The Formation of Three Isomeric Mononitro Derivatives in the Nitration of 2-Thenyl Chloride

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It is commonly assumed that the electrophilic substitution of thiophene derivatives with an *o*-, *p*-directing group in the 2-position occurs almost exclusively at the 5-position because of the overlapping of the directive effects of the nuclear sulfur atom and the substituent; it occurs at the 3-position to only a minor extent. Recently, it has been suggested by the NMR technique that, besides the 5-substituted isomers, considerable amounts of the 3-substituted ones are formed in the nitrations of 2-methylthiophene,¹⁾ 2-thenyl chloride (I)²⁾ and 2-thenyl acetate.³⁾ However, no report on the formation of 4-substituted isomer has been made. A further study of the product obtained from the nitration of I has revealed the formation of, in addition to

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1) R. A. Hoffman and S. Gronowitz, *Arkiv Kemi*, **16**, 563 (1960).

2) T. Sone and Y. Matsuki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 496 (1962).

3) T. Sone, K. Takahashi and Y. Matsuki, This Bulletin, **35**, 1420 (1962).

the 3- and 5-substituted isomers, the 4-substituted isomer, which would not be expected from the assumption mentioned above.

Figure 1 shows the NMR spectrum of the product at 60 Mc. (b. p. 105~109°C/2 mmHg)[2] in the nitration of I by the nitric acid - acetic anhydride procedure. The assignment of the peaks to each of the isomers is based on the ring-coupling constants[1] and on the couplings[4,5] between the methylene protons and the ring protons. A set of four strong peaks, consisting of two triplets and a doublet ($J=4.1_5$ c. p. s. and $J_{\mathrm{CH_2}}=0.8$ c. p. s.), is typical for the ring protons of 5-substituted 2-thenyl derivatives[4,5] and can be assigned to 5-nitro-2-thenyl chloridet (II), the main product. The remainder may be explained as follows. The doublet ($J=5.7$ c. p. s.) centered about 350 c. p. s., with reference to cyclohexane, is clearly due to one[6] of the two ring protons of 3-nitro-2-thenyl chloride (III), while the doublet ($J=1.6$ c. p. s.) on the lowest field side is due to the proton at the 5-position of 4-nitro-2-thenyl chloride (IV).[7] Among the seven peaks in the 367.5 c. p. s.~373.2 c. p. s. region, the two peaks at the two outermost sides are due to one[6] of the two ring protons of III, while the other five peaks are related to the proton at the 3-position of IV; the overlapping of two triplets, which is caused by the coupling of the proton at the 3-position with both that at the 5-position and with the neighboring methylene protons, forms five peaks with an estimated intensity of 1 : 2 : 2 : 2 : 1, and the observed coupling constants ($J_{35}=1.7$ c. p. s. and $J_{2\mathrm{CH_2}-3}=0.8$ c. p. s.) are in accord with the expected ones. The signals correspond well with those of authentic IV (b. p. 105~107°C/2 mmHg, n_D^{20} 1.6065, d_4^{20} 1.4825. Found: C, 33.89; H, 2.02; N, 7.52. Calcd. for $C_5H_4ClNO_2S$: C, 33.81; H, 2.27; N, 7.88%) prepared by the chloromethylation of 3-nitrothiophene, although attempts to isolate IV, itself or as a derivative, from the nitration product were unsuccessful.

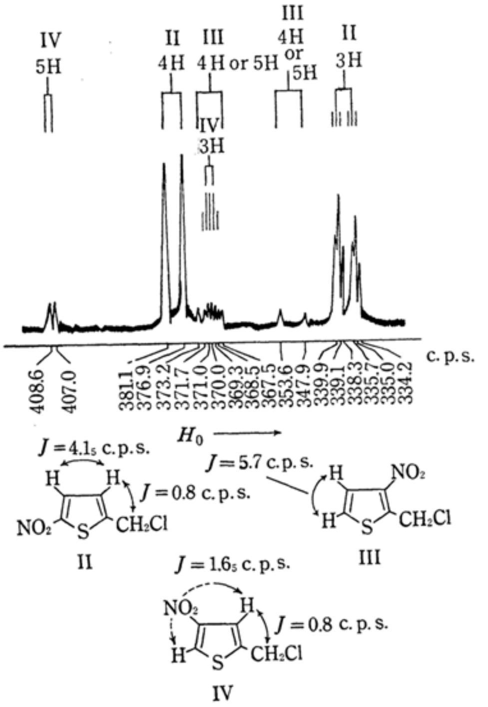

Fig. 1. NMR spectrum of the ring protons of a mixture of 5-nitro-2-thenyl chloride (II), 3-nitro-2-thenyl chloride (III) and 4-nitro-2-thenyl chloride (IV) in carbon tetrachloride at 60 Mc.

The NMR spectrum of the product in the nitration of 2-thenyl acetate also suggests the formation of the 4-nitro derivative as a by-product.[8]

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4) K. Takahashi, T. Sone, Y. Matsuki and G. Hazato, This Bulletin, 36, 108 (1963).

5) Data obtained from the NMR spectra of some thenyl chlorides will be published later.

6) At present, it is not possible to determine which of the doublets should be assigned to the proton at the 5-position or to that at the 4-position.

7) The agreement of the spacing both at 40 Mc. and at 60 Mc. assures the assignment of this doublet to one of the two ring protons of the 4-substituted isomer coupling with the other proton.

8) 4-Nitro isomer: $J_{35}=1.5$ c.p.s. and $J_{2\mathrm{CH_2}-3}=0.6$ c.p.s. In a preceeding paper,[3] two peaks on the lowest field side in the NMR spectrum (40 Mc.) were ascribed to the dinitro isomer.