Study of the zinc action on the 2-chloroethyl 2-bromo-2-perfluoroalkylethanoates

Balsem Jedidi Yaich, Abakar Ould Amanatoullah, Nejib Hussein Mekni and Moufida Romdhani-Younes

Laboratory of Structural Organic Chemistry, Department of Chemistry, Faculty of Science of Tunis, University of Tunis El Manar, Tunis, Tunisia

ABSTRACT

2-Bromo-2-perfluoroalkyl acids are converted into the corresponding esters by a reaction of alcoholysis in the 2-chloroethanol. The action of zinc on perfluoroalkylated bromo-esters resulted in the bromine reduction products formation via zinc organic intermediates. When heated at 100°C, for 48 h, in the presence of an excess of zinc, the bromo-esters produce the symmetrical bis(vinyl perfluoroalkyl ester) ethoxide compounds, resulting from the BrZnF elimination reaction, followed by a dimerization reaction.

1. Introduction

In recent years, a particular interest is accorded to the synthetic methods of highly fluorinated organic compounds. The perfluoroalkyl chains constitute an important source of reagents for these syntheses. These chains have particular chemical [1,2], physical [3–6] and biological [7–10] properties. Their introduction into organic molecules gives them particular properties compared to their non-fluorinated homologues [11].

The organoperfluoroalkyl compounds have a great number of applications in different fields [12–16]. Such compounds are used as surfactants [17–20], agrochemicals [21,22], pharmaceutical [23–27], biological [28] and medical agents [29,30]. While they are detected in human bodies [31,32], municipal water and solid wastes in different industrial areas around the world [33–35] and considered as high polluter for environment and toxic compounds [36,37], perfluoroalkyl acids are interesting compounds used as tensioactifs [38–40], fire-fighting foam [41–43], fluoropolymers [44] and other important applications.

In organic synthesis, some perfluoroalkylated compounds can be easily transformed into their corresponding organometallic derivatives [45,46]. However, their chemical reactivity is relatively complex [47]. Many studies describe different positive [48,49] and negative [50] results on their reactivity, adopting different reaction conditions [48–50].

The perfluoroalkyl carboxylic acids are described as starting material for the synthesis of esters [51–53] and heterocyclic compounds [54,55]. In particular, the 2-bromo-2-perfluoroalkyl acids and esters are described in Reformatsky reaction, conducing to the β-hydroxyesters [56–60] and water elimination reaction products [61].

We have previously described the action of zinc and vinyl zinc bromide on the 2-bromo-2-perfluoroalkylethanoic acid and the methyl 2-bromo-2-perfluoroalkylethanoate compounds [52]. As a continuation, we describe herein an attempt of the synthesis of some perfluoroalkylated lactones [54].
via an intramolecular cyclization reaction, using the 2-chloroethyl 2-bromo-2-perfluoroalkylethanoate substrate with the zinc.

2. Results and discussion

The 2-bromo-2-perfluoroalky acids 1 [51] are transformed into the corresponding 2-chloroethyl 2-bromo-2-perfluoroalkylethanoates 2, in good yields, by an alcoholysis reaction with the 2-chloroethanol in acidic medium for 48 h (Scheme 1).

Compounds 2 are reacted with activated zinc for 6 h at 70°C, in tetrahydrofuran (THF), then hydrolysed. The reaction leads exclusively to the corresponding 2-chloroethyl 2-perfluoroalkylethanoates 3, resulting from the reduction reaction of the bromine atom in middle yields (Scheme 2).

The zinc atom inserts between carbon and bromine atoms, yielding the bromozincic organometallic intermediate. This nucleophilic intermediate is unable to act on the electrophilic chloro-substituted carbon atom. So, the expected perfluoroalkylated lactones 4 are not obtained even by modifying some reaction conditions (zinc amount, temperature and reaction duration).

This result may be explained on the basis of the weak bromozincic carbon atom (CHZnBr) nucleophilicity [62] to act on the chloro-substituted carbon atom, neither via an intramolecular nucleophilic substitution (SN1) to produce the heterocyclic five-membered lactones 4, nor via an intermolecular nucleophilic substitution reaction to yield the dimeric compounds 5 (Scheme 2).

The reaction of the 2-chloroethyl 2-bromo-2-perfluoroalkylethanoate 2 in the presence of a zinc excess, in THF at 100°C for 48 h, conduces to the symmetrical bis(vinyl perfluoroalkyl ester) 6 (Scheme 3) as unique product, resulting from a trans BrZnF elimination reaction, followed by an ethane molecule elimination than an O-alkylation (Scheme 5).

The formation of the esters 3 as well as the dimeric compounds 6 show that the reaction involves in all cases the bromozincic intermediate A (Scheme 4). While fluorine atom elimination reaction is not well frequent, because strength and the short length of the carbon-fluorine covalent single bond, such reaction occurs on compounds 2. The high and prolonged heat, of perfluotoalkylated bromoester 2, conduces exclusively, through an elimination reaction of (BrZnF) to the Z geometrical configuration isomer B, [63] highly stabilized from a conjugated system. The geometrical structure of the bromozincic intermediate A (Scheme 4) is in favour of a trans elimination, because the β-carbon atom is bonded to two fluorine atoms (CF2). So, regardless the absolute configuration of the α-carbon atom, in both cases, there is always a fluorine atom in the trans position to the ZnBr living group (Scheme 4).

