

# Contribution to the study of radical bromination of allyl isothiocyanate

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*Dedicated to Professor RNDr. V. Sutoris, CSc., in honour of his 60th birthday*

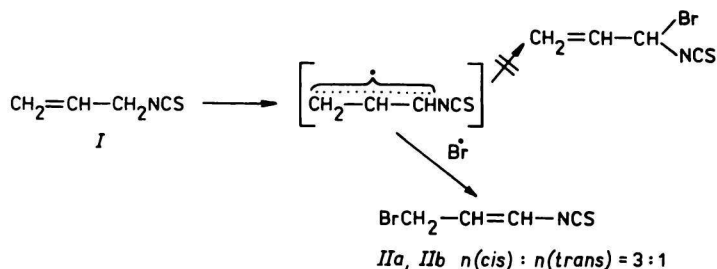
Radical bromination of allyl isothiocyanate results in the mixture of *cis*- and *trans*-3-bromo-1-propenyl isothiocyanates in the amount of substance ratio of 3 : 1, from which the pure *trans* isomer is obtained by freezing out. This reaction represents a new method for preparation of vinyl isothiocyanates with a reactive halogen. In the reaction with KSCN *cis*-3-isothiocyanato-1-propenyl isothiocyanate is formed as the only product. The structures of the synthesized compounds have been determined by spectral methods. The mechanism of the reaction presented has been discussed.

При радикальном бромировании аллилизотиоцианата образуется смесь *цис*- и *транс*-3-бром-1-пропенилизотиоцианатов в соотношении 3 : 1, из которой *транс*-производное можно выделить в чистом виде с помощью вымораживания. Данная реакция представляет собой новый способ получения винилизотиоцианатов с реакционноспособным галогеном. В результате реакции с KSCN образуется в качестве единственного продукта *цис*-3-изотиоцианато-1-пропенилизотиоцианат. Строение синтезированных соединений было установлено с помощью элементарного анализа и спектроскопических методов. В работе обсуждается механизм упомянутой реакции.

Lately, halo isothiocyanates, representing suitable synthons for synthesis of heterocyclic compounds [1, 2], have gained much importance in organic synthesis. Such properties are characteristic also of the new synthon, 2-(bromo-methyl)phenyl isothiocyanate, prepared by radical bromination of *o*-tolyl isothiocyanate in our work [3]. We were interested further in the behaviour of the generally available allyl isothiocyanate under conditions of radical reaction. It is known from the literature that addition of bromine to this compound results in 2,3-dibromopropyl isothiocyanate in high yield [4]. Though it is generally known that the allyl system readily undergoes radical bromination, attempts on radical bromination of allyl isothiocyanate have not been successful so far. *Hussein* and *Jochims* [5, 6] brominated allyl isothiocyanate with *N*-bromosuccinimide (NBS) under irradiation with UV light with negative results. Methyl isothiocyanate did not

react with NBS either. This finding as well as the fact that addition of styrene prevents the otherwise readily proceeding bromination of isopropyl isothiocyanate has been attributed to lower concentration of bromine than required for  $\alpha$ -bromination of isothiocyanates. In the present work we focused on the study of bromination of a generally available source, allyl isothiocyanate, with the possibility to prepare a reactive bifunctional isothiocyanate.

We found that by 1 h heating of allyl isothiocyanate (*I*) with NBS in tetrachloromethane in the presence of dibenzoyl peroxide a mixture of *cis*- and *trans*-3-bromo-1-propenyl isothiocyanates (*IIa*, *IIb*) was formed in the amount of substance ratio of 3 : 1 (Scheme 1). For  $\alpha$ -bromination of isothiocyanates with



Scheme 1

NBS the so-called Goldfinger mechanism was suggested, where the formed radical is stabilized by the NCS group [7] (Scheme 2). We assume that such a stabilization



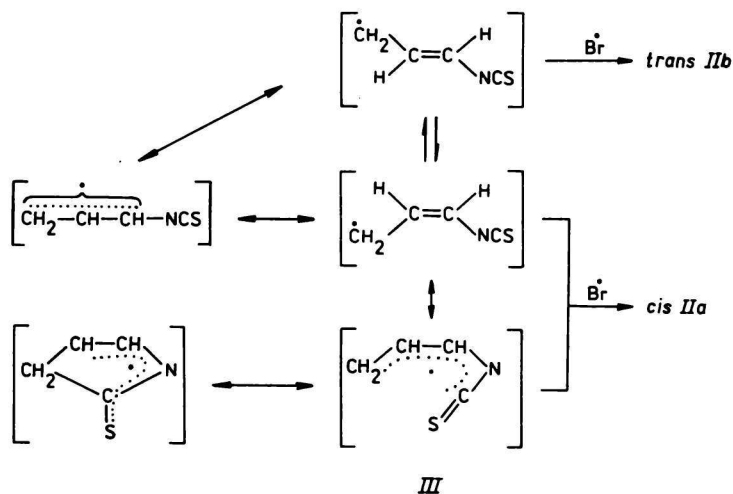
Scheme 2

may operate also in radical bromination of allyl isothiocyanate, in consequence of which the delocalized radical *III* is formed, affording in turn preferentially the *cis* derivative *IIa* (Scheme 3).

