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The Reaction of Olefins with a Mixture of Iodine and Mercury(II) Thiocyanate. Predominant Formation of *vic*-Iodo(isothiocyanato)alkanes

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Treatment of olefins with a mixture of iodine and mercury(II) thiocyanate in benzene or diethyl ether gives *vic*-iodo(isothiocyanato)alkanes and *vic*-iodo(thiocyanato)alkanes in a high yield, the former being predominant. Similar results were obtained by using silver(I) and thallium(I) thiocyanates, though both the yield and the selectivity are slightly lower. By use of potassium thiocyanate and copper(I) isothiocyanate in place of mercury(II) thiocyanate, β-iodo thiocyanates were mainly formed. A reaction scheme involving initial formation of an iodonium ion from olefin and ISCN (formed *in situ*) and a subsequent attack of complex anion $I(SCN)_2^-$ has been proposed to account for this predominant formation of β-iodo isothiocyanates.

We reported previously that $Hg(SCN)_2$ reacts with alkyl halides in solvents of low polarity to afford alkyl isothiocyanates (RNCS) and alkyl thiocyanates (RSCN), with the former being predominant.¹⁾ The preponderant isothiocyanate formation was explained by assuming the reaction of $XHg(SCN)_2^-$ with the alkyl cation. When a mixture of olefin and halogen is used in place of alkyl halides, selective formation of *vic*-iodo(isothiocyanato)-alkanes might be expected in a similar manner. We report here our new findings on this subject. Cambie *et al.* have recently reported that a mixture of I_2 and TlSCN reacts with cyclohexene to give the expected β-iodo isothiocyanate and β-iodo thiocyanate as the main products.²⁾ They have observed an unusual solvent dependence of the isothiocyanate/thiocyanate ratio: In solvents of sulfolane, dichloromethane, or diethyl ether, the ratios were around 1.5 regardless of their polarity, whereas in a suitable mixed solvent ($CHCl_3$ and sulfolane or DMSO with 1 : 1) the ratios were higher (*ca.* 3.0—4.0). Such a trend was not observed in the reaction of alkyl halides with $Hg(SCN)_2$.

Results and Discussion

First of all, we examined the reaction of cyclohexene with a mixture of I_2 and various metal thiocyanates, $M(SCN)_2$, to study the effect of metal salts on the isomer distribution in the expected products. Dry benzene was chosen as a solvent, since we previously observed the favorable formation of isothiocyanates from alkyl halides in less polar solvents. Although I_2 is soluble in benzene, all metal salts examined are only slightly soluble and thus the reaction mixture is heterogeneous in all cases. The reaction was generally carried out in the dark by adding cyclohexene to a pre-stirred (0.5 h) mixture of I_2 and $M(SCN)_2$ in benzene and by stirring the resulting mixture for 18—24 h at room temperature. The products were *trans*-1-iodo-2-isothiocyanatocyclohexane (**1**), *trans*-1-iodo-2-thiocyanatocyclohexane (**2**), and a very small amount of *trans*-1-isothiocyanato-2-thiocyanatocyclohexane (**3**) (Eq. 1). The results are shown in Table 1. $Hg(SCN)_2$ showed the best results for both the total yield of **1** and **2** and the selectivity for the *N*-alkylation product **1**. Among other metal salts examined, AgSCN and TlSCN were found to be fairly effective for the formation of **1**, while almost no reaction occurred using $Ni(NCS)_2$ and $Pb(SCN)_2$, probably due to their poor reactivities toward I_2 (see below). On the contrary, the *S*-alkylation product **2** was mainly formed when KSCN (in ether), CuNCS and $Cu(NCS)_2$ were used. Cambie *et al.* also reported

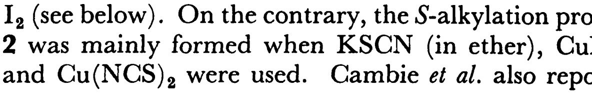

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Table 1. Reaction of cyclohexene with various metal thiocyanates and iodine$^{a)}$

