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A NEW SYNTHESIS OF THIOCYANATOALKYL (METH)ACRYLIC ESTERS

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Abstract: The selective synthesis of thiocyanatoalkyl meth(acrylic) esters were obtained with 71 to 95 % yield under phase transfer catalysis from corresponding chloro- and bromoalkyl (meth)acrylic esters and potassium thiocyanate in presence of potassium iodide.

As part of our program aiming at the synthesis of functionalized acrylic monomers, we wanted to obtain thiocyanato alkyl acrylates and methacrylates starting from the corresponding haloakyl esters, according to Scheme 1.

Such synthesis must satisfy to the following conditions :

i) The nucleophile must selectively substitute the halide without attack of the very reactive unsaturation,

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Scheme 1

1 **2**

R = H, Me ; X = Cl, Br
n= 1 - 12

ii) polymerization must be avoided during the condensation as well as during the isolation of the monomer.

Exploratory experiments were performed with the industrially available chloroethylacrylate (CLEA) 1a (n = 2, X = Cl). We found that in methylethylketone (MEK) at 65 °C and in presence of catalytic amounts of KI (0.1 equiv.) and $Bu_4N^+I^-$ (0.2 equiv.), KSCN (2 equiv.) could be condensed with 1a (1 equiv.) to give 2a in 81 % yield after 63 hours.[1]

Starting from this first result, a systematic study of the reaction, which details will not be reported here, led to the following conclusions : i) NaSCN and NH_4SCN may also be used but lower yields were obtained (73 % and 20 % respectively).

ii) A decrease in the amount of KI or $Bu_4N^+I^-$ increased the reaction time and/or decreased the yield. However, an increase in the amount of one of these catalysts did not improve the condensation.

iii) As far as yields were concerned, the efficiency of the catalyst was found to follow the trend : $Ph_3MeP^+Br^-$ (90 %; 84 h.) > $Bu_4N^+I^-$ (79 %; 63 h.) > $Bu_4N^+Br^-$ (75 %; 71 h.) ≈ $Bu_4N^+Cl^-$ (72 %; 72 h.) ≈ $PhMe_3N^+Br^-$ (73 %; 120 h.) > $Bu_4N^+HSO_4^-$ (55 %; 75 h.) ≥ Aliquat 336 (52 %; 144h.). The reaction was faster with $Bu_4N^+I^-$ (63 h) than with $Ph_3MeP^+Br^-$ (84 h). However the later was preferred. Indeed, it is well known[2] that phosphonium salts are thermally more stable than ammonium, a property which could explain the better yield obtained with $Ph3MeP^+Br^-$.

iv) the influence of the solvent was studied at 65°C using $Ph_3MeP^+Br^-$ as catalyst. The following trend was found : MEK (90 %; 84 h.) ≈ DMA (dimethylacetamide) (90 %; 42 h.) > MeCN, PhCN (76 %; 72 h. and 120 h.) > DMF (dimethylformamide) (68 %; 48 h.) > EtOH (52 %; 120 h.) >> C_6H_{12}, $PhCH_3$ (11 %; 120 h.). In DMA, reaction time were shorter (42 h) than MEK (84 h). However during the workup, MEK may be removed under milder conditions and was thus preferred than DMA on account of the strong propensity of acrylic substrate to polymerize.

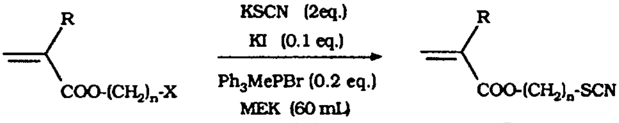
In accord with these above results, the reactions reported in the Table were performed. Starting materials 1 were either industrially available or easily prepared by esterification from (meth)acrylic chloride and chloro- or bromo-alcohols in presence of tertiary amine (see experimental part).

It is noteworthy that under our conditions the formation of the corresponding isothiocyanates was never observed. Moreover, the nucleophilic condensation of thiocyanates was very selective and the formation of by-products or polymers due to the attack of the reactive insaturation was very low. These results support the intermediary formation of iodides derivatives during the performed condensations. The very high reactivity of bromides derivatives compared to chlorides is particularly noteworthy. It must be attributed to a faster bromide-iodide exchange.

Incidentally we will mention that, during control experiments, we found that the interesting bromo- and iodoethyl methacrylates may beeasily obtained according the Scheme 2.

