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Short communication

1,1,3,3,3-Pentafluoro-2-pentafluorophenyl-1,2-epoxypropane and trimethylphosphite: unusual 1,4-dioxan-2,5-dione ring formation

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Abstract

1,1,3,3,3-Pentafluoro-2-pentafluorophenyl-1,2-epoxypropane **1** reacted with trimethylphosphite giving two diastereomers, (*Z*)- and (*E*)-3,6-bis(trifluoromethyl)-3,6-bis(pentafluorophenyl)-1,4-dioxan-2,5-dione **2a**, **b** in a 1:1 ratio, cyclodimerisation product of the intermediately generated α-lactone **4**. Compounds **2a**, **b** were hydrolysed to furnish 3,3,3-trifluoro-2-hydroxy-2-(2,3,4,5,6-pentafluorophenyl)propionic acid **5**. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 1,1,3,3,3-Pentafluoro-2-pentafluorophenyl-1,2-epoxypropane; Trimethylphosphite; Methylphosphonic acid fluoride; 3,6-Bis(trifluoromethyl)-3,6-bis(pentafluorophenyl)-1,4-dioxan-2,5-dione; 3,3,3-Trifluoro-2-hydroxy-2-(2,3,4,5,6-pentafluorophenyl)propionic acid

1. Introduction

Earlier we have shown that the reaction of perfluorinated epoxides with trialkylphosphites generally results into the formation of fluorinated phosphorus ylides concomitant with C–C and C–O bond cleavage in the epoxide ring system [1–3], which was found in the case of 1,1,3,3,3-pentafluoro-2-pentafluorophenyl-1,2-epoxypropane **1** and triethylphosphite [2].

2. Results and discussion

Surprisingly, the reaction of 1,1,3,3,3-pentafluoro-2-pentafluorophenyl-1,2-epoxypropane **1** with trimethylphosphite (Scheme 1) leads to the formation of the liquid, moisture-sensitive (*Z*)- and (*E*)-3,6-bis(trifluoromethyl)-3,6-bis(pentafluorophenyl)-1,4-dioxan-2,5-dione **2a**, **b** in good yield. It is known that the reaction of 1,2-epoxyperfluoropropane with trifluoropyruvate in the presence of tris(dimethylamido)phosphate (HMPT) leads to the formation of a dioxane [4,5]. Probably there will be a MeO/F exchange with trimethylphosphite to give dimethylfluorophosphite which itself rearranges to form the corresponding phosphonic ester fluoride and compound **3** finally splitting off methyl fluoride. The resulting corresponding α-lactone **4** dimerises to furnish the two possible diastereomeric dioxane-diones **2a**, **b** in a 1:1 ratio (the synthesis and some reactions, except cyclodimerisation of perfluorinated α-lactones with similar structure was described earlier [6,7]). Mass spectra and ^{19}F, ^{13}C NMR data are in very good agreement with the proposed structure. The formation of $FP(OMe)_2$ and FP(O)(OMe)Me was confirmed by ^{1}H, ^{19}F and ^{31}P NMR [8,9]. The two diastereomers **2a**, **b** can be clearly distinguished on the basis of their ^{13}C NMR data, since all resonances appear pairwise. Also, the ^{19}F resonances were observed as two sets of signals for the CF_3 group and of the different fluorine nuclei in the phenyl rings.

Hydrolysis of dioxane-diones **2a**, **b** quantitatively (^{19}F and ^{1}H NMR) forms 3,3,3-trifluoro-2-hydroxy-2-(2,3,4,5,6-pentafluorophenyl)propionic acid, which can be used as a reagent for further transformations (cf. [11]).

3. Experimental

NMR spectra were obtained on a Bruker AC 80 instrument operating at 75.39 MHz (^{19}F, internal standard CCl_3F) and a Bruker DPX-200 spectrometer operating at 200.13 MHz for ^{1}H (internal standard TMS), 188.31 MHz for ^{19}F and 50.32 MHz for ^{13}C, internal standard TMS).

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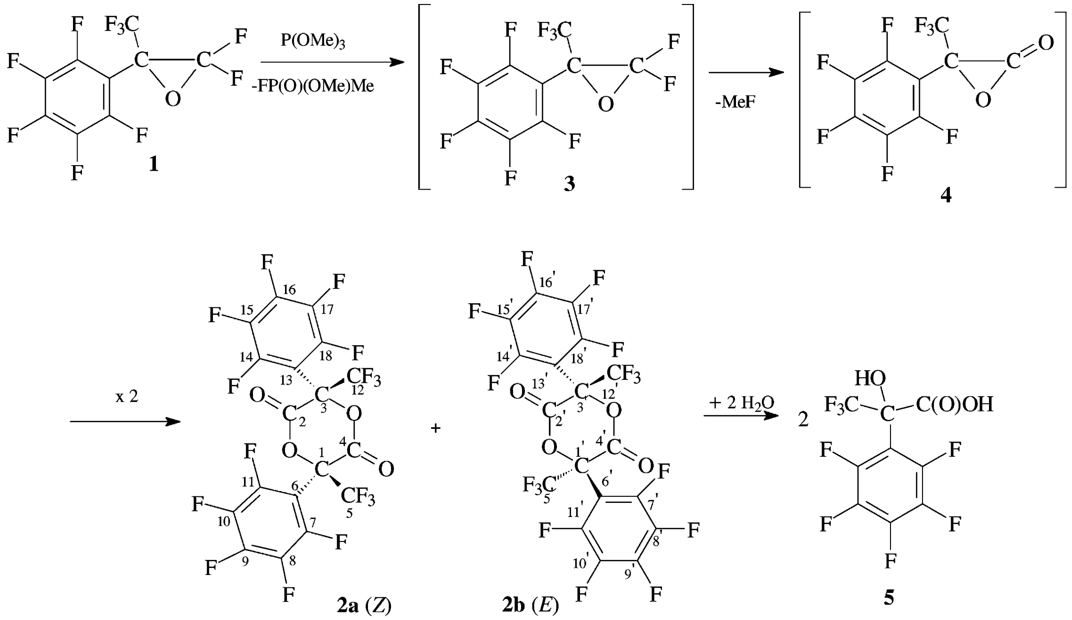

