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Formation of monomeric halogenoaryl acrylates in the presence of hindered pyridine bases

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Abstract

Acylation of perhalogenophenols and pyridinols by acryloyl chloride in the presence of hindered pyridines, such as 2,6-lutidine, afforded the corresponding acrylates which were isolated in a pure form by chromatography on a Florisil® column. This was performed without in situ polymerization of the corresponding acrylates.

Keywords: Halogenoaryl acrylates; Fluorine; Acrylates; Esterification; Photonics

1. Introduction

Polyacrylates of fluorinated alcohols are interesting materials to build waveguides and optical fibers owing to their high transparency in the 1200–1600 nm wavelength region, used in optical communications, as well as their relatively low refractive indices [1]. These properties can be changed by modifying the number of fluorine atoms in the side chain and/or by introducing other, heavier, elements. The use of acrylic aryl esters instead of alkyl esters can also be applied to change the refractive index while increasing the glass transition temperature of the resulting polymer. For the preparation of these polymers or copolymers, the monomers are required to be isolated in a very pure form and the polymerization has to be controlled carefully.

2. Results and discussion

Although α-chloroacrylate, α-fluoroacrylate and methacrylate derivatives of pentafluorophenol are known [1–3], there is no clear description of the corresponding parent (unsubstituted) acrylate.[1] This class of compounds should exhibit higher transparency than methacrylate derivatives owing to their lower hydrogen contents. Their lower intrinsic Tg could however be increased by reticulation. In an attempt to acylate pentafluorophenol **2a** by acryloyl chloride **1** in THF at 0°C in the presence of pyridine, a significant in situ polymerization of pentafluorophenyl acrylate **3a** was observed once it was formed. A possible cause for this undesired reaction could be the Michael addition of pyridine to acrylate **3a**, initiating a probable anionic polymerization. To try to limit this addition reaction, more hindered pyridines were used as proton acceptors. No in situ polymerization of **3a** took place in the presence of 2,6-lutidine (2,6-dimethylpyridine) or of 2,6-di-*tert*-butyl-4-methylpyridine (Scheme 1). Moreover, an excess of these bases could be used to prevent another undesired side reaction: the addition of hydrogen chloride onto the activated double bond of the acrylate.

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[1] The thermal decomposition of poly(pentafluorophenyl)acrylate was reported without any description of its preparation [4]. The acylation of pentafluorophenol in chilled 10% sodium hydroxide solution was claimed to occur by addition of acryloyl chloride over a 1-h period, followed by stirring the mixture for 15 h [5]. No details were given for the crude product thus obtained. Our attempts to repeat this procedure led mainly to pentafluorophenol mixed with a polymeric white solid.

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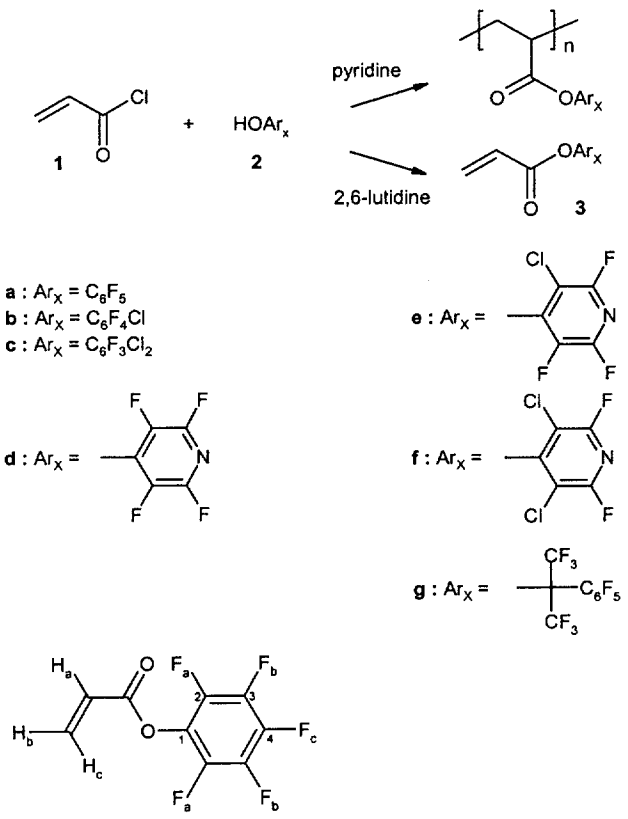

Scheme 1.

Table 1
Halogenoaryl acrylates prepared

Entry	Monomer	Solvent	T (°C)	Time	Yield (%)
1	**3a**	THF	0	5 min	86
2	**3b** [a]	THF	0	45 min	86
3	**3c** [b]	THF	0	20 min	69
4	**3d**	THF	0	45 min	82
5	**3e**	Et_2O	20	45 min	90
6	**3f** [c]	Et_2O	20	1 h	91
7	**3g** [d]	Pentane	20	19 h	66

[a] Mixture of regioisomers (72% 4-chloro, 21% 2-chloro, 7% 3-chloro).
[b] Mixture of regioisomers (80% 2,4-dichloro, 11% 3,4-dichloro, 6% 2,6-dichloro, 3% 2,3-dichloro).
[c] White solid (m.p. 39°C).
[d] White solid (m.p. 38°C).

Aryl esters are easily hydrolyzed [6], especially when the aromatic ring is substituted by electron-withdrawing atoms. Acrylate **3a** did not survive when it was submitted to an aqueous acidic treatment to remove the excess of base. Its hydrolysis was also observed when it was chromatographed on a silica gel column. Fortunately, elution on a Florisil® column[2] allowed its isolation in a very pure form.

