpyrazole-3-carboxylates (2). In the present paper we report the occurrence of similar cyclizations during the electron bombardment of 6-styrylpyridinecarboxylates.

Three compounds were investigated, the first was 3,4-diethoxy-carbonyl-2-methyl-6-styrylpyridine (1), a compound first prepared by Lawson, Perkin, and Robinson



(3) and is here described in the crystalline form and characterized. The second compound was 3-ethoxycarbonyl-2-methyl-6-styrylpyridine-4-carboxylic acid (2) obtained



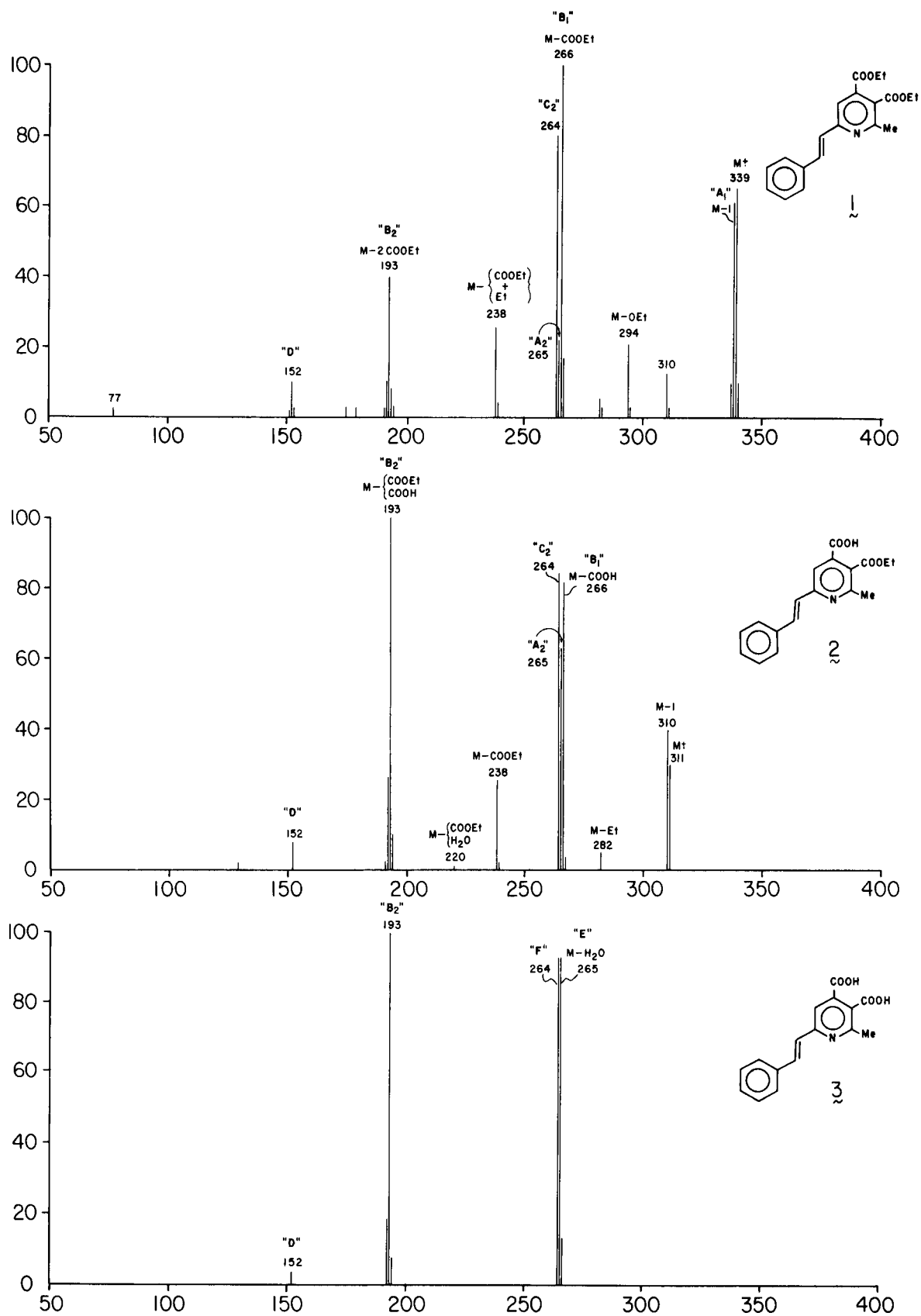
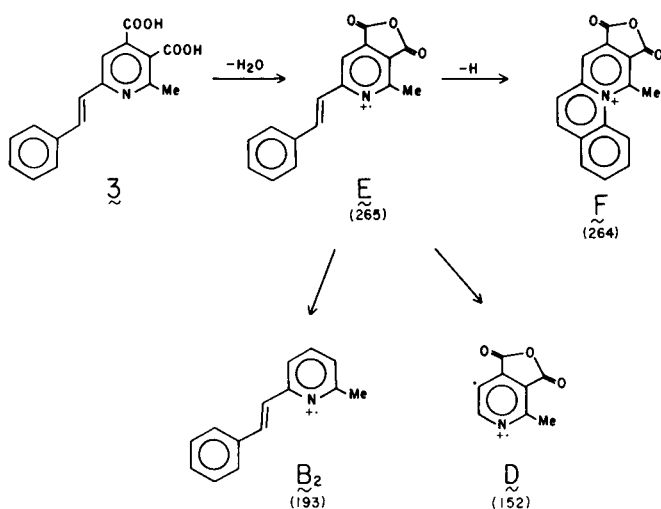


