Pergamon

Tetrahedron Vol. 51, No. 9, pp. 2561-2572, 1995
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0040-4020/95 $9.50+0.00

0040-4020(95)00005-4

New Selective Syntheses of (Meth)Acrylic Monomers: Isocyanates, Isocyanurates, Carbamates and Ureas Derivatives.

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Abstract : *The selective formation of ω-isocyanatoalkyl (meth)acrylates may be conveniently obtained by simple condensation of potassium cyanate with ω-halogeno-alkyl (meth)acrylates under appropriated phase transfer catalytic conditions. Depending on the reaction media and the temperature, these isocyanate derivatives may be isolated, trimerized to the corresponding isocyanurates or trapped in situ as carbamates or ureas compounds.*

INTRODUCTION

The selective functionalizations of the alkoxy part of (meth)acrylic esters CH_2:C(R)-COOΣ where Σ contains nucleophilic or electrophilic functions is an interesting reactivity problem although difficult to be solved. Such reactions are of potential practical interest since they allow the transformation of current (meth)acrylic derivatives into new more elaborated monomers. As part of our program dealing with reactivity and selectivity, we were interested for a few years in this kind of problem and undertook investigations on the chemistry of (meth)acrylic monomers. Thus in the field of the electrophilic reactions we developed a method of selective epoxidation of unsaturated (meth)acrylic esters.[1] On the other hand, we succeeded in the selective nucleophilic thiocyanation of halogenated (meth)acrylic monomers without Michael additions and the corresponding group-transfer polymerizations.[2]

With these results in hand, we turned toward the selective synthesis of isocyanatoalkyl (meth)acrylic esters. Such investigations appeared to us a very interesting for more than one point. Indeed it is well known that (meth)acrylic esters occupy an important position in the synthesis of polymers as well as reagents in fine chemistry.[3] On the other hand, isocyanates as well as their corresponding carbamate, urea and isocyanurate derivatives play an important part in phyto,[4] medicinal [5] and polymer chemistry.[6] Thus compounds comprising one of these functional group with (meth)acrylic esters possess a high application potential.[7]

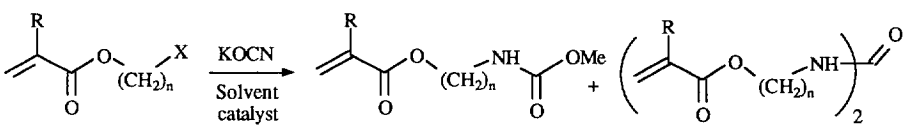
Isocyanates are generally obtained from primary amines and phosgene.[8] Besides the fact that aminoalkyl (meth)acrylates are not convenient substrates, the use of the toxic phosgene was not desirable. On the contrary haloalkyl (meth)acrylates are easily obtained and could be good starting materials if alkali cyanates could be selectively condensed. However it is well known that condensations of alkali cyanates with an alkyl halides are not easy to perform and necessitate rather harsh conditions. In fact such reactions were not often described in the literature [9] and deserved to be investigated.

In a preliminary paper[10] we reported that we succeeded in the condensation of alkali cyanate with halogenoalkyl (meth)acrylates to obtain, depending on the experimental conditions, isocyanates or their derivatives. More details, as well as the scope and limitations of these syntheses, are reported in the present publication.

RESULTS AND DISCUSSION

Exploratory experiments and synthesis of methyl N-(ω-(meth)acrylic alkyl ester) carbamates

We first studied the condensation of sodium cyanate with bromoalkyl (meth)acrylates in DMF at 80°C according to literature conditions.[9] Although the starting halides disappeared slowly and completely from the reaction medium and gave complex untractable mixtures. Attempts to trap the transient isocyanates with methanol gave only low yields in the corresponding carbamates (<20%) near many polar by-products. We then turned towards phase transfer catalysis which, to the best of our knowledge, was never used to perform such condensations in (meth)acrylic series. To avoid difficulties inherent to the instability of the isocyanates we decided to perform the condensations in the presence of methanol in order to obtain carbamates. A systematic study was undertaken with 6-bromohexyl methacrylate **1a** (X=Br; R=Me; n=6). Preliminary experiments showed that KOCN reacted with the substrate and led to the formation of two products according to Scheme 1.



Scheme 1

The formation of ureas by condensation of isocyanates with water is a well known reaction.[11] We thus suspected the presence of water in the reaction medium. Karl-Fisher analysis of the reagents indeed showed they contained some water and it was concluded that this parameter had to be taken into accounts in the systematic study for which the most significant results are given in Table 1. From these data it may be concluded that under our conditions the transient formation of isocyanates took place in good to very good yields. It was found that six equivalents of methanol led to short reaction times. A largest excess (e.g. ten equivalents) only conducted to complex mixtures. However, use of three equivalents of methanol could be used to efficiently trap the transient isocyanate with acceptable reaction times.

From Table 1, as far as overall yields were concerned, acetonitrile (MeCN) and methyl ethyl ketone (MEK) appeared more suited to perform these condensations (run 1-3). In fact MEK is preferred because it leads to shorter reaction times and more convenient workup. Moreover the reaction temperature also played an important part (runs 3-6). Low temperatures (20 to 40°C) led to long reaction times and low conversions. On the contrary at 80°C many by-products were obtained. Thus reactions performed at 60°C gave the best results. In other respects it was expected that a decrease in the water content of the reaction medium would increase the selectivity for **2**. This was verified in MeCN as well as in MEK (runs 7, 8). Finally we examined the influence of the nature of the catalyst (runs 8-13). It is very interesting to note that the nature of the catalyst plays an important part on the yields and the reaction times. The best catalysts were found to be Bu_4NBr and Ph_3MePBr. The latter was preferred as more selective and allowing shorter reaction times.

We then extended these first results to other ω-halogenoalkyl acrylic and methacrylic esters (Table 2).