$M(SCN)_n$	React. temp °C	React. time h	Products and Yields/%$^{b)}$ 1	2	3	Ratio 1 : 2
$Hg(SCN)_2$	18—22	18	67	18	2	79 : 21
$Hg(SCN)_2$$^{c)}$	25—28	17	63	13	0	83 : 17
$Hg(SCN)_2$$^{d)}$	25—27	22	80	8	0	91 : 9
TlSCN	20—25	22	44	9	1	83 : 17
AgSCN	20—25	22	57	24	1	70 : 30
$Cu(NCS)_2$	24—27	21	Trace	16	0	
CuNCS	22—25	22	2	52	0	4 : 96
$Pb(SCN)_2$	20—22	24	0	2	0$^{e)}$	
$Ni(NCS)_2$	25—27	22	0	0	0$^{e)}$	
KSCN$^{f)}$	20—25	21	2	76	0	3 : 97

a) $M(SCN)_n$ (10/n mmol), I_2 (10 mmol), cyclohexene (10 mmol), and dry benzene (25 ml) were used. b) Isolated yield. c) $Hg(SCN)_2$ (2.5 mmol) and cyclohexene (5 mmol) were used. d) $Hg(SCN)_2$ (1 mmol) and cyclohexene (2 mmol) were used . e) *trans*-1,2-Diiodocyclohexane was formed in *ca.* 40% yield. f) Et_2O (25 ml) as solvent.

Table 2. Reaction of cyclohexene with $Hg(SCN)_2$ and I_2 under various conditions[a)]

Solvent (25 ml)	React. temp °C	React. time h	Products and Yields/%[b)] 1	 2	 3	Ratio 1 : 2
Benzene	18—20	1	53	14	1	79 : 21
Benzene	19—21	6	57	15	1	79 : 21
Benzene	18—22	18	67	18	2	79 : 21
Diethyl ether	15—20	1	51	11	1	82 : 18
Diethyl ether	19—20	4	66	14	1	83 : 17
Diethyl ether	2—4	4	52	8	1	87 : 13
Tetrahydrofuran	22—26	5	39	15	Trace	72 : 28

a) $Hg(SCN)_2$ (5 mmol), I_2 (10 mmol), and cyclohexene (10 mmol) were used. b) Determined by GLC and HPLC.

Table 3. Reaction of $Hg(SCN)_2/I_2$ or $KSCN/I_2$ with various olefins[a)]

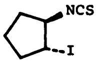
Olefin (10 mmol)	Metal salt	(mmol)	React. temp °C	React. time h	Products and Yields/%[b)] -NCS	 -SCN
Cyclopentene	$Hg(SCN)_2$	5	25—28	22	**4** (69)	**5** (20)
Cyclopentene	KSCN	10	20—26	20	**4** (2)	**5** (76)
Cyclohexene	$Hg(SCN)_2$	5	18—22	18	**1** (67)	**2** (18)
Cyclohexene	KSCN	10	20—25	21	**1** (2)	**2** (76)
Cycloheptene	$Hg(SCN)_2$	5	25—27	16	**6** (65)	**7** (16)
Cycloheptene	KSCN	10	26—27	22	**6** (3)	**7** (71)
trans-3-Hexene	$Hg(SCN)_2$	5	25—28	22	**8** (74)	**9** (10)
trans-3-Hexene	KSCN	10	26—29	20	**8** (3)	**9** (60)

a) I_2 (10 mmol) was used in all cases. Benzene (25 ml) was used as solvent for $Hg(SCN)_2$ and diethyl ether (25 ml) for KSCN. b) Isolated yield.

a predominant formation of β-iodo thiocyanates from some olefins in sulfolane and/or chloroform as a solvent.[2,3)]

Next, the effects of the solvent and the reaction temperature and the time upon the isomer ratio in the products were studied in the reaction using $Hg(SCN)_2$. Table 2 shows that the reaction proceeds smoothly even at shorter reaction times and at a lower temperature in benzene or diethyl ether as solvent, in spite of the heterogeneous reaction system, and that the ratio of **1**/**2** is nearly constant by changing the reaction time. These results suggest that no isomerization between the two isomers occurs under these conditions.[4)] As to the selectivity for the formation of **1**, diethyl ether is superior to benzene as solvent and the reaction at a lower temperature seems to be favorable. The reaction proceeded homogeneously in tetrahydrofuran, but both the product yield and the selectivity for **1** were somewhat lower. No reaction occurred in hexane as solvent.

Extension of the reaction using $Hg(SCN)_2$ to other olefins such as cyclopentene, cycloheptene, and *trans*-3-hexene resulted also in the formation of the expected β-iodo isothiocyanates (**4**, **6**, **8**) and β-iodo thiocyanates (**5**, **7**, **9**), the former being predominant in all cases as in the case of cyclohexene. Similarly, the reaction using KSCN afforded the latter highly selectively. Typical results are summarized in Table 3 together with the data of cyclohexene.