Finally, the result obtained with hydroxyalkylated 1 (n= 2, X= Cl, R= CHOHPh) (run 10) shows that the present reactions conditions may be easily applied to other haloalkyl acrylates.

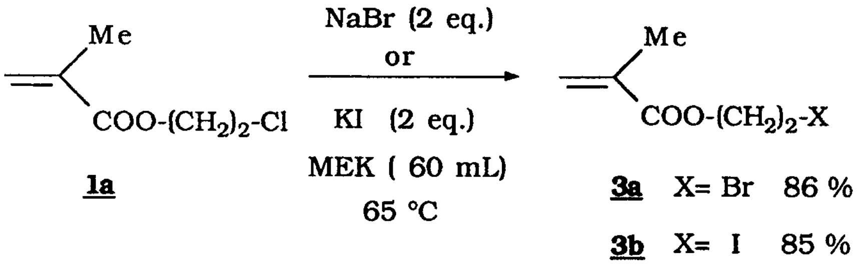
Table : Synthesis of thiocyanatoalkyl (meth)acrylates



1 **2**

Run	Substrate	X	R	n	Reaction time	Product	Isolated yield
1	**1a**	Cl	H	2	84 h.	**2a**	90 %
2	**1b**	Cl	CH_3	2	84 h.	**2b**	76 %
3	**1c**	Cl	H	3	45 h.	**2c**	92 %
4	**1d**	Cl	CH_3	3	26 h.	**2d**	79 %
5	**1e**	Cl	H	4	31 h.	**2e**	75 %
6	**1f**	Cl	CH_3	4	55 h.	**2f**	81 %
7	**1g**	Cl	H	6	30 h.	**2g**	80 %
8	**1h**	Cl	CH_3	6	24 h.	**2h**	82 %
9	**1i**	Cl	CH_3	10	26 h.	**2i**	71 %
10	**1j**	Cl	CH(OH)Ph	2	168 h.	**2j**	74 %
11	**1k**	Br	H	2	2 h.	**2a**	82 %
12	**1l**	Br	CH_3	2	2 h.	**2b**	86 %
13	**1m**	Br	H	5	2 h.	**2m**	89 %
14	**1n**	Br	CH_3	5	2 h.	**2n**	82 %
15	**1o**	Br	H	6	2 h.	**2g**	82 %
16	**1p**	Br	CH_3	6	2 h.	**2h**	90 %
17	**1q**	Br	H	8	2 h.	**2q**	85 %
18	**1r**	Br	CH_3	8	2 h.	**2r**	81 %
19	**1s**	Br	H	10	2 h.	**2s**	84 %
20	**1t**	Br	CH_3	10	2 h.	**2i**	75 %
21	**1u**	Br	H	12	2 h.	**2u**	95 %
22	**1v**	Br	CH_3	12	2 h.	**2v**	91 %

Scheme 2



However, it also appears that alpha substituants may play an important part on the reactivity of the starting material.

EXPERIMENTAL

All (meth)acrylic esters were stabilized with hydroquinone mono- methylether (100 ppm). Choro-2-ethyl acrylate and methacrylate were supplied from ATO (Atochem) and were used as received. Others bromo- and chloroalkyl(meth)acrylates were prepared in 60 to 80 % yield by esterification of (meth)acryloyl chlorides (1.2 eq.) with the corresponding bromo- and chloro alcohols[3] (1 eq.) at 0 °C in presence of triethylamine (2 eq.) in chloroform. Their spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR) were in agreement with the expected formulas and the literature data. Potassium bromide, potassium iodide, methyltriphenylphosphonium bromide, methyl ethyl ketone were available from Aldrich and used without further purification. IR spectra were recorded on a Perkin Elmer 840 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on a Jeol PMX 60 and Bruker AM400 spectrometers respectively. The HRMS were performed on a Finnigan Mat 95Q at the Centre de Recherche Lorraine ATO (Atochem) (Marienau, France).

General procedure: To a slurry of 9.70 g (100 mmol) of potassium thiocyanate, 0.83 g (5 mmol) of potassium iodide and 3.6 g (10 mmol) of triphenylmethylphosphonium bromide in 50 mL of methyl ethyl ketone at room temperature was added 50 mmol of bromo- or chloroalkyl (meth)acrylate 1 in 10 mL of methyl ethyl ketone. The mixture was then heated at 65 °C. The reaction was monitored by GC analysis of small aliquats. The internal standard was hydrocarbon (C_8-C_{18}). GC analyses were performed on a 10-ft OV 101 (10 %) at 80 - 150 °C under 1.25 bar. After completion and cooling, the mixture was diluted with 100 mL water and the organic phase was extracted into methylene chloride, dried over magnesium sulfate. After removal of the solvents, products 2 were separated by flash chromatography (ethyl acetate: 10-15 % / petroleum ether: 90-85 %).

