SYNTHESIS AND PROPERTIES OF ALKYL ISOTHIOCYANATOCARBOXYLATES*

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Synthesis and IR-spectral properties of alkyl isothiocyanatocarboxylates are described. The isothiocyanates have been prepared by the thiophosgene method in aqueous as well as anhydrous solvents. The doublet of the ν(C=O) band is interpreted to be due to the presence of two conformers. The population of the conformers is determined from the ratio of the apparent molar absorptivities, ε^a, of the computer-separated bands.

Some of the isothiocyanates, described in this study, are already known: compounds *II*, *VI–VII*, *XII*, *XVI–XVII*, *XXIV–XXVI* have been synthesized by the thiophosgene method[1–7], compounds *II* and *VIII* by the rhodanide method[8], and compounds *I–III*, *VIII*, *XX*, *XXIII* and *XXV* by the dithiocarbamate method[5,8–13]. Generally, the isothiocyanate group shows a broad complex band in the region 2300–2000 cm^{-1} which is believed to be due vibrational interaction[14]. IR-spectral properties of isothiocyanates with the NCS group bonded to an aromatic[15] or aliphatic residue[15–17] have already been studied.

In this work we tried to find best method for the preparation of the title isothiocyanates and studied the mutual influence of the alkoxycarbonyl and isothiocyanate groups in the α-position. We prepared a series of isothiocyanates of the general formula R^1—CH(NCS)—CO_2R^2 where R^2 is a normal or branched alkyl group with one to four carbons (*I–VI*) and R^1 is a variously substituted, or unsubstituted, alkyl or aralkyl moiety (*VII–XXII*). For comparison we prepared a group of isothiocyanates of the type SCN—$(CH_2)_x$—CO_2R^2 where R^2 is CH_3 or C_2H_5 and x = 2, 3, or 5 (*XXIII–XXVI*). The isothiocyanates were synthesized using two modifications of the thiophosgene method: in water (method *A*) and in an anhydrous medium (method *B*) (Tables I and II). The yields of the isothiocyanates prepared according to the method *A* were 45–75% and the reaction time was four hours. The arising hydrogen chloride was neutralized with powdered sodium hydrogen carbonate. In order to obtain the same yields with calcium carbonate, the necessary reaction time was three times lon-

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TABLE I

Esters of DL-2-Isothiocyanatocarboxylic Acids R^1-CH(NCS)COOR^2

Compound	R^1 R^2	B.p., °C Torr	Yield, % method	Formula (mol. wt.)	Calculated/Found %N	%S
I	H	45—46	58 *A*	$C_4H_5NO_2S$	10·68	24·45
	CH_3	1·5[a]		(131·1)	16·61	24·45
II	H	60·5—61·5	42 *A*	$C_5H_7NO_2S$	9·65	22·08
	C_2H_5	2·0[b]		(145·2)	9·77	21·99
III	H	61—62	58 *A*	$C_6H_9NO_2S$	8·80	20·14
	n-C_3H_7	1·0[a]		(159·2)	8·63	19·88
IV	H	54—55	50 *A*	$C_6H_9NO_2S$	8·80	20·14
	i-C_3H_7	2·0		(159·2)	8·70	20·15
V	H	63—64	63 *A*	$C_7H_{11}NO_2S$	8·08	18·51
	n-C_4H_9	2·0		(173·2)	8·29	18·72
VI	H	32—3	— *A*	$C_7H_{11}NO_2S$	8·08	18·51
	t-C_4H_9	2·0[a]	33 *B*	(173·2)	8·21	18·49
VII	CH_3	39—40	48 *A*	$C_5H_7NO_2S$	9·65	22·08
	CH_3	1·5[a]		(145·2)	9·52	22·15
VIII	CH_3	43·5—45	51 *A*	$C_6H_9NO_2S$	8·80	20·14
	C_2H_5	1·5[b]		(159·2)	8·48	20·37
IX	CH_3	66—68	59 *A*	$C_8H_{13}NO_2S$	7·48	17·12
	s-C_4H_9	2·0		(187·3)	7·65	17·25
X	C_2H_5	49—50	55 *A*	$C_7H_{11}NO_2S$	8·08	18·51
	C_2H_5	1·0		(173·2)	8·17	18·47
XI	i-C_3H_7	46—46·5	46 *A*	$C_8H_{13}NO_2S$	—	17·12[g]
	C_2H_5	0·5[b]	71 *B*	(187·3)	—	16·93
XII	i-C_4H_9	62—63	58 *A*	$C_9H_{15}NO_2S$	—	15·93[g]
	C_2H_5	0·5[c]	90 *B*	(201·3)	—	15·71
XIII	s-C_4H_9	57—58	55 *A*	$C_9H_{15}NO_2S$	—	15·93[g]
	C_2H_5	0·5		(201·3)	—	16·10
XIV	n-C_4H_9	52—53	51 *A*	$C_9H_{15}NO_2S$	—	15·93[g]
	C_2H_5	1·0		(201·3)	—	16·10
XV	$CH_3S(CH_2)_2$	32·0—32·5	57 *A*	$C_8H_{13}NO_2S_2$	6·69	29·24
	C_2H_5	0·001		(219·3)	6·50	29·41
XVI	$C_2H_5O_2CCH_2$	72—73	45 *A*	$C_9H_{13}NO_4S$	—	13·85[g]
	C_2H_5	1·0[d]		(231·3)	—	13·81
XVII	$C_2H_5O_2C(CH_2)_2$	36·0—36·5	54 *A*	$C_{10}H_{15}NO_4S$	5·71	13·07
	C_2H_5	0·002[d]		(245·3)	5·82	13·08