Table 1. Synthesis of methyl N-(6-methacrylic hexyl ester) carbamate 2a (R=Me; n=6).[a]

Entry	solvent	H_2O content (equiv.)b	PTC catalyst	Temp (°C)	time (h.)	Rec. **1a** (%)c	yield **2a** (%)c	yield **3a** (%)c
1	DMF	9	Bu4NBr	60	37	-	27	26
2	MeCN	9	Bu_4NBr	60	40	-	30	31
3	MEK	9	Bu_4NBr	60	24	-	31	27
4	MEK	9	Bu_4NBr	20	400	60	20	(20)
5	MEK	9	Bu_4NBr	40	36	50	20	(20)
6	MEK	9	Bu_4NBr	80	24	-	33	15
7	MeCN	0.6	Bu_4NBr	60	35	-	64	10
8	MEK	0.6	Bu_4NBr	60	24	-	67	nd
9	MEK	0.6	Bu_4NI	60	24	-	57	nd
10	MEK	0.6	Ph_3MeNBr	60	48	-	45	nd
11	MEK	0.6	Aliquat 336	60	26	-	33	nd
12	MEK	0.6	Ph_3MePBr	60	15	-	70	nd
13	MEK	0.6	Bu_4PBr	60	24	30	48	nd

[a] Reaction performed on a 10 mmoles scale with KOCN (15 mmoles), catalyst (2mmoles) and MeOH (60 mmoles) in 20 ml of solvent. [b] Determined by Karl-Fischer analysis. [c] Isolated yields. In parenthesis, yields determined by GC.

Table 2. Synthesis of methyl N-(ω-(meth)acrylic alkyl ester) carbamates 2.[a]

Entry	substrate	R	X	n	Method[b]	time (h)	Rec. 1 (%)c	yield of **2** (%)c	product
1	**1b**	Me	Br	2	A	68	23	37	**2b**
2	**1c**	Me	Br	3	A	20	4	72	**2c**
3	**1d**	Me	Br	4	A	24	3	72	**2d**
4	**1a**	Me	Br	6	A	24	1	83	**2a**
5	**1e**	Me	Br	8	A	24	10	69	**2e**
6	**1f**	H	Br	2	A	45	10	27	**2f**
7	**1g**	H	Br	3	A	24	3	56	**2g**
8	**1h**	H	Br	4	A	24	2	61	**2h**
9	**1i**	H	Br	6	A	16	1	74	**2i**
10	**1j**	H	Br	8	A	16	1	71	**2j**
11	**1k**	Me	Cl	2	B	68	14	20	**2b**
12	**1l**	Me	Cl	4	B	53	8	54	**2d**
13	**1m**	Me	Cl	6	B	88	16	64	**2a**
14	**1n**	Me	Cl	8	B	62	10	58	**2e**
15	**1o**	H	Cl	2	B	72	10	22	**2f**
16	**1p**	H	Cl	4	B	88	5	70	**2h**
17	**1q**	H	Cl	6	B	60	7	60	**2i**
18	**1r**	H	Cl	8	B	24	10	61	**2j**

[a] Reaction performed at 60 °C on a 10 mmoles scale with KOCN (15 mmoles), catalyst (2mmoles), MeOH (60 mmoles) and in 20 ml of MEK. The water content (determined by Karl-Fischer analysis) was equal to 6 mmoles [b] Method A : without addition of KI. Method B: reactions performed in the presence of KI (2mmoles) [c] Isolated yields by flash chromatography.

From a general point of view the best results were obtained with the methacrylic series less sensitive to polymerizations. Chloro derivatives were, as usual [2] less reactive than the corresponding bromides. We previously showed that this lack of reactivity could be compensated by addition of potassium iodide which allow the *in situ* formation of the corresponding iodides.[2] Under these conditions (runs 11 to 18) the carbamates were obtained in good yields. The only limitations were found with **1b, 1f, 1k** and **1o** (n=2) (runs 1, 6, 11, 15). Indeed the reactivity of such substrates are generally lower in nucleophilic condensations. Steric hindrance was invoked to explain such observations.[12]

Synthesis of N,N'-bis-(ω-(meth)acrylic alkyl ester) ureas

Since water was recognized as responsible for urea formation, it was expected that replacing MeOH with H_2O should allow the synthesis of **3**. A short exploratory study of the influence of the amount of water led to interesting conclusions : i) Large excess (6 equivalents) of H_2O led to a mixture of ureas and bisureas ii) With a slight excess (1.2 equivalents) of H_2O ureas were the main or only product isolated. Moreover we also observed that MeCN was more convenient that MEK during the isolation of the ureas. Combining these observations with those obtained from the synthesis of carbamates we then prepared a series of ureas with the results reported in Table 3.

From these data it clearly appears that ureas **3** may be easily obtained in good yields. However, the low reactivity of (meth)acrylates **1b, 1f, 1k** and **1o** (n=2) was again observed. With such substrates, the substitution took place very slowly and was accompanied with a large amount of polymerization.

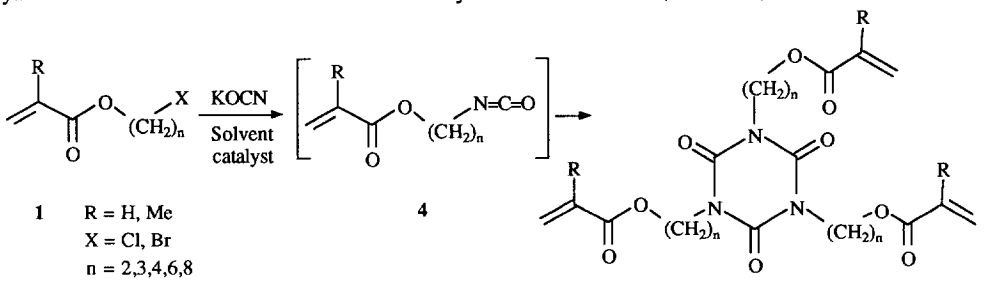
Table 3. Synthesis of N,N'-bis(ω-(meth)acrylic alkyl ester) ureas 3

Entry	substrate	R	X	n	Method[b]	time (h)	Rec. **1** (%)[c]	yield of **3** (%)[c]	product
1	**1b**	Me	Br	2	C	48	-	5	**3b**
2	**1c**	Me	Br	3	C	40	-	83	**3c**
3	**1d**	Me	Br	4	C	44	2	64	**3d**
4	**1a**	Me	Br	6	C	18	traces	86	**3a**
5	**1e**	Me	Br	8	C	24	traces	81	**3e**
6	**1f**	H	Br	2	C	34	10	8	**3f**
7	**1g**	H	Br	3	C	24	10	66	**3g**
8	**1h**	H	Br	4	C	24	6	82	**3h**
9	**1i**	H	Br	6	C	15	5	85	**3i**
10	**1j**	H	Br	8	C	15	4	87	**3j**
11	**1k**	Me	Cl	2	D	62	8	4	**3b**
12	**1l**	Me	Cl	4	D	53	11	60	**3d**
13	**1m**	Me	Cl	6	D	70	10	63	**3a**
14	**1n**	Me	Cl	8	D	62	10	60	**3e**
15	**1o**	H	Cl	2	D	45	21	11	**3f**
16	**1p**	H	Cl	4	D	24	16	71	**3h**
17	**1q**	H	Cl	6	D	64	20	80	**3i**
18	**1r**	H	Cl	8	D	49	14	69	**3j**

[a] Reactions performed at 60 °C on a 10 mmoles scale with KOCN (15 mmoles), catalyst (2mmoles), H_2O (12 mmoles) and in 20 ml of MeCN. [b] Method C: without addition of KI. Method D: reactions performed in the presence of KI (2mmoles) [c] Isolated yields by flash chromatography.

