Isothiocyanates. XLI.
Synthesis and infrared spectra of benzotriazolyl isothiocyanates

A. MARTVOŇ, D. ILAVSKÝ, and M. UHER

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

Received 17 January 1974

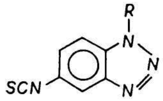
Accepted for publication 9 April 1974

The synthesis of 1-(X-phenyl)-5-benzotriazolyl isothiocyanates and 1-alkyl-5-benzotriazolyl isothiocyanates is described. Characteristic frequencies of infrared spectra of the synthesized derivatives are given.

As mentioned in our previous papers [1, 2], isothiocyanates having their —NCS group bound to a fluorescent active skeleton could be well suited to determine the antibody properties in biological materials. For this reason we synthesized isothiocyanates of

Table 1

1-R-Benzotriazolyl isothiocyanates



Compound	R	Formula	*M*	Calculated/found		Yield	M.p.
				% N	% S	[%]	[°C]
I	Phenyl	$C_{13}H_8N_4S$	252.3	22.24 22.15	12.70 12.59	65.2	150—151
II	Tolyl	$C_{14}H_{10}N_4S$	266.0	21.07 21.06	12.10 12.02	68.2	178—180
III	4-Methoxyphenyl	$C_{14}H_{10}N_4OS$	282.0	19.91 19.92	11.35 11.38	64.0	241—243
IV	4-Ethoxyphenyl	$C_{15}H_{12}N_4OS$	296.1	18.92 19.24	10.81 10.86	62.0	141—142
V	4-Chlorophenyl	$C_{13}H_7ClN_4S$	286.5	19.52 19.35	11.18 11.25	61.0	195—197
VI	4-Bromophenyl	$C_{13}H_7BrN_4S$	331.2	16.91 16.94	9.66 9.73	61.0	205—208
VII	3-Methylphenyl	$C_{14}H_{10}N_4S$	266.0	21.07 21.18	12.10 12.13	66.0	127—129
VIII	3-Chlorophenyl	$C_{13}H_7ClN_4S$	286.5	19.52 19.66	11.18 11.30	60.0	177—178
IX	Methyl	$C_8H_6N_4S$	190.2	29.53 29.62	16.81 16.87	67.0	113—116
X	Ethyl	$C_9H_8N_4S$	204.2	27.45 27.77	13.34 13.14	68.0	127—129
XI	*tert*-Butyl	$C_{11}H_{12}N_4S$	232.2	24.18 24.20	13.76 13.79	65.0	175—177

Table 2

Frequencies of infrared spectra of synthesized isothiocyanates (cm^{-1})

Compound	δ(CH)	$\tilde{\nu}_s$(NCS)	$\tilde{\nu}$(Skelet)		$\tilde{\nu}$(N=N)	$\tilde{\nu}_{as}$(NCS)		Other bands	
I	880, 915	975	1370 1510	1470 1550	1605	2055 2110	2080 2160	1180	
II	870, 890, 905	960	1350 1490	1470 1590	1610	2050 2110	2075	1080 1315	1115
III	850, 880, 905	990	1350 1550	1470 1590	1615	2060	2115 2160	1090 1310	1180
IV	850, 875, 915, 930	975	1350 1490	1390 1530	1610	2070	2115 2160	1080 1300	1120
V	850, 875, 920, 940	970	1505 1595	1540	1600	2050 2115	2080 2160	1110	1180
VI	850, 875, 915, 940	975	1495 1595	1545	1610	2045 2115	2080 2160	1080 1300	1120
VII	830, 890, 930, 910	975	1350 1590	1500	1605	2060 2120	2080 2160	1110 1105	1180 1300
VIII	. 830, 880, 905	975	1350 1495	1450 1540	1590	2050 2110	2080 2160	1080 1105	1090 1300
IX	890, 915, 940	970	1340 1540	1500 1590	1615	2065 2160	2115	1180 1120	1300
X	875, 915	970	1370 1500	1460 1585	1615	2060 2155	2110	1115 1180	1120 1300
XI	830, 875, 905	975	1350 1400 1540	1375 1485	1610	2060 2115	2080 2160	1080 1160	1110 1300

benzotriazolyl type. It is also known that various systems become biologically active by introduction of the —NCS group [1, 3—5].

This paper refers to the synthesis and infrared spectra of benzotriazolyl isothiocyanates substituted in position 1 by an alkyl or aryl.

Isothiocyanates were synthesized by the thiophosgene method: Thiophosgene in heterogeneous mixture water—chloroform—dichloroethane was treated with a chloroform solution of amine. Yields of isothiocyanates thus prepared were 62—68%, what means that the effect of substituents on the reaction of thiophosgene with amine is not notable. All isothiocyanates as listed in Table 1 are white crystalline substances.