TABLE I
(*continued*)

Compound	R^1 R^2	B.p., °C Torr	Yield, % method	Formula (mol. wt.)	Calculated/Found %N	%S
XVIII	$SCN(CH_2)_3$	43·0–44·0	28 *A*	$C_9H_{12}N_2O_2S_2$	11·45	26·22
	C_2H_5	0·002		(244·3)	11·57	26·36
XIX	$SCN(CH_2)_4$	57·5–59·0	76 *A*[e]	$C_{10}H_{14}N_2O_2S_2$	10·84	24·82
	C_2H_5	0·003		(258·4)	10·61	24·51
XX	$C_6H_5CH_2$	84·5	55 *A*	$C_{12}H_{13}NO_2S$	5·95	13·63
	C_2H_5	1·5[b]	85 *B*	(235·3)	5·99	13·75
XXI	$4\text{-}HOC_6H_4CH_2$	62–63	42 *A*	$C_{12}H_{13}NO_2S$	5·57	12·76
	C_2H_5	$CHCl_3$–n-hexane[f]		(251·3)	5·50	12·66
XXII	$4\text{-}HOC_6H_2I_2CH_2$	116–18	72 *A*	$C_{12}H_{11}I_2NO_2S$	2·75	6·30[g]
	C_2H_5	$CHCl_3$–n-hexane[f]		(509·1)	2·81	—

[a] The preparation of compounds *I*, *III*, *VII* is described in ref.[11], preparation of *VI* in ref.[6]; no b.p.'s are given. [b] Ref.[9] gives for *II* 68°C/5 Torr, *VIII* 60°C/5 Torr, *XI* 83°C/4·5 Torr, *XX* 138·5°C/4 Torr. [c] Ref.[3] reports 79°C/0·2 Torr (L-enantiomer). [d] Ref.[5] gives for *XVI* 126°C/2 Torr, *XVII* 86–87°C/2 Torr (L-enantiomer). [e] Reaction time 8 hours. [f] The melting points were determined using a Böetius heated microscope stage and are uncorrected. [g] For *XI* (187·3) calculated: 51·31% C, 6·99% H; found: 51·50% C, 7·07% H. For *XII* (201·3) calculated: 53·70% C, 7·51% H; found: 53·92% C, 7·60% H. For *XIII* (201·3) calculated: 53·70% C, 7·51% H; found: 53·97% C, 7·55% H. For *XIV* (201·3) calculated: 53·70% C, 7·51% H; found: 54·00% C, 7·64% H. For *XVI* (231·3) calculated: 46·80% C, 5·61% H; found: 46·85% C, 5·55% H. For *XXII* (509·1) calculated: 28·31% C, 2·18% H; found: 28·50% C, 2·21% H.

ger; on the other hand, with 0·1M-NaOH the time required was only one hour. The method *B* was used in the synthesis of four isothiocyanates. In the synthesis of the compound *VI* a small amount of dimethylformamide was added to the reaction mixture. The optimum reaction time was determined from the change of the isothiocyanate concentration with time, which was followed IR-spectroscopically in the region 2300–1900 cm^{-1}.

