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SYNTHESIS OF THIOCYANATE AND ISOTHIOCYANATE SUBSTITUTED CARBONATES AND CARBAMATES

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Abstract : Reactions of alkyl 1-chloroethyl carbonates 1 and 1-chloroethyl N,N-dialkyl carbamates 2 with MSCN (M = K, NH_4) in acetone or in protic solvents (MeOH, $HCONH_2$) afforded the corresponding thio- and/or isothiocyano derivatives in good yields.

The origin of the N-bonded compounds is discussed and it is concluded that most of these compounds must be due to a N condensation of the thiocyanate anion.

During this work, we also found a new very mild method for isomerizing in good yields alkyl 1-thiocyanoethyl carbonates and 1-thiocyanoethyl N,N-dialkyl carbamates to their corresponding isothiocyano derivatives.

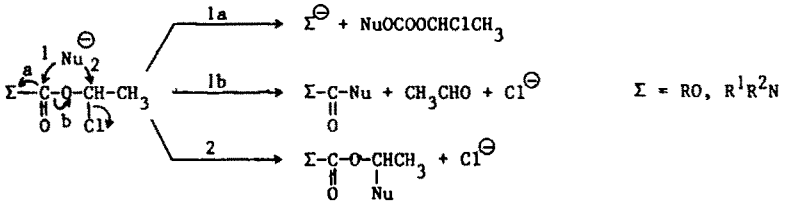
Carbonates and carbamates are widespread compounds in phytosanitary chemistry.[1] The synthesis of such functionalized compounds is currently under active investigation.[2a,b] On the other hand thiocyanates as well as isothiocyanates are also interesting for the same kind of applications.[1,3] Thus it was thought that carbonates or carbamates substituted by a thiocyanate (or an isothiocyanate group) could have interesting phytosanitary properties.

As such, alkyl 1-chloroethyl carbonates 1 and 1-chloroethyl N,N-dialkyl carbamates 2, easily obtained from the corresponding chloroformates[4,5], could be good starting materials by replacement of the chlorine atom by a nucleophile.

$ROCOOCHClCH_3$ — 1

$R^1R^2NCOOCHClCH_3$ — 2

Besides their potential applications, these substrates pose an interesting reactivity problem since they may be attacked by nucleophiles following three different pathways as shown in Scheme 1.



Scheme 1

Moreover, substitutions following path 2 may take place, of course, following an SN_2 mechanism. However the oxygen bonded to the halogenated centre may favour SN_1 or cation-like transition state mechanism by resonance stabilization of the positive charge. Thus two kinds of completely different experimental conditions are expected to give the desired substitutions. We shall see that this was completely confirmed. A short note was previously published on the condensation of MSCN on 1 and 2.[6]

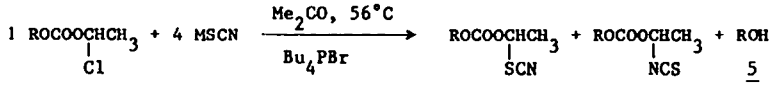
In the present publication, we report the generalization of these first results as well as full details concerning these substitution condensations.

CONDENSATIONS OF ALKALI THIOCYANATES MSCN ON ALKYL 1-CHLOROETHYL CARBONATES 1

We have carefully studied the behavior of alkyl 1-chloroethyl carbonates 1 under aprotic conditions. A number of unreported exploratory experiments rapidly showed us that among aprotic solvents, acetone was the most convenient.

We have gathered in Table I the main results obtained in this solvent in the presence or absence of tetrabutylphosphonium bromide.

Table I : Reactions of alkyl 1-chloroethyl carbonates with MSCN in refluxing acetone



1 a-i 3 a-h 4 a-g

Run	R	M	Bu_4PBr (eq.)	Time (h)	(3+4) %	3[a] %	4[a] %	3/4	5[a] %
1	C_2H_5 (1a)	K	-	19.5	82	74 (3a)	26 (4a)	2.8	-
2	C_2H_5 (1a)	NH_4	-	20	80	75 (3a)	25 (4a)	3	-
3	C_2H_5 (1a)	K	0.2	15	81	62 (3a)	38 (4a)	1.6	-
4	C_2H_5 (1a)	NH_4	0.2	10	82	83 (3a)	17 (4a)	4.9	-
5	tC_4H_9 (1b)	K	-	11.75	86	31 (3b)	69 (4b)	0.4	-
6	tC_4H_9 (1b)	NH_4	-	7.5	86	53 (3b)	47 (4b)	1.1	-
7	tC_4H_9 (1b)	K	0.2	9.5	85	40 (3b)	60 (4b)	0.7	-
8	tC_4H_9 (1b)	NH_4	0.2	4	80	80 (3b)	20 (4b)	4	-
9	nC_8H_{17} (1c)	K	-	35	80	55 (3c)	45 (4c)	1.2	10
10	nC_8H_{17} (1c)	NH_4	-	35	78	67 (3c)	33 (4c)	1.9	12
11	nC_8H_{17} (1c)	K	0.2	25.5	81	65 (3c)	35 (4c)	1.9	11
12	nC_8H_{17} (1c)	NH_4	0.2	4	80	80 (3c)	20 (4c)	4	9
13	$C_6H_5CH_2$ (1d)	K	0.2	26	51	82 (3d)	18 (4d)	4.5	13
14	$C_6H_5CH_2$ (1d)	NH_4	0.2	18.5	60	100 (3d)	0	∞	18
15	 (1e)	K	0.2	24	60	67 (3e)	33 (4e)	2	-
16	 (1e)	NH_4	0.2	15	80	78 (3e)	22 (4e)	3.5	-
17	iC_3H_7 (1f)	NH_4	0.2	19	81	55 (3f)	45 (4f)	1.2	-
18	cC_6H_{11} (1g)	NH_4	0.2	14	80	75 (3g)	25 (4g)	3	-
19	$C_2H_5(OCH_2CH_2)_2$ (1h)	NH_4	0.2	28	60	100 (3h)	0	∞	-
20	C_6H_5 (1i)	NH_4	0.2	168	0	0	0	-	75

