Synthesis of 2-Isothiocyanatotetrahydropyran and Its Reactions with Amines and Alcohols

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By the reaction of $PO(NCS)_3$ or $(PhO)_2PONCS$ with 2-hydroxytetrahydropyran, 2-isothiocyanatotetrahydropyran was formed in a good yield. This, after addition of amines or alkoxides afforded expected thioureas and thiocarbamates, respectively. After addition of substituted anilines, only monosubstituted arylthioureas were isolated from the reaction mixture. Addition of phenol or 2-naphthol gave corresponding 2-tetrahydropyranylaryl ethers. By using of mesitylnitrile oxide, the obtained thioureas and thiocarbamates were converted into the corresponding ureas and carbamates, respectively.

In our previous papers [1, 2], we have found that $PO(NCS)_3$ substitutes smoothly hemiacetal hydroxyl group of 2,6-dimethyl-4-hydroxy-1,3-dioxane, giving rise to 2,6-dimethyl-4-isothiocyanato-1,3-dioxane with —NCS group in the axial position. We have decided to verify general applicability of this reaction and if there is a possibility to extend the scale of products prepared from hemiacetals (described *e.g.* in Ref. [3]) by the action of $PO(NCS)_3$ also for α-isothiocyanato ethers.

In this paper, the results obtained by the study of substitution of hemiacetal hydroxyl group in 2-hydroxytetrahydropyran by —NCS group, are presented. This compound was chosen also for that it represents a deoxypyranose model for the study of reactivity of hemiacetal hydroxyl group in sugar derivatives. A direct substitution of hemiacetal hydroxyl group by —NCS group in carbohydrates would have a considerable significance because it would represent a relatively simple alternative to the synthesis of glycosyl isothiocyanates which are important precursors of different sugar derivatives [4, 5].

EXPERIMENTAL

Melting points of the prepared compounds were determined on a Kofler hot-stage. IR spectra were measured on a Specord IR 75 instrument. ^{1}H NMR spectra were obtained on a Tesla BS 487A instrument at 80 MHz, ^{13}C NMR spectra on a Tesla BS 567 instrument at 23.15 MHz. The used 2-hydroxytetrahydropyran [6], $PO(NCS)_3$ [7], diphenoxyphosphoryl chloride [8], and mesitylnitrile oxide [9] were prepared according to the described methods. The other used chemicals were commercially available products, purified by distillation before using.

Diphenoxyphosphoryl Isothiocyanate

To a solution of diphenoxyphosphoryl chloride (18.0 g; 67 mmol) [8] in dry acetonitrile (50 cm^3), KSCN (6.12 g; 67 mmol) was added and the reaction mixture was heated under reflux for 5 h. After filtration and evaporation of acetonitrile, the residue was distilled *in vacuo* giving diphenoxyphosphoryl isothiocyanate (17.2 g, yield = 88 %), b.p.(0.2 kPa) = 170—172 °C. For $C_{13}H_{10}NO_3PS$ (M_r = 291.27) w_i(calc.): 53.61 % C, 3.46 % H, 4.81 % N; w_i(found): 53.90 % C, 3.67 % H, 4.97 % N. IR spectrum ($CHCl_3$), $\tilde{\nu}$/cm^{-1}: 1974 ν(NCS). ^{1}H NMR spectrum ($CDCl_3$), δ: 7.37 (s, C_6H_5). ^{13}C NMR spectrum ($CDCl_3$), δ: 120.4, 126.2, 130.1, 146.5, 147.3, 149.6, 149.9.

2-Isothiocyanatotetrahydropyran (*I*)

Method A (by the action of $PO(NCS)_3$)