The IR spectra of isothiocyanates, which contain isothiocyanate and alkoxycarbonyl groups in an α-position to each other (*I*–*XXII*), exhibit strong bands in the 2078–2046 cm^{-1} region, $\varepsilon^a = 110-777$ (Table III). The bands are asymmetric on the higher wavenumber side; this indicates the presence of other bands which in the compounds *VIII*–*XI* and *XIII* manifest themselves as shoulders at about 2175 cm^{-1}. As seen from the spectra of compounds *I*–*VI*, branching of the R^2 substituent is accompanied by a marked decrease in ε^a and half-width of the iso-

thiocyanate band. In the spectrum of the compound *VI* the decrease in the spectral characteristics is considerable and is outside the average values. When $R^2 = C_2H_5$, the wavenumber of the band ν_{as}(NCS), as well as the shape and intensity of the other bands in the 2200–2100 cm^{-1} region, depends on the structure of R^1.

The wavenumbers of the strongest band ν_{as}(NCS) in the spectra of compounds *VIII*, *X–XIV*, *XVI* and *XX* are linearly dependent on the +I-effects of the alkyl groups R according to the relation: $\nu_{as}(NCS) = -14{\cdot}27\sigma^* + 2064{\cdot}9\ cm^{-1}$, the the correlation coefficient being $r = 0{\cdot}81 \pm 0{\cdot}17$. The significance of the correlation coefficient reveals itself only when compared with analogous alkyl isothiocyanates where the Taft's σ^* constants of the substituents do not correlate with the wavenumbers ν_{as}(NCS)[18]. The introduction of the steric E_s constants did not improve the correlation significantly (the correlation coefficient r_{σ^*}, E_s is 0·831). The maximum of the band ν_{as}(NCS) in the spectra of compounds *XXIII–XXVI* is shifted towards higher wavenumbers and ranges between 2083 and 2203 cm^{-1} (ε^a 483–413 and $\Delta\nu_{1/2}$ 110–35 cm^{-1}) as shown in Table IV. The comparison of the IR-spectral data of the NCS group in our isocyanates *I–XXII* with that of selected alkyl-[15–19] and aryl isothiocyanates[16,17] shows that they are spectroscopically similar to aryl isothiocyanates. On the contrary, the spectral characteristics of the band ν_{as}(NCS) of the isothiocyanates *XXIII–XXVI* remind that of alkylisothiocyanates[15,18]. The higher values of ε^a and $\Delta\nu_{1/2}$ in the spectra of compounds *XVIII–XIX* indicate the presence of another band. The spectrum of the compound *XVIII* shows a well-discernible symmetric doublet of the main maximum of the band ν_{as}(NCS). Comparison with

TABLE II

Esters of ω-Isothiocyanatocarboxylic Acids, $SCN-(CH_2)_x-CO_2R^2$

Compound	R^2 / x	B.p., °C / Torr	Yield, % / method	Formula (mol. wt.)	Calculated/Found %N	%S
XXIII	CH_3	110[a]	50	$C_5H_7NO_2S$	9·65	22·08
	2	1	*A*	(145·2)	9·50	21·96
XXIV	C_2H_5	54–55[b]	59	$C_6H_9NO_2S$	8·80	20·14
	2	0·5	*A*	(159·2)	8·99	20·16
XXV	C_2H_5	28–29[c]	47	$C_7H_{11}NO_2S$	8·08	18·51
	3	0·001	*A*	(173·2)	8·21	18·54
XXVI	C_2H_5	48[d]	58	$C_9H_{15}NO_2S$	6·96	15·93
	5	0·004	*A*	(201·3)	7·21	15·75

[a] Ref.[12] gives 110–112°C/1 Torr. [b] Ref.[1] reports 90–95°C/1 Torr. [c] Ref.[5] reports 98°C/2 Torr. [d] Ref.[4] reports 126°C/2 Torr, ref.[12] 92–95°C/0·04 Torr.

alkyl isothiocyanates[15,18] and the isothiocyanates *XXIII*–*XXVI* allows to ascribe the higher-wavenumber band to ν_{as} vibrations of the terminal ω-NCS group in the residue R and the lower-wavenumber band to the -NCS group α relative to the ethoxycarbonyl group.