[a]Yield of isolated products by flash chromatography on a silica column

Comparisons of runs 1 to 16 led us to the following conclusions :

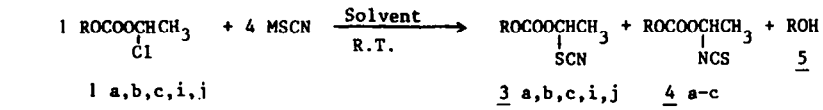
- $Bu_4P^{\oplus}Br^{\ominus}$ increases the reaction rates and favours the formation of thiocyanates 3
- The main side reaction is the nucleophilic attack of the carbonyl group (reaction 1a see Scheme 1)
- Interestingly, NH_4SCN was soluble in acetone whereas the phosphonium catalyst was only slightly soluble. So it seems that the activation observed could be due to a reaction taking place at the surface of the catalyst.

With these results, we then studied the same reaction in protic solvents. Exploratory experiments led us to study methanol and formamide.

Unreported results showed that $Bu_4P^{\oplus}Br^{\ominus}$ which was completely soluble under these conditions was of no interest here.

In Table II are reported the main results obtained.

Table II : Reactions of alkyl 1-chloroethyl carbonates with MSCN in protic solvents at room temperature



Run	R	M	Solvent	Time (h)	(3+4) %	3[a] %	4[a] %	3/4	5[a] %
21	C_2H_5 (1a)	K	MeOH	23	58	100 (3a)	0	∞	-
22	C_2H_5 (1a)	NH_4	MeOH	73	78	100 (3a)	0	∞	-
23	C_2H_5 (1a)	K	$HCONH_2$	4	76	83 (3a)	17 (4a)	4.9	-
24	C_2H_5 (1a)	NH_4	$HCONH_2$	4.75	86	85 (3a)	15 (4a)	5.7	-
25	tC_4H_9 (1b)	K	MeOH	5	82	81 (3b)	19 (4b)	4.3	-
26	tC_4H_9 (1b)	NH_4	MeOH	12	80	88 (3b)	12 (4b)	7.3	-
27	tC_4H_9 (1b)	K	$HCONH_2$	12	82	81 (3b)	19 (4b)	4.3	-
28	tC_4H_9 (1b)	NH_4	$HCONH_2$	17	89	79 (3b)	21 (4b)	3.8	-
29	nC_8H_{17} (1c)	K	MeOH	73	70	93 (3c)	7 (4c)	13.31	-
30	nC_8H_{17} (1c)	NH_4	MeOH	27	64	100 (3c)	0	∞	22
31	nC_8H_{17} (1c)	K	$HCONH_2$	168	62	65 (3c)	35 (4c)	1.9	23
32	nC_8H_{17} (1c)	NH_4	$HCONH_2$	72	85	59 (3c)	41 (4c)	1.4	-
33	C_6H_5 (1i)	NH_4	$HCONH_2$	72	51	100 (3i)	0	∞	35
34	4-ClC_6H_4 (1j)	NH_4	$HCONH_2$	20	44[b]	100 (3j)	0	∞	c

[a] Yield of isolated product by flash chromatography on a silica column

[b] Reaction performed at 50°C

[c] 4-Chlorophenol in undetermined amount.

Clearly it appears that ammonium thiocyanate in formamide constitutes the best experimental conditions, leading with one exception (run 32) to a better selectivity towards 3 than in aprotic solvents. The side reaction due to the nucleophilic attack on the carbonyl group also took place with some carbonates. However formamide has the advantage over acetone that it allows the formation of thiocyanates 3 from phenyl and 4-chlorophenyl 1-chloroethyl carbonates (runs 33, 34).

A study of the behavior of carbonates 1 under solvolytic conditions in methanol showed that these compounds were totally decomposed after 48 hours at room temperature.

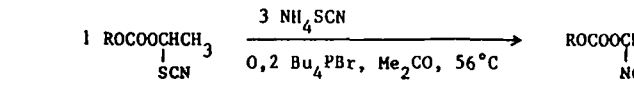
The comparison of the results obtained in methanol and formamide are shown in Table II and led us to favour a cation-like transition state SN_2 mechanism rather than an SN_1 process.

