Unexpected Course of Thiocyanation of 1,6-Methano[10]annulene. Elimination of Thiocyanogen from a Diisothiocyanate

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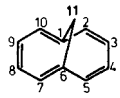
The isolation of the *syn,syn*-adduct **5** in the reaction of 1,6-methano[10]annulene (**1**) with the bulky pseudo-halogen $(SCN)_2$ indicates a preferred *exo* attack of electrophiles on **1**, in spite of a possible steric interference with the methylene bridge. The formation of the unexpected isothiocyanates **4** and **5** is explained in terms of an addition-isomerization-elimination sequence. The novel elimination of $(SCN)_2$ from a diisothiocyanate is investigated.

Unerwarteter Rhodanierungsverlauf an 1,6-Methano[10]annulen. Dirhodan-Eliminierung aus einem Diisothiocyanat

Die Isolierung des *syn,syn*-Addukts **5** bei der Reaktion von 1,6-Methano[10]annulen (**1**) mit dem raumbeanspruchenden Dirhodan weist auf einem bevorzugten *exo*-Angriff, trotz einer möglichen sterischen Wechselwirkung mit der Methylenbrücke. Die Bildung unerwarteter Isothiocyanate **4** und **5** wird durch eine Additions-Isomerisierungs-Eliminierungs-Sequenz erklärt. Die neuartige Eliminierung von $(SCN)_2$ aus einem Diisothiocyanat wird untersucht.

Literature data about the stereochemistry of electrophilic attack on 1,6-methano[10]annulene (**1**) appear to be conflicting. In an earlier report[1] on the protonation of **1**, the π electron density was assumed to be greater on the *endo* side of the annulene ring, by analogy with the related bicyclo[4.3.1]decatetraenyl (1,5-methano-[9]annulenyl) anion **2**. Upon quenching with D_2O, the latter had been found to be deuterated stereospecifically on the *endo* side[2]. Subsequent work with **2**[3], however, invalidated the initial interpretation[2] of NMR data and evidenced exclusive *exo* incorporation of various electrophiles. The mere analogy with **2** seems now to suggest, therefore, *exo* stereochemistry for the electrophilic attack on **1**.



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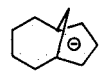

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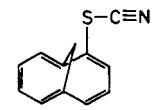
The kinetic isotope effect found in the sulfonation of **1**, larger than that observed for naphthalene, was interpreted to result, however, from an opposite stereochemistry[4]. In a σ-complex formed by *endo* addition of the sulfonating agent, the expulsion of the *exo*-2 proton was thought to be hindered by the methylene bridge. An attack from the *exo* side of the molecule was later reaffirmed as improbable, on steric grounds[5].

In contrast to the inferred *endo* stereochemistry of sulfonation, the addition of bromine to **1** was found to take place at the *exo* face. In a 2,5-dibromo adduct, trapped with a strong dienophile, both atoms added were shown to exhibit *syn* configuration with respect to the bridge[6].

In order to see how decisive is the steric factor, we tried to obtain an adduct of **1** with a bulky electrophile. Thiocyanogen, $(SCN)_2$, was chosen as reaction partner, not only for its large steric requirements, but also for its low electrophilicity. The reagent could thus be expected to discriminate between the *exo* and the *endo* region, if an unequally distributed electron density, and not the steric hindrance of the bridge, controls the stereochemistry. At the same time thiocyanogen was used hoping to obtain a stable addition product, displaying only a low re-aromatization tendency (by HNCS elimination), since $-SCN$ is a relatively poor leaving group.

Results and Discussion

We reported briefly[7] on the reaction of **1** with $(SCN)_2$ (the latter obtained from lead thiocyanate and bromine). In addition to thiocyanate **3** (the normal substitution product), two unusual products were found: the aromatic isothiocyanate **4** and the diisothiocyanato adduct **5**.



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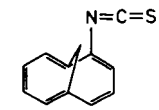

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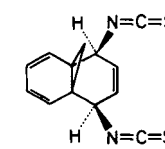

5

The *syn* configuration of the two $-N=C=S$ groups in adduct **5** indicates that the *exo* addition is the preferred stereochemical course of the electrophilic attack on **1**, in spite of a possible steric interference with the methylene bridge.