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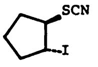

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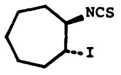

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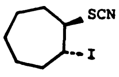

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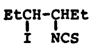
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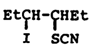
$$\underset{I}{EtCH}-\underset{SCN}{CHEt}$$

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Though it is known that $Pb(SCN)_2$ effectively reacts with Br_2 to give thiocyanogen [$(SCN)_2$][5,6)] and with excess Cl_2 to afford thiocyanogen chloride (ClSCN), few similar reactions with I_2 have been reported, except for the case of the Ag salt.[7,8)] Cambie *et al.*[2)] recently stated that, in the reaction of 2-phenylpropene with I_2 and TlSCN in chloroform–sulfolane solvent, the total yield of the β-isothiocyanato thiocyanate and the dithiocyanate predominated over the yield of the β-iodo isothiocyanate, but no evidence was given for the generation of $(SCN)_2$ species from a mixture of I_2 and TlSCN.

We have obtained some information regarding the formation of some active species including $(SCN)_2$ from I_2 and metal thiocyanates as shown below. When an equimolar quantity of I_2 was added gradually to a stirred suspension of $Hg(SCN)_2$ in benzene and then the stirring was continued for a further 0.5 h at 25 °C, the red color of I_2 in solution almost disappeared and a red solid separated. Treatment of the filtrate, after the removal of the solid, with cyclohexene (1 equiv) for 17 h at 16—19 °C under stirring afforded **3** (19%) along with **1** (12%) and **2** (2%). In contrast to this, the use of 2 mol of I_2 in the above experiment resulted in a different product distribution: *i.e.*, **1** (57%), **2** (16%), and **3** (1%). The total yield of **1** and **2** is somewhat lower than that in the reaction without filtration of the red solid, but the ratio of **1**/**2** is nearly the same in both cases. Quite similar results were obtained in the I_2–TlSCN system as well. These observations clearly indicate that the generation of $(SCN)_2$ from an equivalent mixture of I_2 and $Hg(SCN)_2$ or TlSCN (possibly the Ag(I) salt as well) is fairly rapid in spite of a heterogeneous reaction, and that under the presence of excess I_2 the *vic*-iodothiocyanation and *vic*-iodoisothiocyanation occur substantially with only a little or without any formation of the olefin–$(SCN)_2$ and olefin–I_2 adducts. Thus the most probable species for addition to olefin would be the ISCN species, which is formed by the following scheme (Eqs. 2 and 3). Here, the equilibrium shown in Eq. 3 is already known.[8]

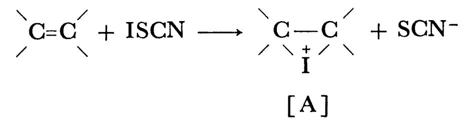
$$Hg(SCN)_2 + I_2 \longrightarrow (SCN)_2 + HgI_2\downarrow$$

$$2TlSCN + I_2 \longrightarrow (SCN)_2 + 2TlI\downarrow \quad (2)$$

$$(SCN)_2 + I_2 \rightleftarrows 2\,ISCN \quad (3)$$

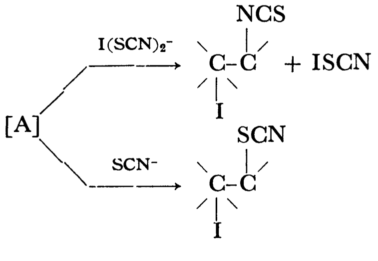
However, in the cases of $Pb(SCN)_2$ and $Ni(SCN)_2$ the generation of $(SCN)_2$ by Eq. 2 seemed to be difficult, since no appreciable decolorization of the reaction mixture was observed and no principal products other than *vic*-diiodide were found (see Table 1).