Chlorotetrafluorophenyl acrylate **3b** and dichlorotrifluorophenyl acrylate **3c** were prepared from the isomeric mixture of their corresponding phenols **2b** and **2c** [7] (see Table 1). Tetrafluoropyridyl acrylate **3d** could also be obtained in THF at 0°C in the presence of 2,6-lutidine. An attempt to use the same conditions for the preparation of acrylates **3e** or **3f** from perhalogenopyridinols [8] met with little success owing to their polymerization. However, the same reaction performed in the less polar diethyl ether at room temperature did lead to the corresponding monomers. This method could also be used for the preparation of the more hindered acrylate **3g** [9]; in this particular case, the reaction was rather slow and was therefore performed in the even less polar pentane at room temperature.

Usually, the pyridine employed in esterification reactions activates the acylation agent by formation of an intermediate acylpyridinium salt [10]. In the present case, its action could be rather different because the perhalogenophenols are very acidic.[3] For example, the formation of an insoluble complex between phenol **2f** and 2,6-lutidine[4] was observed in diethyl ether at 0°C. The higher basicity of 2,6-lutidine compared to pyridine should increase the extent of deprotonation of the perhalogenophenol. In initial experiments, a small amount of the even more basic 4-dimethylaminopyridine was added as catalyst to the medium. However, it appeared that 2,6-lutidine alone is sufficient to perform the acylation reaction.

All acrylates were obtained as oils except **3f** and **3g** which were solids having low melting points. They could be stored pure at room temperature for several days. When stabilized by 0.1% monobenzylhydroquinone (chosen for its high boiling point) their life-time at −30°C was longer than one year. A simple short path distillation under vacuum can be applied to remove the stabiliser and to render these new halogenoaryl acrylate monomers ready for UV initiated polymerization or copolymerization. The copolymers formed from acrylate **3b** mixed with 25 to 45% acrylate **3a** proved to be stable in the air at room temperature. They were found to be three to four times more transparent than polymethylmethacrylate in the 1200–1600 nm region [14].

3. Experimental

3.1. General

^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were determined in $CDCl_3$ as solvent on a Bruker AC 300 spectrometer at 300.1, 75.5, and 282.4 MHz, respectively. Chemical shifts are reported in δ (ppm) from internal TMS (^{1}H and ^{13}C) and from $CFCl_3$ (^{19}F), respectively. Mass spectra were measured at the mass spectrometry service of the University of Paris VI.

[2] Florisil® is an activated magnesium silicate. The 60–100 mesh reagent grade from Aldrich (Ref. 22-074-4) was used.

[3] The pK_a values of pentafluorophenol and pentachlorophenol in water are 5.2 and 4.5, respectively [11,12].

[4] The pK_a values of the conjugated acids of pyridine, 2,6-dimethylpyridine and 4-dimethylaminopyridine in water are 5.2, 6.7 and 9.7, respectively [13].

IR spectra were obtained on a Perkin Elmer 1420 spectrometer with solutions of CCl_4 in a cell of Na. UV spectra were recorded on a Shimadzu UV-160 spectrometer with *n*-hexane as solvent. Gas chromatography analyses were performed on a Shimadzu GC-14A apparatus with SE30 (30%) 25 m fused silica capillary column. Microanalyses were performed by the analytical service of the University of Paris VI. Melting points were measured on a Mettler-FP61 apparatus.

3.2. Typical procedure

Freshly prepared acryloyl chloride [15] (14.8 g, 164 mmol) was added dropwise, to a stirred solution of pentafluorophenol (15.1 g, 82 mmol) and 2,6-lutidine (13.2 g, 123 mmol) in THF (200 ml) at 0°C. After 5 min stirring at the same temperature, the precipitate was filtrated and washed with THF (100 ml). Then, the solvent was removed under reduced pressure and the residue was purified by chromatography on a Florisil® [2] column, using pentane as the eluent. Pentafluorophenyl acrylate **3a** was obtained as a colourless oil (16.7 g, 86%). Its purity was found higher than 99.5% by glc analysis. (Found: C, 45.45; H, 1.4. $C_9H_3F_5O_2$ requires C, 45.4; H, 1.3%); ν_{max} (CCl_4) 1775 cm^{-1}; λ_{max} (hexane) 256 nm (ϵ 400); ^1H NMR: 6.73 (1H, dd, J_{HH} = 17.2 and 0.9, H_c), 6.37 (1H, dd, J_{HH} = 17.2 and 10.5, H_a) and 6.19 (1H, dd, J_{HH} = 10.5 and 0.9, H_b) ppm; ^{19}F NMR: −153.1 (2F, d, J_{FF} = 18, F_a), −158.4 (1F, t, J_{FF} = 22, F_c) and −162.8 (2F, dd, J_{FF} = 22 and 18, F_b) ppm; ^{13}C NMR: 161.6 (1C, s, *C*O), c.a. 141 (2C, dm, $^1J_{CF} \approx 250$, C_2), 139.6 (1C, dtt, J_{CF} = 253, 14 and 4, C_4), ca. 138 (2C, dm, $^1J_{CF} \approx 250$, C_3), 135.1 (1C, s, CH_2), 125.3 (1C, s, *C*H) and 125.1 (1C, tdt, J_{CF} = 15, 5 and 2, C_1) ppm; CIMS (isobutane, m/z) 239 (MH^+, 100), 155 (26), 117 (60) and 93 (22%).

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