Synthesis of tris-(ω-(meth)acrylic alkyl ester) isocyanurates

During the above study dealing with the influence of the amount of water we observed that in the presence of less than 1 equivalent of water new products appeared. They were identified as the corresponding isocyanuric acid derivatives due to the classical isocyanates trimerization (Scheme 2).



Scheme 2

Thus we turned our attention toward the one pot preparation of these compounds. From a not reported systematic study it was observed that condensations of halogenoalkyl (meth)acrylic esters with KOCN in the presence of Ph_3MePBr or preferentially Bu_4NBr, in MeCN at 65°C and in the presence of only 0.3 equivalent of H_2O led to selective formation of **5**. We observed that the trimerization of the isocyanate took place easily and the isocyanuric derivatives were obtained in good yields (Table 4).

Table 4. Synthesis of *tris*-(ω-(meth)acrylic alkyl ester) isocyanurates 5.[a]

Entry	substrate	R	X	n	Method[b]	time (h)	yield of 5 (%)[c]	product	yield of 3 (%)[c]
1	**1b**	Me	Br	2	E	42	49	**5b**	-
2	**1c**	Me	Br	3	E	40	69	**5c**	11
3	**1d**	Me	Br	4	E	42	70	**5d**	12
4	**1a**	Me	Br	6	E	62	75	**5a**	10
5	**1e**	Me	Br	8	E	24	62	**5e**	15
6	**1f**	H	Br	2	E	38	44	**5f**	-
7	**1g**	H	Br	3	E	48	62	**5g**	10
8	**1h**	H	Br	4	E	40	60	**5h**	12
9	**1i**	H	Br	6	E	48	72	**5i**	14
10	**1j**	H	Br	8	E	21	62	**5j**	10
11	**1k**	Me	Cl	2	F	52	52	**5b**	-
12	**1l**	Me	Cl	4	F	58	56	**5d**	10
13	**1m**	Me	Cl	6	F	42	63	**5a**	10
14	**1n**	Me	Cl	8	F	72	61	**5e**	10
15	**1o**	H	Cl	2	F	69	41.5	**5f**	-
16	**1p**	H	Cl	4	F	70	59	**5h**	15
17	**1q**	H	Cl	6	F	62	60	**5i**	15
18	**1r**	H	Cl	8	F	43	75	**5j**	10

[a] Reactions performed at 65°C on a 10 mmoles scale with KOCN (15 mmoles), catalyst (2mmoles) and in 20 ml of MeCN. The water content (determined by Karl-Fischer analysis) was equal to 3 mmoles [b] Method E : without addition of KI. Method F: reactions performed in the presence of KI (2mmoles) [c] Isolated yields by flash chromatography.

It is noteworthy that even with **1b, 1f, 1k** and **1o** (n = 2) yields were fair and higher than those obtained during the preparation of carbamates or ureas. This result deserves some comment. We mentioned above that β-halogenoethyl (meth)acrylates were found of low reactivity in nucleophilic substitutions. This property is related to the structure of the substrate as well as to the reaction medium. Presently the condensations were performed under aprotic conditions with a very low content of water. Such experimental conditions considerably favor SN_2. On the other hand comparison of the reaction times with those of Tables 2 and 3, shows that they are shorter but the differences are not large enough to explain the large increase of yields observed in Table 4. Thus, it must be assumed that, under aprotic conditions, the isocyanatoalkyl (meth)acrylates are less prone to polymerization.

Synthesis of ω-isocyanatoalkyl (meth)acrylates 4.

These synthetically interesting reactions occur in good yields. In order to isolate the very sensitive isocyanate products, it is important that water be excluded and that the reaction temperature be as low as possible. Exploratory experiments using such conditions demonstrated that lowering the amount of water down to 0.3 equivalent led to the formation of small amounts of the expected isocyanate (detected by GCMS).

From these very encouraging results a systematic study was performed and the conclusion was that ω-(meth)acrylic isocyanatoalkyl esters **4** accompanied with more or less significant amounts of ureas **3** and isocyanurates **5** could be obtained provided the water containt was equal to or less than 0.1 equivalent. An optimal reaction temperature of 55°C was found to allow the best compromise between the desired nucleophilic substitution and undesired polymerization. On an other hand, the reaction times depended on the structure of the starting material. The optimal reaction time was determined for each substrate by monitoring the reactions by GC. Extended reaction times led to formation of isocyanurate derivatives, thus demonstrating the high reactivity of product **4**.

Table 5. Synthesis of ω-(meth)acrylic isocyanatoalkyl esters 4.[a]

Entry	substrate	R	X	n	Method[b]	time (h)	Rec. 1 (%)[c]	yield of 4 (%)[c]	product	yield of 3 (%)[c]	yield of 5 (%)[c]
1	**1c**	Me	Br	3	G	8	-	52	**4c**	12	18
2	**1d**	Me	Br	4	G	12	-	48	**4d**	12	14
3	**1a**	Me	Br	6	G	22	15	51	**4a**	10	18
4	**1e**	Me	Br	8	G	21	-	59	**4e**	11	32
6	**1g**	H	Br	3	G	8	-	44	**4g**	13	22
7	**1h**	H	Br	4	G	14	-	43	**4h**	12	24
8	**1i**	H	Br	6	G	17	22	42	**4i**	10	18
9	**1j**	H	Br	8	G	38	10	55	**4j**	10	9
12	**1l**	Me	Cl	4	H	58	32	41	**4d**	10	9
13	**1m**	Me	Cl	6	H	72	28	33	**4a**	11	31
14	**1n**	Me	Cl	8	H	72	22	37	**4e**	10	31
16	**1p**	H	Cl	4	H	46	-	45	**4h**	12	13
17	**1q**	H	Cl	6	H	72	-	45	**4i**	10	29
18	**1r**	H	Cl	8	H	72	19	53	**4j**	11	20

[a] Reactions performed at 55°C on a 10 mmoles scale with KOCN (15 mmoles), catalyst (2mmoles) and in 20 ml of MeCN. The water content (determined by Karl-Fischer analysis) was equal to 1 mmole [b] Method A : without addition of KI. Method B: reactions performed in the presence of KI (2mmol.) [c] Isolated yields by flash chromatography.

