Isothiocyanates. XXXV. 3-Substituted rhodanines derived from (p-isothiocyanatophenyl)alkyl sulfides and sulfones

V. KNOPPOVÁ and M. UHER

Department of Organic Chemistry, Slovak Technical University, 880 37 Bratislava

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The preparation of 13 new 3-substituted rhodanines derived from isothiocyanates containing sulfur beside that in the functional group is described in this work. Infrared and ultraviolet spectra of the synthesized derivatives are interpreted.

In connection with the preceding works [1, 2] dealing with nucleophilic addition of OH⁻ ions and amino groups, respectively, to isothiocyanates (ITC), it seemed useful to study also the reaction of ITC with thioglycolic acid [3].

So far, rhodanines on a large scale were prepared by reaction of the appropriate dithiocarbamate with monochloroacetic acid [4] and isothiocyanate with thioglycolic acid [5], respectively. However, thioglycolic acid is quantitatively added to isothiocyanates under exactly defined conditions. This fact was utilized in the microsynthesis of 3-substituted rhodanines. In this work, thioglycolic acid was added to (p-isothiocyanatophenyl)alkyl sulfides and sulfones.

Experimental

The appropriate (p-isothiocyanatophenyl)alkyl sulfides and (p-isothiocyanatophesnyl)alkyl sulfones prepared from the corresponding amines by thiophosgene method [6] were used as starting products for the synthesis of rhodanines.

Infrared absorption spectra of the synthesized derivatives were obtained on a double-beam UR-20 (Zeiss, Jena) spectrophotometer in the $700-3600~\rm cm^{-1}$ range. The used concentration of compounds in chloroform was $0.025~\rm M$.

Ultraviolet absorption spectra were taken with a Spectrd UV VIS spectrometer at $200-350\,\mathrm{nm}$ using $10\mathrm{-mm}$ cells. The concentration of the measured compounds in methanol was $5\times10^{-5}\,\mathrm{m}$. The used methanol contained 1% of glacial acetic acid to prevent decomposition of rhodanines.

3-Substituted rhodanines

The isothiocyanate (1 mole) was dissolved in acetone (20 ml) under cooling and triethylamine buffer (20 ml) (1.6 ml of 2 N acetic acid and 0.96 ml of triethylamine filled with water up to 20 ml) containing thioglycolic acid (1.04 mmole) was added. The reaction mixture of pH 10 was placed into a water bath at 30°C for 1 hour. Then the solvent

was distilled off under reduced pressure and the residue was dissolved in glacial acetic acid (10 ml) saturated with gaseous hydrogen chloride. When the solvent was again vacuum-distilled, a crude rhodanine was obtained and crystallized from the acidified (1% glacial acetic acid) ethanol.

Results and discussion

The synthesized 3-substituted rhodanines and their physicochemical properties are presented in Table 1. The preparation of both series of rhodanines *i.e.* sulfides and sulfones was accomplished under exactly defined conditions (buffered medium) so that a 100% yield was obtained regarding the starting isothiocyanate. We mentioned this fact in our preceding work already [7].

 $\begin{tabular}{ll} Table 1 \\ The synthesized 3-substituted rhodanines \\ \end{tabular}$

$$\begin{array}{c|c}
R-Z-& \bigcirc & -N-C=S \\
& | & | \\
O=C & S \\
& & \downarrow \\
CH_{2}
\end{array}$$

No.	R	z	Formula	M	Calculated/found		M.p.
					% N	% S	[°C]
I	Methyl	s	$\mathrm{C_{10}H_{9}NOS_{3}}$	255.4	5.48	37.66	150-153
II	Ethyl	s	$\mathrm{C_{11}H_{11}NOS_3}$	269.4	5.42 5.19	37.58 35.33	118-119
III	Isopropyl	S	$\mathrm{C_{12}H_{13}NOS_3}$	283.4	4.94 4.94 4.85	35.10 33.93 33.81	162.5 — 163.5
IV	n-Hexyl	S	$\mathrm{C_{15}H_{19}NOS_3}$	325.5	4.30 4.28	29.55 29.58	110-115
V	$n ext{-}\mathrm{Octyl}$	S	$\mathrm{C}_{17}\mathrm{H}_{23}\mathrm{NOS}_3$	353.6	3.96 4.00	27.20 27.19	113-115
VI	$n ext{-}\mathrm{Decyl}$	S	$C_{19}H_{27}NOS_3$	381.6	3.61 3.56	25.20 25.01	120 - 121
VII	Methyl	SO_2	$\mathbf{C_{10}H_9NO_3S_3}$	287.4	4.87 4.78	33.47 33.35	158 - 160
VIII	Ethyl	SO_2	$\mathrm{C}_{11}\mathrm{H}_{11}\mathrm{NO_3S_3}$	301.4	4.66 4.64	$31.88 \\ 31.98$	161-164
IX	Isopropyl	SO_2	$\mathrm{C}_{12}\mathrm{H}_{13}\mathrm{NO_3S_3}$	315.4	4.44 4.40	$30.40 \\ 30.33$	168-170
X	n-Butyl	SO_2	$\mathrm{C_{13}H_{15}NO_{3}S_{3}}$	329.4	$\frac{4.30}{4.32}$	$29.18 \\ 29.02$	180 - 182
ΧI	n-Hexyl	SO ₂	$\mathrm{C_{15}H_{19}NO_3S_3}$	357.5	$\frac{3.91}{4.07}$	$26.91 \\ 26.97$	168-168.5
XII	n-Octyl	SO ₂	C ₁₇ H ₂₃ NO ₃ S ₃	385.6	3.63 3.58	24.94 24.69	115-116
XIII	$n ext{-} ext{Decyl}$	SO_2	C_{1} , $H_{27}NO_{3}S_{3}$	413.6	$\frac{3.38}{3.28}$	$23.25 \\ 23.30$	100 - 105

