Dimroth rearrangement in the thiadiazole—triazole system

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Kinetically controlled rearrangement of substituted 5-amino-1,2,3-thiadiazoles to the corresponding 1,2,3-triazoles under the conditions of a pseudomonomolecular reaction is described. Based upon the found rate constants k' the mechanism of the rearrangement is discussed.

В работе изучалась кинетика перегруппировки замещенных 5-амино--1,2,3-тиадиазолов в 1,2,3-триазолы в условиях псевдомономолекулярной реакции. Исходя из измеренных констант скоростей k' обсуждается механизм перегруппировки.

Dimroth rearrangement in a thiadiazole—triazole system was first observed by *Kindt—Larsen* and *Pedersen* [1] when 5-mercapto-1-phenyl-1,2,3-triazole was formed from 5-anilino-1,2,3-thiadiazole. A similar rearrangement has been observed to take place with 4-substituted 5-amino-1,2,3-thiadiazoles [2] and 4-acyl-5-arylamino-1,2,3-thiadiazoles [3].

In the present work the kinetics of the rearrangement of substituted 5-amino-1,2,3-thiadiazoles to 1,2,3-triazoles in piperidine or its methanolic solution has been monitored under the conditions of a pseudomonomolecular reaction (excess of piperidine).

The rate of the rearrangement was followed by the u.v. spectroscopy in the range 35—60°C. Below 30°C the rearrangement was a slow reaction. The course of the reaction was deduced from the decrease of the extinction of the corresponding 1,2,3-thiadiazole in the range (~300—340 nm) where the formed triazole shows no absorption maximum.

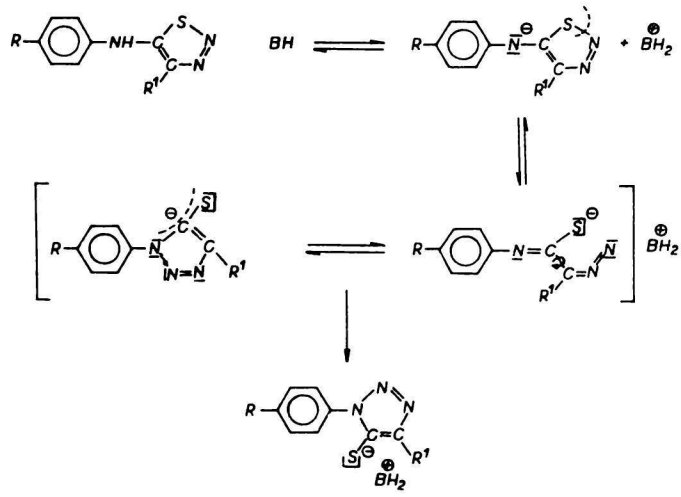
The rearrangement was studied on two types of compounds: one of them was the conversion of 5-(R-amino)-1,2,3-thiadiazoles to 1-R-5-mercapto-1,2,3-triazoles and the other was that of 4-methyl-5-(R-amino)-1,2,3-thiadiazoles to 1-R-4-methyl-5-mercapto-1,2,3-triazoles.

The objective of the kinetic measurements was to ascertain whether the substituents at the position C-4 of the benzene ring affect the rate of the rearrangement *i.e.* the rate of the cleavage of the 1,2,3-thiadiazole ring (the S—N bond) and, based on the found data, to discuss the mechanism of the process. The

Table 1. Rate constants of the conversion of 1,2,3-thiadiazoles to 5-mercapto-1,2,3-triazoles