To a solution of 2-hydroxytetrahydropyran (10.0 g; 18 mmol)[6] in dry ether (20 cm^3), a solution of $PO(NCS)_3$ (7.3 g; 33 mmol) [7] in ether (15 cm^3) was added dropwise at – 40 °C under stirring in the atmosphere of nitrogen. In the course of 2 h, the reaction mixture was left to warm up to room temperature and then it was heated under reflux for 1 h. After evaporation of ether, the resulting oil was extracted with petroleum ether (5 × 30 cm^3). Combined extracts were washed with 10 mass % $NaHCO_3$, dried and the solvent was evaporated. The residue was distilled giving isothiocyanate *I* (10.1 g, yield = 72 %), b.p.(2.67 kPa) = 115—116 °C. For C_6H_9NOS (M_r = 143.21) w_i(calc.): 50.32 % C, 6.34 % H, 9.78 % N; w_i(found): 50.54 % C, 6.49 % H, 9.54 % N. IR spectrum ($CHCl_3$), $\tilde{\nu}$/cm^{-1}: 2060 ν(NCS). ^{1}H NMR

spectrum ($CDCl_3$), δ: 1.71 (m, 6H, CH_2), 3.75 (t, 2H, CH_2—O), 5.25 (t, 1H, O—CH—N). ^{13}C NMR spectrum ($CDCl_3$), δ: 18.5, 25.3, 30.8, 63.6, 83.8, 138.8.

Method B (by the action of $(PhO)_2PONCS$)

Diphenoxyphosphoryl isothiocyanate (5.7 g; 22 mmol) was added dropwise under stirring at room temperature in the atmosphere of nitrogen to 2-hydroxytetrahydropyran (2.0 g; 2 mmol). After 15 h of stirring, distillation of the reaction mixture afforded 1.7 g (63 %) of compound identical at all with the above-described isothiocyanate *I*.

Thioureas *II—V*

To a solution of isothiocyanate *I* (0.75 g; 5 mmol) in dry ether (10 cm^3), a solution of corresponding amine (5 mmol) in dry ether (10 cm^3) was added dropwise under stirring at – 40 °C in the atmosphere of nitrogen. In the course of 2 h, the reaction mixture was left to warm up to room temperature and then it was stirred for additional 2 h. After evaporation of ether, the product was chromatographed on a column of silica gel with ether—petroleum ether (φ_r = 3 : 1) as an eluent. Characteristics of the obtained thioureas *II—V* are given in Table 1, their spectral data are summarized in Table 2.

When isothiocyanate *I* was treated with aromatic amines under the same reaction conditions, only following arylthioureas were obtained after evaporation of ether: phenylthiourea *VI* (from aniline; yield = 83 %), m.p. = 149—151 °C (m.p. = 152 °C [10]); 4-tolylthiourea *VII* (from 4-methylaniline; yield = 80 %), m.p. = 184—185 °C (m.p. = 182 °C [11]), and 4-methoxyphenylthiourea *VIII* (from 4-methoxyaniline; yield = 85 %), m.p. = 211—213 °C (m.p. = 213 °C [12]).

Thiocarbamates *IX* and *X*

A solution of sodium alkoxide prepared by dissolving of sodium (0.11 g; 4.9 mmol) in absolute methanol or ethanol (30 cm^3) was added dropwise under stirring at 0 °C in the atmosphere of nitrogen to a solution of isothiocyanate *I* (0.7 g; 4.9 mmol) in benzene. After 2 h of stirring at room temperature, the solvents were evaporated, the residue was dissolved in water, carefully neutralized with dilute HCl (1 : 1) and extracted with chloroform. Organic layer was dried, solvent evaporated and the product was chromatographed on a column of silica gel using cyclohexane—ether (φ_r = 3 : 1) as an eluent. Characteristics of the prepared thiocarbamates *IX* and *X* are given in Table 1 and their spectral data in Table 2.

Phenylthiocarbamate (*XI*) and 2-Tetrahydropyranylphenyl ether (*XII*)

A solution of sodium alkoxide prepared by dissolving of sodium (0.11 g; 4.9 mmol) in dry methanol (20 cm^3) was added dropwise in the atmosphere of nitrogen to a solution of phenol (0.46 g; 4.9 mmol) in dry benzene (5 cm^3). Then the solvents were evaporated *in vacuo*, the residue was dissolved in benzene (10 cm^3) and added under stirring at 0 °C in the atmosphere of nitrogen to a solution of isothiocyanate *I* (0.70 g; 4.9 mmol) in benzene (15 cm^3). Reaction mixture was worked up as in the case of the above-given experiment and after chromatography, thiourethane *XI* (0.50 g, 43 %) and 2-tetrahydropyranylphenyl ether *XII* (0.46 g, 40 %) were isolated. Their characteristics and spectral data are given in Tables 1 and 2.