Control experiments showed that when **4a** was added to the reaction, product **5a** was obtained nearly quantitatively after 24 hours. Finally ω-(meth)acrylic isocyanatoalkyl esters **4** may be obtained in fair to good isolated yields (Table 5) by allowing the monomers to trimerize or polymerize. However, it must be noted, these reactions did not allow for the isolation of the very sensitive β-isocyanato-ethyl (meth)acrylic esters.

CONCLUSION

The present work shows that isocyanates may be conveniently formed and trapped or isolated by simple condensation of alkyl halides with alkali cyanates under PTC conditions. Such a synthesis works well with the sensitive halogenoalkyl (meth)acrylic esters and avoids use of the difficult to prepare amino derivatives as well as the use of the phosgene.

Moreover we also showed that with simple changes in the experimental conditions it is very easy to obtain either (meth)acrylic carbamates, ureas, isocyanuric acid derivatives or isocyanates. These results are of considerable interest for the synthesis of new acrylic monomers.

EXPERIMENTAL PART

Gas chromatography analyses were performed using a Shimadzu GC-8A apparatus, equipped with a Merck D-2500 data processor, with a column of silicone OV-101 (10 %) - chromosorb W (3 m) (N_2 as carrier gas). ^1H and ^{13}C NMR spectra were measured for $CDCl_3$ or CCl_4 solutions containing tetramethylsilane (as an internal standard) on a Jeol PMX 60, Bruker AM 300 or Bruker AM 300 spectrometer respectively. Chemical shifts are expressed in ppm (δ)). IR spectra were recorded on a 580B Perkin Elmer spectrophotometer. High resolution mass spectra were conducted on a Finnigan MAT 95 Q mass spectrometer at the Centre de Recherches Lorraine of Elf-Atochem (Marienau, France). Exact mass were determined by ESCAN method. Chemical ionization (CI) mass spectra were recorded on a Hewlett-Packard 5971 apparatus equipped with quadropole moment detection and with helium as carrier gas. T.l.c. analyses were performed with hexane - ethyl acetate mixtures (80:20 to 30:70). Products were purified by silica flash chromatography on Kieselgel 60 (230-400 mesh) with petroleum ether - ethyl acetate mixtures as eluent (80:20 to 30:70). NaOCN, Bu_4NBr and KI were dried over 16 h at 110°C under 5 mbar. Acetonitrile or methyl ethyl ketone was distilled over P_2O_5. Methanol was distilled over Mg. All acrylic esters used as substrates were prepared by esterification of acryloyl chloride with the corresponding alcohol (1.1 equivalents) in the presence of triethylamine (3 equivalents) at 10 °C in $CHCl_3$ for 12 hours. Pure products (GC analysis) were obtained after usual workup and flash chromatography. All spectroscopic data (IR, ^1H and ^{13}C NMR) were in agreement with the expected formulas and the literature data. (Meth)acrylic esters were used under air atmosphere after stabilization with hydroquinone monomethyl ether (100 ppm) to avoid polymerisation.

General procedures for the selective syntheses of 2 or 3 or 4 or 5.

Method A: To a slurry of NaOCN (15 mmoles) and Bu_4NBr (2 mmoles) in 15 mL of methyl ethyl ketone at room temperature was added **1** (10 mmoles) in 5 mL of methyl ethyl ketone. It must be verified (by Karl-Fischer analysis) that the water content do not exceeded 0.6 equivalent. The mixture was then heated at 60°C. The reactions were monitored by G.C. analysis of small aliquots. After completion and cooling, the mixture was filtered, the precipitate was washed with methylene chloride, and concentrated under vacuum. Products **2** were then separated by flash chromatography (ethyl acetate/petroleum ether (30/70)).

Method B: The method A was employed with an additionnal amount of KI (2 mmoles).

Method C: To a slurry of NaOCN (15 mmoles) and Bu_4NBr (2 mmoles) in 15 mL of MeCN at room temperature was added **1** (10 mmoles) in 5 mL of MeCN. The water content was ajusted at 12 mmoles (1.2 equivalent). The mixture was then heated at 60°C. The reactions were monitored by G.C. analysis of small aliquots. After completion and cooling, the mixture was filtered, the precipitate was washed with methylene

chloride, and concentrated under vacuum. Products **3** were separated by flash chromatography (ethyl acetate / petroleum ether (80/20)).

Method D: The method C was employed with an additionnal amount of KI (2 mmoles).

Method E: To a slurry of NaOCN (15 mmoles) and Bu_4NBr (2 mmoles) in 15 mL of MeCN at room temperature was added **1** (10 mmoles) in 5 mL of MeCN. It must be verified (by Karl-Fischer analysis) that the water content do not exceeded 0.5 equivalent. The mixture was then heated at 65°C. The reactions were monitored by G.C. analysis of small aliquots. After completion and cooling, the mixture was filtered, the precipitate was washed with methylene chloride, and concentrated under vacuum. Products **5** were separated by flash chromatography (ethyl acetate / petroleum ether (30/70)).

Method F: The method E was employed with an additionnal amount of KI (2 mmoles).

Method G: To a slurry of NaOCN (15 mmoles) and Bu_4NBr (2 mmoles) in 15 mL of MeCN at room temperature was added **1** (10 mmoles) in 5 mL of MeCN. It must be verified (by Karl-Fischer analysis) that the water content do not exceeded 0.1 equivalent. The mixture was then heated at 55°C. The reactions were monitored by G.C. analysis of small aliquots. After completion and cooling, the mixture was filtered, the precipitate was washed with methylene chloride, and concentrated under vacuum. Products **4** were separated by flash chromatography (ethyl acetate / petroleum ether (10/90)).

Method H: The method G was employed with an additionnal amount of KI (2 mmoles).

Methyl N-[6-(2-methyl 2-propenoic acid) hexyl ester] carbamate (**2a**) : IR (neat) 3357 (NH) 2935-2861, 1720 (CO_2), 1700 (CO), 1638 (C=C), 1531 (C-N-H), 1254, 1168, 941 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 6.1 (s, 1H), 5.7-5.9 (m, 1H, NH), 5.5 (s, 1H), 4.0-4.2 (t, 2H, J = 6Hz), 3.6 (s, 3H), 3.1-3.25 (m, 2H), 1.9 (s, 3H), 1.2-1.7 ppm (m, 8H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 166.8 (CO_2), 156.8 (CO), 135.9 (C=), 124.7 (CH_2=), 64.0 (CH_2OCO), 51.2 (OCH_3), 40.3, 30.0, 25.8, 25.1 (4 CH_2), 17.6 ppm (CH_3); HREIMS : $C_{12}H_{21}NO_4$. M exp. 243.1474 ; M req. 243.14706.

