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2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl methacrylate

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Abstract

The title monomer (**4**) was prepared from the trimer of hexafluoropropene-1,2-oxide, 2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonanoyl fluoride (**1**), via methyl ester **2** that was reduced by sodium borohydride to the corresponding alkanol **3**, which was finally acylated by methacryloyl chloride.

Keywords: Borohydride reduction; Fluoroalkyl methacrylate; 2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl methacrylate

1. Introduction

Polymers and copolymers of acrylates and methacrylates of fluorinated alcohols have been used in a number of applications, viz. textile finishing [1], special polymerization surfactants [2], microelectronics [3,4], optoelectronics [5], oxygen carriers [6], human prosthetics [6,7], and highly sensitive electron-beam and X-ray resists [4,8,9].

In this paper we report the preparation of a new methacrylate monomer (**4**) with a branched perfluorinated ether linkage in the ester. The perfluoroether group should significantly modify the material properties [10] of the corresponding polymers when compared with simple (perfluoroalkyl)methyl methacrylates.

2. Results

We started the synthesis of the monomer **4** with the preparation of the formal trimer of hexafluoropropene-1,2-oxide, 2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonanoic fluoride (**1**), using our previously reported procedure [11,12], viz. caesium fluoride as a catalyst and tetraglyme as a solvent. The acid fluoride **1**, which is also an industrial intermediate [10,13], is easily converted to the corresponding methyl ester **2**, as reported previously [14,15]. For the transformation of esters of perfluorocarboxylic or perfluorodicarboxylic acids to the corresponding alcohols or diols, reductions with complex metal hydrides and diborane have been reported [16,17]. In the case of the ester **2**, we applied here the reduction with sodium borohydride in diethyl ether–methanol mixture. This reagent appeared to be [9,18] sufficiently efficient to reduce completely the ester group in esters of fluorinated acids, but also sufficiently mild to avoid the attack of α C–F or C–Cl bonds as has been sometimes observed [17] during lithium aluminum hydride reductions of fluorinated esters. The reduction of **2** afforded the corresponding 2,4,4,5,7,7,8,8, 9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonan-1-ol (**3**) in 81% yield. No byproducts were detected in the reaction mixture. The acylation of alcohol **3** with methacryloyl chloride was performed under conditions similar to those that were successfully applied recently in the acylation of fluoroalcohols or diols [2,9,19,20] afforded the corresponding methacrylate **4** in 82% yield when an excess of the acid chloride was employed. An equimolar amount of the reactants (see Section 4, Procedure A) afforded a mixture of the starting alcohol **3** and methacrylate **4** that were separated by repeated fractional distillation.

3. Conclusion

A convenient synthesis of 2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl methacrylate (**4**) has been developed from industrial intermediate **1**.

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4. Experimental details

4.1. General experimental procedures

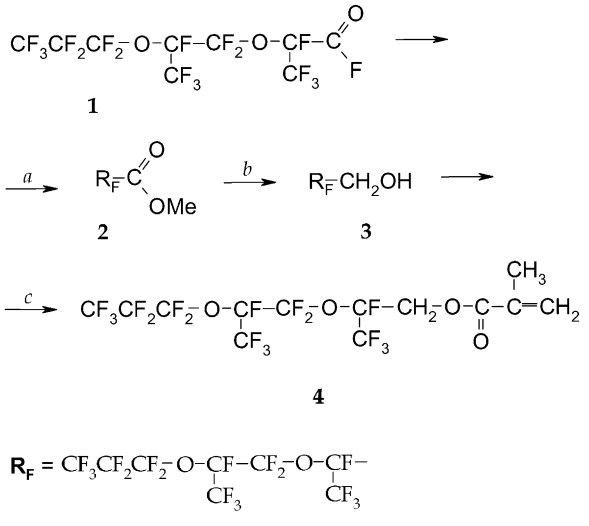
The temperature data were uncorrected. Distillations of high boiling compounds were carried out on a Vacuubrand RC5 high vacuum oil pump. GC analyses were performed on a Micromat HRGC 412 (GCa, Nordion Analytical; 25 m glass capillary column, SE-30). NMR spectra were recorded on a Bruker 400 AM (FT, ^{19}F at 376.6 MHz), Varian Gemini 300 HC (FT, ^{1}H at 300.07 MHz) instruments using TMS and $CFCl_3$ as the internal standards, chemical shifts in ppm (s: singlet, d: doublet, t: triplet, m: multiplet), coupling constants J in Hz, solvent $CDCl_3$.

The chemicals were used as follows: sodium borohydride (Lachema, Brno), methanol (fractionally distilled, bp 42 °C), diethyl ether (distilled over Na), methacryloyl chloride (Aldrich, distilled before use), triethylamine (distilled over NaOH, bp 88 °C), 1,1-diphenyl-2-picrylhydrazyl (DPPH, Aldrich) (Scheme 1).

