

Furan derivatives. XXXIX.

The isomerization of substituted 5-phenyl-2-furfurylthiocyanates to the corresponding isothiocyanates

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Received 15 July 1971

The isomerization of substituted 5-phenyl-2-furfurylthiocyanates to the corresponding isothiocyanates was investigated from the kinetic point of view. The measured rate constants were correlated with Hammett σ constants.

The isomerization of thiocyanates to isothiocyanates was already known in the last century; the rate and the mechanism of this reaction was, however, studied only recently. Thus *Rao* and *Balasubrahmanyam* [1] reported the first kinetic measurements of isomerization of methylthiocyanate. The isomerization of allyl and benzyl substituted thiocyanates was investigated more intensively than that of saturated thiocyanates [2–9]. Some authors rationalized this fact by a greater ability of unsaturated thiocyanate systems to isomerize and furnish proper isothiocyanates [10, 11]. The isomerization mechanism of some types of thiocyanates was already suggested by *Iliceto et al.* [2–7] and also by *Smith* and *Emerson* [11, 12]. The above-mentioned authors [2–7] explained the isomerization of allyl substituted thiocyanates by an intramolecular mechanism involving a transitive formation of a six-membered ring. When investigating the isomerization of benzhydrylic thiocyanates by means of kinetic measurements using ^{35}S , these authors found this reaction to proceed by a monomolecular mechanism. Bimolecular mechanism was considered to be improbable due to the low nucleophilicity of the nitrogen atom in the organic thiocyanate.

The structure of the appropriate carbenes formed during the isomerization was evidenced by *Spurlock* and co-workers [13–15] on the basis of results obtained when examining single types of thiocyanates. Also the rearrangement of furfurylthiocyanate to furfurylisothiocyanate was reported by the same author [14]. The rearrangement of 5-substituted furfurylthiocyanates was studied by further authors [16, 17] as well.

Experimental

The preparation of 5-phenyl-2-furfurylthiocyanates and some reference isothiocyanates was published earlier [18]. The purity of thiocyanates was checked on a silica gel thin-layer plate before each kinetic measurement [19].

The determination of rate constants

The isomerization rate constants of substituted 5-phenyl-2-furfurylthiocyanates to the proper isothiocyanates were determined by means of infrared spectroscopy with an SP-100 Unicam Spectrophotometer in the main NCS-band region at approximately 2060 cm^{-1} . The apparatus was calibrated with a polystyrene foil $25\text{ }\mu\text{m}$ thick.

The kinetic examination procedure

The proper thiocyanate was dissolved in a spectral grade chloroform to give a $5 \times 10^{-3} \text{ mol l}^{-1}$ solution and poured into a flask provided with a reflux condenser. The flask was placed in a bath the temperature of which was kept at $60 \pm 1^\circ\text{C}$. Samples were withdrawn in 10–60 min. periods according to preliminarily estimated rates of rearrangement. The rearrangement was measured in cells 5.276 mm in width to a constant absorbance.

Results and discussion

We found that substituted 5-phenyl-2-furfurylthiocyanates easily undergo isomerization during preparation. The course of isomerization of the synthesized thiocyanates was investigated in the main NCS-band region at approximately 2060 cm^{-1} [18]. Instead

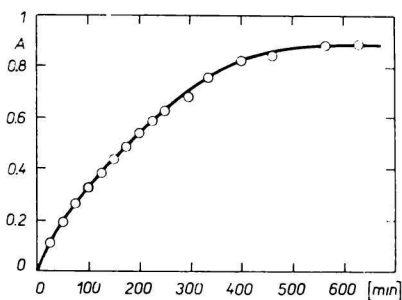


Fig. 1. The isomerization course of 5-(4-bromophenyl)-2-furfurylthiocyanate to isothiocyanate.

The time-depending absorbance at $\bar{\nu} = 2071 \text{ cm}^{-1}$.

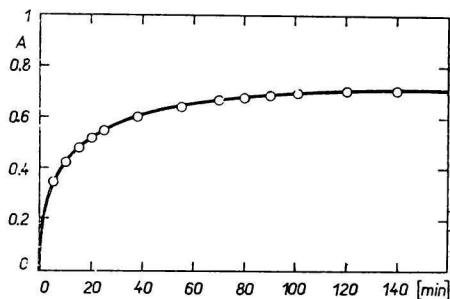


Fig. 2. The isomerization course of 5-(4-tolyl)-2-furfurylthiocyanate to isothiocyanate.

The time-depending absorbance at $\bar{\nu} = 2069 \text{ cm}^{-1}$.

Table 1

Rate constants of rearrangement of substituted 5-(X-phenyl)-2-furfurylthiocyanates to the corresponding isothiocyanates
Measured in CHCl_3 at 60°C . The initial concentration of thiocyanate $5 \times 10^{-3} \text{ mol l}^{-1}$

No.	X	$k \times 10^4 \text{ min}^{-1}$	σ
I	4- NO_2	4.37	0.778
II	3- NO_2	5.06	0.71
III	4-Cl	41.6	0.227
IV	3-Cl	34.0	0.37
V	4-Br	44.8	0.232
VI	H	184.0	0
VII	4- CH_3	423.2	-0.17

of concentration, we put the absorbance into the kinetic equation since from the calibration curve it is evident that there is a linear dependence between concentration and absorbance in the concentration region under study. The relationship between concentration and absorbance of 5-(4-nitrophenyl)-2-furfurylisothiocyanate was the basis for construction of the calibration curve. The course of some kinetic measurements could be seen in Figs. 1 and 2. The measured data were evaluated using the first order kinetic equation, since it was found that the rate constant is not concentration dependent. The measured values of rate constants are listed in Table 1.

The statistical evaluation of the measured values of rate constants with Hammett σ_p and σ_m constants gave the following results: $\rho = -2.1$, correlation coefficient $r = -0.99$ and standard deviation 0.083. These results indicate the effect of various substituents attached to benzene ring to be transmitted through the conjugated benzene and furan system on the rhodanomethyl group and that substituents markedly influence its reactivity.

From the measured rate constants (Table 1) it could be assumed that a monomolecular reaction course is involved in the case of isomerization of substituted 5-phenyl-2-furfurylthiocyanates. In support of this assumption electron-donor substituents favour the isomerization, whereas electron-acceptor substituents retard the rearrangement what is evident from the values of rate constants.

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Translated by Z. Votický