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Abstract

Full Text

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ADDITION OF THIOUREA AND SELENOUREA TO UNSATURATED ELECTROPHILIC REAGENTS

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In studying the properties of thiourea it was observed that it gives two series of derivatives, substituted at nitrogen and at sulfur, which gave grounds for assuming the existence of a tautomeric equilibrium between the thione and thiol forms:

$$NH_2{-}C(=S){-}NH_2 \rightleftharpoons NH_2{-}C(=NH){-}SN$$

However, investigation of the infrared and ultraviolet absorption spectra of thiourea (^{1}) showed that, both in the crystalline state and in aqueous solutions, regardless of the pH of the medium, it is a stable thione form. Thus, all reactions of thiourea leading to the formation of S-derivatives should be regarded as a process proceeding with transfer of the reaction center to the sulfur atom (^{2}). As is known, S-derivatives of thiourea are usually obtained by its interaction with halogen-substituted addends. The direct interaction of thiourea with unsaturated electrophilic systems should be considered unstudied, since the scattered data available in the literature on the ability of thiourea to enter into a cyanoethylation reaction have not been confirmed and are disputed (^{3}).

In 1951, a report appeared by Beringer and Zillikens (^{4}) on the interaction of thiourea with acrylic acid in the presence of hydrogen chloride; however, the authors do not discuss the mechanism of the reaction.

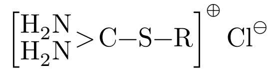
For a more detailed study of the reaction of thiourea with unsaturated electrophilic reagents, we carried out experiments on the addition of thiourea to acrylic acid (I), its nitrile (II) and methyl ester (III), methacrylic acid (IV) and methyl methacrylate (V), maleic and fumaric (VI) acids, dimethyl maleate, and propiolic acid (VII) (see Table 1). From the analytical data it follows that all the adducts have a composition corresponding to addition of thiourea to the addends in a 1:1 ratio.

To prove the S-structure of the adducts, ultraviolet spectra were recorded for thiourea *(1)*, its hydrochloride *(2)*, N-allylthiourea *(3)*, and the adducts of thiourea with acrylonitrile *(4)*, propiolic acid *(5)*, and allyl chloride *(6)* (see Fig.

1). On the basis of these spectra it was concluded that all the addition products obtained by us have an S-structure. Indeed, the absorption region of thiourea and N-allylthiourea has $\lambda_{\max}$242.5 mμ $\left(\varepsilon^{(1)}_{\lambda_{\max}} = 11{,}900 \text{ and } \varepsilon^{(3)}_{\lambda_{\max}} = 14{,}200\right)$, whereas the spectra of the adducts *(4, 6)* have no absorption maximum in the region studied by us, 225–290 mμ. The intense absorption with a shift of $\lambda_{\max}$ to the region of 257.5 mμ for *(5)* should evidently be attributed to an electronic transition due to the presence in (VII) of a conjugated system. Of definite interest is the IR spectrum of adduct (VII) (see Fig. 2), since with its aid one can, to a certain extent, draw a conclusion about the geometrical configuration of the double bond in adduct (VII). In fact, the presence of absorp-

Table 1

Derivatives of isothiuronium chloride



$$\left[\begin{matrix}H_2N\\H_2N\end{matrix}\!>C{-}S{-}R\right]^{\oplus} Cl^{\ominus}$$

Compound no.	R	Solvent	Yield, %	M.p., °C	Empirical formula	S, % found*	S, % calcd.
I	$-CH_2-CH_2-COOH$	Alcohol, water	96.5	145	$C_4H_9O_2SN_2Cl$	–	–
II	$-CH_2-CH_2-CN$	Alcohol	93	161	$C_4H_8N_3SCl$	19.51 19.29	19.33
III	$-CH_2-CH_2-COOCH_3$	Alcohol	97.9	117	$C_5H_{11}O_2N_2SCl$	16.46	16.12
IV	$-CH_2-CH(CH_3)-COOH$	Acetic acid	86	168	$C_5H_{11}N_2O_2SCl$	16.01 15.97	16.12
V	$-CH_2-CH(CH_3)-COOCH_3$	Alcohol	80	156-157	$C_6H_{13}O_2N_2SCl$	15.51	15.03
VI	$-CH(COOH)-CH_2-COOH$	Alcohol	82	200(decomp.)	$C_5H_9O_4N_2SCl$	13.81 13.72	14.00
VII	$-CH=CH-COOH$(trans)	Water	91.7	163	$C_4H_7N_2O_2SCl$	15.69	17.53