Compound	R	R^1	$k'_{35°C} \cdot 10^3$ min^{-1} 3+log $k_{35°C}$	$t_{1/2}$ min	$k'_{45°C} \cdot 10^3$ min^{-1} 3+log $k_{45°C}$	$t_{1/2}$ min	$k'_{60°C} \cdot 10^3$ min 3+log $k_{60°C}$	t_1 min
I	H	H	9.93±0.134 0.9969	68.7	54.35±1.62 1.7352	12.8	176.40±0.225 2.2465	3.9
II	*p*-CH_3CO	H	29.94±4.80 1.4762	23.1	142.73±2.05 2.1544	4.8	442.63±3.04 2.6460	1.6
III	*p*-C_2H_5O	H	5.37±0.50 0.7299	129.0	23.84±0.81 1.3773	29.0	133.99±0.49 2.1268	5.2
IV	*p*-NO_2	H	52.40±0.22 1.7200	13.2	302.00±1.73 2.4800	2.3	916.36±10.25 2.9620	0.75
V	*p*-$(CH_3)_2N$	H	3.43±0.04 0.5352	202.0	13.13±1.14 1.1182	52.8	59.44±2.04 1.7740	11.6
VI	*p*-CH_3CONH	H	10.10±0.68 1.0043	68.6	37.63±0.50 1.5755	18.4	190.45±1.05 2.2796	3.6
VII	*p*-CH_3OCO	H	25.84±1.93 1.4122	26.8	96.72±2.30 1.9855	7.2	535.36±2.36 2.7286	1.3
VIII	*p*-C_2H_5OCO	H	30.35±3.05 1.4821	22.8	84.72±6.47 1.9279	8.2	465.31±0.80 2.6677	1.5
IX	*p*-CH_3S	H	15.35±0.15 1.1861	45.1	59.53±0.60 1.7747	11.6	184.90±0.28 2.2669	3.7
X	*p*-CH_3O	H	6.21±0.16 0.7930	111.6	32.36±1.34 1.5106	21.4	131.95±8.05 2.1202	5.2
XI	*p*-Br	H	25.41±1.38 1.4050	27.3	111.23±5.25 2.0453	6.2	384.59±2.28 2.5850	1.8
XII	*p*-C_2H_5—S	H	10.63±0.08 1.0268	65.2	39.86±0.71 1.6005	17.4	259.77±8.52 2.4144	2.7
XIII	H	CH_3	0.635±0.001 0.8027	1091.3	1.349±0.032 1.3001	513.7	6.839±0.002 1.8349	101.3
XIV	*p*-CH_3O	CH_3	0.506±0.022 0.7041	1369.5	1.128±0.005 1.0523	614.4	4.191±0.02 1.6223	165.3
XV	*p*-Cl	CH_3	1.646±0.052 1.2164	421.0	4.076±0.015 1.6102	170.0	19.50±0.200 2.2900	35.5

possibility of the opening of the ring generally depends upon the electronic properties of the substituents and our results are in accord with this theory. The found rate constants (Table 1) show that electron-withdrawing substituents, making it more acidic, faciliate the abstraction of the hydrogen atom, and *vice-versa*. We assume that the opening of the thiadiazole ring occurs *via* the cleavage of the S—N bond the ease of which depends upon the electronic effects of the *p*-sub-



BH = piperidine.

Scheme 1

stituents on the benzene ring and on R^1 (Scheme 1). This is supported by the linear correlation of the rate constant logarithms with σ_p Hammett constants of the substituents found at three temperatures ($r_{35°C} = 0.96$; $r_{45°C} = 0.95$, and $r_{60°C} = 0.98$). The ϱ values at these temperatures were found to be close enough ($\varrho_{35°C} = 0.815$, $\varrho_{45°C} = 0.815$, $\varrho_{60°C} = 0.758$) to indicate a uniform reaction course (Fig. 1).

The following values could be considered, taking into account the correlation dependences: the equations for the rearrangement under investigation,

$$35 \pm 0.2°C: y = 1.076 + 0.315x,$$
$$\text{with the deviations } S_x = 0.425$$
$$S_y = 0.359$$

and the point scatterings = 0.098,

$$45 \pm 0.2°C: y = 1.711 + 0.815x,$$
$$\text{with the deviations } S_x = 0.425$$
$$S_y = 0.365$$

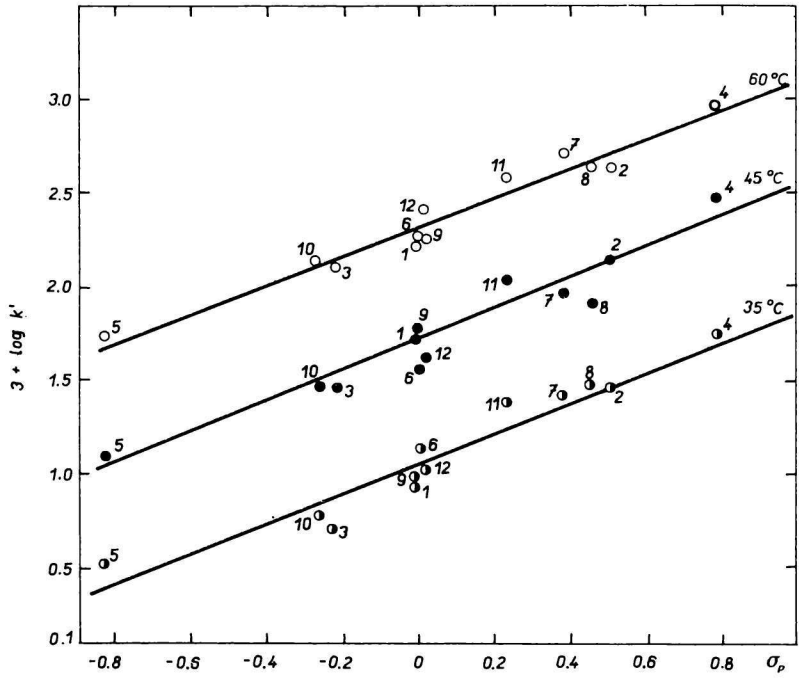


Fig. 1. Correlation dependence of log k' upon σ_p of the rearrangement in the thiadiazole—triazole system.
The substances are numbered as in Table 1. The σ_p values were taken from [4], for derivative *XII* from [5].