TABLE III

IR Spectral Data of Alkyl 2-Isothiocyanatocarboxylates

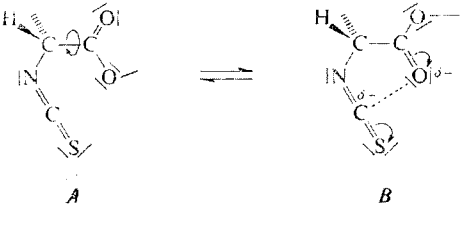
Compound	ν_{as}(—N=C=S)						ν(C=O)			
	$\tilde{\nu}_1$	ε_1^a	$\tilde{\nu}_2$	ε_2^a	$\Delta\nu_{1/2}$	$\tilde{\nu}_3$	ε_3^a	$\tilde{\nu}_4$	ε_4^a	$\Delta\nu_{1/2}$
I	—	—	2 066	537	105	1 777·0	213	1 757·0	352	34
II	—	—	2 065	507	108	1 768·0	288	1 751·0	366	31
III	—	—	2 072	445	104	1 768·5	282	1 751·0	347	34
IV	—	—	2 068	510	110	1 762·0	246	1 753·0	292	37
V	—	—	2 065	410	95	1 762·0	234	1 746·0	344	40
VI	—	—	2 067	110	90	1 767·5	101	1 750·5	117	36
VII	—	—	2 055	472	130	1 768·5	268	1 754·0	414	28
VIII	2 122	190	2 062	499	130	—	—	1 746·5	419	28
IX	2 126	182	2 066	474	135	—	—	1 747	242	35
X	2 165	94	2 064	565	130	1 761·0	284	1 746·0	424	26
XI	2 217	49	2 070	487	115	1 758·0	241	1 743·5	369	29
	2 174	50								
	2 132	220								
XII	—	—	2 065	442	120	1 759·0	253	1 746·5	363	28
XIII	2 215	43	2 072	500	140	1 759·0	279	1 743·5	401	29
	2 122	182	2 072	500	140	1 759·0	279	1 743·5	401	29
XIV	—	—	2 064	477	133	1 758	246	1 746·0	306	32
XV	—	—	2 052	456	115	1 761·0	234	1 751·0	317	33
XVI	—	—	2 056	507	115	—	—	1 751	765	29
XVII	—	—	2 052	497	113	—	—	1 747	680	34
XVIII	2 196	140	2 078	741	133	1 761	250	1 751	285	29
			2 056	741						
XIX	2 202	140	2 078	777	132	1 761	243	1 750	230	34
XX	—	—	2 065	423	128	1 761	242	1 748	322	33
XXI	—	—	2 064	415	145	1 760	227	1 749	305	37
XXII	—	—	2 046	—	—	1 761	—	—	—	—

The bands ν(C=O) of compounds *I*–*III*, *V*–*VIII*, *X*–*XIII* were measured on a Unicam SP-100G instrument; $\tilde{\nu}$ and $\nu\Delta_{1/2}$ given in cm^{-1}, ε^a in 1 mol^{-1} cm^{-1}.

TABLE IV
IR Spectral Data of Alkyl ω-Isothiocyanatocarboxylates

Compound	ν_{as}(N=C=S)					ν(C=O)		
	$\tilde{\nu}_1$	ε_1^a	$\tilde{\nu}_2$	ε_2^a	$\Delta\nu_{1/2}$	$\tilde{\nu}_3$	ε_3^a	$\Delta\nu_{1/2}$
XXIII	2 215 2 175	97 96	2 084	452	100	1 751	385	28
XXIV	2 214 2 160	96 96	2 083	478	95	1 746	503	20
XXV	2 200	105	2 100 2 068	433 282	95	1 744	473	21
XXVI	2 203	120	2 093	413	100	1 744	496	24