* The sulfur analysis was carried out by the method of N. V. Sokolova and V. A. Orestova (^{5}), improved at the Scientific Research Institute of the Rubber Industry.

···tion in the region of 913 cm^{-1} (and 920 cm^{-1} for the adduct of selenourea with propiolic acid) indicates the trans configuration of adduct (VII)*, and consequently a cis mechanism of addition.

It proved interesting to observe the geometrical isomerization of dimethyl maleate to dimethyl fumarate, of maleic acid to fumaric acid, and of citraconic acid to mesaconic acid in the course of thiourea addition. There is no basis for attributing the cause of this phenomenon to the catalytic action of hydrogen chloride, since a blank experiment in the absence of thiourea gave a negative result. The reverse process of isomerization of trans acids into cis isomers is not observed, for fumaric acid reacts normally with thiourea, giving an addition product.

We have for the first time studied, under analogous conditions, the interaction of selenourea with acrylic acid (VIII) and its nitrile (IX), as well as with propiolic acid (X), which apparently proceeds by an analogous mechanism (see Table 2).

Fig. 1. UV absorption spectra: 1 –thiourea, 2 –thiourea hydrochloride, 3 – *N*-allylthiourea, 4 –thiourea adducts with acrylonitrile, 5 –propiolic acid, 6 – allyl chloride.

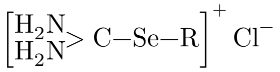
In conclusion, the authors express their gratitude to E. G. Yarkova and R. M. Mamina for recording the IR spectra.

Experimental Part

All addition reactions were carried out in methyl alcohol or glacial acetic acid saturated with hydrogen chloride, or in a 3.5 *N* aqueous hydrochloric acid solution. The reaction time was 1 day.

Table 2

Derivatives of chlorinated isoselenourea



$$\left[\begin{matrix}H_2N\\H_2N\end{matrix}\!> C\text{–}Se\text{–}R\right]^+ Cl^-$$

Compound No.	R	Solvent	Yield, %	M.p., °C	Gross formula	Cl⁻, % found	Cl⁻, % calc.
VIII	$-CH_2-CH_2-COOH$	Glacial acetic acid	65	151-152	$C_4H_9O_2SeN_2Cl$	15.23 15.26	15.32
IX	$-CH_2-CH_2-CN$	Glacial acetic acid	51	167-168	$C_4H_8SeN_3Cl$	16.56 16.54	16.69
X	$-CH=CH-COOH$ (trans)	Water	94.4	184	$C_4H_7O_2SeN_2Cl$	15.53 15.57	15.46

at room temperature. The addition products were isolated by concentrating the solutions in vacuo, filtered off, and recrystallized from methyl alcohol. All adducts are colorless needle-shaped crystals, stable in air and light, soluble in water, ethyl alcohol, and glacial acetic acid (on heating).

Fig. 2. IR absorption spectra of the adducts with propiolic acid of thiourea (*1*) and selenourea (*2*).

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* The corresponding absorption band for a trans-ethylene bond in α-crotonic acid also lies in the region of 912 cm^{-1} (^{6}).

Fig. 2. IR absorption spectra of the adducts with propiolic acid of thiourea (1) and selenourea (2)

Figure 1: Fig. 2. IR absorption spectra of the adducts with propiolic acid of thiourea (1) and selenourea (2)

The IR absorption spectra were recorded on a double-beam H-800 spectrophotometer (Hilger) in the range 700–2000 cm^{-1} with a sodium chloride prism. The substances were introduced as a fine suspension in Vaseline oil.

The UV absorption spectra were recorded on an SF-4 spectrophotometer in alcoholic solutions.

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