2-Tetrahydropyranyl-2-naphthyl ether (*XIII*)

By the reaction of 2-naphthol (0.70 g; 4.9 mmol) with isothiocyanate *I* (0.70 g; 4.9 mmol) using the same procedure as above, β-naphthyl ether *XIII* (0.45 g, 40 %) was isolated. Its characteristics and spectral data are given in Tables 1 and 2.

Ureas *XIV—XVII* and Carbamates *XVIII—XX*

To a solution of corresponding thiourea *III—V* or thiocarbamate *IX—XI* (5 mmol) in dry acetonitrile (20 cm^3), a solution of mesitylnitrile oxide (6 mmol) in acetonitrile (15 cm^3) was added dropwise in the atmosphere of nitrogen. Reaction mixture was stirred for 1 h, acetonitrile was evaporated and the resulting products were purified by crystallization from the ether—hexane mixture or (compounds *XIX* and *XX*) by chromatography on silica gel using hexane—ether (φ_r = 5 : 1) as an eluent. Characteristics and spectral data of the prepared ureas *XIV—XVII* and carbamates *XVIII—XX* are given in Tables 1 and 2.

RESULTS AND DISCUSSION

By the action of $PO(NCS)_3$ on the known 2-hydroxytetrahydropyran [6] in ethereal solution at – 10 °C, 2-isothiocyanatotetrahydropyran *I* was formed smoothly, isolated in 72 % yield as a stable compound having b.p.(2.67 kPa) = 115—116 °C. Further, we have found that hemiacetal hydroxyl group can be substituted not only by using $PO(NCS)_3$ but also *e.g.* by the help of $(PhO)_2PONCS$ because the reaction of this compound with 2-hydroxytetrahydropyran also afforded the same isothiocyanate *I*. The presence of —NCS group in the compound *I* is confirmed in

Table 1. Characterization of the Prepared 2-Tetrahydropyranyl Thioureas, Thiocarbamates, Ureas, and Carbamates

Compound	Formula	M_r	w_i(calc.)/% w_i(found)/%			Yield	M.p.
			C	H	N	%	°C
II	$C_{10}H_{20}N_2OS$	216.35	55.52 55.80	9.32 9.61	12.95 13.15	85	Oil
III	$C_{13}H_{18}N_2OS$	250.37	62.37 62.55	7.25 7.51	11.19 11.43	80	119—122
IV	$C_{10}H_{20}N_2OS$	216.35	55.92 55.81	9.32 9.14	12.95 13.18	89	Oil
V	$C_{11}H_{20}N_2OS$	228.36	57.86 58.04	8.83 8.97	12.27 12.46	91	140—143
IX	$C_7H_{13}NO_2S$	175.26	49.97 50.19	7.48 7.73	7.99 8.21	85	Oil
X	$C_8H_{15}NO_2S$	189.28	50.76 50.98	7.99 8.14	7.40 7.68	90	Oil
XI	$C_{12}H_{15}NO_2S$	237.33	60.73 60.96	6.37 6.64	5.90 6.08	43	Oil
XII	$C_{11}H_{14}O_2$	178.23	74.13 74.38	7.92 8.14	–	40	Oil
XIII	$C_{15}H_{16}O_2$	228.29	78.92 79.17	7.06 7.32	–	40	Oil
XIV	$C_{10}H_{20}N_2O_2$	200.29	59.97 60.19	10.07 10.33	13.99 14.12	90	65—68
XV	$C_{13}H_{18}N_2O_2$	234.30	66.64 66.87	7.74 7.95	11.96 12.08	93	115—118
XVI	$C_{10}H_{20}N_2O_2$	200.29	59.97 60.16	10.07 10.25	13.99 13.74	91	92—93
XVII	$C_{11}H_{20}N_2O_2$	212.30	62.23 62.51	9.50 9.78	13.20 13.48	93	143—145
XVIII	$C_7H_{13}NO_2$	159.20	52.82 53.01	8.80 9.04	8.23 8.49	92	82—84
XIX	$C_8H_{15}NO_3$	173.22	55.47 55.69	8.73 8.96	8.09 8.34	94	Oil
XX	$C_{12}H_{15}NO_3$	221.26	65.14 65.39	6.83 6.97	6.33 6.49	75	Oil

particular by the IR spectra where the characteristic band of stretching vibrations of this group at $\tilde{\nu}$ = 2060 cm^{-1} is observed and by the ^{13}C NMR spectra where the signal of carbon atom of —NCS group is registered at δ = 138.8. The other signals in the ^1H and ^{13}C NMR spectra are in full accordance with the structure of 2-isothiocyanatotetrahydropyran *I*.