Similar results are obtained in the reaction of **1** with thiocyanogen generated in situ from ammonium thiocyanate and bromine. However, the low yield (ca. 4%) of isolated adduct **5** does not reflect the actual composition of the reaction mixture, being rather due to the difficulty of separation from **3** as well as to decomposition during workup. In a crude mixture the ratio **3**/**5** was found, by means of NMR, to be 1.8, which would correspond to a 29% yield of adduct **5**.

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The presence of the two unexpected isothiocyanates **4** and **5** prompted us to investigate the influence of several reaction parameters upon the course of thiocyanation of **1**. Since the yields of isolated compounds did not afford reliable information concerning the product distribution, the reaction was monitored by means of thin-layer chromatography. Adduct **5** was thus found, together with thiocyanate **3** (major product) and isothiocyanate **4** (minor product), under a wide range of reaction conditions: a) Temperature between −30 and +20°C (at higher temperatures polymerization of thiocyanogen was observed, especially at longer reaction times and with increasing polarity or acidity of solvent); b) reaction time between 1 min and 2 days; c) darkness, diffuse daylight, or irradiation; d) solvents of different polarity: benzene, dichloromethane, diethyl ether, THF, nitromethane, acetonitrile, acetic acid; e) presence or absence of finely divided iron as a catalyst.

TLC monitoring carried out at short reaction times showed that the first products formed are thiocyanate **3** and adduct **5**, isothiocyanate **4** appearing only in later stages of the reaction.

The change from unpolar to very polar solvent did not appear to affect the product distribution seriously. The constant presence of the *syn,syn*-adduct **5** under these conditions seems to point to a concerted *syn* addition, since the drastic change of solvent polarity did not modify the stereochemical outcome of the reaction.

It is interesting to note that the presence of iron [which reacts with $(SCN)_2$, affording ferric thiocyanate], although repressing partially the formation of adduct **5**, could not prevent it entirely in favour of a substitution course. However, when stronger electrophilic catalysts were used ($AlCl_3$, $FeCl_3$ or $SnCl_4$), **5** was no longer found in the reaction mixture (see Table 1). In the presence of $FeCl_3$ or $SnCl_4$ small amounts of isothiocyanate **4** were still isolated, but with $AlCl_3$ only traces of it could be detected. (Anhydrous $AlCl_3$ was found to cause decomposition of **1** as well as polymerization of thiocyanogen. In order to prevent this, the catalyst was partially deactivated with diethyl ether.)

Table 1. Product yields (%) in the catalytic thiocyanation of **1** (ratio catalyst/**1** = 0.5; 1 h, room temp., 1,2-dichloroethane)

Catalyst	3	4	5
$AlCl_3/Et_2O$	17.5	traces	–
$FeCl_3$	24	3.7	–
$SnCl_4$	21	3.1	–

The above observations show that the "abnormal" products **4** and **5** are not the result of a particular combination of reaction conditions, but constant components of the thiocyanation mixture. The formation of a relatively high proportion of **5** is significant in view of its possible intervention as intermediate in an addition-elimination mechanism.

As an explanation for the formation of the unexpected isothiocyanate **4** the possibility of an isomerization of the normal product **3** was first taken into consideration. In the aliphatic series the isomerization of thiocyanates into the thermodynamically more stable isothiocyanates is a well-known transformation[8,9]. With aromatic derivatives, however, isomerization appears to require strong electron-attracting groups (e.g. NO_2), which allow a nucleophilic attack of thiocyanate ions (SNAr mechanism)[10]. Our control experiments showed that thiocyanate **3** cannot isomerize to isothiocyanate **4**. In the presence of a threefold excess of KSCN and in a solvent (DMF) which insures a high activity for the anion, no trace of **4** could be detected after two days of stirring.