Methyl N-[2-(2-methyl 2-propenoic acid) ethyl ester] carbamate (**2b**) : IR (neat) 3350, 2956, 1702, 1638, 1536, 1261, 943 cm^{-1} ; ^1H NMR (60 MHz, CCl_4) δ 6.0 (s, 1 H), 5.6-6.0 (m, 1H, NH), 5.5 (m, 1H), 4.0-4.2 (t, 2H, J = 6Hz), 3.5 (s, 3H), 3.2-3.5 (m, 2H), 1.9 ppm (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.5, 156.5, 135.3, 125.1, 62.9, 51.2, 39.3, 17.3 ppm ; Anal. Calcd. C 51.33, H 6.99, N 7.48. Found C 50.83, H 6.85, N 7.41.

Methyl N-[3-(2-methyl 2-propenoic acid) propyl ester] carbamate (**2c**) : IR (neat) 3358, 2958, 1704, 1639, 1535, 1454, 1378, 1170, 1038 cm^{-1}; ^1H NMR (400 MHz, CCl_4) δ 6.11 (m, 1H), 5.6 (m, 2H), 4.2 (t, 2H, J = 6Hz), 3.6 (s, 3H), 3.3 (m, 2H), 1.9 (s, 3H), 1.9 ppm (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 167.2, 157.3, 136.2, 125.7, 62.2, 52.0, 37.9, 29.1, 18.3 ppm ; Anal. Calcd. C 53.7 , H 7.51, N 6.96, Found C 53.88, H 7.47, N 7.20.

Methyl N-[4-(2-methyl 2-propenoic acid) butyl ester] carbamate (**2d**) : IR (neat) 3361, 2955, 1708, 1639, 1536, 1453, 1405, 1169, 1035 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 6.0 (m, 1H), 5.5 (m, 2H), 4.2 (t, 2H, J = 6Hz), 3.5 (s, 3H), 3.2 (q, 2H, J = 6Hz), 1.9 (s, 3H), 1.5-1.7 ppm (m, 4H) ; ^{13}C NMR (300 MHz, $CDCl_3$) δ 167.2, 157.3, 136.2, 125.2, 64.2, 51.7, 40.4, 26.4, 25.8, 18.1 ppm ; Anal. Calcd. C 55.60, H 7.96, N 6.50 . Found C 55.22, H 7.74, N 6.35.

Methyl N-[8-(2-methyl 2-propenoic acid) octyl ester] carbamate (**2e**) : IR (neat) 3352, 2931, 2858, 1717, 1702, 1639, 1531, 1253, 1165, 940 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 6.3 (m, 1H), 5.9-6.3 (m, 1H, NH), 5.7 (m, 1H), 4.3 (t, 2H, J = 6Hz), 3.8 (s, 3H), 3.2-3.5 (q, 2H, J = 6Hz), 2.2 (s, 3H), 1.4-2.0 ppm (m. 12H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.0, 156.3, 135.5, 123.9, 63.6, 50.4, 39.5, 28.9, 28.2, 28.2, 27.6, 25.7, 24.9, 17.1 ppm ; Anal. Calcd. C 61.97, H 9.28, N 5.10. Found C 62.11, H 9.25, N 4.88.

Methyl N-[2-(2-propenoic acid) ethyl ester] carbamate (**2f**) : IR (neat) 3350, 2957, 1709, 1637, 1535, 1407, 1189 cm^{-1}; ^1H NMR (60 MHz, CCl_4) δ 5.5-6.5 (m, 4H) ; 4.0-4.3 (t, 2H, J = 6Hz) ; 3.5 (s, 3H) ; 3.2-3.4 ppm (q, 2H, J = 6Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 165.3, 156.7, 130.4, 127.4, 62.4, 51.2, 39.2 ppm ; Anal. Calcd. C 48.55, H 6.40, N 8.08. Found C 48.31, H 6.37, N 7.61.

Methyl N-[3-(2-propenoic acid) propyl ester] carbamate (**2g**) : IR (neat) 3353, 2957, 1725, 1620, 1410, 1192, 984 cm^{-1}; ^1H NMR (60 MHz, CCl4) δ 5.5-6.5 (m, 4 H) ; 4.1-4.3 (t, 2H, J = 6Hz) ; 3.5 (s, 3H) ; 3.0-3.2 (q, 2H, J = 6Hz) ; 1.62 ppm (t, 2H, J = 6Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 165.3, 156.6, 129.9, 127.6, 61.3, 50.9, 36.9, 28.2 ppm ; Anal. Calcd. C 51.33, H 6.99, N 7.48. Found C 51.27, H 7.33, N 6.94.

Methyl N-[4-(2-propenoic acid) butyl ester] carbamate (**2h**) : IR (neat) 3350, 2953-2090, 1724, 1637, 1534, 1452, 1410, 1195 , 985 cm^{-1}; ^1H NMR (60 MHz, CCl4) δ 5.5-6.5 (m, 4H), 4.0-4.2 (t, 2H, J = 6Hz), 3.5 (s, 3H), 3.0-3.2 (q, 2H, J = 6Hz), 1.6-1.8 ppm (m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 165.5, 156.7, 130.0, 127.8, 63.5, 51.1, 39.8, 25.8, 25.2 ppm; Anal. Calcd. C 53.72, H 7.51, N 6.96 Found C 53.56, H 7.48, N 6.96.

Methyl N-[6-(2-propenoic acid) hexyl ester] carbamate (**2i**) : IR (neat) 3353, 2940-2862, 1727, 1700, 1638, 1620, 1536, 1271, 985 cm^{-1}; ^1H NMR (60 MHz, CCl4) δ 5.7-6.8 (m, 3H), 5.2-5.8 (m, 1H, NH), 4.2 (t, 2H, J = 6Hz), 3.7 (s, 3H), 3.15 (q, 2H, J = 6Hz), 0.9-2.0 ppm (m, 8 H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 165.5, 156.67, 129.7, 128.0, 63.8, 51.1, 40.3, 29.2, 27.9, 25.7, 25.0 ppm; HREIMS $C_{11}H_{19}NO_4$. M obsd. 229.1308 ; M req. 229.13141.