As to the product-determining step, Cambie *et al.* suggested a probable pathway for the reaction with a mixture of I_2 and $(SCN)_2$. This pathway involves the initial formation of a bridged iodonium ion, and a subsequent attack by SCN^- leading to *β*-iodo thiocyanate and the attack by ISCN or $(SCN)_2$ to *β*-iodo isothiocyanate.[3] However, we believe that a nucleophile $I(SCN)_2^-$, which is in equilibrium with SCN^- and ISCN,[9] is a more conceivable species for the latter attack. If this complex ion serves as a source of SCN^-, the reaction with cationic species would occur mainly at either of the two terminal N atoms, which are the sterically favorable and more electronegative sites (Eqs. 4 and 5). Further, when a large excess of I_2 was used in the reaction of cyclohexene, a further increase in the *N*-selectivity was observed (see Table 1). This might be attributed to the concentration of another active species $I_2(SCN)^-$, but the phenomenon was not so general for other olefins.



$$\gt C{=}C\lt + ISCN \longrightarrow \gt C{-}\underset{\overset{+}{I}}{}{-}C\lt + SCN^- \quad (4)$$

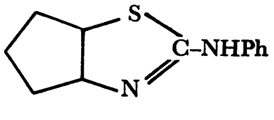
[A]



$$[A] \xrightarrow{I(SCN)_2^-} \gt C(I){-}C(NCS)\lt + ISCN$$
$$[A] \xrightarrow{SCN^-} \gt C(I){-}C(SCN)\lt \quad (5)$$

For comparison with the data using the I_2–$Hg(SCN)_2$ system, we also examined the reaction using an equimolar mixture of I_2 and $(SCN)_2$ (prepared by a known method[5] separately). The reaction in benzene at 17—24 °C for 20 h afforded the products **1** (53%), **2** (16%), and **3** (1%). A slight excess in the total yield of **1** and **2** and in the *N*-selectivity in the I_2–$Hg(SCN)_2$ cases compared to this case can be explained by assuming the competitive thiocyanation with a complex anion of $Hg(SCN)_2$ such as $IHg(SCN)_2^-$ or $Hg(SCN)_3^-$, though no direct evidence of this is available.

It is known that *vic*-iodo(isothiocyanato)alkanes react with aniline and methanol to afford 2-anilino-2-thiazoline and 2-thiazolidinone respectively.[10] By the reported methods we could prepare the corresponding new compounds such as **10** and **12** from **4** and **11** and **13** from **6** respectively.



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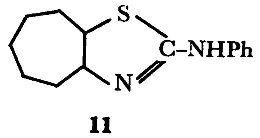

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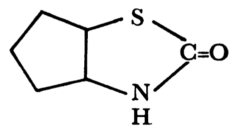

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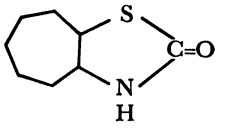

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Experimental

All organic substances were distilled immediately before use. Diethyl ether and tetrahydrofuran were dried over sodium and then distilled. Commercial metal thiocyanates and isothiocyanates, HgI_2, and bromine were used without further purification.

The ^1H NMR spectra were recorded with JEOL JNM FX-100 (100 MHz) instruments on solutions in $CDCl_3$ with Me_4Si as internal standard. The ^{13}C NMR spectra were taken at 25.1 MHz with a JEOLCO ^{13}C Fourier transform NMR system and were recorded on solutions in $CDCl_3$, after 250—1000 pulses with intervals of 2.7—2.8 s. The GLC analyses were carried out with a Yanagimoto G-2800 apparatus using SE-30 (1 m) and EGSS-X (1 m) columns (H_2 as carrier gas), benzyl isothiocyanate ($PhCH_2NCS$) being used as an internal standard. The IR spectra were recorded with a Hitachi SPI-G3 spectrometer. The liquid chromatographic analyses were carried out with a Waters HPLC system equipped with a 6000A solvent delivery system and a Model 440 absorbance detector (at 254 nm) with a μ-Porasil (3.9 mm × 0.3 m) column [hexane–chloroform (3 : 1) as eluent]. The mass spectra were measured on a JEOL JMS-D300 mass spectrometer, the ionization voltage being 10 and 70 eV.

The yield of *vic*-iodo(isothiocyanato)alkanes was determined by GLC, while *vic*-iodo(thiocyanato)alkanes were decomposed at the GLC conditions. Therefore, the yield of the iodothiocyanates was evaluated by HPLC using a calibration curve between the two isomers which are stable enough for HPLC determination. The isolation of products was carried out by column chromatography using silica gel (Wakogel C-200; benzene as eluent), the isothiocyanates being eluted first.