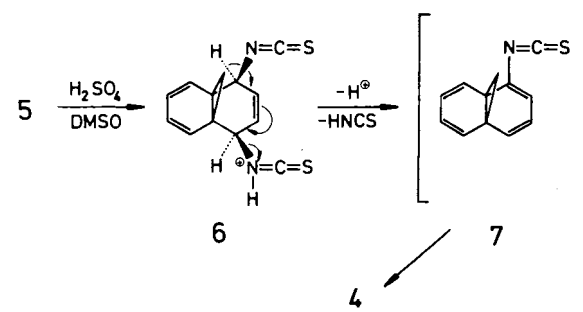
Elimination of isothiocyanic acid, HNCS, from adduct **5** was also considered as a possible source of isothiocyanate **4**. Freshly purified **5** was stirred in dry benzene at longer times than actually used in the thiocyanation of **1**, but neither this treatment nor heating a shorter time in refluxing toluene could lead to any elimination product. A spontaneous thermal decay of **5** cannot account, therefore, for the thiocyanation products of **1**. This remarkable stability reflects probably the poor leaving group ability of the isothiocyanato group and the difficulty of breaking the C−N bond.

Further elimination experiments, under acid or base catalysis, were carried out under standard conditions: 20°C, 0.2 mol **5**/l (a concentration in the range of those used in preparative thiocyanations of **1**), DMSO as solvent. (DMSO was chosen for its good solvent properties towards the salts used as catalyst. Similar results, however, could be observed with acetic acid or acetonitrile.) Unconventional bases, with a low nucleophilicity towards the thiocarbonyl group, were chosen as catalysts in order to avoid any addition to the C=S bond.

Preliminary experiments indicated the possibility of a competitive $(SCN)_2$ elimination. Since the terminal atom in the −N=C=S group could be expected to be the target of catalyst attack, elimination agents were chosen also for their affinity for sulfur. Large, easily polarizable anions, like thiocyanate, SCN^-, or lower halides, I^- and Br^-, appeared thus to be suitable catalysts.

The composition of elimination mixtures was determined by ^{1}H-NMR analysis, taking advantage of the good resolution of characteristic signals in spectra recorded at 250 MHz.

Since the substitutive thiocyanation of **1** yields, in addition to **3**, an equivalent amount of HNCS, the possibility of an acid-catalyzed elimination from adduct **5** was first examined. The acid used (H_2SO_4) was expected to lead to iso-



(1)

thiocyanate **4**, acting as shown in eq. (1). Surprisingly, the reaction mixture was actually found to contain, in addition to **4**, the isomeric thiocyanate **3**, as well as small amounts of unsubstituted hydrocarbon **1** (see Table 2).

Table 2. Product distribution (%) in catalytic eliminations from **5** (initial concentration of **5**: 0.2 mol/l; DMSO, 20°C)

Catalyst (C)	C/5	Time [h]	5	3	4	1	5/4	3/4
		1.75	80	12	6.8	0.6	12	1.8
H_2SO_4	0.25	5	46	37	16	1.0	2.9	2.3
		24	–	71	26	3.5	–	2.7
KSCN	0.5	15	30	51	14	4.0	2.1	3.6
		24	11	69	15	5.0	0.8	4.5
KI	3.0	24	–	8.0	6.0	85	–	1.2
KBR	3.0	24	1.4	52	44	3.0	0.03	1.2

Following remarks can be made concerning the results of acid-catalyzed elimination:

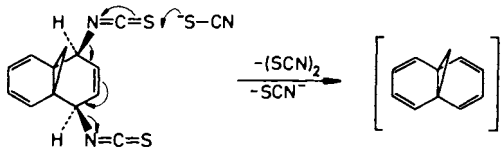
a. The decay of adduct **5** is rather slow, so that the compound can survive a long time under the conditions used in the thiocyanation of **1**.

b. As the reaction proceeds, the proportion of thiocyanate **3** appears to increase more rapidly than that of isothiocyanate **4** (as shown by the raising value of **3/4**). Even after 24 h, however, the ratio **3/4** remains considerably lower than the values (10 – 17) observed in the thiocyanation of **1**. Although the formation of **3** from **5** is demonstrated, this does not appear to be the only reaction path leading to **3**.

c. Elimination of HNCS from adduct **5** seems to be, indeed, a plausible explanation for the formation of the "abnormal" product **4**. Moreover, the ratio **5/4** observed in the thiocyanation of **1** (6 – 9) does not disagree with the results obtained in the elimination experiment.

d. The formation of unsubstituted hydrocarbon **1**, although in very reduced amounts, is an intriguing feature, since an acid (electrophilic) catalysis of $(SCN)_2$ elimination, involving expulsion of a positive SCN rest, is difficult to conceive.

