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SELECTIVE SYNTHESIS OF NEW ω-PHALIMIDOALKYL (METH)ACRYLIC ESTERS

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Abstract: The selective synthesis of ω-phtalimidoalkyl meth(acrylic) esters was obtained in 71 to 81 % yields under phase transfer catalysis from corresponding bromoalkyl (meth)acrylates and potassium phtalimide. Chloro-derivatives gave the same products in the presence of catalytic amount of potassium iodide.

Functional (meth)acrylic monomers are of particular interest in the synthesis of polymeric materials.[1] On the nature of the functional group anchored to the (meth)acrylic part depends the application of a particular monomer. As part of our program aiming at the synthesis of new (meth)acrylates,[2,3,4] we planned to prepare ω-phtalimidoalkyl (meth)acrylates starting from the corresponding ω-haloalkyl esters and a phtalimide alkali salt.

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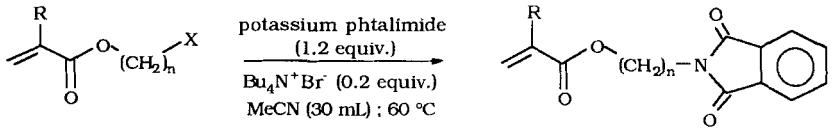
In such selective functionalization, Michael addition of the nucleophile to the acrylic part or/and anionic group transfer polymerizations are the main side-reactions.

We describe in the present communication a synthesis of ω-phtalimidoalkyl (meth)acrylates in which solid-liquid phase transfer catalysis (PTC) allows preventing these drawbacks. The best results obtained with various bromo and chloro-alkyl (meth)acrylates (industrially available or easily prepared according to experimental section) are gathered in the Table.

From runs 1 to 10, it appeared that under our conditions the nucleophilic condensation of potassium phtalimide with bromo compounds was very selective and the formation of by-products or polymers due to the attack of the very reactive insaturation was very slow. Indeed the obtained isolated yields were ranged from 71 % to 81 % either in methacrylic or in acrylic series. Compared with our previous work concerning condensation of thiocyanate,[3] it is interesting to underline the unusually high reactivity of 2-bromoethyl methacrylic or acrylic esters. Under aprotic conditions used, the steric hindrance was decreased in 2-halogenoethyl methacrylates[3b] and only electronic effects and the δ-assistance of the carbonyl group in the transition state governed the substitution. On an other hand, the lower reactivity of methacrylate *versus* acrylate confirmed that alpha substituent plays an important part on the reactivity of these substrates. [3,4]

When we tried to apply this kind of reaction to some industrial ω-choroalkyl (meth)acrylates (runs 11 to 16), we

Table. Synthesis of ω-phtalimidoalkyl (meth)acrylates from bromo and chloroalkyl derivatives.[a]



Run	Substrate	R	X	n	Reaction time	Product	Isolated yield
1	**1a**	H	Br	2	8 h.	**2a**	71 %
2	**1b**	H	Br	3	20 h.	**2b**	78 %
3	**1c**	H	Br	5	20 h	**2c**	76 %
4	**1d**	H	Br	6	20 h.	**2d**	81 %
5	**1e**	H	Br	8	18 h.	**2e**	80 %
6	**1f**	CH_3	Br	2	13 h.	**2f**	81 %
7	**1g**	CH_3	Br	3	15 h.	**2g**	73 %
8	**1h**	CH_3	Br	5	22 h.	**2h**	78 %
9	**1i**	CH_3	Br	6	26 h.	**2i**	81 %
10	**1j**	CH_3	Br	8	25 h.	**2j**	80 %
11	**1k**	H	Cl	2	20 h.	**2a**	37 %
12	**1l**	H	Cl	6	34 h.	**2d**	30 %
13	**1m**	CH_3	Cl	2	14 h	**2f**	75 %
14	**1n**	CH_3	Cl	6	28 h.	**2i**	79 %
15	**1k**	H	Cl	2	10 h.	**2a**	51 %[b]
16	**1l**	H	Cl	6	24 h.	**2d**	50 %[b]