2a : IR (neat) : 2957 cm^{-1} (C-H) ; 2157 cm^{-1} (S-C≡N) ; 1727 cm^{-1} (C=O) ; 1638 cm^{-1} (C=C) ; 1620-1190 cm^{-1} (C-O) ; 985 cm^{-1} (CH=). ^1H NMR (CCl_4) (δ ppm) : 5.67-6.67 (m, 3 H) ; 4.38 (t, 2 H, J = 6.5 Hz) ; 3.21 (t, 2 H, J = 6.5 Hz). ^{13}C NMR ($CDCl_3$) (δ ppm) : 164.64 (CO_2) ; 131.34 (CH_2=) ; 126.87 (CH=) ; 111.13 (SCN) ; 61.62 (CH_2OCO) ; 31.91 (CH_2SCN). HRMS : Calcd for $C_6H_8NO_2S$: 158.0279; Found : 158.0276

2b : IR (neat) : 2958 cm^{-1} (CH_2) ; 2158 cm^{-1} (SCN) ; 1723 cm^{-1} (CO_2) ; 1640 cm^{-1} (C=C). ^1H NMR (CCl_4) (δ ppm) : 6.19 (sl, 1 H) ; 5.64 (sl, 1 H) ; 4.47 (t, 2 H, J = 6 Hz) ; 3.30 (t, 2 H, J = 6 Hz) ; 1.98 (sl, 3 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 165.75 (CO_2) ; 134.76 (C=C) ; 125.83 (H_2C=) ; 111.0891 (SCN) ; 61.79 (CH_2OCO) ; 32.00 (CH_2SCN) ; 17.30 (CH_3). HRMS : calcd for $C_7H_{10}NO_2S$: 172.0430; Found : 172.0432.

2c : IR (neat) : 2965 cm^{-1} (CH_2) ; 2155 cm^{-1} (SCN) ; 1725 cm^{-1} (CO_2) ; 1638 cm^{-1} (C=C). ^1H NMR (CCl_4) (δ ppm) : 5.63-6.57 (m, 3 H) ; 4.23 (t, 2 H, J = 6 Hz) ; 3.00 (t, 2 H, J = 6 Hz) ; 2.16 (q, 2 H, 6 Hz). ^{13}C NMR ($CDCl_3$) (δ ppm) : 165.78 (CO_2) ; 131.40 (CH_2=) ; 127.78 (CH=) ; 111.70 (SCN) ; 61.49 (CH_2OCO) ; 30.62 (CH_2SCN) ; 28.96 (CH_2). HRMS : Calcd for $C_7H_{10}NO_2S$: 172.043033; Found : 172.043228

2d : IR (neat) : 2962 cm^{-1} (CH_2) ; 2155 cm^{-1} (SCN) ; 1718 cm^{-1} (CO_2) ; 1639 cm^{-1} (C=C). ^1H NMR (CCl_4) (δ ppm) : 6.05 (sl, 1 H) ; 5.53 (sl, 1 H) ; 4.27 (t, 2 H, J = 6 Hz) ; 3.05 (t, 2 H, J = 6 Hz) ; 2.19 (q, 2 H, 6 Hz) ; 1.91 (sl, 3 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 166.20 (CO_2) ; 135.31 (C=) ; 125.21 (H_2C=) ; 111.28 (SCN) ; 61.25 (CH_2OCO) ; 30.16 (CH_2SCN) ; 28.44 (CH_2) ; 17.36 (CH_3). HRMS : Calcd for $C_8H_{12}NO_2S$: 186.0589; Found : 186.0589.

2e : IR (neat) : 2957 cm^{-1} (CH_2) ; 2154 cm^{-1} (SCN) ; 1723 cm^{-1} (CO_2) ; 1638 cm^{-1} (C=C) ; 1620 cm^{-1}. ^1H NMR (CCl_4) (δ ppm) :

5.62-6.55 (m, 3 H) ; 4.13 (m, 2 H) ; 2.99 (m, 2 H) ; 1.59-2.23 (m, 4 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 165.90 (CO_2) ; 130.80 (CH_2=) ; 128.16 (CH=) ; 111.73 (SCN) ; 63.18 (CH_2OCO) ; 33.47 (CH_2SCN) ; 26.90 (CH_2) ; 26.50 (CH_2). HRMS : Calcd for $C_8H_{12}NO_2S$: 186.0588; Found: 186.0589.