As an explanation for the presence of **1** and **3** in the elimination mixture a reaction similar to the halogen elimination from dihalogen derivatives could be imagined. Ionization of the acid (H – NCS), released in the course of thiocyanation of **1**, should afford SCN^- anions, which could act as a thiophile and promote $(SCN)_2$ elimination from adduct **5**, as shown in eq. (2). The free thiocyanogen and the unsubstituted annulene formed could then react in a further step, yielding thiocyanate **3**.



5 8 (2)

$$\rightarrow 1 \xrightarrow{(SCN)_2} 3 + HNCS$$

In order to test this hypothesis, under conditions which exclude acid catalysis, **5** was treated with a neutral source of thiocyanate ions (KSCN). The results, presented in Table 2, show that SCN^- can act both as base and thiophile, promoting HNCS and $(SCN)_2$ elimination, respectively. As in the previous experiment the reaction appears to proceed at a relatively slow rate.

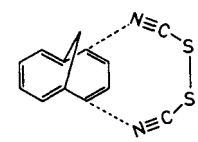
Thiocyanate **3** is again the major product, but the ratio **3/4**, although nearly twice as large as under acid catalysis, is still definitely lower than in the thiocyanation of **1**. This indicates that the decay of **5** can only account for a fraction of product **3**. Low, but significant concentrations of hydrocarbon **1** were constantly found, pointing to $(SCN)_2$ elimination.

Obviously, larger amounts of elimination product **1** would be more convicing evidence for the assumed thiocyanogen elimination from diisothiocyanate **5**. Since **1** was supposed to disappear as a result of reaction with the liberated $(SCN)_2$, we tried to suppress this step by using, instead of SCN^-, an anion with a lower oxidation potential (a thiocyanogen scavenger). An experiment carried out with potassium iodide led thus to a high yield of annulene **1** (85.2%), together with small amounts of **3** and **4**.

The basic assumptions underlying these experiments were further confirmed when an anion (Br^-) with a higher oxidation potential than SCN^- was used to promote elimination. The results were reversed, as compared to the previous case, as a high yield of **3** and a low yield of **1** were observed.

Thiocyanogen elimination is not restricted to 1,4-diisothiocyanates. We are currently investigating the similar reaction of the normal addition products of alkenes.

After having found a possible reaction path for the unexpected substitution product **4**, we have still to account for the intriguing structure of its precursor, the unprecedented diisothiocyanato adduct **5**. The *syn* configuration of the two functional groups, which – as shown above – remains unchanged under a large variety of reaction conditions, appears to rule out the intervention of an open carbenium ion. A cyclic 1,4-sulfenium ion is equally unlikely, since it should favour a *trans* addition. The concerted addition of the two groups appears to be, therefore, a plausible alternative.



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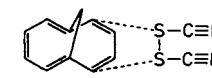

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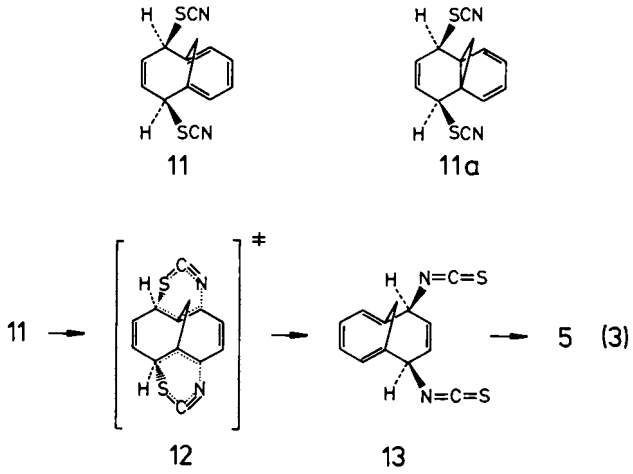
The attack of the nitrogen atom on the π system of **1**, as shown in the hypothetical encounter complex **9**, appears to be rather improbable, not only in view of the low electrophilicity of N terminals in the nitrile groups, but also because of the unfavourable entropy change involved in attaining the macrocyclic transition state. Besides, a diisothiocyanate

does not appear to have ever been observed in a thiocyanogen addition. For the first step one should rather envisage, therefore, the addition of the electrophilic sulfur atoms (**10**).