The bands ν(C=O) of compounds *I*–*XXII* exhibit two maxima in the region 1 777 – 1 744 cm^{-1} (Table III). In all cases the wavenumbers of the ν(C=O) bands are markedly higher as compared with the ν(C=O) bands in the spectra of analogous esters of carboxylic acids[20–22], however, the ε^a values of the studied compounds differ only little from that of the esters of the saturated carboxylic acids[23]. Since the electronic effect of the substituents R^1 and R^2 is small, the higher wavenumbers of the bands ν(C=O) are caused by the presence of isothiocyanate group in α-position relative to the ethoxycarbonyl group. The bands ν(C=O) of the methyl esters (*I*, *VII* and *XXIII*) are considerably shifted toward the higher wavenumbers. This shifts is characteristic of methyl esters, as follows from the spectra of methyl esters derived from carboxylic acids[24], substituted carboxylic acids and dicarboxylic acids[25]. The bands ν(C=O) of the compounds with a branched substituent R^2 (*IV*, *VI*)



A *B*

FIG. 1
Conformations of 2-Isothiocyanatocarboxylates

exhibit markedly lower ε^a values compared to *I*, *II*, *VII* and *VIII* where it is not necessary to consider the steric situation on the C—O—C ester bond[26]. In the spectra of compounds *XVI* and *XVII*, where the substituent R^1 contains another ethoxycarbonyl group, we were able to identify only the lower wavenumber maximum. However, the asymmetry of the band on the higher wavenumber side, together with a substantial increase of the ε^a values, indicates the presence of other bands. In compounds *XVIII* and *XIX* the splitting of the band is relatively pronounced and on the basis of comparison with other isothiocyanates *I*–*XXII* it is possible to assume that the isothiocyanate group in the substituent R^1 has no effect on the splitting of the band ν(C=O). The spectra of compounds *XXIII*–*XXVI* (Table IV) exhibit symmetrical, nonsplitted bands ν(C=O) in the region 1 751 – 1 744 cm^{-1}. The ε^a values of these bands are markedly higher (503–385) whereas their $\Delta\nu_{1/2}$ values are lower than those found for the compounds *I*–*XXII*. From the comparison of the spectral characteristics of the bands ν(C=O) in all the studied compounds another proof is obtained that the complex nature of this band is due to the interaction between isothiocyanate and ethoxycarbonyl groups in the α-position relative to each other. The higher wavenumbers of the carbonyl band in the spectra of *I*–*XXII* are in accord with the electron-acceptor effect of the isothiocyanate group[27,28]. The bands ν(C=O), measured in tetrachloromethane, are splitted into two maxima, that at the higher wavenumber being invariably less intensive. The intensity of the maxima varies with the nature of the substituent R^2. It can be assumed that the band splitting is due to the existence of the conformers *A* and *B* (Fig. 1). The reasons for this as-

TABLE V

IR Spectral Data of the Separated Bands ν(C=O) for Some Alkyl 2-Isothiocyanatocarboxylates

Compound	$\tilde{\nu}_3$	ε_3^a	$\Delta\nu_{1/2}$	$\tilde{\nu}_4$	ε_4^a	$\Delta\nu_{1/2}$	$\varepsilon_3^a/\varepsilon_4^a$
I	1 776·0	189	7·0	1 757·0	335	6·3	0·562
II	1 768·5	255	5·5	1 751·0	328	5·5	0·777
III	1 768·5	241	6·0	1 750·5	319	5·9	0·757
IV	1 763·0	203	7·0	1 746·0	313	6·5	0·647
VI	1 767·5	57	6·0	1 748·8	81	6·0	0·703
VII	1 768·0	225	6·0	1 754·0	381	6·0	0·592
VIII	1 762·0	173	6·3	1 746·7	408	6·5	0·423
X	1 760·0	208	6·5	1 745·0	362	6·5	0·577
XI	1 758·0	215	7·5	1 743·5	366	6·0	0·586
XII	1 759·0	194	5·0	1 745·0	344	7·0	0·556
XIII	1 758·0	229	7·5	1 743·5	372	5·7	0·614

sumption are the following: *a*) certain similarity exists between the shape and the wavenumbers of the bands of α-substituted carbonyl compounds[29-34], *b*) the conformational isomerism is facilitated by the electron deficit at the carbon atom in the -NCS group; this deficit is made greater by the electron-acceptor effect of the alkoxycarbonyl group in the α-position. The interaction of the carbon in the isothiocyanate group with the free electron pair of the carbonyl oxygen should hinder the free rotation around the σ-bonds, and this would lead to an energetically advantageous five-membered ring arrangement (Fig. 1).