Typical experimental procedures and analytical data of new compounds are given below.

a) The Reaction of $Hg(SCN)_2$ and I_2 with Cyclopentene in Benzene. To a suspension of $Hg(SCN)_2$ (1.58 g, 5 mmol) and benzene (5 ml) was slowly added a benzene (20 ml) solution of I_2 (2.53 g, 10 mmol) under stirring at room temperature. After 30 min, cyclopentene (0.68 g, 10 mmol) was added to the mixture by keeping the temperature within the range of 18—22 °C (a slight heat evolution was observed during the addition) and the resulting mixture was stirred for 18 h at that temperature. All operations described above were carried out in the dark by wrapping the flask with aluminium foil.

The precipitated red solid (mainly HgI_2) was filtered and the filtrate was washed with aqueous KI, aqueous $Na_2S_2O_3$, and brine successively, and then dried over $MgSO_4$. Evaporation of the solvent from the filtrate left a yellow oil, an aliquot of it being analyzed by GLC and HPLC; *trans*-1-iodo-2-isothiocyanatocyclopentane (**4**) (7.29 mmol, 73% yield) and *trans*-1-iodo-2-thiocyanatocyclopentane (**5**) (2.13 mmol, 21%). These were isolated respectively by column chromatography: **4** (1.75 g, 6.91 mmol, 69%) and **5** (0.49 g, 1.95 mmol, 20%). **4**; A colorless oil, IR 2050 ($\nu_{\text{-NCS}}$, br) cm^{-1}. ^{1}H NMR δ=1.6—2.7 (m, 6H), 4.1—4.5 (m, 2H). ^{13}C NMR δ=22.2 (t), 27.8 (d, $>\underline{\mathrm{C}}$HI), 31.3 (t), 36.3 (t), 66.8 (d, $>\underline{\mathrm{C}}$HNCS), 134.4 (s, -N$\underline{\mathrm{C}}$S). Mass (*m/e*) 253 (M^+), 195 (M^+−NCS), 126 (M^+−I). Found: C, 28.49; H, 3.27; N, 5.71%. Calcd for C_6H_8INS: C, 28.47; H, 3.19; N, 5.53%. **5**; A colorless oil, IR 2150 ($\nu_{\text{-SCN}}$) cm^{-1}. ^{1}H NMR δ=1.6—2.7 (m, 6H), 3.93 (td. 1H, *J*=4.5 and 7.2 Hz, $>\underline{\mathrm{C}}$HSCN), 4.40 (td. 1H, *J*=4.5 and 6.0 Hz, $>\underline{\mathrm{C}}$HI). ^{13}C NMR δ=22.9 (t), 29.0 (d, $>\underline{\mathrm{C}}$HI), 30.6 (t), 37.0 (t), 57.1 (d, $>\underline{\mathrm{C}}$HSCN), 110.4 (s, -SCN). Mass (*m/e*) 254 (M^++1), 195 (M^+−SCN), 126 (M^+−I). Found: C, 28.33; H, 3.16; N, 5.84%.

The analytical data of *trans*-1-iodo-2-isothiocyanatocycloheptane (**6**) and *trans*-1-iodo-2-thiocyanatocyloheptane (**7**) are as follows. **1**, **2**, **8**, and **9** are known compounds[2,3] and the spectral and analytical data are completely the same as those of each authentic sample.

6; A colorless oil, IR 2050 ($\nu_{\text{-NCS}}$, br) cm^{-1}. ^{1}H NMR δ=1.64 (br s, 6H), 1.8—2.3 (m, 4H), 4.20 (ddd 1H, *J*=7.5, 7.0, and 3.2 Hz, $>\underline{\mathrm{C}}$HNCS), 4.46 (td 1H, *J*=7.5 and 4.0 Hz, $>\underline{\mathrm{C}}$HI). ^{13}C NMR δ=22.3 (t), 26.3(t), 26.6 (t), 32.6 (t), 35.7 (d, $>\underline{\mathrm{C}}$HI), 36.3 (t), 67.1 (d, $>$C$\underline{\mathrm{H}}$NCS), 133.1 (-N$\underline{\mathrm{C}}$S). Mass (*m/e*) 281 (M^+), 233 (M^+−NCS), 154 (M^+−I). Found: C, 34.24; H, 4.49; N, 5.20%. Calcd for $C_8H_{12}INS$: C, 34.18; H, 4.30; N, 4.98%.