2f : IR (neat) : 2957 cm^{-1} (CH_2) ; 2154 cm^{-1} (SCN) ; 1716 cm^{-1} (CO_2) ; 1638 cm^{-1} (C=C) ; 1618 cm^{-1}. ^{1}H NMR (CCl_4) (δ ppm) : 6.02 (sl, 1 H) ; 5.52 (sl, 1 H) ; 3.02 (m, 2 H) ; 1.92 (sl, 2 H) ; 1.67-2.17 (m, 4 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 166.11 (CO_2) ; 135.45 (C=) ; 124.70 (H_2C=) ; 111.14 (SCN) ; 62.72 (CH_2OCO) ; 32.72 (CH_2SCN) ; 26.14 (CH_2) ; 25.88 (CH_2) ; 17.47 (CH_3). HRMS : Calcd for $C_9H_{14}NO_2S$: 200.0744; Found : 200.0745.

2g : IR (neat) : 2939 cm^{-1} (CH_2) ; 2863 cm^{-1} ; 2154 cm^{-1} (SCN) ; 1723 cm^{-1} (CO_2) ; 1638 cm^{-1} (C=) ; 1620. ^{1}H NMR (CCl_4) (δ ppm) : 5.61-6.65 (m, 3 H) ; 4.1 (t, 2 H, 6 Hz) ; 2.96 (t, 2 H, 6 Hz) ; 1.07-2.13 (m, 8 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 165.57 (CO_2) ; 130.10 (CH_2=) ; 128.02 (HC=) ; 111.77 (SCN) ; 63.70 (CH_2OCO) ; 33.33 (CH_2SCN) ; 29.25 (CH_2) ; 27.85 (CH_2) ; 26.99 (CH_2) ; 24.78 (CH_2). HRMS : Calcd for $C_{10}H_{16}NO_2S$: 214.0902; Found : 214.0902.

2h : IR (neat) : 2937 + 2861 cm^{-1} (CH_2) ; 2154 cm^{-1} (SCN) ; 1717 cm^{-1} (CO_2) ; 1678-1638 cm^{-1} (C=C). ^{1}H NMR (CCl_4) (δ ppm) : 6.17 (sl, 1 H) ; 5.50 (sl, 1 H) ; 4.10 (t, 2 H, 6 Hz) ; 2.95 (t, 2 H, 6 Hz) ; 1.92 (sl, 3 H) ; 1.25-2.20 (m, 8 H).^{13}C NMR ($CDCl_3$) (δ ppm) : 166.37 (CO_2) ; 135.65 (C=) ; 124.50 (H_2C=) ; 111.44 (SCN) ; 63.61 (CH_2OCO) ; 33.08 (CH_2SCN) ; 29.06 (CH_2) ; 27.64 (CH_2) ; 26.75 (CH_2) ; 24.61 (CH_2) ; 17.57 (CH_3). HRMS : Calcd for $C_{11}H_{18}NO_2S$: 228.1057; Found : 228.1058

2i : IR (neat) : 2930 + 2856 cm^{-1} (CH_2) ; 2154 cm^{-1} (SCN) ; 1717-1678 cm^{-1} (CO_2) ; 1639 cm^{-1} (C=C). ^{1}H NMR (CCl_4) (δ ppm) : 5.97 (sl, 1 H) ; 5.43 (sl, 1 H) ; 4.05 (t, 2 H, 6 Hz) ; 2.91

(t, 2 H, 6 Hz) ; 1.89 (sl, 3 H) ; 1.13-2.12 (m, 16 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 166.75 (CO_2) ; 135.98 (C=) ; 124.60 (CH_2=) ; 111.73 (SCN) ; 64.17 (CH_2OCO) ; 33.50 (CH_2SCN) ; 29.40 (CH_2) ; 29.85 (CH_2) ; 28.76 (CH_2) ; 28.66 (CH_2) ; 28.35 (CH_2) ; 28.09 (CH_2) ; 27.39 (CH_2) ; 25.45 (CH_2) ; 17.81 (CH_3). HRMS : Calcd for $C_{15}H_{26}NO_2S$: 284.1685; Found : 284.1684