The presence of a zinc excess in the reaction with the ester 2, in the above-described reaction conditions, gives rise also to a second zinc insertion reaction between chlorine and carbon atoms. As a result, the intermediate B transforms into the intermediate C (Scheme 5). This latter transforms in its turn into the corresponding ionic acid salt intermediate C′, via an elimination reaction of an ethene molecule.

Scheme 1. Alcoholysis reaction of 2-bromo-2-perfluoroalky acids 1 with the 2-chloroethanol.

Scheme 2. Action of zinc on the 2-chloroethyl 2-bromo-2-perfluoroalkylethanoates 2 at 70°C.
The anionic species intermediate $C'$ acts on the intermediate $B$, yielding the corresponding symmetric bis(vinyl perfluoroalkyl) ethoxide compound $6$ (Scheme 5).

The NMR spectroscopic data confirm the obtained structures. In particular, the $^1$H NMR spectra show a doublet at 6.05 ppm, corresponding to the two enonic protons ($=$CH), coupled with the single vinylic fluorine atom ($=$CF, $J_{HF}$trans $\sim$ 31 Hz). The $^{19}$F NMR spectra are in agreement with the $^1$H NMR spectra and show a signal corresponding to two vinylic fluorine atoms at $-108$ ppm. The $^{13}$C NMR spectra show a singlet at $\sim106$ ppm, attributed to the enonic (HC=) carbon atoms and a doublet of multiplet at $152$ and $156$ ppm, relative to fluorinated vinylic carbon atoms ($=$CF) with a coupling constant $J_{FC}$ $\sim$ 285 Hz.

3. Conclusion

The 2-chloroethyl 2-bromo-2-perfluoroalkylethanoates 2 are synthesized by an alcoholysis reaction of 2-bromo-2-perfluoroalkyl acids 1 in the 2-chloroethanol. Reacted with the zinc in middle conditions, the bromo-esters 2, yield the bromine atom reduction products 3 and no trace of the desired perfluoroalkyl lactones 4 is detected. Such results justify again the low reactivity of the zincic carbon atom to act as a nucleophile on the primary chloro-substituted carbon atom. The prolonged heat of the same reagents 2 with a zinc excess, yield the bis(vinyl perfluoroalkyl) oxyethylene 6 as exclusive products.

The highly fluorinated obtained compounds 2-perfluoroalkyl acids 3 and bis(vinyl perfluoroalkyl ester) ethoxides 6, among many others applications, may have interesting surface properties [64–66] and can also undergo some interesting reactions, particularly in the synthesis of organofluorinated heterocyclic compounds [67,68].

4. Experimental

$^1$H, $^{13}$C and $^{19}$F NMR spectra were realized in CDCl$_3$ on a Bruker AC 300 spectrometer at 300, 75 and 282 MHz, respectively, for $^1$H, $^{13}$C (TMS) and $^{19}$F (C$_6$F$_6$). IR spectra were determined with PerkinElmer Paragon 1000 PC in CHCl$_3$ spectrometer. HRMS spectra were realized on a Finnigan MAT 95 mass spectrometer in
chemical ionization mode (CI). The used silicagel is of Merck 7734 type. The HRMS spectra were realized in the Institut National de Recherches et d’Analyse Physico-Chimiques (INRAP), Sidi Thabet 2020 Tunisia. The 2-bromo-2-perfluoroalkyl acids 1 were prepared according to the method described in Ref. [51].

4.1. Synthesis of 2-chloroethyl 2-bromo-2-perfluoroalkylethanoate 2a

A solution of 0.05 mmol of 2-bromo-2-perfluoroalkyl acid 1, dissolved in 4 mL of 2-chloroethanol and 0.1 mL of concentrated H2SO4 is refluxed for 48 h. The mixture is cooled and diluted with 20 mL of water. The crude is extracted with (3 × 50 mL) diethyl ether, then dried over MgSO4. The diethyl ether is evaporated and the residue is distilled, yielding ester 2a as yellowish liquid.

2-Chloroethyl 2-bromo-2-perfluoroalkylethanoate 3a

IR (CHCl3): νCl = 1750 cm-1; 1H NMR (CDCl3), δ: 3.13 (t, 2H, CH2), 3JHF = 17.6 Hz), 3.72 (t, 2H, CH2), 4.44 (m, 2H, –O), 4.50 (m, 2H, CH2=), 13C NMR (CDCl3), δ: 163.0 (s, C = O), 110.0–120.0 (m, CF3O), 65.8 (s, CH2=O), 39.7 (s, –CH2–Cl) and 35.0 (s, CH2–O); 19F NMR (CDCl3), δ: –82.9 (t, 3F, CF3), –113.1 (m, 2F, CF2o), –121.9 (m, 2F, CF2p), –123.6 (m, 4F, 2CF2p), –127.0 (m, 2F, CF2o); HRMS: Calcd. for C10H6F13O2Cl: 439.98847, found 439.98524.