7; A Colorless oil, IR 2150 ($\nu_{\text{-SCN}}$) cm^{-1}. ^{1}H NMR δ=1.4—2.0 (m, 6H), 2.0—2.5 (m, 4H), 3.89 (ddd, 1H, *J*=7.3, 7.1, and 3.3 Hz, $>$C$\underline{\mathrm{H}}$SCN), 4.63 (dt, 1H, *J*=7.1 and 5.0 Hz, $>$C$\underline{\mathrm{H}}$I). ^{13}C NMR δ=24.2 (t), 25.7 (t), 26.7 (t), 32.2 (t), 36.5 (d, $>\underline{\mathrm{C}}$HI), 36.7 (t), 60.0 (d, $>\underline{\mathrm{C}}$HSCN), 110.9 (s, -S$\underline{\mathrm{C}}$N). Mass (*m/e*) 281 (M^+), 223 (M^+−SCN), 154 (M^+−I). Found: C, 34.14; H, 4.42; N, 5.06%.

b) The Reaction of KSCN and I_2 with Cyclopentene in Diethyl Ether. The reaction was carried out in a similar manner to that given above, using dry KSCN (0.98 g, 10 mmol), I_2 (2.53 g, 10 mmol), and cyclopentene (0.68 g, 10 mmol) in diethyl ether (25 ml) as solvent at 20—26 °C for 20 h. The products were **4** and **5**; the isolated yields of **4** and **5** were 0.04 g (0.17 mmol, 2%) and 1.91 g (7.56 mmol, 76%), respectively.

c) The Reaction of a Mixture of I_2 and Thiocyanogen with Cyclohexene. The solution of thiocyanogen (10 mmol) in benzene (20 ml) was prepared by the reported method[5] using $Pb(SCN)_2$ (3.60 g, 11 mmol) and Br_2 (1.60 g, 10 mmol). To this solution was added a benzene (20 ml) solution of I_2 (2.53 g, 10 mmol) at 10—17 °C under stirring. After 30 min, cyclohexene (0.82 g, 10 mmol) was added and the resulting mixture was stirred for 20 h at 17—24 °C in the dark and then worked up as in the case of a). The GLC and HPLC analysis revealed the presence of 1-iodo-2-isothiocyanatocyclohexane (**1**) (5.30 mmol, 53%), 1-iodo-2-thiocyanatocyclohexane (**2**) (1.90 mmol, 19%), and 1-isothiocyanato-2-thiocyanatocyclohexane (**3**) (0.10 mmol, 1%) as products. Each product was isolated by column chromatography. **3**; A colorless semisolid (lit,[11] a colorless solid), IR 2130 ($\nu_{\text{-SCN}}$) and 2050 ($\nu_{\text{-NCS}}$) cm^{-1}. ^{1}H NMR δ=1.1—2.0 (m, 6H), 2.1—2.6 (m, 2H), 3.10 (ddd, 1H, *J*=4.0, 10.5, and 11.5 Hz, $>$C$\underline{\mathrm{H}}$SCN), 3.76 (td, 1H, *J*=10.5 and 4.0 Hz, $>$C$\underline{\mathrm{H}}$NCS). ^{13}C NMR δ=23.5 (t), 25.2 (t), 32.5 (t), 34.2 (t), 52.3 (d, $>\underline{\mathrm{C}}$HSCN), 59.9 (d, $>\underline{\mathrm{C}}$HNCS), 109.5 ($>$S$\underline{\mathrm{C}}$N), 135.5 (-N$\underline{\mathrm{C}}$S). Found: C, 48.24; H, 5.09; N, 14.24%. Calcd for $C_8H_{10}N_2S_2$: C, 48.46; H, 5.08; N, 14.13%.