(a) Reactions performed on a 10 mmoles scale. (b) Reactions performed in the presence of 0.2 equiv. of KI.

observed that less sensitive methacrylates can be converted into phtalimido derivatives with excellent yields (runs 13 and 14) while acrylic derivatives gave only poor yields (runs 11 and 12). Indeed a large amount of polymers were detected in these last experiments showing high reactivity of the conjugated insaturation of these monomers. We tried to accelerate the nucleophilic substitution by a catalytic addition of potassium iodide (0.2 equiv.). Then, the isolated yields were reached up to 50 % (runs 15 and 16). In these cases, the previous conversion of chlorides into bromides or iodides[3c] must be preferred.

In summary, a convenient and selective method under phase transfer catalysis conditions has been developed for the preparation of ω-phtalimidoalkyl (meth)acrylates starting from the corresponding halogenoalkyl derivatives. Examination of the potential ability of these monomers to polymerize are in current investigations.

EXPERIMENTAL

General. All (meth)acrylic esters were stabilized with 100 ppm of hydroquinone monomethyl ether. 2-Chloroethyl acrylate and methacrylate were supplied from Elf-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 equiv.) with corresponding bromo- or chloro alcohols (1 equiv.) at 0 °C in the presence of triethylamine (2 equiv.) in chloroform. Their spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR) were in agreement with the expected formulas and

the literature data. Potassium phtalimide was prepared from KOH and phtalimide.[5]

Tetrabutylammonium bromide, methyltriphenylphosphonium bromide, acetonitrile, methyl ethyl ketone were available from Aldrich and used without further purification. IR spectra were recorded on a Perkin Elmer 840 spectrophotometer. ^{1}H and ^{13}C NMR were obtained on Bruker AM 400 spectrometer (with Me_4Si as internal standard). Elemental analysis were recorded by CNRS laboratory (Vernaison). Melting points were determined on a Totoli melting point apparatus and are uncorrected.

General procedure. To a slurry of 2.22 g (12 mmol.) of potassium phtalimide, (2 mmol.) of tetrabutyl ammonium bromide in 25 mL of MeCN at room temperature was dropwise added 10 mmoles of bromoalkyl methacrylate in 5 mL MeCN. The mixture was then heated at 60 °C. The reaction was monitored by GC analysis of small aliquats using an internal standard method (C8-C18). GC analyses were performed on a 10-ft OV 101 (10 %) at 80 -150 °C under 1.5 bar. After completion and cooling, the mixture was diluted with 100 mL water and the organic phase was extracted into methylene chloride and dried over magnesium sulfate. After removal of the solvents, products 2 were separated by flash chromatography (ethyl acetate : 15-20 % / petroleum ether : 85-80 %).

2-propenoic acid, 2-phtalimidoethyl ester **2a** : M.p. = 97 °C. IR (neat) ν : 2948, 1774-1728, 1638, 1464, 1187 and 717 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.9 (m, 2H, J = 7 Hz) ; 7.7 (m, 2 H, J = 7 Hz) ; 6.4-5.8 (m, 3 H) ; 4.4 (t, 2H, J = 7 Hz) and 4.0 ppm (t, 2 H, J = 7 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ : 167.9 (CO); 165.7 (CO_2); 134.0; 131.9; 131.3 (CH_2=); 127.9 (CH=); 123.3; 61.6 ($\underline{C}H_2OCO$) and 36.9 ppm (CH_2N). Elemental anal. Calc.: C 63.67, H 4.52, N 5.71; Found : C 63.22, H 4.41, N 5.46.

2-propenoic acid, 3-phtalimidopropyl ester **2b** : IR (neat) ν : 3064, 2959, 1954, 1774-1723, 1638, 1619, 1468, 1191 and 721 cm^{1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.8-7.7 (m, 4 H); 6.4-

5.8 (m, 3 H); 4.2 (t, 2 H, J = 7 Hz); 3.8 (t, 2 H, J = 7 Hz) and 2.1 ppm (t, 2 H, J = 7 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ : 167.2 (CO); 164.9 (CO_2); 133.2; 131.25; 130.0 (CH_2=); 127.5 (C=); 122.3; 61.3 ($\underline{C}H_2OCO$); 34.25 (CH_2N) and 26.8 ppm (CH_2). Elemental anal. Calc. C 64.86, H 5.05, N 5.40; Found : C 65.05, H 5.06, N 5.39.