It is generally known that amines and alcohols easily enter into addition reactions with isothiocyanates under formation of thioureas or thiocarbamates. These compounds, as well as their oxygen analogues, *i.e.* ureas or carbamates are interesting because they exhibit different biological activity [13, 14]. In the reactions of 2-isothiocyanatotetrahydropyran, it can be expected that —NCS group can also behave like pseudohalide, that means it can also enter into substitution or elimination reactions, similarly like 2-halotetrahydropyrans [15, 16]. Therefore, we have decided to examine reactivity of 2-isothiocyanatotetrahydropyran with amines and alcohols, respectively, with the aim to find out if this isothiocyanate is suitable as a starting compound for the preparation of new thioureas and thiocarbamates, respectively and subsequently ureas and carbamates, too.

As expected, by the reaction of aliphatic primary as well as secondary amines, corresponding thioureas *II*—*V* were formed smoothly (Scheme 1). Their structure was confirmed unambiguously by elemental analysis and ^1H and ^{13}C NMR spectra. On the other hand, after reaction with aromatic amines, only monosubstituted arylthioureas *VI*—*VIII* were isolated from the reaction mixture.

We assume that in both cases, addition to isothiocyanate *I* takes place but in the case of aromatic amines, the formed thioureas are so labile that *N*-arylthiourea is split off from tetrahydropyran ring even under room temperature.

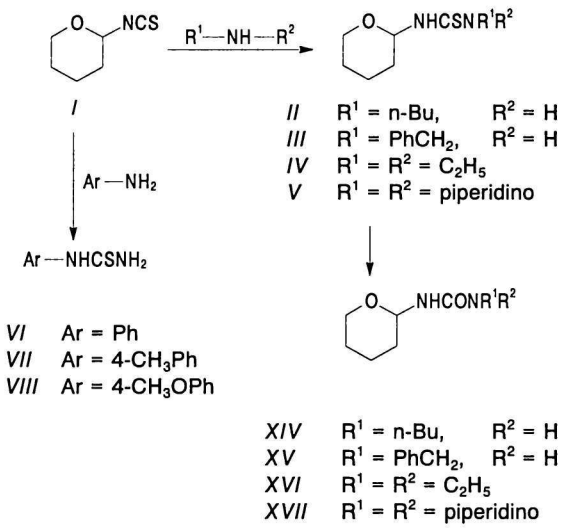
Isothiocyanate *I* reacted in a different way also with aliphatic and aromatic alkoxides (Scheme 2). With alcohol itself, *e.g.* with methanol, isothiocyanate *I* did not react even after 2 h of boiling. However, sodium methoxide (likewise sodium ethoxide) reacted with isothiocyanate *I* smoothly under formation of thiocarbamates *IX* and *X*. Structure of thiocarbamates *IX* and *X* was confirmed unambiguously by ^1H and ^{13}C NMR spectra.

Table 2. NMR Spectral Data and IR Carbonyl Vibrations of 2-Tetrahydropyranyl Ureas, Carbamates, Thioureas, and Thiocarbamates