Attempts to separate both isomers chromatographically were unsuccessful due to their very similar  $R_f$  values. In spite of that, we succeeded in obtaining the pure *trans* isomer by freezing it out from the reaction mixture. The residue was composed of *cis* isomer and 19 % *trans* isomer. Isolation of pure *trans* isomer *IIb* made possible to distinguish the *cis* and *trans* isomers unambiguously and determine their ratio by means of gas chromatography.

The IR spectra of the investigated isothiocyanates showed broad absorption maxima  $\nu_{\text{as}}(\text{NCS})$  in the region of  $\tilde{\nu} \approx 2102 \text{ cm}^{-1}$  as well as absorption bands at

$\tilde{\nu} \approx 1620 \text{ cm}^{-1}$  belonging to  $\nu(\text{C}=\text{O})$  vibrations and at  $\tilde{\nu} \approx 925 \text{ cm}^{-1}$  belonging to bending vibrations of the ethylene CH bond of the *trans* isomer. The  $^1\text{H NMR}$  spectrum of the *trans* derivative revealed beside the multiplet for ethylene hydrogens at  $\delta = 5.95\text{--}6.25 \text{ ppm}$  (*trans*  $J_{\text{AB}} = 13.53 \text{ Hz}$ ) also a signal for the methylene group at  $\delta = 3.95 \text{ ppm}$ . Having the pure *trans* isomer, it was possible to assign the respective resonance signals to the *cis* derivative in the mixture of both isomers (see Experimental). In the mass spectrum of 3-bromo-1-propenyl isothiocyanate molecular peaks with  $m/z = 179$  (for  $^{79}\text{Br}$ ) and 177 were present and the base maximum was the fragmentation ion formed by splitting-off of bromine ( $[\text{M} - \text{Br}]^+$   $m/z = 98, 100 \%$ ).



Scheme 3

By the reaction mentioned above it is possible to prepare halo isothiocyanates of the vinyl type, which cannot be obtained in usual way. For example, the analogous 3-chloro-1-propenyl isothiocyanate was prepared by Schulze *et al.* [8, 9] from the rarely attainable 1,3-dichloropropene with KSCN.

The synthesized 3-bromo-1-propenyl isothiocyanate (II) represents a compound with highly reactive halogen of the allyl type which, by the reaction with KSCN and subsequent distillation of the crude product, affords *cis*-3-isothiocyanato-1-propenyl isothiocyanate (IV) (*cis*  $J_{\text{AB}} = 7.90 \text{ Hz}$ ). Because of the complex nature of the  $\nu_{\text{as}}(\text{NCS})$  band, only one broad maximum at  $\tilde{\nu} = 2050 \text{ cm}^{-1}$  was observed in the IR spectrum of this compound.

## Experimental

IR spectra were measured in chloroform solutions with a Specord 75 IR (Zeiss, Jena) apparatus.  $^1\text{H}$  NMR spectra were recorded in deuteriochloroform solutions with a Tesla BS 487 A (80 MHz) and  $^{13}\text{C}$  NMR spectra with a Tesla BS 567 (25.12 MHz) spectrometers using tetramethylsilane as internal standard. Mass spectra were measured on a MAT 111 (Varian) spectrometer at 80 eV and ion source temperature 200 °C. The composition of the products was monitored by gas chromatography with a C. Erba Fractovap chromatograph with a steel column (1.5 m  $\times$  2 mm) of Chromosorb WHP coated with 3 % OV-17. The sample injection temperature was 210 °C, column temperature 120 °C, and nitrogen carrier-gas flow rate 15 cm<sup>3</sup> min<sup>-1</sup>.

