On the Nitration of 2-Thenyl Acetate

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A recent paper[1] has reported that the nitration of 2-thenyl acetate with acetic anhydride-nitric acid at 10°C gives a 65% yield of 5-nitro-2-thenyl acetate (I), b.p. 132°C/0.3 mmHg, m.p. 35°C, but also that in spite of some attempts, the formation of 3-nitro-2-thenyl acetate (II), which can be expected from the presence of the *o*-, *p*-directing acetoxymethyl group in the 2-position of the thiophene ring, is not observed.

During the identification and the structural investigation of thenyl derivatives by means of the NMR technique, we early examined the same reaction and observed, unlike the paper mentioned above, the formation of II as a by-product in a relatively high proportion. To a solution of 2-thenyl acetate (15.6 g.) in acetic anhydride (30 ml.), a mixture of nitric acid ($d=1.50$, 6 ml.) and acetic anhydride (12 ml.) was added at −10°C, and the reaction mixture was stirred at −5~0°C for 2.5 hr. Nitro-2-thenyl acetate was obtained as a pale yellow oil (13.6 g., 67.6%), b.p. 120~125°C/2~2.5 mmHg (Found: C, 42.02; H, 3.27; N, 6.47%), which, on being left standing, partially solidified to colorless needles, m.p. 38~39°C[2] (from low boiling petroleum ether). The NMR spectrum (Fig. 1a[3], 40 Mc., cyclohexane as an internal reference) of the oil shows several lines with a medium intensity in the aromatic region, in addition to the four lines (227.8, 231.9, 252.7 and 256.6 c.p.s., $J=4.0$ c.p.s.) on the basis of which the major part of the oil can be identified as I, 2,5-disubstituted thiophene[4]. Besides these, two lines (155 and 168 c.p.s.) due to the methylene group and a line (31 c.p.s.) due to the methyl group are observed at the high field side. This indicates the presence of an isomer other than I. Upon treating the acetate (b.p. 120~125°C/2~2.5 mmHg) with 10% sulfuric acid, the corresponding nitro-2-thenyl alcohol (b.p. 115~118°C/2 mmHg) was obtained in a 72% yield (Found: C, 38.03; H, 2.87; N, 8.61; Calcd. for $C_5H_5 \cdot NO_3S$: C, 37.73; H, 3.17; N, 8.80%). Benzoate, m.p. 97.5~99°C (from alcohol) (Found: N, 5.25; Calcd. for $C_{12}H_9NO_4S$: N, 5.32%). In the NMR spectrum (Fig. 1b) of the alcohol, the shifts and the coupling constants ($J=4.1$ and 5.4 c.p.s.) obviously show the alcohol to be a mixture of 5-nitro- and 3-nitro-2-thenyl alcohol. Thus, it is evident that the original nitro-2-thenyl acetate is also a mixture of I and II. From the relative peak area of the NMR spectra, the ratio of II to I in the nitration products of 2-thenyl acetate under the conditions studied is of the order of 1 to 8 or higher. There has been hitherto little systematic or quantitative investigation of the ratio of isomer formed in the electrophilic substitution of thiophene derivatives with an *o*-, *p*-directing group in the 2-position; it has been assumed that the substitution occurs almost exclusively at the 5-position and at the 3-position, if at all, to a minor extent. However, from the results of the nitration of 2-methoxy thiophene[5] and 2-thenyl chloride[6] and of the present study, it seems that 3-substitution occurs in a relatively higher proportion than had been expected.

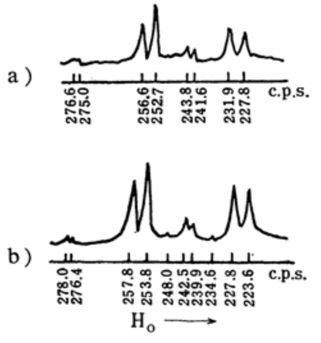

Fig. 1. NMR spectra in the aromatic region of:
- a) A mixture of 3-nitro-, and 5-nitro-2-thenyl acetate
- b) A mixture of 3-nitro-, and 5-nitro-2-thenyl alcohol

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[1] M. Berçot-Vatteroni, R. C. Moreau and P. Reynaud, *Compt. rend.*, **252**, 2419 (1961).

[2] The lines due to II are not observed in the NMR spectrum.

[3] The two extra peaks at the low field side are probably due to the presence of the dinitro isomer.

[4] S. Gronowitz and R. A. Hoffman, *Arkiv. Kemi.*, **13**, 279 (1958); ibid., **16**, 563 (1960); K. Takahashi, Y. Matsuki, T. Mashiko and G. Hazato, This Bulletin, **32**, 156 (1959); K. Takahashi, Y. Matsuki, Y. Miyake and G. Hazato, ibid., **34**, 1599 (1961).

[5] J. Sicé, *J. Am. Chem. Soc.*, **75**, 3697 (1953).

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