2j : IR (neat) : 3484 cm^{-1} (O-H) ; 3087-2953 cm^{-1} (C-H, C-H) ; 2157 cm^{-1} (C≡N) ; 1721 cm^{-1} (C=O) ; 1630-1603 cm^{-1} (C=C) ; 1493, 1455 cm^{-1} (C=C) ; 766, 701 cm^{-1} ; 917 cm^{-1}. ^{1}H NMR (CCl_4) (δ ppm) : 7.24 (sl, 5 H) ; 6.34 (sl, 1 H) ; 5.87 (sl, 1 H) ; 5.48 (m, 1 H) ; 4.32 (t, 2 H, J = 6 Hz) ; 3.04 (t, 2 H, J = 6 Hz) ; 2.89-3.2 (m, 1 H, OH). ^{13}C NMR ($CDCl_3$) (δ ppm) : 165.47 (CO_2) ; 141.44 , 141.15 (C=) ; 128.44 , 127.92 , 127.16 , 126.63 (C=C) ; 111.24 (SCN) ; 72.76 (CH) ; 62.29 (CH_2OCO) ; 32.51 (CH_2SCN).

2m : IR (neat) : 2944 cm^{-1} (CH_2) ; 2865 cm^{-1} ; 2154 cm^{-1} (SCN) ; 1722 cm^{-1} (CO_2) ; 1637 cm^{-1} (C=C) ; 1619 cm^{-1}. ^{1}H NMR (CCl_4) (δ ppm) : 5.60-6.60 (m, 3 H) ; 4.1 (t, 2 H, 6 Hz) ; 2.93 (t, 2 H, 6 Hz) ; 1.23-2.1 (m, 6 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 165.11 (CO_2) ; 129.89 (CH_2=) ; 127.76 (CH=) ; 111.38 (SCN) ; 63.20 (CH_2OCO) ; 32.96 (CH_2SCN) ; 28.79 (CH_2) ; 27.17 and 23.62 (CH_2). HRMS : Calcd for $C_9H_{14}NO_2S$: 200.0743; Found : 200.0745

2n : IR (neat) : 2946 cm^{-1} (CH_2) ; 2864 cm^{-1} ; 2154 cm^{-1} (SCN) ; 1716 cm^{-1} (CO_2) ; 1638 cm^{-1} (C=C). ^{1}H NMR (CCl_4) (δ ppm) : 6.02 (sl, 1 H) ; 5.33 (sl, 1H) ; 4.12 (t, 2 H, 6 Hz) ; 2.97 (t, 2 H, 6 Hz) ; 1.90 (sl, 3 H) ; 1.33-2.13 (m, 6 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 166.15 (CO_2) ; 135.53 (C=) ; 124.44 (H_2C=); 111.26 (SCN) ; 63.27 (CH_2OCO) ; 32.91 (CH_2SCN) ; 28.73 (CH_2) ; 27.10 (CH_2) ; 23.59 (CH_2) ; 17.41 (CH_3). HRMS : Calcd for $C_{10}H_{16}NO_2S$: 214.0901; Found : 214.0902.

2q : IR (neat) : 2932-2858 cm^{-1} (CH_2) ; 2154 cm^{-1} (SCN) ; 1724 cm^{-1} (CO_2) ; 1637 cm^{-1} (C=C) ; 1620 cm^{-1}. ^{1}H NMR (CCl_4) (δ ppm) : 5.60-6.53 (m, 3 H) ; 4.07 (t, 2 H, 6 Hz) ; 2.93 (t, 2 H, 6 Hz) ; 1.17-2.00 (m, 12 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 165.11 (CO_2) ; 129.61 (CH_2=) ; 127.90 (CH=C) ; 111.38 (SCN) ; 63.63 (CH_2OCO) ; 33.15 (CH_2SCN) ; 29.11 (CH_2) ; 28.20 (CH_2) ; 27.98 (CH_2) ; 27.80 (CH_2) ; 26.99 (CH_2) ; 25.03 (CH_2). HRMS : Calcd for $C_{12}H_{20}NO_2S$: 242.1213; Found : 242.1215.