2-propenoic acid, 5-phtalimidopentyl ester **2c** : IR (neat) ν : 3062, 2942-2864, 1774-1712, 1637, 1619, 1467, 1192 and 719 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ : 7.8 (m, 2 H); 7.7 (m, 2 H); 6.4-5.8 (m, 3 H); 4.15 (t, 2 H, J = 7 Hz); 3.7 (t, 2 H, J = 7 Hz); 1.75 (qt, 4 H, J = 7 Hz) and 1.4 ppm (qt, 2 H, J = 7 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) d : 168.1 (CO); 166.0 (CO_2); 133.7; 131.9; 130.3 (CH_2=); 128.3 (CH=); 122.9; 64.0 ($\underline{C}H_2OCO$); 37.5 (CH_2N); 28.0; 27.9 and 23.0 ppm (CH_2). Elemental anal.: Calc. C 66.89, H 5.96, N 4.87; Found : C 67.03, H 6.03, N 4.86.

2-propenoic acid, 6-phtalimidohexyl ester **2d** : IR (neat) ν : 3060, 2941-2862, 1774-1713, 1637, 1619, 1468, 1189 and 720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ : 7.8-7.7 (m, 4 H); 6.4-5.8 (m, 3 H); 4.1 (t, 2 H, J = 7 Hz); 3.7 (t, 2 H, J = 7 Hz); 1.7 (m, 4 H) and 1.4 ppm (m, 4 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ : 168.0 (CO); 165.8 (CO_2); 133.6; 131.7; 129.9 (CH_2=); 128.5 (CH=); 122.7; 64.2 ($\underline{C}H_2OCO$); 37.5 (CH_2N); 28.2; 26.2; and 25.3 ppm (CH_2). Elemental anal. Calc.: C 67,76. H 6.35, N 4.65; Found : C 67.47, H 6.28, N 4.50.

2-propenoic acid, 8-phtalimidooctyl ester **2e** : IR (neat) ν : 3062, 2933-2857, 1774-1709, 1637, 1619, 1468, 1189 and 719 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ : 7.8 (m, 2 H); 7.7 (m, 2 H); 6.4-5.8 (m, 3 H); 4.1 (t, 2 H, J = 7 Hz); 3.7 (t, 2 H, J = 7 Hz); 1.7 (m, 4 H) and 1.3 ppm (m, 8 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ : 167.9 (CO); 165.75 (CO_2); 133.4; 131.8; 130.0 (CH_2=); 128.3 (CH=); 122.7; 64.2 ($\underline{C}H_2OCO$); 37.5 (CH_2N); 28.7; 28.6; 28.2; 26.3 and 25.5 ppm. Elemental anal.: Calc.: C 69.28, H 7.04, N 4.25; Found : C 69.24, H 7.10, N 4.31.

2-methyl-2-propenoic acid, 2-phtalimidoethyl ester **2f** : M. p. = 90 °C. IR (neat) ν : 3060-3044, 2931-2905, 1779-1707, 1633,

1468, 1172 and 719 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ : 7.9 (m, 2 H, J = 7 Hz); 7.75 (m, 2 H, J = 7 Hz); 6.1 (s, 1 H); 5.55 (s, 1H); 4.4 (t, 2H, J=7 Hz); 4.0 (t, 2H, J=7 Hz) and 1.9 ppm (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ : 168.0 (CO); 167.0 (CO_2); 135.8; 134.0; 132.0 (C=); 126.1 (CH_2=); 123.3; 61.9 ($\underline{C}H_2OCO$); 36.9 (CH_2N) and 18.1 ppm (CH_3). Elemental anal. Calc.: C 64.80, H 5.05, N 5.40; Found : C 64.65, H 4.82, N 5.22.