Figure 1. Mass Spectra of Compounds 1, 2, and 3.



here for the first time by mild alkaline hydrolysis of diester (1). Since the rate of alkaline hydrolysis of ethoxycarbonylpyridines is fastest for the 4-carboxylic ester followed by the 2-carboxylic ester and is slowest for the 3-carboxylic ester (4,5), it was concluded that mild alkaline hydrolysis would hydrolyze the ester group on position 4 rather than that in position 3 and the monoester obtained was accordingly given structure (2). The last compound studied was the known (3) 2-methyl-6-styrylpyridine-3,4-dicarboxylic acid (3) obtained by the acid hydrolysis of diester (1) or monoester (2).

The mass spectra of the 6-styrylpyridine carboxylates studied (see Figure 1) showed strong evidence of the cyclization of the styryl side chain to form azaphenanthrenes, either through the formation of a bridge between the *ortho* position of the phenyl ring and the *beta* position of the pyridine ring with a loss of two protons as in ion "C₂" or by forming a bridge between the *ortho* position of the phenyl ring and the nitrogen of the pyridine ring with a loss of one proton as in ion "A". Due to the steric effect of the carboxylate or carboxylic acid group present in position 4 in compounds 1, 2, and 3, the azaphenanthrene of type "A" prevailed in those compounds having a carboxylate group in position 4; whereas the f-benzoquinolines of type "C₂" seemed to be formed only after the carboxylate group attached to position 4 of the pyridine was removed.

The mass spectrum of compound 1 showed a strong molecular peak at *m/e* 339 which was followed by an M-1 peak of equal intensity which was assigned to the azaphenanthrene "A₁". Although the loss of a proton from the side chain of alkylpyridines is not uncommon (6), the magnitude of the M-1 peak in compounds 1 and 2 is much greater than would be expected for such a fragmentation mode. A more plausible explanation is the cyclizations of the styryl side chain to form azaphenanthrenes. The type of the cyclization "A" or "C₂" being influenced by steric effects.

The M⁺ and M-1 peaks were followed by two relatively weak peaks corresponding to M-Et at 310 and M-OEt at 294. The base peak in the spectrum appeared at *m/e* 266 and was assigned to M-COOEt. At *m/e* 265, a moderately strong peak appeared which was assigned to a loss of COOEt from the cyclized azaphenanthrene (A₂). It is known (7) that decarboxylation of pyridine-2,3,4-tricarboxylic acid occurs preferentially at position 2 followed by position 4 and is most difficult for position 3. Accordingly we have tentatively assigned the *m/e* 266 peak to a 3-ethoxycarbonyl-2-methyl-6-styrylpyridine radical cation "B₁". The assumption that the carboxylate group in position 4 was the one eliminated could help explain why the major peak appeared at *m/e* 264, two mass units less than the M-COOEt. This fragment was represented by ion "C₂" produced by forming a bridge between the *ortho* position of the phenyl ring and *beta* position of the pyridine ring. This cyclization is now favored because the bulky substituent in the 4 position has been removed. A peak of moderate intensity appeared at *m/e* 238 which corresponded to the loss of COOEt and Et and a stronger one at *m/e* 193 corresponded to the loss of the two ethoxycarbonyl groups. Finally, a small peak at 152 appeared in all three spectra and was assigned to a 2-methylpyridine-3,4-dicarboxylic acid anhydride radical cation (D).