Finally it appears, from the literature data, that $SCN^{\ominus}$ is an ambident anion with a high propensity to condense on a sulfur atom to give thiocyanate derivatives.[7a,b,c] Moreover it is also well known that thiocyanates may isomerize to isothiocyanates under rather drastic conditions.[8a,b]

These results led us to study the stability of thiocyanates 3 under our experimental conditions, in order to determine the origin of isothiocyanates 4.

The results obtained in acetone are given in Table III.

Table III : Stability of carbonates 3 under their preparation conditions in refluxing acetone



3 a-i 4 a,b,c,e,f,g,h

Run	R	Time (h)	4[a] %	Unreacted 3 %
35	C_2H_5 (3a)	53	12 (4a)	40
36	iC_3H_7 (3f)	96	27 (4f)	20
37	tC_4H_9 (3b)	26	41 (4b)	0
38	cC_6H_{11} (3g)	39	44 (4g)	26
39	nC_8H_{17} (3c)	48	20 (4c)[b]	50
40	nC_8H_{17} (3c)	49	29 (4c)	52
41	$C_2H_5(OCH_2CH_2)_2$ (3h)	77	13 (4h)	15
42	 (3e)	55	35 (4e)	52
43	C_6H_5 (3i)	108	0[c]	0
44	$C_6H_5CH_2$ (3d)	38	0[d]	0

[a]Yield of isolated products by flash chromatography on a silica column
[b]Reaction performed without Bu_4PBr
[c]Presence of 53 % of phenol isolated by flash chromatography on a silica column
[d]Presence of 59 % of benzyl alcohol isolated by flash chromatography on a silica column.

It appears that with few exceptions isothiocyanates are formed in rather low yields. Moreover, the reaction times needed to perform these transformations are much longer than the reaction times reported in Table I. Finally significant decompositions were observed.

From these results we concluded that most isothiocyanates 4 must be due to a N condensation of the thiocyanate anion.

The same experiments when performed in protic solvents (MeOH or $HCONH_2$) did not lead to the formation of isothiocyanates 4 but rather gave large amounts of decomposition products. Thus it appears that isothiocyanates 4 are due only to N condensation of thiocyanate anions.

Moreover a specific solvation of $SCN^{\ominus}$ on nitrogen, which is the hardest basic site of the anion accounts for the highest selectivity observed in the formation of thiocyanates 3.

CONDENSATION OF ALKALI THIOCYANATES ON 1-CHLOROETHYL N,N-DIALKYL CARBAMATES 2

The results obtained in acetone as well as in protic solvents are reported in Table IV.

Condensations on carbamates were, like condensations on carbonates, catalyzed by Bu_4PBr in acetone. It appears that in this solvent, potassium thiocyanate strongly favoured the formation of isothiocyanates 7 which in a number of cases were the only product formed.

In protic solvents the reaction are much faster and the formation of thiocyanates 6 was favoured. Study of the behaviour of carbamates 2 under solvolytic conditions in MeOH showed decomposition of these compounds.

We also concluded that an SN_2 reaction with high cationic transition state character must take place instead of SN_1 reaction during the thiocyanate condensation.

Table IV : Reactions of 1-chloroethyl N,N-dialkyl carbamates with MSCN in acetone or in protic solvents at room temperature

2 a,b 6 a,b 7 a,b

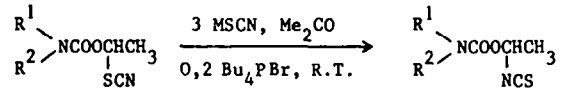
Run	R^1	R^2	M	Bu_4PBr (eq)	Solvent	Time (h)	(6+7) %	6[a] %	7[a] %	6/7
45	C_2H_5	C_2H_5 (2a)	K	-	Me_2CO	8.5	75	0	100(7a)	0
46	C_2H_5	C_2H_5 (2a)	NH_4	-	Me_2CO	7.5	68	78(6a)	22(7a)	3.5
47	C_2H_5	C_2H_5 (2a)	K	0.2	Me_2CO	5.5	74	7(6a)	93(7a)	0.08
48	C_2H_5	C_2H_5 (2a)	NH_4	0.2	Me_2CO	3.75	87	67(6a)	33(7a)	2
49	$-(CH_2)_5-$	(2b)	K	-	Me_2CO	24	79	0	100(7b)	0
50	$-(CH_2)_5-$	(2b)	NH_4	-	Me_2CO	27	35	71(6b)	29(7b)	2.4
51	$-(CH_2)_5-$	(2b)	K	0.2	Me_2CO	25	85	0	100(7b)	0
52	$-(CH_2)_5-$	(2b)	NH_4	0.2	Me_2CO	18	73	38(6b)	62(7b)	0.6
53	C_2H_5	C_2H_5 (2a)	K	-	MeOH	b	72	79(6a)	21(7a)	3.8
54	C_2H_5	C_2H_5 (2a)	NH_4	-	MeOH	b	64	63(6a)	37(7a)	1.7
55	C_2H_5	C_2H_5 (2a)	K	-	$HCONH_2$	b	67	67(6a)	33(7a)	2
56	C_2H_5	C_2H_5 (2a)	NH_4	-	$HCONH_2$	b	71	54(6a)	46(7a)	1.1
57	$-(CH_2)_5-$	(2b)	K	-	MeOH	b	66	59(6b)	41(7b)	2.2
58	$-(CH_2)_5-$	(2b)	NH_4	-	MeOH	b	66	82(6b)	18(7b)	4.5
59	$-(CH_2)_5-$	(2b)	K	-	$HCONH_2$	b	36	39(6b)	61(7b)	0.6
60	$-(CH_2)_5-$	(2b)	NH_4	-	$HCONH_2$	b	64	44(6b)	56(7b)	0.8

[a]Yield of isolated product by flash chromatography on a silica column
[b]Instantaneous reaction.