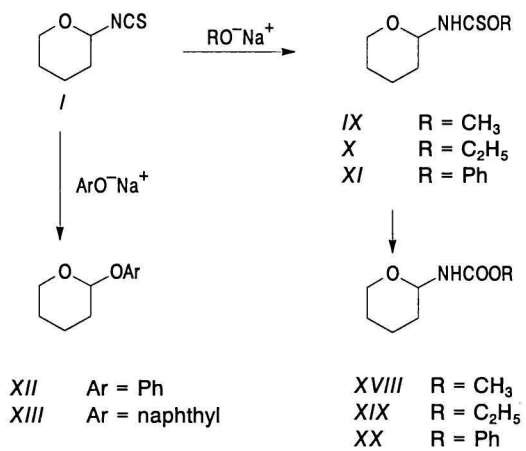
Compound	δ		IR, $\tilde{\nu}$/cm^{-1}
	^{1}H NMR	^{13}C NMR	ν(C=O)
II	0.93 (t, 3H, CH_3), 1.23—2.13 (m, 10H, CH_2), 3.63 (q, 2H, CH_2N), 3.96 (t, 2H, CH_2O), 5.10 (t, 1H, NCHO), 7.02 (m, 2H, NH)	13.8, 20.1, 20.5, 25.0, 29.8, 31.13, 45.0, 63.9, 81.3, 183.2	–
III	1.3—2.05 (m, 6H, CH_2), 3.85 (t, 2H, CH_2O), 4.88 (d, 2H, CH_2Ph), 5.07 (t, 1H, OCHN), 6.90 (bs, 1H, NH), 7.42 (bs, 6H, Ph + NH)	20.3, 24.9, 29.7, 49.2, 63.7, 81.0, 127.6, 128.6, 137.6, 183.7	–
IV	1.20 (t, 3H, CH_3), 1.38—2.13 (m, 6H, CH_2), 3.68 (q, 2H, NCH_2), 3.93 (t, 2H, OCH_2), 5.73 (t, 1H, OCHN), 6.18 (d, 1H, NH)	12.6, 23.1, 25.2, 31.6, 45.3, 67.5, 84.0, 179.7	–
V	1.13—2.13 (m, 12H, CH_2), 3.48—4.23 (m, 4H, NCH_2, OCH_2), 5.80 (t, 1H, OCHN), 6.15 (d, 1H, NH)	22.6, 23.1, 24.2, 25.5, 31.7, 49.2, 67.6, 84.1, 180.7	–
IX	1.13—2.18 (m, 6H, CH_2), 4.08 (s, 3H, OCH_3), 4.18 (t, 2H, OCH_2), 5.50 (t, 1H, OCHN), 6.82 (m, 1H, NH)	22.7, 25.4, 30.1, 57.1, 67.5, 83.2, 191.5	–
X	1.3 (t, 3H, CH_3), 1.46—2.25 (m, 6H, CH_2), 4.05 (t, 2H, OCH_2), 4.58 (q, 2H, OCH_2CH_3), 5.53 (t, 1H, OCHN), 6.58—7.05 (m, 1H, NH)	14.1, 22.6, 25.0, 31.0, 66.4, 67.4, 82.9, 190.6	–
XI	1.35—2.28 (m, 6H, CH_2), 4.09 (t, 2H, OCH_2), 5.55 (t, 1H, OCHN), 6.88—7.5 (m, 5H, Ph)	22.6, 25.0, 30.1, 67.5, 83.1, 115.4, 120.6, 129.6, 155.8, 191.6	–
XII	1.45—2.15 (m, 6H, CH_2), 3.63 (t, 2H, OCH_2), 5.54 (t, 1H, OCHO), 7.05—7.45 (m, 5H, Ph)	18.9, 25.3, 30.5, 62.2, 96.5, 116.6, 121.7, 129.4, 157.2	–
XIII	1.55—2.25 (m, 6H, CH_2), 3.85 (t, 2H, OCH_2), 5.69 (t, 1H, OCHO), 7.28—8.00 (m, 7H, naphthyl)	18.8, 25.3, 30.5, 62.0, 96.5, 110.6, 119.2, 123.8, 126.2, 127.1, 127.6, 129.2, 129.5, 134.6, 154.9	–
XIV	0.95 (t, 3H, CH_3), 1.28—2.13 (m, 10H, CH_2), 3.26 (q, 2H, CH_2N), 3.73 (t, 2H, OCH_2), 5.0 (t, 1H, OCHN), 5.6 (t, 1H, NH), 5.94 (d, 1H, NH)	13.9, 20.1, 22.5, 25.3, 31.2, 32.2, 39.9, 65.7, 79.6, 158.3	1675
XV	1.05—2.0 (m, 6H, CH_2), 3.84 (t, 2H, OCH_2), 4.35 (d, 2H, $PhCH_2$), 4.85 (t, 1H, OCHN), 5.58 (d, 1H, NH), 7.26 (s, 5H, Ph)	22.1, 25.2, 31.0, 44.1, 65.5, 79.7, 127.1, 127.4, 128.5, 139.5, 158.0	1667
XVI	1.15 (t, 3H, CH_3), 1.38—2.10 (m, 6H, CH_2), 3.35 (q, 2H, NCH_2), 4.03 (t, 2H, OCH_2), 5.13 (m, 2H, OCHN + NH)	13.8, 23.4, 25.3, 32.1, 41.2, 67.3, 79.8, 155.9	1650
XVII	1.28—2.08 (m, 12H, CH_2), 3.39 (t, 4H, 2 × NCH_2), 4.03 (t, 2H, OCH_2), 5.18 (m, 2H, OCHN + NH)	23.4, 24.4, 25.3, 25.6, 32.0, 44.8, 67.3, 79.9, 156.1	1650
XVIII	1.20—2.13 (m, 6H, CH_2), 3.80 (s, 3H, OCH_3), 4.03 (t, 2H, OCH_2), 4.95 (t, 1H, OCHN), 5.35—5.68 (m, 1H, NH)	22.8, 25.1, 31.5, 52.3, 67.0, 80.0, 156.0	1720
XIX	1.23 (t, 3H, CH_3), 1.43—2.20 (m, 6H, CH_2), 3.75 (t, 2H, OCH_2), 4.28 (q, 2H, OCH_2CH_3), 5.10 (t, 1H, OCHN), 5.35—5.75 (m, 1H, NH)	14.6, 23.0, 25.1, 31.5, 61.1, 67.0, 80.1, 155.7	1725
XX	1.13—2.20 (m, 6H, CH_2), 3.93—4.25 (m, 2H, OCH_2), 5.00 (t, 1H, OCHN), 6.83—7.63 (m, 5H, Ph)	22.7, 24.9, 31.2, 66.8, 80.0, 115.3, 119.8, 129.3, 156.2, 156.4	1730