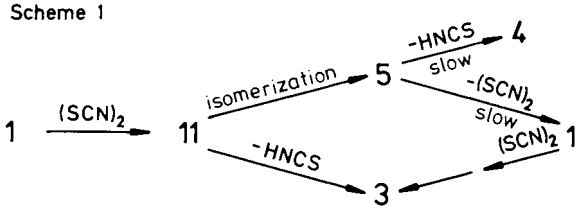
The primary addition product can be formulated as **11** or **11a**. In the bicyclic form **11**, the triene system has two double bonds which are favourably positioned for an allylic rearrangement. The latter, which is a well-documented example of thiocyanate isomerization[8,9,11], may well explain the formation of the "abnormal" diisothiocyanato adduct, as shown in eq. (3).



Allyl thiocyanates have been shown to isomerize at rates independent of solvent polarity, electronic effects, or concentration of salt, which points to a non-ionic, cyclic mechanism[11]. In our case, the concerted character of the rearrangement accounts well for the retention of the *syn* configuration in the final structure **5**.

The course of thiocyanation of **1**, as discussed above, is summarized in Scheme 1. The major part of thiocyanate **3** is assumed to be formed by elimination from the primary dithiocyanato adduct **11**. HNCS and $(SCN)_2$ eliminations from the rearranged adduct **5** appear to proceed at a slower pace than the preceding steps, since **5** is found to survive a relatively long time in the reaction mixture.

Scheme 1



The mechanism outlined above appears to be confirmed by the results of catalytic thiocyanation. If **4** is formed as a result of elimination from adduct **5**, then this abnormal substitution product should no longer be found if the formation of its precursor is prevented. This is precisely what appears to happen when the thiocyanation of **1** is carried out in the presence of Lewis acid catalysts (see Table 1). While in absence of catalysts the reaction route leading to **4** and **5** accounts for over 30% of total products, a sharp decline of it is observed in the presence of $AlCl_3$, $FeCl_3$, or $SnCl_4$. With $AlCl_3$ no trace of **5** and only traces of **4** could be detected. By complexing and polarizing the molecule of $(SCN)_2$ the catalyst generates probably a stronger electrophile, so that instead of a concerted addition the reaction adopts the course of a conventional SEAr process. It is interesting to note, however, that even under these conditions a residual addition-elimination route can be observed, as shown by the presence of small amounts of **4**.

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Experimental

Melting points (uncorrected): Reichert (Wien) hot-stage apparatus. – NMR spectra: Bruker WM 250 and HX-90 E (TMS internal standard). – IR spectra: Perkin-Elmer 325. – Mass spectra: Varian MAT 311 A. – TLC analyses: plastic sheets Polygram SIL G/UV_{254} (Macherey-Nagel). – Solvents were purified and dried by standard procedures.

Reaction of **1** *with "Nascent" Thiocyanogen:* To a solution of 5.32 g (70 mmol) of ammonium thiocyanate (dried in vacuo for ca. 12 h over phosphorus pentoxide) and 2.84 g (20 mmol) of **1** in 40 ml of glacial acetic acid a solution of 3.19 g (20 mmol) of bromine in 10 ml of glacial acetic acid was added dropwise with stirring at 20°C. After 45 min further stirring the mixture was diluted with 300 ml of water and extracted with dichloromethane (3 × 30 ml). The organic layer was washed twice with water, then with a 5% aqueous solution of $NaHCO_3$. After drying with $MgSO_4$ and removal of solvent the residue was further worked up as described in ref.[7] Yields: 1.12 g (28%) of **3**, m.p. 50°C; 0.11 g (2.7%) of **4**, m.p. 29°C; 0.24 g (4.6%) of **5**, m.p. 108°C. – MS, IR, and NMR data were in agreement with those previously determined[7].

In order to obtain an analytical sample of **3**, 0.40 g of the product was dissolved in 0.5 ml of acetone, the solution was diluted with 2 ml of petroleum ether (40–60°C), and the white solid formed was removed by filtration. The filtrate was further diluted with 0.3 ml of petroleum ether and left for ca. 12 h in the refrigerator. Filtration, washing with petroleum ether/acetone (20:1, v/v) and drying in vacuo yielded 0.35 g of light-yellow crystals, m.p. 51°C.

Attempts to recrystallize **5** from benzene/petroleum ether or acetone/petroleum ether mixtures led to decomposition.