and the point scatterings = 0.121,

$$60 \pm 0.2°C: y = 2.325 + 0.758x,$$
with the deviations $S_x = 0.425$
$S_y = 0.329$

and the point scatterings = 0.068.

The studied rearrangement was not accompanied by side reactions which was substantiated by the fact that during the kinetic measurements the u.v. spectra of the reaction mixtures showed merely the decrease of the band corresponding to the 1,2,3-thiadiazoles and the increase of the band of the produced 1,2,3-triazoles.

Based on the above-mentioned fact and the found rate constants k' the following mechanism (Scheme 1) is suggested for the conversion under study.

The mechanism was further supported by the found higher entropy values (Table 2) and mainly by the fact that in the case of the rearrangement of 4-methyl-5-(R-amino)-1,2,3-thiadiazoles the found rate constants were by an

Table 2

Activation energies and entropies of the conversion of 1,2,3-thiadiazoles to 5-mercapto-1,2,3-triazoles

R	R^1	E_A kJ mol^{-1}	$\Delta S^{\neq}$ (e.u.)		
			35°C	45°C	60°C
H	H	43.29	−36.16	−33.92	−33.14
p-CH_3CO	H	37.09	−38.83	−36.68	−35.78
p-C_2H_5O	H	40.11	−39.91	−37.97	−35.99
p-NO_2	H	14.90	−54.88	−51.84	−50.22
p-$(CH_3)_2N$	H	42.96	−38.59	−37.03	−35.57
p-CH_3CONH	H	44.21	−35.46	−33.98	−32.35
p-CH_3OCO	H	45.64	−32.49	−31.04	−29.21
p-CH_3S	H	37.47	−39.85	−38.13	−37.24
p-CH_3O	H	47.14	−34.15	−32.08	−30.98
p-Br	H	39.52	−37.26	−35.36	−34.31
p-C_2H_5OCO	H	41.45	−35.41	−34.45	−32.55
p-C_2H_5S	H	37.76	−40.33	−38.69	−36.33
H	CH_3	35.00	−43.51	−42.15	−40.15
p-CH_3O	CH_3	32.57	−45.84	−45.11	−43.69
p-Cl	CH_3	37.22	−39.91	−39.08	−37.31

order of magnitude lower (Table 1). This may be explained by the less pronounced acidity of the hydrogen of the amino group as a result of its conjugation due to the +I effect of the methyl group, making the S—N bond cleavage in the thiadiazole ring more difficult.

Experimental

The starting 5-(R-amino)-1,2,3-thiadiazoles and 4-methyl-5-(R-amino)-1,2,3-thiadiazoles were obtained by reacting the corresponding isothiocyanates with diazomethane [6] or diazoethane [7]. Prior to the kinetic measurements the substances were recrystallized and dried under reduced pressure. Piperidine or its 0.04 M methanolic solution was used as the base.

The kinetics of the conversions were monitored by spectrophotometry using a Specord UV VIS (Zeiss, Jena) instrument, by running the reactions directly in the tempered instrument cells at 35 ± 0.2, 45 ± 0.2, and 60 ± 0.2°C.

The reaction mixtures consisted of 9.5 ml methanolic 0.04 M piperidine and 0.5 ml methanolic solution of corresponding thiadiazole (final concentration of the substrate ranging from 2 to 5×10^{-5} M).

The conversion was conducted under the conditions of a pseudomonomolecular reaction (constant concentration of the base) and the rate constants were calculated according to the equation of first-order reactions. Since extinction E is a linear function of the concentration, in the kinetic equation the changes of the concentration of the corresponding thiadiazole could be substituted with the differences in the extinction (keeping the wavelength, cell thickness, and the temperature constant).

The rate constants k' (min^{-1}) found for the Dimroth rearrangement in the thiadiazole—triazole system and the $t_{1/2}$ values (min) are listed in Table 1.

From the linear dependence of k' upon $1/T$ in the range 35—60°C the activation energies and entropies (Table 2) were calculated according to the modified Arrhenius equation.

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