4.2. 2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonanoyl fluoride (1)

Acid fluoride **1** was prepared by ionic oligomerization of hexafluoropropene-1,2-oxide in tetraglyme in the presence of caesium fluoride as catalyst according to [12]. During storage of **1**, partial hydrolysis to the corresponding acid occurred. Fluoride **1** was purified by distillation in vacuum, bp 40–41 °C/30 mmHg (literature: [21], bp 115–117 °C; [22], bp 112–115 °C/760 mmHg).

^{19}F NMR (376.60 MHz, $CDCl_3$): δ 26.69 (*d*, 1F, COF), −86.38 (*m*, 2F, $CF_3CF_2\mathbf{CF_2}$), −79.11 (*m*, 2F, $OCF(CF_3)\mathbf{CF_2}$), −80.57 (*m*, 3F, $OCF(\mathbf{CF_3})CF_2$), −81.89 (*s*, 3F, $OCF(\mathbf{CF_3})$-COF), −82.31 (*s*, 3F, $\mathbf{CF_3}CF_2$), −130.14 (*s*, 2F, $\mathbf{CF_2}CF_3$), −131.26 (*t*, 1F, **C**FCOF), −145.78 (*t*, 1F, O**C**FCF_3).



Scheme 1. (a) MeOH, r.t.; (b) $NaBH_4$, Et_2O, MeOH, reflux, (c) methacryloyl chloride, Et_2O, Et_3N, r.t.

4.3. Methyl 2,4,4,5,7,7,8,8,9,9,9-undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonanoate (2) [14,15]

A three-necked round bottomed flask (250 ml, magnetic spinbar) equipped with a separatory funnel and efficient water-cooled reflux condenser was charged with methanol (20 g, 0.63 mol), diethyl ether (30 ml), silica gel (5 g), Na_2CO_3 (3 g) and powdered $MgSO_4$ (1 g). A solution of acid fluoride **1** (71.1 g, 0.14 mol) in diethyl ether (50 ml) was added dropwise to keep the mixture slightly boiling and after that the mixture was stirred overnight. After working up, the raw product was fractionally distilled on a packed column (Berle saddles, heated jacket, splitter head) to afford methyl ester **2**, bp 60–63 °C/11 mmHg, yield 62.3 g (86.3%) (literature [14,15]: yield 78.8%, bp 154–155 °C).

^{1}H NMR (300.07 MHz, $CDCl_3$): δ 3.99 (*s*, 3H, $COOCH_3$).

^{19}F NMR (376.60 MHz, $CDCl_3$): δ −85.55 (*m*, 2F, $CF_3CF_2\mathbf{CF_2}$), −79.31 (*m*, 2F, $OCF(CF_3)\mathbf{CF_2}$), −80.63 (*d*, 3F, $OCF(\mathbf{CF_3})CF_2$), −82.05 (*m*, 3F, $OCF(\mathbf{CF_3})COOMe$), −82.89 (*d*, 3F, $\mathbf{CF_3}CF_2$), −130.05 (*s*, 2F, $\mathbf{CF_2}CF_3$), −131.87 (*t*, 1F, **C**FCOOMe), −145.31 (*t*, 1F, O**C**FCF_3).

4.4. 2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonan-1-ol (3)

A two-necked round bottomed flask (250 ml, magnetic spinbar) equipped with Dimroth reflux condenser fitted with drying tube was charged with diethyl ether (100 ml), $NaBH_4$ (4.4 g, 115.7 mmol). A solution of methylester **2** (59 g, 115.7 mmol) in methanol (5 ml) and diethyl ether (50 ml) was then added dropwise while vigorously stirring and the mixture subsequently gently refluxed for 12 h. The cooled mixture was washed with dilute HCl (1:1, 50 ml) and the water layer was extracted with diethyl ether (3 × 50 ml), the organic solutions were combined and dried over $MgSO_4$, which was filtered-off next day. Ether was removed from the filtrate by atmospheric distillation. The residue was fractionally distilled on a packed column (Berle saddles, heated jacket, splitter head) to afford alcohol **3**, bp 61–63 °C/13 mmHg, yield 44.6 g (81.1%).

^{1}H NMR (300.07 MHz, $CDCl_3$): δ 2.17 (*s*, 1H, OH), 4.16 (*d*, 2H, CH_2, $^{3}J_{HF} = 11.5$ Hz).