Determination of the Proportion of **3** *and* **5** *in the Thiocyanation Mixture of* **1**: The above experiment was repeated using a different chromatography procedure for the residue of the dichloromethane extract. After elution with petroleum ether of a mixture of **1** and **4** (the first yellow zone), flash chromatography was continued (the second yellow zone) using petroleum ether/acetone (20:1, v/v). Evaporation of solvent afforded 3.6 g of a mixture of **3** and **5**. A ^{1}H-NMR spectrum ($CDCl_3$, 90 MHz) allowed to determine the proportion of products as ca. 65% **3** and 35% **5**, corresponding to 53.2 and 28.6% yields, respectively. Attempts to separate the two prod-

ucts and to purify them (by recrystallization or chromatography) led, as in the preceding experiment, to considerable loss of material.

TLC Monitoring of the Thiocyanation of **1**: The reaction of **1** with $(SCN)_2$ obtained from lead thiocyanate and bromine[7] was carried out under different reaction conditions using the following standard starting composition: 0.28 g (2.0 mmol) of **1** in 2 ml of solvent and 0.23 g (2.0 mmol) of thiocyanogen in 5 ml of solvent. The anhydrous solvents and the temperatures used were: benzene (20°C), dichloromethane (−30, 0, 20°C), 1,2-dichloroethane (−10, 20°C), diethyl ether (−10, 20°C), THF (−30, 20°C), nitromethane (−10, 20°C), acetonitrile (20°C), and acetic acid (0, 20°C). In a run carried out in dichloromethane, at −30°C, the reaction mixture was irradiated for 30 min with a 500-W lamp placed at 20 cm from the reaction flask. Four runs (dichloromethane, −30 and 20°C; nitromethane, −10°C; benzene, 20°C) were performed also in the presence of 11 mg (0.2 mmol) of finely divided iron. Two mobile phases were used for TLC monitoring: petroleum ether for the separation of **4** (R_f 0.48) from unreacted **1** (R_f 0.54, violet fluorescence at 254 nm), and petroleum ether/benzene (2:1, v/v) for **3** (R_f 0.25, dark-blue fluorescence at 366 nm), **4** (R_f 0.82), and **5** (R_f 0.55). As R_f values show, no clean separation of **4** from **1** could be achieved. For reactions carried out in different solvents and at various temperatures, but in the absence of iron, TLC indicated no substantial differences in the proportion of **3**, **4**, and **5**, compound **4** being always a minor component. In the presence of iron a distinctly lower proportion of **5** was observed.

Thiocyanation of **1** *Catalyzed by Deactivated Anhydrous* $AlCl_3$: 266 mg (2.0 mmol) of anh. $AlCl_3$ was dissolved carefully, with stirring, in a cooled solution of 220 mg (0.32 ml; 6 mmol) of anhydrous diethyl ether in 3 ml of dry 1,2-dichloroethane. The mixture was added with stirring to a solution of 568 mg (4.0 mmol) of **1** in 3 ml of dry 1,2-dichloroethane, cooled to −30°C. A cooled solution of 581 mg (5.0 mmol) of thiocyanogen in 10 ml of dry 1,2-dichloroethane was added immediately. The dark-violet mixture was stirred for 15 min at −30°C, then the temperature was raised to 20°C, and stirring was continued for 1 h. TLC of the reaction mixture (carried out under the conditions described above) indicated the absence of **5** and only traces of **4**. Workup according to the procedure used for the uncatalyzed thiocyanation of **1**[7] yielded, after repeated flash-chromatography, 140 mg (17.5%) of **3**.

Thiocyanation of **1** *Catalyzed by Anhydrous* $FeCl_3$: To a solution of 568 mg (4.0 mmol) of **1** in 8 ml of dry 1,2-dichloroethane, cooled to −30°C, 324 mg (2.0 mmol) of anh. $FeCl_3$ was added with stirring, followed by a solution of 581 mg (5.0 mmol) of thiocyanogen in 10 ml of dry 1,2-dichloroethane (the mixture turned dark-violet). After stirring for 15 min at −30°C, then for 1 h at 20°C, TLC indicated the absence of **5**. The same workup as above yielded 191 mg (24%) of **3** and 30 mg (3.7%) of **4**.