The infrared spectra of 1-substituted benzotriazoles are relatively little systematically described in the literature. *O'Sullivan* [6] reports for 1-phenylbenzotriazole an absorption in the 1500 to 1670 cm^{-1} range, consisting of three characteristic absorption bands ($\tilde{\nu}$(C=C) 1673 cm^{-1}, $\tilde{\nu}$(N=N) 1601 cm^{-1}, and $\tilde{\nu}_{arom}$ 1509 cm^{-1}). As seen in Table 2 our derivatives reveal characteristic vibrations of $\tilde{\nu}$(C=C) neither at about 1670 cm^{-1}, nor within the 1640—1630 cm^{-1} range as is the case with 2-phenyl substituted derivatives of benzotriazole [1], what indicates a quite significant interaction of the —NCS group with the benzotriazole ring, providing that it is substituted by an aryl in position 1. Similar conclusions could be deduced, in accordance with [7], also for 1-alkyl substituted benzotriazoles.

In the 2200—2000 cm^{-1} range a strong absorption band, attributable to $\tilde{\nu}_{as}$(NCS), could be observed. If the —NCS group was located in position 5 of the benzotriazole ring, then 4 absorption maxima due to splitting of the maximum at about 2060 cm^{-1}

similar to that of benzothiazolyl isothiocyanates [8] were seen. Splitting did not occur if electron-donating substituents were in position 1. Another two absorption maxima of the complex band in the 2200—2000 cm^{-1} range did not differ from other isothiocyanates of aromatic systems [9].

Experimental

Infrared spectra were measured with a double-beam UR-20 spectrophotometer in the 3660 to 800 cm^{-1} range in chloroform ($c = 2.5 \times 10^{-2}$ M, 0.427 mm cell thickness). The apparatus was calibrated with a polystyrene foil.

Intermediates needed for the synthesis of isothiocyanates were prepared according to [10—17].

1-R-5-Benzotriazolyl isothiocyanates

A solution of the proper amine (0.1 mole) in chloroform (120 ml) was gradually added to a mixture of water (200 ml), chloroform (150 ml), dichloroethane (150 ml), and thiophosgene (12 g; 0.105 mole) under vigorous stirring. While adding, the temperature of the reaction medium was kept in the 5—10°C range and the pH value was adjusted with solid calcium carbonate to 7. Stirring was continued after addition of the amine solution for 2 hrs at room temperature; the organic layer was then separated, dried with anhydrous calcium chloride, and removed. The dry residue was crystallized from the mixture benzene—light petroleum 3 : 1. Characteristic data of the prepared isothiocyanates and frequencies of their infrared spectra are listed in Tables 1 and 2.

References

1. Martvoň, A., Antoš, K., and Uher, M., *Collect. Czech. Chem. Commun.* ***37***, 2967 (1972).
2. Martvoň, A., *Zborník prác Chemickotechnologickej fakulty SVŠT.* (Collection of Communications, Section Chemistry, Slovak Technical University.) Bratislava, in press.
3. Logemann, W. and Galimbert, S., *Biol. Med.* ***3***, 227 (1960).
4. Mackie, A., *Manufacturing Chemist.* ***31***, 97 (1960).
5. Hata, J. and Tsuruoko, M., *J. Pharm Soc. Jap.* ***74***, 245 (1954).
6. O'Sullivan, O. G., *J. Chem. Soc.* ***1960***, 3655.
7. Molnár, I., *Helv. Chim. Acta* ***46***, 1473 (1963).
8. Martvoň, A. and Skačáni, I., *Chem. Zvesti* ***27***, 387 (1973).
9. Kristian, P., Antoš, K., and Kováč, Š., *Chem. Zvesti* ***17***, 747 (1963).
10. Leymann, H., *Ber.* ***15***, 1234 (1882).
11. Van Romborgh, O., *Rec. Trav. Chim. Pays-Bas* ***2***, 104 (1883).
12. Reissert, A. and Goll, G., *Ber.* ***38***, 93 (1905).
13. Zincke, L., *Justus Liebigs Ann. Chem.* ***313***, 264 (1900).
14. Bremer, O., *Justus Liebigs Ann. Chem.* ***514***, 279 (1934).
15. Cartez, P. H., Katritzky, A. R., and Plant, S. G., *J. Chem. Soc.* ***1955***, 337.
16. Pinov, A. and Koch, R., *Ber.* ***30***, 2852 (1897).
17. Beretta, J., *Gazz. Chim. Ital.* ***55***, 742 (1925).

Translated by Z. Votický