Finally we studied the stability of thiocyanates 6 under our reaction conditions.

The results obtained in acetone are summarized in Table V.

Table V : Stability of 1-thiocyanoethyl N,N-dialkyl carbamates 6a,b under their preparation conditions in acetone



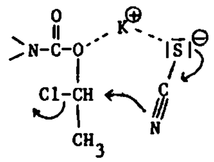
6 a,b 7 a,b

Run	R^1	R^2	M	Time (h)	7[a] %
61	C_2H_5	C_2H_5 (6a)	K	42	44 (7a)
62	C_2H_5	C_2H_5 (6a)	NH_4	72	70 (7a)
63	$-(CH_2)_5-$	(6b)	K	33	48 (7b)
64	$-(CH_2)_5-$	(6b)	NH_4	70	75 (7b)

[a]Yield of isolated product by flash chromatography on a silica column.

It may be seen that isomerization takes place with potassium as well as ammonium thiocyanates. However the isomerization was much slower than the condensation of the alkaline thiocyanates. Thus we concluded that a large amount of isothiocyanates were formed by N condensations.

The very high selectivity observed with potassium thiocyanate could be explained by the cyclic transition state shown :



In protic solvents we never observed the isomerization of thiocyanates 6 to isothiocayanates 7, but decomposition. . Thus the formation of isothiocyanates 7 during the condensations must be due to N-condensations. The specific solvation of nitrogen must also be responsible for the S-condensation selectivity observed with both potassium as well as ammonium thiocyanates.

A VERY MILD THIOCYANATES - ISOTHIOCYANATES ISOMERIZATION

The reactions described above allow the easy preparation of thiocyanates Σ-C(=O)-O-CH(SCN)CH$_3$ with Σ = RO, R^1R^2N.

However, with a few exceptions, the corresponding isothiocyanates cannot be synthesized in this way. Among the few methods given in the literature to isomerize thiocyanates to isothiocyanates, the only one successfully used with some of our substrates was heating at 160°C in decalin in the presence of $ZnCl_2$. The results thus obtained are given in Table VI.

Table VI : Isomerization of thiocyanates 3 to isothiocyanates 4 according to a literature procedure

ROCOOCH(SCN)CH$_3$ —(Decalin , 160°C; $ZnCl_2$ 0.1 eq.)→ ROCOOCH(NCS)CH$_3$

3 a,f,c,d, → 4 a,f,c

Run	R	Time (h)	4[a] %
65	C_2H_5 (3a)	2	78 (4a)
66	iC_3H_7 (3f)	0.5	80 (4f)
67	nC_8H_{17} (3c)	2	66 (4c)
68	$C_6H_5CH_2$ (3d)	0.35	0

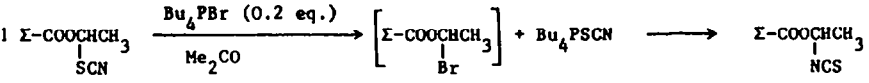
[a]Yield of isolated product by flash chromatography on a silica column.

However these drastic experimental conditions cannot be used with sensitive thiocyanates. For example benzyl 1-thiocyanoethyl carbonate was completely destroyed and isomerization was never observed.

During the study of the stability of thiocyanates 3 and 6 under their formation conditions we surprisingly found that in acetone, in the presence of Bu_4PBr but in the absence of alkali thiocyanates, thiocyanates 3 and 6 were readily transformed under mild conditions to the corresponding isothiocyanates 4 and 7 respectively. The results thus obtained are gathered in Table VII.

Even sensitive substrates were isomerized in fair yield. Interestingly, the isomerization also took place in the presence of Et_4NBr although this catalyst was a little less efficient. On the contrary no isomerization we observed in the presence of Et_4NPF_6. So it appears that the bromide anion is needed for the isomerization to take place. On the other hand it is well known that substrates such as Σ-COOCH(Br)CH$_3$ (Σ = RO, R^1R^2N) are extremely reactive reagents.[9]

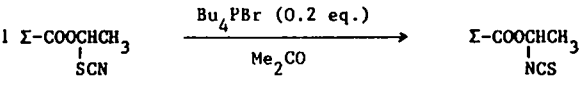
Taking into account these data, we propose the two step mechanism given in Scheme 2 to observed isomerization



Scheme 2

Concerning the N condensation selectivity observed during the second step, there is no obvious simple explanation. However, it could be suggested that replacing chlorine atom by bromine atom would lead to a more marked cationic like transition state . Thus according to the HSAB theory[10a,b,c] the substrate would be attacked by the hardest side of thiocyanate anion, that is to say the nitrogen atom.