Methyl N-[8-(2-propenoic acid) octyl ester] carbamate (**2j**) : IR (neat) 3350, 2939-2856, 1708, 1638, 1534, 1466, 1408, 1194, 985 cm^{-1}; ^1H NMR (60 MHz, CCl4) δ 5.5-6.5 (m, 4H), 4.0-4.2 (t, 2H, J = 6Hz), 3.5 (s, 3H), 2.8-3.2 (q, 2H, J = 6Hz), 1.0-1.9 ppm (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 164.8, 156.0, 129.1, 127.4, 63.3, 50.4, 39.7, 28.7, 27.9, 27.4, 25.4, 24.6 ppm ; Anal. Calcd. C 60.68. H 9.01. N 5.44. Found C 60.21, H 8.89, N 5.33.

N, N'-[6-(2-methyl 2-propenoic acid) hexyl ester] urea (**3a**) : IR (neat) 3328 (NH), 2936-2861, 1720 (CO), 1618 (C=C), 1571, 1163, 942 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.0 (s, 2H), 5,5 (s, 2H), 5,4-5,6 (m, 2H, NH), 4,1 (t, 4H, J = 6Hz), 3,2 (q, 4H, J = 6Hz), 1,9 (s, 6H), 1,3-1,8 ppm (m, 16H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 167.2 (CO_2), 158.2 (CO), 136.1 (CH_2=), 124.9 (C=), 64.2 (CH_2OCO), 39.9 (CH_2N), 29.8, 28.2, 26.1, 25.3 (4 CH_2), 17.9 ppm (CH_3); Anal. Calcd. C 63.60, H 9.16, N 7.06. Found C 63.32, H 9.18, N 6.93.

N, N'-[2-(2-methyl 2-propenoic acid) ethyl ester] urea (**3b**) : IR (neat) 3338, 2956, 1723, 1638, 1455, 1172, 945 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.1 (s, 2H), 5.5 (s, 2H), 5.5 (m, 2H, NH), 4.3 (t, 4H, J = 6Hz), 3.5 (q, 4H, J = 6Hz), 1.9 ppm (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.8, 154.9, 135.5, 125.5, 63.6, 38.9, 17.8 ppm; CI/MS: m/e (%) 325 (5, M^++41), 313 (12, M^++29), 285(59, M^+), 267 (97), 199 (100), 156 (15), 130 (65), 113 (29), 87 (15), 69 (62).

N, N'-[3-(2-methyl 2-propenoic acid) propyl ester] urea (**3c**) : IR (neat) 3338, 2930-2878, 1710, 1631, 1453, 1174, 947 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.1 (s, 2 H), 5.5 (s, 2H), 4.9 (m, 2H, NH), 4.25 (t, 4H, J = 6Hz), 3.25 (q, 4H, J = 6Hz), 1.94 (s, 6 H), 1.87 ppm (m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 167.6, 158.2, 136.1, 125.7, 62.1, 37.0, 29.4, 18.3 ppm ; Anal. Calcd. C 57.70, H 7.74, N 8.98. Found C 57.42, H 7.60, N 9.24.

N, N'-[4-(2-methyl 2-propenoic acid) butyl ester] urea (**3d**) : IR (neat) 3326, 2950-2866, 1709, 1639, 1572, 1168, 938 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.0 (s, 2 H), 5.5 (s, 2H), 5.4-5.6 (m, 2H, NH), 4.2 (t, 4H, J = 6Hz), 3.2 (q, 4H, J = 6Hz), 1.9 (s, 6H), 1.7 ppm (m, 8H), ^{13}C NMR (300 MHz, $CDCl_3$) δ 167.0, 158.9, 135.8 , 125.0, 63.8, 39.4, 26.4, 25.6, 17.8 ppm ; Anal. Calcd. C 59.98, H 8.29, N 8.29. Found C 59.43, H 8.48, N 8.48.

N, N'-[8-(2-methyl 2-propenoic acid) octyl ester] urea (**3e**) : IR (neat) 3336, 2927-2851, 1716, 1614, 1573, 1164, 967 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.0 (s, 2H), 5.4 (s, 2H), 4.8-5.1 (m, 2H, NH), 4.1 (t, 4H, J = 6Hz), 3.1 (m, 4H), 1.9 (s, 6H), 1.2-1.5 ppm (m, 24H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 167.8, 158.9, 136.7, 125.5, 65.0, 40.6, 30.5, 29.4, 29.4, 28.8, 27.1, 26.1, 18.5 ppm; Anal. Calcd. C 66.34, H 9.80, N 6.19. Found C 66.47, H 9.82, N 6.15.

N, N'-[2-(2-propenoic acid) ethyl ester] urea (**3f**) : IR (neat) 3335, 2950, 1728, 1546, 1407, 1184, 990 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 5.8-6.5 (m, 6H), 5.5 (m, 2H, NH), 4.25 (t, 4H, J = 6Hz), 3.5 ppm (q, 4H, J = 6Hz), ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.2 (CO_2), 158.3 (CO), 131.4 (C=), 127.9 (CH_2=), 63.8 (CH_2OCO), 39.3 ppm (CH_2N); CI/MS: m/e (%) 298 (4, M^++41), 286 (7, M^++29), 257 (37, M^+), 185 (68), 116 (100), 88 (48), 73 (15), 69 (8).

N, N'-[3-(2-propenoic acid) propyl ester] urea (**3g**) : IR (neat) 3339, 2860, 1723, 1638, 1571, 1491, 1189, 984 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 5.5-6.5 (m, 6H), 5.4-5.6 (m, 2H, NH), 4.2 (t, 4H, J = 6Hz), 3.3 (q, 4H, J = 6Hz), 1.9 ppm (q, 4H, J = 6Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 166.5, 158.9, 131.1, 128.5, 62.3, 37.1, 29.6 ppm ; Anal. Calcd. C 54.92, H 9.85, N 7.09. Found C 55,07, H 9.84, N 7.12.

N, N'-[4-(2-propenoic acid) butyl ester] urea (**3h**) : IR (neat) 3329, 2950-2860, 1720, 1638, 1574, 1164, 984 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 5.5-6.5 (m, 6 H), 5.1 (m, 2H, NH), 4.1 (t, 4H, J = 6Hz), 3.1 (q, 4H, J = 6Hz), 1.6 ppm (m, 8H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.1, 158.7, 130.6, 128.1, 64.0, 39.7, 26.7, 25.9 ppm ; Anal. Calcd. C 57.68, H 7.74, N 8.97. Found C 57.41, H 7.73, N 9.02.