d) The Reaction of trans-*1-Iodo-2-isothiocyanatocyclopentane (**4**) with Aniline.* *Preparation of* **10**: Aniline (0.76 g, 8 mmol) and (**4**) (1.02 g, 4 mmol) were dissolved in diethyl ether (25 ml) and the resulting solution was kept for 3 d at room temperature in the dark, during which period a yellow semisolid appeared at the bottom of the flask.[10] The whole mixture was washed with aqueous K_2CO_3 (in order to liberate the product from its HI salt) and brine, and then dried over $MgSO_4$. Evaporation of the solvent left a white solid of *cis*-2-anilino-4,5-trimethylenethiazoline (**10**) which was recrystallized from benzene–hexane: yield; 0.665 g, 3.05 mmol (76%). Mp 117—118 °C, IR (KBr disk) 3420 ($\nu_{\text{N-H}}$), 1620 $\nu_{(\text{C=N})}$ cm^{-1}. ^{1}H NMR δ=1.3—2.2 (m, 6H), 3.9—4.2 (m, 1H), 4.4—4.7 (m, 1H), 6.2 (br s, 1H), 6.9—7.4 (m, 5H). ^{13}C NMR δ=23.5 (t), 34.6 (t), 36.1 (t), 49.7 (d, $>\underline{\mathrm{C}}$H-S), 68.2 (d, $>\underline{\mathrm{C}}$H-N), 121.5 (d), 122.9 (d), 128.8 (d), 147.6 (s), 160.9 (s, -N=$\underline{\mathrm{C}}$-S). Mass (*m/e*) 218 (M^+). Found: C, 66.01; H, 6.44; N, 13.25%. Calcd for $C_{12}H_{14}N_2S$: C, 66.02; H, 6.46; N, 12.83%.

By similar treatment of **6** with aniline, *cis*-2-anilino-4,5-pentamethylenethiazoline (**11**) was obtained in an isolated yield of 84%. A colorless solid from diethyl ether–hexane (1 : 2). Mp 124.5—125.5 °C, IR (KBr disk) 3420 (ν_{NH}), 1630 ($\nu_{\text{C=N}}$) cm^{-1}. ^{1}H NMR δ=1.0—1.5 (m, 3H), 1.5—2.0 (m, 7H), 3.7—4.2 (m, 2H), 5.55 (br s, 1H), 6.9—7.4 (m, 5H). Mass (*m/e*) 247 (M^++1). Found: C, 68.15; H, 7.41; N, 11.68%. Calcd for $C_{14}H_{18}N_2S$: C, 68.25; H, 7.36; N, 11.37%.

e) The Reaction of **4** *with Methanol.* *Preparation of* **12**: The mixture of **4** (1.56 g, 6.2 mmol), methanol (10 ml), and tetrachloroethylene (20 ml) was refluxed for 3 d in the dark.[10] Evaporation of the solvent left a yellow oil which was subjected to column chromatography [silica gel, $CHCl_3$ as eluent] to give a pure *cis*-4,5-trimethylene-2-thiazolidinone (**12**) as a pale yellow oil: yield, 0.47 g, 3.3 mmol (53%). IR (neat) 3221 (ν_{NH}, br), 1660 ($\nu_{\text{C=O}}$, br) cm^{-1}. ^{1}H NMR δ=1.5—2.3 (m, 6H), 4.0—4.3 (m, 2H), 7.26 (br s, NH). ^{13}C NMR δ=23.1 (t), 34.5 (t), 36.2 (t), 47.5 (d, $>\underline{\mathrm{C}}$H-S), 60.0 (d, $>\underline{\mathrm{C}}$H-N), 175.4 ($>\underline{\mathrm{C}}$=O). Mass (*m/e*) 143 (M^+). Found: C, 49.93; H, 6.60; N, 10.10%. Calcd for C_6H_9NOS: C, 50.32; H, 6.34; N, 9.78%.

By similar treatment of **6** with methanol, *cis*-4,5-pentamethylene-2-thiazolidinone (**13**) was obtained in an isolated yield of 42% by column chromatography as above. Mp 94—95 °C, IR (KBr disk) 3200 (ν_{NH} br), 1660 ($\nu_{\text{C=O}}$, br) cm^{-1}. ^{1}H NMR δ=1.0—2.1 (m, 10H), 3.9—4.1 (m, 2H), 7.18 (br s, 1H). ^{13}C NMR δ=24.8 (t), 27.3 (t), 30.4 (t), 31.2 (t), 32.5 (t), 49.5 (d, $>\underline{\mathrm{C}}$H-S), 59.3 (d, $>\underline{\mathrm{C}}$H-N), 174.5 ($>\underline{\mathrm{C}}$=O). Mass (*m/e*) 171 (M^+). Found: C, 56.82; H, 7.94; N, 8.29%. Calcd for $C_8H_{13}NOS$: C, 56.11; H, 7.65; N, 8.18%.

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On the other hand, the isomerization of the thiocyanate to the thermodynamically more stable isothiocyanate is known to occur, especially by catalysis of the various acids and metal salts such as $BF_3 \cdot Et_2O$ and $ZnCl_2$: see Refs. 1 and 2 and references therein.

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