2r : IR (neat) : 2934 + 2858 cm^{-1} (CH_2) ; 2154 cm^{-1} (SCN) ; 1716 cm^{-1} (CO_2) ; 1638 cm^{-1} (C=C). ^{1}H NMR (CCl_4) (δ ppm) : 5.95 (sl, 1 H) ; 5.42 (sl, 1 H) ; 4.04 (t, 2 H, 6 Hz) ; 2.93 (t, 2 H, 6 Hz) ; 1.89 (sl, 3 H) ; 1.04-2.21 (m, 12 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 166.44 (CO_2) ; 135.79 (C=) ; 124.42 (H_2C=) ; 111.48 (SCN) ; 63.88 (CH_2OCO) ; 33.28 (CH_2SCN) ; 29.20 (CH_2) ; 28.30 (CH_2) ; 28.09 (CH_2) ; 27.88 (CH_2) ; 27.11 (CH_2) ; 25.18 (CH_2) ; 17.62 (CH_3). HRMS : Calcd for $C_{13}H_{22}NO_2S$: 256.1368; Found : 256.1371.

2s : IR (neat) : 2927-2856 cm^{-1} (CH_2) ; 2154 cm^{-1} (SCN) ; 1727 cm^{-1} (CO_2) ; 1637 cm^{-1} (C=C) ; 1620 cm^{-1}. ^{1}H NMR (CCl_4) (δ ppm) : 5.60-6.53 (m, 3 H) ; 4.05 (t, 2 H, 6 Hz) ; 2.93 (t, 2 H, 6 Hz) ; 1.03-2.13 (m, 16 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 165.03 (CO_2) ; 129.49 (CH_2=) ; 127.91 (CH=) ; 111.28 (SCN) ; 68.65 (CH_2OCO) ; 33.16 (CH_2SCN) ; 29.14 (CH_2) ; 28.58 (CH_2) ; 28.50 (CH_2) ; 28.40 (CH_2) ; 28.08 (CH_2) ; 27.84 (CH_2) ; 27.08 (CH_2) ; 25.12 (CH_2). HRMS : Calcd for $C_{14}H_{24}NO_2S$: 270.1527; Found : 270.1528.

2u : IR (neat) : 2927-2856 cm^{-1} (CH_2) ; 2155 cm^{-1} (SCN) ; 1724 cm^{-1} (CO_2) ; 1637 cm^{-1} (C=C) ; 1622 cm^{-1}. ^{1}H NMR (CCl_4) (δ ppm) : 5.60-6.53 (m, 3 H) ; 4.07 (t, 2 H, 6 Hz) ; 2.92 (t, 2 H, 6 Hz) ; 1.07-2.13 (m, 20 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 165.43 (CO_2) ; 129.74 (CH_2=) ; 128.13 (HC=) ; 111.60 (SCN) ; 63.97 (CH_2OCO) ; 33.43 (CH_2SCN) ; 29.36 (CH_2) ; 28.92 (3 CH_2) ; 28.81 (CH_2) ; 28.68 (CH_2) ; 28.34 (CH_2) ; 27.07 (CH_2) ; 27.35 (CH_2) ; 25.37 (CH_2). HRMS : Calcd for $C_{16}H_{28}NO_2S$: 298.184100; Found : 298.184078

2v : IR (neat) : 2929 + 2856 cm^{-1} (CH_2) ; 2154 cm^{-1} (SCN) ; 1719-1678 cm^{-1} (CO_2) ; 1639 cm^{-1} (C=C). ^{1}H NMR (CCl_4) (δ ppm) : 6.02 (sl, 1 H) ; 5.46 (sl, 1 H) ; 4.07 (t, 2 H, 6 Hz) ; 2.93 (t, 2 H, 6 Hz) ; 1.92 (sl, 3 H) ; 1.03-2.20 (m, 20 H). ^{13}C NMR ($CDCl_3$) (δ ppm) : 166.70 (CO_2) ; 135.99 (C=) ; 124.55 (CH_2=) ; 111.67 (SCN) ; 64.18 (CH_2OCO) ; 33.51 (CH_2SCN) ; 29.41 (CH_2) ; 28.98 (3 CH_2) ; 28.86 (CH_2) ; 2873 (CH_2) ; 28.39 (CH_2) ; 28.11 (CH_2) ; 27.41 (CH_2) ; 25.47 (CH_2) ; 17.80 (CH_3). HRMS : Calcd for $C_{17}H_{30}NO_2S$: 312.1998; Found : 312.1997

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References and notes:

1- Without catalyst, yield only reached 35 % in 72 hours.

2- E.V. Dehmlow, S. S. Dehmlow " Phase Transfer Catalysis. Monographs in Modern Chemistry", Vol. 11 Verlag Chemie, 1980.

3- Bromoalcohols were prepared according the procedure described by S. K. KANG, Synthesis, 1985, 1161.

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