Scheme 1.

Highfield shifts from TMS and CCl_3F were given negative signs. MS spectra were obtained on a Varian MAT CH7A instrument at 70 eV.

3.1. *E,Z-3,6-Bis(trifluoromethyl)-3,6-bis-pentafluorophenyl-1,4-dioxane-2,5-dione* ***2a, b***

Trimethylphosphite (1.6 g, 12.9 mmol) and 2.0 g (6.4 mmol) of **1** were heated at 60 °C for 20 h. Distillation gave 1.57 g (84%) of **2a**, **b** (bp 78–80 °C/0.01 Torr). MS: *m/e* (%): 584 (M^+), 292 [$C_6F_5(CF_3)C(O)CO^+$], 276 [$C_6F_5(CF_3)C(O)C^+$], 248 [$C_6F_5(CF_3)C^+$], 198 [$C_6F_5(CF_3)$-C^+–CF_2], 195 [$C_6F_5C(O)^+$], 179 ($C_6F_5C^+$), 167 ($C_6F_5{}^+$), 93 ($C_3F_7{}^+$), 69 ($CFF_3{}^+$), 28 (CO). HRMS: calculated mass = 583.9541. Found mass = 583.9537. Analysed calculated for $C_{18}F_{16}O_4$ (584.17): C, 37.00; F, 52.04%. Found: C, 36.94; F, 52.17%.

2a: NMR: ^{19}F: $\delta = -75.8$ (CF_3, t, $^4J_{FF} = 11.8$ Hz), -131.8 ($F^{8,10,17,15}$ br.s), -142.5 ($F^{9,16}$,m), -156.5 ($F^{7,11,14,18}$, q); ^{13}C: (C1, 3) q, 78.9, $J^2 = 33.8$ Hz; (C2, 4) s, 152; (C5, 12) q, 120.0, $J^1 = 287.0$ Hz; (C6, 13) t, 103, $J^2 = 12.0$ Hz; (C7, 11, 14, 18) dt, 145, $J^1 = 258.9$ Hz, $J^2 = 14.1$ Hz; (C8, 10, 15, 17) ddd, 137.8, $J^1 = 254.6$ Hz, $J^2 = 12.6$ Hz, $J^{2'} = 7.1$; (C9, 16) dt, 143.0, $J^1 = 262$, $J^2 = 12.6$ Hz.

2b: NMR: ^{19}F: $\delta = -73.4$ (CF_3, t, $^4J_{FF} = 13.5$ Hz), -133.1 ($F^{8',10',17',15'}$ br.s), -143.5 ($F^{9',16'}$, m), -157.3 ($F^{7',11',14',18'}$, q); ^{13}C: (C1′, 3′) q, 80.5, $J^2 = 33.4$ Hz; (C2′, 4′) s, 152.6; (C5′, 12′) q, 120.1, $J^1 = 289$ Hz; (C6′, 13′) t, 105.5, $J^2 = 12$ Hz; (C7′, 11′, 14′, 18′) dt, 145, $J^1 = 258.9$, $J^2 = 14.1$ Hz; (C8′, 10′, 15′, 17′) ddd, 138.3, $J^1 = 255.0$, $J^2 = 12.6$, $J^{2'} = 6.9$ Hz; (C9′, 16′) dt, 143.4, $J^1 = 264$, $J^2 = 12.6$ Hz.

3.2. *3,3,3-Trifluoro-2-hydroxy-2-(2,3,4,5,6-pentafluorophenyl)propionic acid* ***5***

(*E,Z*)-3,6-Bis(trifluoromethyl)-3,6-bis(pentafluorophenyl)-1,4-dioxan-2,5-dione **2a**, **b** (0.03 g) and 0.5 ml H_2O was heated 4 h at 80 °C. Evaporation of the $CDCl_3$ extract gave 0.020 g of solid **5**; mp 141–142 °C [10]. NMR: ^{19}F: $\delta = -77.0$ (CF_3, t, $^4J_{FF} = 17.2$ Hz), -139.1 (2F, m), -154.2 (1F, m), -163.3 (F, m). ^{1}H: 4.67 s; 4.69 br.s.

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