On the basis of the above assumptions we ascribed the higher-wavenumber band ν(C=O) to the conformer *A* and the lower wavenumber band to the conformer *B* (Fig. 1). The ratio $\varepsilon_3^a/\varepsilon_4^a$ (Table III) of these two bands can serve as a rough estimate of the conformer population. The relative intensities, corresponding to the two conformers, depend on the substituents R^1 and R^2. The determination of the conformer population was carried out in the case of the derivatives *I–IV, VI–VIII, X–XIII* (Table V) where the bands ν(C=O) were separated by means of computer[35]. The effect of the substituent R^1 on the conformational equilibrium $A \rightleftharpoons B$ is mainly electronic whereas the substituents R^2 exert both electronic and steric influence. For compounds where $R^2 = C_2H_5$ it follows from the ratio $\varepsilon_3^a/\varepsilon_4^a$ that substituents R^1 stabilise the conformer *B* and their effect is more marked than in the cases where $R^1 = H$ and R^2 varies (*I–IV, VI*). As expected, the higher +I effect of branched alkyl group R^2 (*IV*) manifested itself in a higher population of conformer *B* as compared with the compounds containing n-alkyl groups (*I–III*). In the compounds *VI*, where R^2 = tert-butyl, the further increase in the +I effect of the R^2 substituent did not lead to a further increase in the population of the conformer *B* because this conformer is destabilised by steric interactions.

EXPERIMENTAL

The amino acids were commercial products (Lachema, Brno, and Nutritional Biochemicals Corporation, Ohio). Amino ester hydrochlorides were prepared by esterification of amino acids in an excess of the corresponding alcohol saturated with hydrogen chloride[36]. The thiophosgene was dried and rectified at normal pressure. The fraction, boiling at 73·5–74°C, was stored in glass ampoules (sealed after cooling with dry ice). Prior to the reaction, the content of the ampoule was dissolved in chloroform (10 g of $CSCl_2$ in 100 ml of $CHCl_3$). The isothiocyanates were synthesized in a reactor, equipped with a cooling jacket, a teflon stirrer and an outlet stopcock[37]. The purity of the prepared isothiocyanates was checked, besides elemental analysis, by thin layer chromatography (silica gel with 10% gypsum; ethyl acetate–hexane 1·2 : 8·8). The IR-spectra were measured on UR-20 Zeiss and Unicam SP-100G instruments in tetrachloromethane (spectral grade) at room temperature, using NaCl cells of various thickness. The instruments were calibrated using polystyrene foil, the accuracy being ± 1 cm^{-1} for UR-20 and $\pm 0{\cdot}5$ cm^{-1} for Unicam SP-100G. The bands were separated on a Hewlett-Packard computer.

Alkyl Isothiocyanatocarboxylates

Method A: A solution of the corresponding amino-ester hydrochloride (1 g) in water (10 ml) was mixed with chloroform (10 ml) and a stock solution of thiophosgene (1·05 mol-equivalent) was added under stirring with simultaneous addition of a reagent neutralising the hydrogen chloride, liberated during the reaction ($NaHCO_3$, $CaCO_3$ or 0·01M-NaOH). The addition was carried out at such a rate as to maintain the coloration of the reaction mixture due to an excess of thiophosgene. After the carbon dioxide evolution had ceased, the chloroform layer was separated, washed successively with 0·1M-HCl (2× 10 ml) and water (3× 10 ml), dried over sodium sulphate and taken down at 25°C. The oily residue was distilled under diminished pressure, or, alternatively, the solid compound was crystallized from a suitable solvent.

Method B: To a cooled and stirred suspension of amino ester hydrochloride (1 g) in chloroform (10 ml) a solution of thiophosgene (1·05 mol-equivalent) was added, followed by the dropwise addition of a calculated amount (3 equivalents) of triethylamine in chloroform (10 ml) at −20°C. The mixture was stirred for 15 minutes and then 0·1M-HCl (10 ml) was added. The organic layer was separated and washed several times with water, dried over sodium sulphate, taken down and the residue was distilled under reduced pressure.

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