4.2. Synthesis of 2-chloroethyl 2-perfluoroalkylethanoate 3

A solution of 0.05 mmol of 2-bromo-2-perfluoroalkyl acid 1, dissolved in 4 mL of 2-chloroethanol and 0.1 mL of concentrated H2SO4 is refluxed for 48 h. The mixture is cooled and diluted with 100 mL of diethyl ether. The solution is washed with water (2 × 50 mL) then dried on MgSO4. The crude is extracted with (3 × 50 mL). The solution is dried on Na2SO4, then the solvent is evaporated. The product is purified by chromatography using the mixture petroleum ether/diethyl ether (70/30). The pure compounds 3 are obtained as yellowish liquids.

2-Chloroethyl 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctanoate 3b

IR (CHCl3): νCl = 1750 cm-1; 1H NMR (CDCl3), δ: 3.15 (t, 2H, CH2), 3JHF = 17.6 Hz), 3.75 (t, 2H, CH2–Cl), 4.48 (m, 2H, CH2=O), 13C NMR (CDCl3), δ: 163.3 (s, C = O), 110.0–120.0 (m, CF3O), 60.5 (s, CH2–O), 40.7 (s, –CH2–Cl) and 35.5 (t, 1C, CH2–CF2, 2JCF = 86.1 Hz); 19F NMR (CDCl3), δ: –82.7 (t, 3F, CF3), –113.0 (m, 2F, CF2o), –121.1 (m, 6F, 3CF2), –123.6 (m, 4F, 2CF2p), –126.9 (m, 2F, CF2o); HRMS: Calcd. for C13H6F17O2Cl: 539.97848, found 539.97877.

4.3. Synthesis of bis(allylperfluoroalkyl) ethoxide 6

0.26 g (4 mmol) of activated zinc powder and 10 mL of dry THF under nitrogen atmosphere, (4 mmol) of 2-chloroethyl 2-bromo-2-perfluoroalkylethanoate 2 are placed in a 100 mL erlenmeyer. The mixture is vigorously stirred during 48 h at 100°C, then cooled, filtered and diluted with 100 mL of diethyl ether. The solution is washed with water (2 × 50 mL) then dried on MgSO4. The solvents are evaporated and the obtained crude is purified on chromatographic column using the mixture petroleum ether/diethyl ether (70/30). Compounds 6 are isolated as yellowish solids.

(ZZ,ZZ)-ethane-1,2-diyi bis(3,4,4,5,5,6,6,7,7,8,8,8-dodecafluorooct-2-enoate): 6a

Mp = 67°C; 1H NMR (CD2Cl2), δ: 6.01 (d, 2H, 2CH = CF, 3JHF = 31.1 Hz), 4.50 (s, 4H, 4CH2 = CF, 3JHF = 163.3 Hz), 13C NMR (CD2Cl2), δ: 160.9 (s, 2C, C = O), 152.3 and 156.2 (d.m., 2C, 2FC=, 1JCF = 285.1 Hz), 105.7 (s, 2C, 2CH=), 110.0–120.0 (m, 10C, CF3F13), 65.0 (s, 2C, 2CH2=O), 19F NMR (CDCl3), δ: –82.6 (t, 6F, 2CF2p), –108.3 (m, 2F, 2CF2), –120.4 (m, 4F, 4CF2), –124.4 (m, 8F, 4CF2), –127.9 (m, 4F, 4CF2); HRMS: Calcd. for C18H10F12O4: 741.98828, found 741.98853.

(ZZ,ZZ’)-ethane-1,2-diyi bis(3,4,4,5,5,6,6,7,7,8,8,8,10,10-hexadecafluorodec-2-enoate): 6b

Mp = 85°C; 1H NMR (CD2Cl2), δ: 6.08 (d, 2H, 2CH = CF, 3JHF = 31.4 Hz), 4.60 (s, 4H, 4CH2 = CF, 3JHF = 163.5 Hz), 13C NMR (CD2Cl2), δ: 163.5 (s, 2C, C = O), 152.3 and 156.2 (d.m., 2C, 2FC=, 1JCF = 286.7 Hz), 105.7 (s, 2C, 2CH=), 110.0–120.0 (m, 14C, CF3F13), 65.1 (s, 2C, 2CH2=O), 19F NMR (CDCl3), δ: –82.5 (t, 6F, 2CF2p), –108.3 (m, 2F, 2CF2), –120.4 (m, 4F, 4CF2), –123.6 (m, 8F, 4CF2), –124.4 (m, 8F, 4CF2), –127.9 (m, 4F, 4CF2); HRMS: Calcd. for C20H10F12O4: 841.99062, found 841.99043.
(m., 8F, 4CF₂), −127.8 (m., 4F, 2CF₂); HRMS: Calcd. for C₁₂₅H₁₁₀F₃₂O₄: 941.97551, Found 941.97589.

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No potential conflict of interest was reported by the authors.

ORCID
Nejib Hussein Mekni http://orcid.org/0000-0003-2924-3551

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