N, N'-[6-(2-propenoic acid) hexyl ester] urea (**3i**) : IR (neat) 3331, 2938-2860, 1724, 1660-1631, 1573, 1162, 984 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 5.7-6.8 (m, 6H), 4.8-5 (m, 2H, NH), 4.2 (t, 4H, J = 6Hz), 3.2 (m, 4H), 0.9-2.1 ppm (m, 16H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 165.9, 158.8, 130.2, 128.1, 64.0, 39.6, 29.9, 28.1, 26.1, 25.2 ppm ; HREIMS $C_{19}H_{32}N_2O_5$. M obsd. 368.23096 ; M req. 368.23113.

N, N'-[8-(2-propenoic acid) octyl ester] urea (**3j**) : IR (neat) 3329, 2932-2851, 1728, 1618, 1580, 1192, 984 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 5.5-6.5 (m, 6H), 4.7 (m, 2H, NH), 4.2 (t, 4H, J = 6Hz), 3.2 (q, 4H, J = 6Hz), 1.2-1.8 ppm (m, 24H), ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.1, 158.8, 130.3, 128.4, 64.4, 40.0, 30.1, 29.0, 28.9, 28.3, 26.7, 25.6 ppm ; Anal. Calcd. C 65.06, H 9.49, N 6.60. Found C 64.58, H 9.2, N 6.53

tris-[6-(2-methyl 2-propenoic acid) hexyl ester] isocyanuric acid ester (**5a**) : IR (neat) 2931-2857, 1702 (CO), 1639 (C=C), 1466, 1404, 1166, 940 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6,0 (s, 3H), 5.5 (s, 3H), 3.7-4.4 (m, 12H), 1.9 (s, 9H), 1.3-1.9 ppm (m, 24 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.2 (CO_2), 147.9 (CO), 135.5 (CH_2=), 124.1 (C=), 63.5 (CH2OCO), 41.7 (CH_2N), 27.5, 26.7, 25.3, 24.6 (4 CH2), 17.3 ppm (CH3); Anal. Calcd. C 62.54, H 8.11, N 6.63. Found C 62.40, H 8.13, N 6.31.

tris-[2-(2-methyl 2-propenoic acid) ethyl ester] isocyanuric acid ester (**5b**) : IR (neat) 2964-2960, 1703, 1639, 1461, 1158, 944 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.0 (s, 3H), 5.5 (s, 3H), 4.2 (m, 12H), 1.9 ppm (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.4, 148.2, 135.2, 125.4, 60.6, 41.1, 17.5 ppm ; Anal. Calcd. C 54.19, H 5.85, N 9.03. Found C 54.21, H 5.97, N 8.83.

tris-[3-(2-methyl 2-propenoic acid) propyl ester] isocyanuric acid ester (**5c**) : IR (neat) 2963-2930, 1702, 1638, 1461, 1176, 944 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 5.9 (s, 3 H), 5.4 (s, 3H), 4.0 (m, 6H) ; 3.9 (m, 6H), 1.9 ppm (m, 15H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.2, 148.3, 135.6, 124.6, 61.4, 39.6, 26.4, 17.5 ppm ; Anal. Calcd. C 56.80, H 6.55, N 8.28. Found C 56.59, H 6.59, N 8.23

tris-[4-(2-methyl 2-propenoic acid) butyl ester] isocyanuric acid ester (**5d**) : IR (neat) 2960, 1723, 1693, 1639, 1465, 1404, 1165, 940 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.0 (s, 3H), 5.5 (m, 3H), 3.7-4.3 (m, 12H), 1.9 (s, 9 H), 1.6-1.8 ppm (m, 12 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 167.3, 148.9, 136.9, 125.5, 64.0, 42.7, 26.0, 25.4, 18.3 ppm ; Anal. Calcd. C 59.00, H 7.15, N 7.645. Found C 59.15, H 7.27, N 7.40.

tris-[8-(2-methyl 2-propenoic acid) octyl ester] isocyanuric acid ester (**5e**) : IR (neat) 2933-2857, 1719, 1638, 1466, 1404, 1161, 938 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6,0 (s, 3H), 5.4 (s, 3H), 4.0 (t, 6H) ; 3.8 (m, 6H), 1.9 (s, 9H), 1.3 ppm (m, 36H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.8, 148.5, 136.0, 124.6, 64.2, 42.4, 28.7, 28.6, 28.6, 27.3, 26.1, 25.4, 17.8 ppm; Anal. Calcd. C 65.25, H 8.84, N 5.85. Found C 65,12. H 8.93, N 5.48.

tris-[2-(2-propenoic acid) ethyl ester] isocyanuric acid ester (**5f**) : IR (neat) 2966, 1727, 1692, 1637, 1459, 1407, 1183, 984 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 5.9-6.5 (m, 9H), 4.0-4.4 ppm (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.11, 149.10, 131.69, 128.14, 61.33 , 42.12 ppm; Anal. Calcd. C 51.06, H 4.99, N 9.82. Found C 51.01, H 5.20, N 9.40.

tris-[3-(2-propenoic acid) propyl ester] isocyanuric acid ester (**5g**) : IR (neat) 2967, 1726, 1693, 1637, 1467, 1410, 1197, 986 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.8-6.4 (m, 9H), 4.2 (t, 6H, J = 6Hz), 4.0 (t, 6H, J = 6Hz), 2.1 ppm (m, 6 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 165.5, 148.5, 130.6, 127.8, 61.6, 39.9, 26.6 ppm; Anal. Calcd. C 54.19, H 5.85, N 9.02. Found C 54.30, H 5.80, N 8.83.

tris-[4-(2-propenoic acid) butyl ester] isocyanuric acid ester (**5h**) : IR (neat) 2962, 2873, 1687, 1638, 1459, 1413, 1194, 986 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 6.4-5.4 (m, 9 H), 4.1 (t, 6H), 3.8 (t, 6H), 1.7 ppm (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 165.1, 148.5, 129.9, 127.8; 63.1, 41.7, 25.1, 23.2 ppm; Anal. Calcd. C 56.80, H 6.55, N 8.28. Found C 56.88, H 6.40, N 7.98.

tris-[6-(2-propenoic acid) octyl ester] isocyanuric acid ester (**5i**) : IR (neat) 2940-2861, 1725, 1689, 1638, 1466, 1409, 1192, 985 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.8-6.4 (m, 9 H), 4.1-4.2 (t, 6H, J = 6Hz), 3.8-3.9 (t, 6H, J = 6Hz), 1.6-1.75 (q, 12H, J = 6Hz), 1.3-1.5 ppm (m, 12H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 165.4, 148.3, 129.7, 127.9, 63.6, 42.1 , 27.7, 26.9, 25.6, 24.8 ppm; Anal. Calcd. C 60.90, H 7.66, N 7.10. Found C 60.93, H 7.77, N 6.88.

tris-[8-(2-propenoic acid) octyl ester] isocyanuric acid ester (**5j**) : IR (neat) 2932-2857, 1728, 1686, 1638, 1467, 1408, 1194, 985 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5,8-6.4 (m, 9H), 4.1-4.2 (t, 6H, J = 6Hz), 3.8-3.9 (t, 6H, J = 6 Hz), 1.5-1.7 (q, 12H, J = 7Hz), 1.3 ppm (s, 24 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 165.0, 148.0, 129.3, 127.7, 63.5, 41.8, 28.1, 27.9, 27.6, 26.8, 25.6, 24.8 ppm, Anal. Calcd. C 63.98, H 8.50, N 6.21. Found C 63.94, H 8.45, N 6.32.