Table VII : Isomerization of compounds 3 and 6 to their corresponding N-bonded derivatives in acetone in presence of Bu_4PBr



3 a-i or 6 a,b — 4 a-i or 7 a,b

Run	Σ	T°C	Time (h)	4 or 7[a] %
69	C_2H_5O (3a)	56	72	81 (4a)
70	iC_3H_7O (3i)	56	17	85 (4i)
71	$cC_6H_{11}O$ (3g)	56	24	82 (4g)
72	tC_4H_9O (3b)	56	13	81 (4b)
73	$nC_8H_{17}O$ (3c)	56	48	82 (4c)
74	$C_2H_5(OCH_2CH_2)_2O$ (3h)	56	26	45 (4h)
75	 (3e)	56	38	81 (4e)
76	C_6H_5O (3i)	56	99	42[b] (4i)
77	$C_6H_5CH_2O$ (3d)	56	26	56 (4d)
78	$(C_2H_5)_2N$ (6a)	25	96	80 (7a)
79	 (6b)	25	80	78 (7b)

[a]Yield of isolated product by flash chromatography on a silica column

[b]Presence of 15 % of unreacted starting material.

CONCLUSION

The present work describes the easy preparations of derivatives containing both carbonates or carbamates and thiocyanates or isothiocyanates groups which could present an interest in phytosanitary chemistry. A number of the compounds thus prepared are under investigation in this way.

EXPERIMENTAL

IR spectra were measured as films unless otherwise stated on a Perkin Elmer 580 B instrument. ^1H NMR spectra were recorded with TMS as an internal standard in CCl_4 at 60 MHz on a Perkin Elmer R 12 B spectrometer or at 80 MHz on a Bruker AW 80 spectrometer. The chemical shifts are given in ppm. Mass spectra were recorded with a Nermag-Sidar V 30 spectrometer at 70 eV. GLC was carried out on a Carlo Erba GI 452 gas chromatograph with a FID detector (3 m 10 % SE_{30} column or 1 m 10 % OV_{101} glass column). TLC was performed on a Merck Kieselgel 60 F_{254} (eluent : petroleum ether/ethyl acetate 85/15). Flash chromatography[11] was carried out on a silica column packed with Merck Kieselgel (230-400 mesh) (eluent : petroleum ether/ethyl acetate 92-70/8-30).

Solvents were distilled in the presence of appropriate drying reagents before use. MSCN (M = K, NH_4), Bu_4PBr and $ZnCl_2$ were dried under vacuo at 100°C one night before use.

All the starting materials 1a-j, and 2a,b were prepared according to the literature procedures.[4,5,12] The products 1e, 1h, 1j are unknown.

Allyl 1-chloroethylcarbonate 1e :
1e was obtained with 85 % yield. BP_2 : 54-55°C ; IR (cm^{-1}) 3100, 1770, 1655
^1H NMR : 1.8 d (3 H, J = 6 Hz) ; 4.65 d (2 H, J = 5.3 Hz) ; 5.14-5.6 m (2 H) ; 5.77-6.65 m (2 H with q 6.45, J = 6 Hz)
Anal. Calc. for $C_6H_9ClO_3$: C 43.79 ; H 5.51 ; Cl 21.54. Found : C 43.77 ; H 5.44 ; Cl 21.64.

2-(2-Ethoxyethoxy)ethyl 1-chloroethylcarbonate 1h :
1h was obtained with 82 % yield. BP_4 : 128°C ; IR (cm^{-1}) 1765
^1H NMR : 1.14 t (3 H, J = 6.3 Hz) ; 1.8 d (3 H, J = 6 Hz) ; 3.26-3.88 m (8 H) ; 4.17-4.48 m (2 H) ; 6.4 q (1 H, J = 6 Hz)
Anal. Calc. for $C_9H_{17}ClO_5$: C 44.91 ; H 7.12 ; Cl 14.73. Found : C 44.83 ; H 7.28 ; Cl 14.93.

4-Chlorophenyl 1-chloroethylcarbonate 1j :
1j was obtained with 77 % yield. BP_3 : 129-130°C ; MP : 53°C ; IR (KBr, cm^{-1}) 1790
^1H NMR : 1.84 d (3 H, J = 6 Hz) ; 6.4 q (1 H, J = 6 Hz) ; 7-7.5 m (4 H)
Anal. Calc. for $C_9H_8Cl_2O_3$: C 45.99 ; H 3.43 ; Cl 30.16. Found : C 46.20 ; H 3.19 ; Cl 29.99.

1. Reactions of 1a-i with MSCN in refluxing acetone. Synthesis of alkyl 1-thiocyanoethylcarbonates 3a-h and alkyl 1-isothiocyanoethylcarbonates 4a-g (Table I) - Compounds 1a-i (10 mmoles) diluted in 10 ml of acetone were added to a magnetically stirred mixture of MSCN (40 mmoles M = K, 3.88 g ; M = NH_4, 3.04 g) with Bu_4PBr (2 mmoles, 0.67 g) in refluxing acetone (20 ml). Some reactions were also performed without Bu_4PBr (see Table I). After completion of the reactions (monitored by GLC), the reaction mixture was allowed to cool to room temperature and water was added. The organic layer was extracted with Et_2O and the extracts were washed (water) dried (anhyd. $MgSO_4$) and concentrated under reduced pressure. Flash chromatography of the crude product (eluent : petroleum ether/ethyl acetate 92-70/8-30) gave pure 3a-h and 4a-g.