Thiocyanation of **1** *Catalyzed by Anhydrous* $SnCl_4$: The above run was repeated using as catalyst 680 mg (2.0 mmol) of anh. $SnCl_4$ in 3 ml of dry 1,2-dichloroethane. No addition product **5** could be detected by means of TLC. Yields: 167 mg (21%) of **3** and 24 mg (3.1%) of **4**.

Eliminations from Adduct **5**: Elinination mixtures were analyzed by means of ^1H NMR using characteristic signals from the following list (δ, ppm): **1**: −0.58 (s, 2H), 7.07−7.11 (m, 4H), 7.49−7.53 (m, 4H); **3**: −0.47 (d_c, 1H), 7.43 (d_c, 1H), 7.74 (d_c, 1H), 7.86 (d_c, 1H); **4**: −0.62 (d_c, 1H); **5**: 0.09 (d_c, 1H), 1.91 (d_c, 1H), 4.91 (s, 2H), 5.73 (s, 2H), 6.16−6.22 (m, 2H), 6.25−6.31 (m, 2H). The composition of the elimination mixtures is shown in Table 2. KSCN, KI, and KBr were dried for 24 h in vacuo over phosphorus pentoxide.

a) *Acid-catalyzed Elimination:* A solution of 25.8 mg (0.10 mmol) of **5** and 2.4 mg (0.025 mmol) of sulfuric acid in 0.5 ml of $[D_6]$-DMSO, kept at 20°C, was NMR-analyzed after 1.75, 5, and 24 h.

b) *SCN^--catalyzed Elimination:* 25.8 mg (0.10 mmol) of **5** and 4.8 mg (0.05 mmol) of dry potassium thiocyanate were dissolved in 0.5 ml of $[D_6]$DMSO, and the mixture was kept at 20°C. ^1H-NMR spectra were recorded after 15 and 24 h.

c) *I^--promoted Elimination:* An experiment similar to the above one was carried out using 50 mg (0.30 mmol) of dry KI (instead of KSCN). The elimination mixture was analyzed after 24 h.

Br^--catalyzed Elimination: Experiment c) was repeated with 35.7 mg (0.30 mmol) of dry KBr instead of KI.

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1: 2443-46-1 / **3**: 115163-01-4 / **4**: 115163-02-5 / **5**: 115163-03-6 / $(SCN)_2$: 505-14-6 / $AlCl_3$: 7446-70-0 / Et_2O: 60-29-7 / $FeCl_3$: 7705-08-0 / $SnCl_4$: 7646-78-8 / H_2SO_4: 7664-93-9 / KSCN: 333-20-0 / KI: 7681-11-0 / KBr: 7758-02-3

[1] P. Warner, S. Winstein, *J. Am. Chem. Soc.* **91** (1969) 7785.
[2] P. Radlick, W. Rosen, *J. Am. Chem. Soc.* **89** (1967) 5308.
[3] K. Takahashi, K. Takase, T. Kagawa, *J. Am. Chem. Soc.* **103** (1981) 1186.
[4] K. Lammertsma, H. Cerfontain, *J. Am. Chem. Soc.* **100** (1978) 8244.
[5] H. Cerfontain, H. Goossens, A. Koeberg-Telder, C. Kruk, H. J. A. Lambrechts, *J. Org. Chem.* **49** (1984) 3097.
[6] T. Scholl, J. Lex, E. Vogel, *Angew. Chem.* **94** (1982) 924; *Angew. Chem. Int. Ed. Engl.* **21** (1982) 920.
[7] R. Neidlein, T. Constantinescu, R. Boese, D. Bläser, *Chem. Ber.* **121** (1988) 1699.
[8] A. Fava in *The Chemistry of Organic Sulfur Compounds* (N. Kharasch, C. Y. Meyers, Eds.), Vol. 2, Chap. 3, Pergamon Press, Oxford 1966.
[9] R. G. Guy in *The Chemistry of Cyanates and their Thio Derivates* (S. Patai, Ed.), Part 2, Chap. 18, J. Wiley, New York 1977.
[10] D. E. Giles, A. J. Parker, *Aust. J. Chem.* **23** (1970) 1581; **26** (1973) 273.
[11] D. E. Giles in Lit.[9], Chap. 12.

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