2-methyl 2-propenoic acid, 6-isocyanatohexyl ester (**4a**) : IR (neat) 2939-2859 (CH_2), 2272 (NCO), 1719 (CO), 1638 (C=C), 1453 (CH_2), 1405 (CH3) (C=C), 1166 (CO), 940 cm^{-1}(C=C); ^1H NMR (400 MHz, $CDCl_3$) δ 6.1 (s, 1H), 5.55 (s, 1H), 4.15 (t, 2H, J = 6Hz), 3.3 (t, 2H, J = 6Hz), 1.95 (s, 3H), 1.6-1.75 (m, 4H), 1.4 ppm (m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.9 (CO_2), 130.2 (CH_2), 124.8 (CH_2=), 64.1 (CH_2OCO), 42.5 (CH_2N), 30.8, 28.1, 25.8, 25.1 (4 CH_2), 17.8 ppm (CH_3); Anal. Calcd. C 62.54, H 8.11, N 6.63. Found C 62.28, H 8.15, N 6.65.

2-methyl 2-propenoic acid, 3-isocyanatopropyl ester (**4c**) : IR (neat) 2961-2928, 2271, 1723, 1638, 1454, 1164, 941 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6,1 (s, 1H), 5.6 (s, 1H), 4.25 (t, 2H, J = 6Hz), 3.5 (t, 2H, J = 6Hz), 2.23 (q, 2H, J = 6Hz), 1.98 ppm (s, 3H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 166.1, 135.6, 124.7, 60.6, 39.3, 29.6, 17.4 ppm ; Anal. Calcd. C 56.80, H 6.55, N 8.28. Found C 56,97, H 6.61, N 8.36.

2-methyl 2-propenoic acid, 4-isocyanatobutyl ester (**4d**) : IR (neat) 2958, 2276, 1718, 1637, 1453, 1163, 939 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6,1 (s, 1H), 5.5 (ps, 1H), 4.2 (t, 2H, J=6Hz) ; 3.6 (t, 2H, J = 6Hz), 1.9 (s, 3H), 1.85 (m, 2H), 1.75 ppm (m, 2H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 166.4, 135.9, 124.6, 63.2, 43.8, 28.7, 25.5, 17.6 ppm; Anal. Calcd. C 59.98, H 7.15, N 7.64. Found C 59.76, H 7.20, N 7.33.

2-methyl 2-propenoic acid, 8-isocyanatooctyl ester (**4e**) : IR (neat) 2931-2857, 2272, 1719, 1639, 1466, 1403, 1166, 940 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.1 (s, 1H), 5.5 (s, 1H), 4.1 (t, 2H, J = 6Hz), 3.3 (t, 2H, J = 6Hz), 1.9 (s, 3H), 1.5-1.7 (m, 4H), 1.35 ppm (m, 8H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.8, 136.1, 124.5, 64.2, 42.5, 30.8, 28.6, 28.4, 28.1, 26.0, 25.4, 17.7 ppm; Anal. Calcd. C 65.25, H 8.84, N 5.65. Found C 64.89, H 8.86, N 5.74.

2-propenoic acid, 3-isocyanatopropyl ester (**4g**) : IR (neat) 2967, 2280, 1728, 1638, 1466, 1409, 1188, 984 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.85-6.45 (m, 3H), 4.3 (t, 2H, J = 6Hz), 3.5 (t, 2H, J = 6Hz) ; 2.0 ppm (q, 2H, J = 6Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 165.9, 131.0, 128.1, 61.2 , 39.8, 30.1 ppm ; Anal. Calcd. C 54.19, H 5.85, N 9.07. Found C 54.19, H 5.64, N 8.73.

2-propenoic acid, 4-isocyanatobutyl ester (**4h**) : IR (neat) 2960-2875, 2277, 1719, 1638, 1460, 1408, 1187, 983 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.8-6,3 (m, 3H), 4.16 (t, 2H, J = 6Hz), 3.55 (t, 2H, J = 6Hz) ; 1.8 ppm (m, 4H); ^{13}C NMR (250 MHz, $CDCl_3$) δ 166.0, 130.9, 128.3, 63.6, 44.4, 28.1, 26.0 ppm; Anal. Calcd. C 56.80, H 6.55, N 8.28 . Found C 57.08, H 6.64, N 8.40.

2-propenoic acid, 6-isocyanatohexyl ester (**4i**) : IR (neat) 2943-2862, 2274, 1727, 1638, 1463, 1409, 1196, 985 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.8-6,4 (m, 3H), 4,15 (t, 2H, J = 6Hz), 3.3 (t, 2H, J = 6Hz) ; 1.6-1.7 (m, 4H), 1.4 ppm (m, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 165.7, 130.0, 128.2, 63.9, 42.4, 30.7, 28.1, 25.8, 24.9 ppm; Anal. Calcd. C 60.91, H 7.66, N 7.10 Found C 60.39, H 7.60, N 7.10.

2-propenoic acid, 8-isocyanatooctyl ester (**4j**) : IR (neat) 2933-2859, 2274, 1726, 1638, 1467, 1408, 1191, 985 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.8-6.4 (m, 3H), 4.15 (t, 2H, J = 6Hz), 3.3 (t, 2H, J = 6Hz) ; 1.7 (m, 2H, J = 6Hz), 1.1-1.5 ppm (m, 8H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.1, 130.3, 128.5, 64.4, 42.8, 31.1, 28.9, 28.7, 28.4, 25.7 ppm ; Anal. Calcd. C 63.98, H 8.50, N 6.22, Found C 63.87, H 8.27, N 6.29.

Acknowledgements : The authors are grateful to ElF-Atochem for financial support. We thank Dr. N. Ferret (Elf-Atochem) for helpfull discussions during this work. We also thank referees for help and comments.

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(*Received in Belgium* 28 *June* 1994; *accepted* 26 *October* 1994)