## *Thermal Isomerization of 2-Thenylthiocyanate*

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During the studies of the structural investigation and the identification of thenyl derivatives by means of the NMR technique, we happened upon the occurrence of the thermal isomerization of 2-thenylthiocyanate at about 150°C.

Resonance was observed at 40 mc, the apparatus and the procedure were similar to those previously described¹⁾, and in every sample, cyclohexane was used as an internal reference. The spectrum of the raw product synthesized from thiophene by the procedure of thiocyanomethylation, is shown in Fig. 1a. The lines coming from the aromatic hydrogens in thiophene ring spread over the range of about 20 cps at the low-field side of the spectrum. At the high-field side two lines at 107.5 and 125 cps, referred to cyclohexane signal, are assumed to be the lines coming from the hydrogens of the methylene group. We had expected formerly to be observed only one line coming from this group; whereas, the experimental result showed that the methylene peak was divided into two lines, corresponding to two isomers respectively. After this measurement, the sample was heated at about 150°C for two hours by immersing in a constant temperature bath. In the spectrum of the heated sample, the two lines coming from the methylene hydrogens were found at the same positions but there was a marked difference in their intensities as compared with the non-heated sample, as shown in Fig. 1b. This result indicates the occurrence of a thermal isomerization between two compounds of which our synthesized product consists. The thermal isomerization in allylthiocyanate was firstly shown by Gerlich²⁾. Here we have studied the benzyl thiocyanate which shows the thrmal isomerization at about 250°C, reported already by Hennicke³⁾. Its spectrum shows two lines coming from methylene and aromatic hydrogens at 96 and 229 cps, referred to cyclohexane signal, respectively. By heating of this compound at about 150°C for two hours, no change of its NMR spectrum was observed in comparison with 2-thenyl derivative, but after heating at about 250°C for two hours, the line coming from the methylene group was found at 111 cps with the other small neighboring peaks, and the lines of the aromatic hydrogens were found at 224 and 228 cps. This phenomenon is assumed as the isomerization from thiocyanate to isothiocyanate which is promoted by heating, the same is the case with that observed in 2-thenyl derivative. The isomerization in question here observed in the NMR spectrum is represented by the shift of the line coming from the methylene group to the lower field, which is attributed to the change of the electronegativity and of the second-order high frequency paramagnetism of the adjacent group. The detailed result on the thiocyanomethylation of thiophene will be published in the Journal of the Chemical Society of Japan, Ind. Chem. Sec.

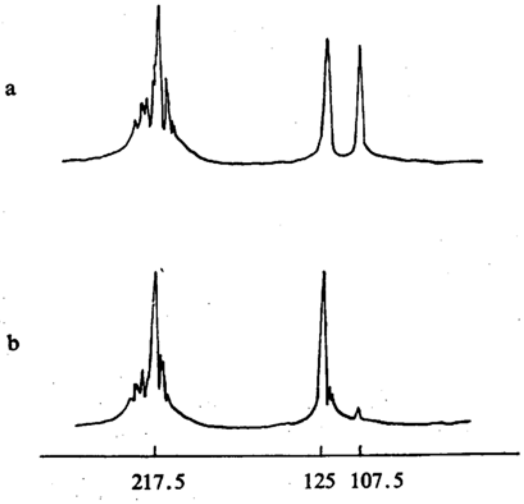

Fig. 1. The proton magnetic resonance spectra of the raw product synthesized from thiophene by thiocyanomethylation, (a) before heating; (b) after heating at about 150°C for two hours. Applied magnetic field increasing from left to right.

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1) K. Takahashi, Y. Matsuki, T. Mashiko and G. Hazato, This Bulletin, 32, 156 (1959).

2) G. Gerlich, *Ann.*, 178, 83 (1875).

3) H. Hennicke, ibid., 344, 24 (1906).