Unlike the aliphatic alkoxides, after reaction with sodium phenoxide, a mixture of two compounds (according to the NMR spectra, in the ratio of $x_r \approx 1:1$) was obtained which were separated using chromatography on a column of silica gel. Based on the data of elemental analysis, ^{1}H and ^{13}C NMR spectra, one of the isolated compounds had a structure of expected phenylthiocarbamate *XI*. The ^{1}H and ^{13}C NMR spectra of the second compound were in accordance with the structure of phenyl ether *XII*. This structure was confirmed by the independent synthesis because after an addition of phenol to dihydropyran according to the described method [17], we have obtained a compound in all characteristics identical with compound *XII*. After addition of sodium 2-naphthoxide to isothiocyanate *I*, no thiocarbamate was isolated from the reaction mixture but only β-naphthyl ether *XIII*.

The prepared thioureas *II*—*V* as well as thiocarbamates *IX*—*XI* were transformed to the corresponding oxygen derivatives, *i.e.* ureas *XIV*—*XVII* and carbamates *XVIII*—*XX*, respectively. This replacement of sulfur atom by the atom of oxygen can be accomplished under very mild reaction conditions by the action of mesitylnitrile oxide in the solution of acetonitrile [18, 19] when the intermediary cycloadduct to



Scheme 1



Scheme 2

the C=S bond decomposes to the corresponding oxygen derivative and mesitylisothiocyanate already at laboratory temperature. The replacement of sulfur atom by the atom of oxygen is unambiguously confirmed by the presence of C=O group in the IR as well as ^{13}C NMR spectra of compounds *VI* and *VII*.

From the obtained results it is evident that $PO(NCS)_3$ or $(PhO)_2PONCS$ represent easily available agents by the help of which hemiacetal hydroxyl at tetrahydropyran ring can be smoothly substituted by the —NCS group. Synthesized isothiocyanate *I* willingly enters into usual addition reactions when it reacts with aliphatic amines and alkoxides, respectively. The products of side reactions are formed by the reactions with aromatic amines and phenoxides, respectively.

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