$m{Table} 2$									
Infrared and ultraviolet spectra of the synthesized 3-substituted rhodanines									

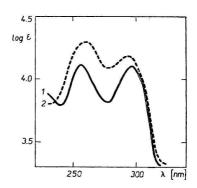
No.	$\lambda_{\max I}$ [nm]	\logarepsilon	$\lambda_{\max 11}$ [nm]	log ε	$ ilde{v}(\mathrm{C}\!=\!\mathrm{O})$ [cm ⁻¹]	$ ilde{v}_{as}(\mathrm{SO}_2) \ [\mathrm{cm}^{-1}]$	$ ilde{v}_{\mathrm{s}}(\mathrm{SO}_2) \ [\mathrm{cm}^{-1}]$
I	262	4.30	293	4.18	1746	_=	-
II	263	4.29	294	4.23	1743	-	11
III	265	4.25	293	4.26	1754		_
IV	264	4.30	293	4.26	1755	-	
V	264	4.27	293	4.22	1748		-
VI	264	4.26	293	4.20	1752		_
VII	257	4.11	297	4.10	1754	1317	1154
VIII	256	4.09	296	4.09	1753	1319	1142
IX	257	4.12	296	4.10	1765	1323	1146
\boldsymbol{X}	257	4.08	297	4.08	1764	1322	1158
XI	257	4.13	297	4.12	1759	1326	1163
XII	264	4.27	294	4.22	1750	1325	1130 v
XIII	264	4.21	294	4.19	1746	1325 w	1133 v

w - weak, vw - very weak.

It is evident from our observation that the lengthening of the alkyl chain does not make difficult the preparation of these compounds. All the prepared 3-substituted rhodamines after isolation from the reaction medium were yellow crystalline compounds.

Two absorption bands in the ultraviolet region at 256-265 and 293-297 nm, respectively (Table 2) were characteristic of the prepared 3-substituted rhodanines. The first absorption maximum (~ 260 nm) could be attributed to the so-called "N" conjugation (thioamide band) and the second one (~ 295 nm) to the "S" conjugation (dithiocarbamate band). Both bands were of high intensity (log ε above 4). Introduction of the -S-R group (due to the free electron pair on the sulfur atom, a mesomeric "S" conjugation was possible) into the molecule of 3-phenylrhodanine caused a bathochromic shift of the first absorption band (with 3-phenylrhodanine λ_1 258 nm) while introduction of the $-SO_2-R$ group (electron acceptor) manifested itself hypsochromically (except for derivatives XII and XIII with a long alkyl chain). The position of the second band practically did not change (Fig. 1).

Fig. 1. Ultraviolet absorption spectra.
1. 3-(4-methylphenylthio)rhodanine;
2. 3-(4-methylphenylsulfonyl)rhodanine.
5 × 10⁻⁵ M solutions in methanol (with 1% glacial acetic acid).



The characteristic wavenumbers of bonds of the prepared rhodanines are given in Table 2. With the increasing alkyl, bands belonging to stretching vibrations of C-H bonds were negligibly shifted to lower wavenumbers. The spectra of all investigated rhodanines showed very intensive absorption bands of stretching vibrations of C=O groups in the $1764-1743~\rm cm^{-1}$ range. In case $Z=SO_2$, a shift to higher wavenumbers was observed (derivative I, when Z=S, showed a band at $1746~\rm cm^{-1}$ while VII with $Z=SO_2$ at $1754~\rm cm^{-1}$) due to the electron-accepting properties of the functional SO_2 group. The bands belonging to vibrations of the C=C bonds of the aromatic system were observed at $1600-1500~\rm cm^{-1}$, the absorption band at $1500~\rm cm^{-1}$ being much more intensive than that at $1600~\rm cm^{-1}$. The absorption bands belonging to deformation vibrations of C-H bonds of alkyl groups appeared in the range of $1478-1384~\rm cm^{-1}$ being insignificant with some derivatives. With derivatives VII-XIII ($Z=SO_2$), intensive absorption bands $\bar{\nu}_{us}(SO_2)$ were observed in the region $1326-1317~\rm cm^{-1}$ and a very intensive band $\bar{\nu}_s(SO_2)$ at $1163-1130~\rm cm^{-1}$. The position of these bands was not dependent on the character of the alkyl chain.

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