2-methyl-2-propenoic acid, 3-phtalimidopropyl ester **2g** : IR (neat) ν : 3064, 2960-2899, 1776-1710, 1639, 1616, 1468, 1174 and 721 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ : 7.8 (m, 2 H, J = 7 Hz); 7.7 (m, 2 H, J = 7 Hz); 6.1 (s, 1 H); 5.5 (s, 1 H); 4.2 (t, 2 H, J = 7 Hz); 3.8 (t, 2 H, J = 7 Hz); 2.1 (qt, 2 H, J = 7 Hz) and 1.9 ppm (s, 3 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ : 167.9 (CO); 166.8 (CO_2); 155.8; 133.7; 131.7 (C=); 125.2 (CH_2=); 122.9; 61.7 ($\underline{C}H_2OCO$); 34.7 (CH_2N); 27.3 (CH_2) and 17.9 ppm (CH_3). Elemental anal. Calc.: C 65.92, H 5.53, N 5.12; Found : C 66.30, H 5.54, N 5.14.

2-methyl-2-propenoic acid, 5-phtalimidopentyl ester **2h** : IR (neat) ν : 2942-2863, 1775-1703, 1638, 1618, 1468, 1172 and 720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ : 7.8 (m, 2 H, J = 7 Hz); 7.7 (m, 2 H, J = 7 Hz); 6.1 (s, 1 H); 5.5 (s, 1 H); 4.1 (t, 2 H, J = 7 Hz); 3.7 (t, 2 H, J = 7 Hz); 1.9 (s, 3 H); 1.7 (qt, 4 H, J = 7 Hz) and 1.5 ppm (qt, 2 H, J = 7 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ : 168.2 (CO); 167.2 (CO_2); 136.2; 133.7; 131.9 (C=); 125.1 (CH_2=); 122.9; 64.2 ($\underline{C}H_2OCO$); 37.5 (CH_2N); 28.0; 27.9; 23.1 (CH_2) and 18.1 ppm (CH_3). Elemental anal. Calc.: C 67.76, H 6.35, N 4.65; Found : C 67.46, H 6.24, N 4.53.

2-methyl-2-propenoic acid, 6-phtalimidohexyl ester **2i** : IR (neat) ν : 2931, 1771-1713, 1638, 1618, 1470, 1170 and 720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ : 7.8 (m, 2 H, J = 7 Hz); 7.7 (m, 2 H, J = 7 Hz); 6.1 (s, 1 H); 5.5 (s, 1 H); 4.1 (t, 2 H, J = 7 Hz); 3.7 (t, 2 H, J = 7 Hz); 1.9 (s, 3 H); 1.7 (qt, 4 H, J = 7 Hz) and 1.4 ppm (m, 4 H, J = 7 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ : 168.25 (CO); 167.3 (CO_2); 136.3; 133.7; 132.0 (C=C); 125.1 (CH_2=); 123.0; 64.5 ($\underline{C}H_2OCO$); 37.7 (CH_2N); 28.3; 26.4; 25.5

(CH_2) and 18.2 ppm (CH_3). Elemental anal. Calc.: C 68.55, H 6.71, N 4.44; Found : C 68.31, H 6.78, N 4.49.

2-methyl-2-propenoic acid, 8-phtalimidooctyl ester **2j** : IR (neat) ν : 2932-2857, 1775-1703, 1638, 1618, 1468, 1167 and 719 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ : 7.8 (m, 2 H, J = 7 Hz); 7.7 (m, 2 H, J = 7 Hz); 6.1 (s, 1 H); 5.5 (s, 1 H); 4.1 (t, 2 H, J = 7 Hz); 3.7 (t, 2 H, J = 7 Hz); 1.9 (s, 3 H); 1.7 (m, 4 H) and 1.35 ppm (m, 8 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ : 168.1; 167.1 (CO_2); 136.2; 133.6; 131.8 (C=); 124.9 (CH_2=); 122.8; 64.4 ($\underline{C}H_2OCO$); 37.7 (CH_2N); 28.8; 28.7; 28.3; 26.5; 25.6 (CH_2) and 18.1 ppm (CH_3). Elemental anal. Calc.: C 69.95, H 7.34, N 4.08; Found : C 69.95, H 7.35, N 4.03.

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