^{19}F NMR (376.60 MHz, $CDCl_3$): δ −82.63 (*m*, 2F, $CF_3CF_2\mathbf{CF_2}$), −79.97 (*m*, 2F, $OCF(CF_3)\mathbf{CF_2}$), −80.58 (*m*, 3F, $OCF(\mathbf{CF_3})CF_2$), −81.97 (*m*, 3F, $OCF(\mathbf{CF_3})CH_2OH$), −82.92 (*d*, 3F, $\mathbf{CF_3}CF_2$); −130.2 (*s*, 2F, $\mathbf{CF_2}CF_3$), −136.49 (*m*, 1F, **C**FCH_2OH), −145.51 (*m*, 1F, O**C**FCF_3). Anal. Calcd. for $C_9H_3F_{17}O_3$: C, 22.4; H, 0.6. Found: C, 22.6; H, 0.9%.

4.5. 2,4,4,5,7,7,8,8,9,9,9-Undecafluoro-2,5-bis(trifluoromethyl)-3,6-dioxanonyl methacrylate (4)

4.5.1. Procedure A

A three-necked round bottomed flask (250 ml, magnetic spinbar) equipped with a Dimroth reflux condenser fitted

with drying tube was charged with methacryloyl chloride (8.33 g, 79.7 mmol), triethylamine (8.06 g, 79.7 mmol), diethyl ether (50 ml) and a stabilizer DPPH (10 mg) and the mixture was stirred at r.t. for 1 h. A solution of fluoroalkanol **3** (35.8 g, 72.4 mmol) in diethyl ether (50 ml) was then added dropwise and the mixture was stirred at r.t. for 12 h. The reaction mixture was neutralized with aqueous $NaHCO_3$ and the water layer was separated and extracted with diethyl ether (3×30 ml). The organic solutions were combined and dried over $MgSO_4$, which was filtered-off after 10 h. Diethyl ether was removed from the filtrate by rotary evaporator and the residue was trap-to-trap distilled in vacuum to afford a mixture of unreacted **3** and product **4**, bp 38–55 °C/1.2 mmHg. This raw material was repeatedly fractionally distilled on a packed column (see compound **3**): the first distillation afforded pure **3** (bp 61–63 °C/13 mmHg), and a residue (mixture of **3** and **4**), which was fractionally distilled to give two fractions, which each gave two fractions. The result was as follows: pure **3** (9.7 g, 27.2%); a mixture of **3** and **4** (6.22 g); almost pure **4**, bp 91–93 °C/22 mmHg, yield 1.82 g (4.5%), purity 96%; pure **4**, bp 92–93 °C/22 mmHg, yield 10.13.2 g (24.9%). Stabilizer was added to all distilled fractions.

4.5.2. Procedure B

A mixture of methacryloyl chloride (15.7 g, 150 mmol), triethylamine (15.2 g, 150 mmol), fluoroalkanol **3** (24.7 g, 50 mmol), diethyl ether (100 ml) and stabilizer DPPH (10 mg) was prepared as in Procedure A and stirred at r.t. for 4 h when a complete conversion of fluoroalkanol was attained (by ^{19}F NMR). Methanol (1.6 g, 50 mmol) was then added and the mixture was stirred for an additional hour. Water (2×100 ml) was then added slowly to the mixture, the ethereal layer was separated, the water layer was extracted with diethyl ether (3×50 ml); the ethereal solutions were combined and dried over $MgSO_4$. Diethyl ethyl ether was evaporated by rotary evaporator, triethylamine, methanol and methyl methacrylate were removed by distillation in vacuum (20–40 mmHg) and the residue was trap-to-trap distilled as above. The raw product was fractionally distilled as above to afford product **4** in a yield of 23.1 g (82%), bp 77–79 °C/13 mmHg.

^1H NMR (300.07 MHz, $CDCl_3$): δ 1.96 (*s*, 3H, CH_3), 4.68 (*d*, 1H, CH_2, $^3J_{HF} = 5$ Hz), 4.72 (*d*, 1H, CH_2, $^3J_{HF} = 3.9$ Hz), 5.7 (*s*, 1H, CH_2=C), 6.19 (*s*, 1H, CH_2=C).

^{19}F NMR (376.60 MHz, $CDCl_3$): δ −82.38 (*m*, 2F, $CF_3CF_2\mathbf{CF_2}$), −80.85 (*m*, 2F, $OCF(CF_3)\mathbf{CF_2}$), −80.57 (*m*, 3F, $OCF(\mathbf{CF_3})CF_2$), −81.89 (*m*, 3F, $OCF(\mathbf{CF_3})CH_2O$–), −83.48 (*d*, 3F, $\mathbf{CF_3}CF_2$), −130.21 (*s*, 2F, $\mathbf{CF_2}CF_3$), −134.44 (*m*, 1F, $\mathbf{CF}CH_2O$–), −145.69 (*m*, 1F, $O\mathbf{CF}CF_3$).

Anal. Calcd. for $C_{13}H_7F_{17}O_4$: C, 28.4; H, 1.3. Found: C, 28.6; H, 1.5%.

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