Ethyl 1-thiocyanoethylcarbonate 3a :
IR (cm^{-1}) 2170, 1760
^1H NMR : 1.42 t (3 H, J = 6.7 Hz) ; 1.88 d (3 H, J = 6 Hz) ; 4.29 q (2 H, J = 6.7 Hz) ; 6.00 q (1 H, J = 6 Hz)
Anal. Calc. for $C_6H_9NO_3S$: C 41.13 ; H 5.17 ; N 7.99 ; S 18.30. Found : C 40.97 ; H 5.29 ; N 7.79 ; S 18.40.

Ethyl 1-isothiocyanoethylcarbonate 4a :
IR (cm^{-1}) 2050, 1760
^1H NMR : 1.40 t (3 H, J = 6.7 Hz) ; 1.58 d (3 H, J = 6 Hz) ; 4.24 q (2 H, J = 6.7 Hz) ; 5.93 q (1 H, J = 6 Hz)
Anal. Calc. for $C_6H_9NO_3S$: C 41.13 ; H 5.17 ; N 7.99 ; S 18.30. Found : C 41.25 ; H 5.07 ; N 8.07 ; S 18.60.

Terbutyl 1-thiocyanoethylcarbonate 3b :
IR (cm^{-1}) 2170, 1765
^1H NMR : 1.53 s (9 H) ; 1.87 d (3 H, J = 6 Hz) ; 5.92 q (1 H, J = 6 Hz)
Anal. Calc. for $C_8H_{13}NO_3S$: C 47.27 ; H 6.45 ; N 6.89 ; S 15.77. Found : C 47.38 ; H 6.39 ; N 6.84 ; S 15.46.

Terbutyl 1-isothiocyanoethylcarbonate 4b :
IR (cm^{-1}) 2040, 1765
^1H NMR : 1.51 s (9 H) ; 1.66 d (3 H, J = 6 Hz) ; 5.96 q (1 H, J = 6 Hz)
Anal. Calc. for $C_8H_{13}NO_3S$: C 47.27 ; H 6.45 ; N 6.89 ; S 15.77. Found : C 47.31 ; H 6.38 ; N 6.91 ; S 15.86.

n-Octyl 1-thiocyanoethylcarbonate 3c :
IR (cm^{-1}) 2170, 1760
^1H NMR : 0.6-2.1 m (18 H with d at 1.87, 3 H, J = 6 Hz) ; 4.14 m (2 H) ; 5.96 q (1 H, J = 6 Hz)
Anal. Calc. for $C_{12}H_{21}NO_3S$: C 55.71 ; H 8.16 ; N 5.40 ; S 12.36. Found : C 55.74 ; H 8.40 ; N 5.27 ; S 11.99.

n-Octyl 1-isothiocyanoethylcarbonate 4c :
IR (cm^{-1}) 2040, 1765
^1H NMR : 0.6-2.1 m (18 H with d at 1.6, 3 H, J = 6 Hz) ; 4.1 m (2 H) ; 5.95 q (1 H, J = 6 Hz)
Anal. Calc. for $C_{12}H_{21}NO_3S$: C 55.71 ; H 8.16 ; N 5.40 ; S 12.36. Found : C 55.74 ; H 8.62 ; N 5.13 ; S 12.03.

Benzyl 1-thiocyanoethylcarbonate 3d :
IR (cm^{-1}) 2170, 1765
^1H NMR : 1.79 d (3 H, J = 6 Hz) ; 5.11 s (2 H) ; 5.86 q (1 H, J = 6 Hz) ; 7.3 br.s (5 H)
Anal. Calc. for $C_{11}H_{11}NO_3S$: C 55.69 ; H 4.67 ; N 5.90 ; S 13.51. Found : C 55.88 ; H 4.87 ; N 5.99 ; S 13.61.

Benzyl 1-isothiocyanoethylcarbonate 4d :
IR (cm^{-1}) 2040, 1760
^1H NMR : 1.57 d (3 H, J = 6 Hz) ; 5.07 s (2 H) ; 5.87 q (1 H, J = 6 Hz) ; 7.32 br.s (5 H)
Anal. Calc. for $C_{11}H_{11}NO_3S$: C 55.69 ; H 4.67 ; N 5.90 ; S 13.51. Found : C 55.54 ; H 4.73 ; N 5.65 ; S 13.22.

Allyl 1-thiocyanoethylcarbonate 3e :
IR (cm^{-1}) 3100, 2170, 1760, 1655
^1H NMR : 1.9 d (3 H, J = 6 Hz) ; 4.67 d (2 H, J = 4.7 Hz) ; 5.15-5.6 m (2 H) ; 5.65-6.7 q (2 H with q at 5.97, 1 H, J = 6 Hz)
Anal. Calc. for $C_7H_9NO_3S$: C 44.91 ; H 4.85 ; N 7.48 ; S 17.13. Found : C 45.04 ; H 4.98 ; N 7.48 ; S 16.59.