The mass spectrum of 3-ethoxycarbonyl-2-methyl-6-styrylpyridine-4-dicarboxylic acid (2) was quite similar to that of diester (1). However, the molecular peak was of smaller intensity due to the relative ease of decarboxylation of a carboxylic acid relative to an ester. The molecular peak at *m/e* 311 was followed by a peak of stronger intensity at *m/e* 310 corresponding to the azaphenanthrene and a small peak at *m/e* 282 corresponding to M-Et. A major peak appeared at *m/e* 262 and was assigned to M-COOH. This was followed by the two azaphenanthrene peaks, one at *m/e* 265 and one at 264. A smaller peak appeared at *m/e* 238 and was assigned to the loss of COOEt. Since the loss of a carboxylic acid is more facile than the loss of an ethoxycarbonyl group, the M-COOH peak was larger than the M-COOEt peak. The base peak in the spectrum of compound (2) was at *m/e* 193 which corresponded to the loss of both COOH and COOEt groups. The radical cation (D) at *m/e* 152 also appeared in the spectrum.

The mass spectrum of 2-methyl-6-styrylpyridine-3,4-dicarboxylic acid (3) showed no molecular peak, but showed an intense peak corresponding to the loss of water at *m/e* 265, probably due to the formation of the anhydride. Since position 4 of the pyridine ring was occupied, no [*f*]-benzoquinoline was observed but instead an azaphenanthrene (F) was observed at *m/e* 264. The base peak showed at *m/e* 193 and as in the spectra of compounds 1 and 2, it corresponded to the formation of the 2-methyl-6-styrylpyridine cation diradical (B₂). It was followed by a peak

at m/e 152 assigned to radical cation "D".

EXPERIMENTAL

Melting points were measured on a Kofler block and are uncorrected. Ir spectra were recorded with Unicam SP200 and Perkin-Elmer 621 spectrophotometers. Mass spectra were run on a Varian M-60 spectrometer by Mr. M. P. Gilles, Department of Chemistry and Chemical Engineering, Michigan Technological University, who also carried out the microanalyses on a Perkin-Elmer 240 Elemental Analyzer.

3,4-Diethoxycarbonyl-2-methyl-6-styrylpyridine (1).

This diester was obtained by the method of Lawson, Perkin and Robinson (3) from ethyl 2,4-dioxo-6-phenylhex-4-enoate (10.0 g.) and ethyl β -aminocrotonate (5.2 g.). It was isolated as a canary yellow picrate (6.0 g.) m.p. 147° (lit. (3) m.p. $147-148^\circ$). The picrate was decomposed by shaking with dilute aqueous ammonia and extracted with ether several times. The ethereal extract was washed by shaking three times with 500 ml. portions of water then dried. After distillation of the ether, the pale-brownish oil that separated was extracted four times with petroleum-ether (b.p. $40-60^\circ$). Upon concentration of the solution, compound (1) separated out (3.1 g.) and was crystallised from light petroleum (b.p. $50-70^\circ$) in colorless needles m.p. 68° ; ν max (potassium bromide): 1724 cm^{-1} (C=O).

Anal. Calcd. for $\text{C}_{20}\text{H}_{21}\text{NO}_4$: C, 70.78; H, 6.24; N, 4.3. Found: C, 71.02; H, 6.30; N, 4.03.

3-Ethoxycarbonyl-2-methyl-6-styrylpyridine-4-carboxylic Acid (2).

One mole of diester (1) was refluxed for three hours in 50 ml. of ether containing 1.5 mole of sodium ethoxide. After evaporating the ether, the residue was acidified with 10% hydrochloric acid and extracted with ether. When the ether was removed, the residue

crystallised from benzene or methanol in colourless needles m.p. 196° ; ν max (potassium bromide): 1723 cm^{-1} (C=O).

Anal. Calcd. for $\text{C}_{18}\text{H}_{17}\text{NO}_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.36; H, 5.53; N, 4.43.

2-Methyl-6-styrylpyridine-3,4-dicarboxylic Acid (3).

This dicarboxylic acid was obtained when diester (1) or monoester (2) were refluxed for 15 minutes with excess 10% sodium methoxide in methanol. The solution was concentrated, diluted with water, cooled and acidified with acetic acid. 2-Methyl-6-styrylpyridine-3,4-dicarboxylic acid (0.32 g.) separated out and was crystallised from dilute acetic acid in pale yellow hydrated crystals, m.p. $220-221^\circ$ (lit. (3) m.p. 220°); ν max (potassium bromide): $1720; 1710\text{ cm}^{-1}$ (C=O).

Anal. Calcd. for $\text{C}_{16}\text{H}_{13}\text{NO}_4 \cdot \text{H}_2\text{O}$: C, 63.78; H, 5.02; N, 4.62. Found: C, 63.58; H, 4.93; N, 4.58.

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