### *3-Bromo-1-propenyl isothiocyanate II*

The mixture of redistilled allyl isothiocyanate (9.9 g; 0.1 mol), *N*-bromosuccinimide (19.58 g; 0.11 mol), and dibenzoyl peroxide (2.42 g; 0.01 mol) in dry tetrachloromethane (40 cm<sup>3</sup>) was boiled under reflux for 1 h. To the cooled reaction mixture petroleum ether (150 cm<sup>3</sup>) was added and the precipitate was sucked. The petroleum ether solution was purified by charcoal and evaporated to dryness. The residue was distilled *in vacuo*. The fraction with b.p. (13.3 kPa) = 98–100 °C was collected. Yield = 54.2 %. The amount of substance ratio of *cis* and *trans* isomers, determined by gas chromatography, was 3 : 1. For C<sub>4</sub>H<sub>4</sub>NSBr ( $M_r = 178.06$ )  $w_i(\text{calc.})$ : 26.97 % C, 2.26 % H, 7.86 % N, 18.00 % S, 44.88 % Br;  $w_i(\text{found})$ : 26.89 % C, 2.24 % H, 7.81 % N, 18.05 % S, 44.91 % Br. IR (CHCl<sub>3</sub>),  $\bar{\nu}/\text{cm}^{-1}$ : 2102 (NCS), 1623 (C=C).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>),  $\delta/\text{ppm}$ : 27.9 (CH<sub>2</sub>), 120.9 (CH), 127.6 (CH). Mass spectrum,  $m/z$  ( $I_r/\%$ ): 179 (10,  $^{79}\text{Br}$ ), 177 (10), 98 (100), 72 (24), 39 (40).

### *trans-3-Bromo-1-propenyl isothiocyanate IIb*

*trans*-3-Bromo-1-propenyl isothiocyanate crystallized from the mixture on standing at -30 °C for several hours. The colourless crystals obtained from petroleum ether had m.p. = 24–28 °C. For C<sub>4</sub>H<sub>4</sub>NSBr ( $M_r = 178.06$ )  $w_i(\text{calc.})$ : 26.97 % C, 2.26 % H, 7.86 % N, 18.00 % S, 44.88 % Br;  $w_i(\text{found})$ : 26.95 % C, 2.29 % H, 7.90 % N, 18.03 % S, 44.80 % Br.  $^1\text{H}$  NMR (CDCl<sub>3</sub>),  $\delta/\text{ppm}$ : 3.95 (CH<sub>2</sub>, d, 2H), 5.95 (CH, m, 1H), 6.26 (CH, m, 1H),  $J_{\text{trans}}(\text{CH}=\text{CH}) = 13.53$  Hz. IR (CHCl<sub>3</sub>),  $\bar{\nu}/\text{cm}^{-1}$ : 2102 (NCS), 1623 (C=C).

### *cis-3-Bromo-1-propenyl isothiocyanate IIa*

After separating the crystalline *trans*-3-bromo-1-propenyl isothiocyanate, the mixture contained 81 % of *cis*-3-bromo-1-propenyl isothiocyanate and 19 % of the *trans* derivative (GC). The mixture could not be separated by column or thin-layer chromatography on SiO<sub>2</sub> due to almost identical  $R_f$  values of both isomers. For C<sub>4</sub>H<sub>4</sub>NSBr ( $M_r = 178.06$ )  $w_i(\text{calc.})$ : 26.97 % C, 2.26 % H, 7.86 % N, 18.00 % S, 44.88 % Br;  $w_i(\text{found})$ : 26.89 % C, 2.21 % H, 7.88 % N, 18.07 % S, 44.94 % Br.  $^1\text{H}$  NMR (CDCl<sub>3</sub>),  $\delta/\text{ppm}$ : 4.05 (CH<sub>2</sub>, d,

2H), 5.68 (CH, m, 1H), 6.10 (CH, m, 1H),  $J_{cis}(\text{CH}=\text{CH}) = 7.38$  Hz. IR ( $\text{CHCl}_3$ ),  $\bar{\nu}/\text{cm}^{-1}$ : 2101 (NCS), 1622 (C=C).

### *cis*-3-Isothiocyano-1-propenyl isothiocyanate IV

To the solution of 3-bromo-1-propenyl isothiocyanate (0.03 mol) in dry acetone (30 cm<sup>3</sup>) KSCN (0.035 mol) was added and stirred for 1 h. After the reaction was complete, acetone was distilled off at reduced pressure and the residue was extracted with ether (50 cm<sup>3</sup>) and filtered. Then ether was distilled off and the residue was distilled *in vacuo*. The fractions distilling in the temperature range of 96—100 °C/0.67 kPa were collected. The colourless crystals had m.p. = 31—34 °C (petroleum ether); yield = 44 %. For  $\text{C}_5\text{H}_4\text{N}_2\text{S}_2$  ( $M_r = 156.23$ )  $w_i(\text{calc.})$ : 38.43 % C, 2.58 % H, 17.93 % N, 41.04 % S;  $w_i(\text{found})$ : 38.48 % C, 2.49 % H, 18.00 % N, 44.06 % S. IR ( $\text{CHCl}_3$ ),  $\bar{\nu}/\text{cm}^{-1}$ : 2050 (NCS), 1625 (C=C). <sup>1</sup>H NMR ( $\text{CDCl}_3$ ),  $\delta/\text{ppm}$ : 3.73 (2H, d,  $\text{CH}_2$ ), 5.51 (1H, dd, CH), 6.27 (1H, d,  $\text{CH}-\text{NCS}$ ),  $J_{cis}(\text{CH}=\text{CH}) = 7.90$  Hz.

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