Allyl 1-isothiocyanoethylcarbonate 4e :
IR (cm^{-1}) 3100, 2050, 1760, 1655
^1H NMR : 1.7 d (3 H, J = 6 Hz) ; 4.71 d (2 H, J = 4.7 Hz) ; 5.2-5.7 m (2 H) ; 5.8-6.3 m (2 H with q at 6.04, 1 H, J = 6 Hz)
Anal. Calc. for $C_7H_9NO_3S$: C 44.91 ; H 4.85 ; N 7.48 ; S 17.13. Found : C 44.70 ; H 5.29 ; N 7.46 ; S 16.68.

Isopropyl 1-thiocyanoethylcarbonate 3f :
IR (cm^{-1}) 2170, 1765
^1H NMR : 1.35 d (6 H, J = 6 Hz) ; 1.89 d (3 H, J = 6 Hz) ; 4.64-5.15 m (1 H) ; 5.9 (1 H, J = 6 Hz)
Anal. Calc. for $C_7H_{11}NO_3S$: C 44.43 ; H 5.86 ; N 7.40 ; S 16.94. Found : C 44.12 ; H 6.02 ; N 7.24 ; S 16.48.

Isopropyl 1-isothiocyanoethylcarbonate 4f :
IR (cm^{-1}) 2050, 1765
^1H NMR : 1.33 d (6 H, J = 6 Hz) ; 1.62 d (3 H, J = 6 Hz) ; 4.62-5.13 m (1 H) ; 5.91 (1 H, J = 6 Hz)

Anal. Calc. for $C_7H_{11}NO_3S$: C 44.43 ; H 5.86 ; N 7.40 ; S 16.94. Found : C 44.39 ; H 5.91 ; N 7.16 ; S 16.77.

Cyclohexyl 1-thiocyanoethylcarbonate 3g :
IR (cm^{-1}) 2170, 1760
^1H NMR : 1.02-2.34 m (13 H with d at 1.88, 3 H, J = 6 Hz) ; 4.35-5 m (1 H) ; 5.95 q (1 H, J = 6 Hz)
Anal. Calc. for $C_{10}H_{15}NO_3S$: C 52.60 ; H 6.18 ; N 6.14 ; S 14.05. Found : C 52.46 ; H 6.66 ; N 6.15 ; S 13.77.

Cyclohexyl 1-isothiocyanoethylcarbonate 4g :
IR (cm^{-1}) 2040, 1760
^1H NMR : 0.8-2.25 m (13 H with d at 1.62, 3 H, J = 6 Hz) ; 4.27-4.91 m (1 H) ; 5.95 q (1 H, J = 6 Hz)
Anal. Calc. for $C_{10}H_{15}NO_3S$: C 52.60 ; H 6.18 ; N 6.14 ; S 14.05. Found : C 52.12 ; H 6.52 ; N 6.09 ; S 13.66.

2-(2-Ethoxyethoxy)ethyl 1-thiocyanoethylcarbonate 3h :
IR (cm^{-1}) 2170, 1760
^1H NMR : 1.12 t (3 H, J = 6.3 Hz) ; 1.9 d (3 H, J = 6 Hz) ; 3.2-3.95 m (8 H) ; 4.2-4.6 m (2 H) ; 5.95 q (1 H, J = 6 Hz)
Anal. Calc. for $C_{10}H_{17}NO_5S$: C 45.60 ; H 6.51 ; N 5.32 ; S 12.18. Found : C 45.46 ; H 6.47 ; N 5.59 ; S 12.59.

2. Reactions of alkyl 1-chloroalkyl carbonates 1a,b,c,i,j with MSCN in protic solvents. Synthesis of alkyl 1-thiocyanoethylcarbonates (3a,b,c,i,j) and alkyl 1-isothiocyanoethylcarbonates (4a,b,c) - Compounds 1 (10 mmoles) diluted in 10 ml of methanol or formamide were added to a magnetically stirred solution of MSCN (40 mmoles) in methanol or formamide at room temperature. After completion of the reactions (monitored by GLC) and the work up described above, the products 3a,b,c,i,j and 4a-c were isolated pure by flash chromatography. 3i,j were new products.

Phenyl 1-thiocyanoethylcarbonate 3i :
IR (cm^{-1}) 2170, 1770
^1H NMR : 1.9 d (3 H, J = 6 Hz) ; 5.92 q (1 H, J = 6 Hz) ; 7-7.52 m (5 H)
Anal. Calc. for $C_{10}H_9NO_3S$: C 53.80 ; H 4.06 ; N 6.12 ; S 14.36. Found : C 53.88 ; H 4.17 ; N 6.27 ; S 14.36.

4-Chlorophenyl 1-thiocyanoethylcarbonate 3j :
IR (cm^{-1}) 2170, 1775
^1H NMR : 1.9 d (3 H, J = 6 Hz) ; 5.94 q (1 H, J = 6 Hz) ; 7-7.47 m (4 H)
Anal. Calc. for $C_{10}H_8ClNO_3S$: C 46.61 ; H 3.13 ; N 5.43 ; S 12.44. Found : C 46.66 ; H 3.12 ; N 5.31 ; S 12.04.

3. Stability of thiocyanates 3a-i under their preparation conditions. Reactions performed in refluxing acetone (Table III) - In a 50 ml round bottom flask, we stirred magnetically a mixture of 5 mmoles of alkyl 1-thiocyanoethylcarbonates 3a-h, 15 mmoles of NH_4SCN (1.14 g) and 1 mmole of Bu_4PBr (0.34 g) in refluxing acetone (15 ml). For the reaction time given in Table III, the reaction did not progress more (except run 37). After the usual aqueous work up, the compounds 4a,b,c,e,f,g,h were isolated by flash chromatography. All these compounds have been already described above except 4h which was a new one.

2-(2-Ethoxyethoxy)ethyl 1-isothiocyanoethylcarbonate 4h :
IR (cm^{-1}) 2040, 1760
^1H NMR : 1.12 t (3 H, J = 7 Hz) ; 1.65 d (3 H, J = 6 Hz) ; 3.26-3.8 m (8 H) ; 4.17-4.4 m (2 H) ; 6 q (1 H, J = 6 Hz)
m/e M^+ +1 264

4. Reactions of 1-chloroethyl N,N-dialkylcarbamates 2a,b with MSCN in acetone or in protic solvents. Synthesis of 1-thiocyanoethyl N,N-dialkylcarbamates 6a,b and 1-isothiocyanoethyl N,N-dialkylcarbamates (Table IV) - In acetone, we operated at room temperature. The procedure was the same as that used for carbonates 1. In protic solvents, carbamates 2a,b must not be diluted in the choiced solvent before addition to the reaction mixture. Otherwise the procedure was the same as that described in experimental part (section 2).

5. Stability of carbamates 6a,b under their preparation conditions in acetone (Table V) - The procedure was the same as that used in section 3 for carbonates 3. The products isolated by flash chromatography were pure. Their spectroscopic data are given below.

6. Isomerization of some alkyl 1-thiocyanoethylcarbonates to their corresponding isothiocyano derivatives according to a procedure described in the literature[6b] (Table VI) - To a magnetically stirred solution of $ZnCl_2$ (0.5 mmole, 68 mg) in decaline (5 ml) at 160°C, we added dropwise carbonates 3a,c, d,f (5 mmoles). After completion of the reaction (monitored by GLC), the solvent was removed by distillation under reduced pressure. The expected products were isolated by flash chromatography. Their spectroscopic data (IR, NMR) were identical to those described previously in section 1.

7. Isomerization of compounds 3a-i and 6a,b to their corresponding isothiocyano derivatives in acetone containing Bu_4PBr (Table VII) - In a 50 ml round bottom flask, we stirred magnetically a mixture of carbonates 3a-i (5 mmoles) and Bu_4PBr (1 mmole, 0.34 g) in acetone (15 ml) at the temperature given in Table VII. After completion of the reactions (monitored by GLC or TLC), the products were isolated by flash chromatography. Their spectroscopic data (IR, NMR) were identical to those described in section 1 and 4 except 4i which was a new one.

Phenyl 1-isothiocyanoethylcarbonate 4i :
IR (cm^{-1}) 2040, 1775
^1H NMR : 1.57 d (3 H, J = 6 Hz) ; 5.95 q (1 H, J = 6 Hz) ; 6.95-7.6 m (5 H)
Anal. Calc. for $C_{10}H_9NO_3S$: C 53.80 ; H 4.06 ; N 6.12 ; S 14.36. Found : C 53.72 ; H 4.12 ; N 6.38 ; S 14.40.

1-Thiocyanoethyl N,N-diethylcarbamate 6a :
IR (cm^{-1}) 2170, 1715
^1H NMR : 1.13 t (6 H, J = 7.3 Hz) ; 1.88 d (3 H, J = 6 Hz) ; 3.29 q (4 H, J = 7.3 Hz) ; 6.05 q (1 H, J = 6 Hz)
MS m/e M^+ 202.

1-Isothiocyanoethyl N,N-diethylcarbamate 7a :
IR (cm^{-1}) 2050, 1720
^1H NMR : 1.13 t (6 H, J = 7.3 Hz) ; 1.6 d (3 H, J = 6 Hz) ; 3.28 q (4 H, J = 7.3 Hz) ; 6.08 q (1 H, J = 6 Hz)
MS m/e M^+ 202

The products 6a and 7a were unstable and gave unsatisfactory C, H, N, S microanalysis.

1-Thiocyanoethyl N-piperidylcarbamate 6b :
IR (cm^{-1}) 2170, 1715
^1H NMR : 0.8-2.05 m (9 H with d at 1.83, 3 H, J = 6.3 Hz) ; 3.14-3.7 m (4 H) ; 6.02 q (1 H, J = 6.3 Hz)
MS m/e M^+ 214.

1-Isothiocyanoethyl N-piperidylcarbamate 7b :
IR (cm^{-1}) 2040, 1715
^1H NMR : 1.1-1.8 (9 H with d, 3 H, J = 6 Hz) ; 3.1-3.6 m (4 H) ; 6.03 q (1 H, J = 6 Hz)
MS m/e M^+ 214.

The products 6b and 7b were unstable and gave unsatisfactory C, H, N, S microanalysis.

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