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Unusual conversion of perfluoromethylepoxycyclopentane into a linear β-aminovinylketone by C–C bond cleavage

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Abstract

2,3,3,4,4,5,5-Heptafluoro-1-trifluoromethyl-1,2-epoxycyclopentane reacted with 2-*iso*propyl-acetophenone imine giving 2,3,3,4,4,5,5-heptafluoro-2-trifluoromethyl-1-(2′-*iso*propylimino-2′-phenylethane) cyclopentan-1-ol, which in its turn underwent an intramolecular rearrangement yielding the linear 4,4,5,5,6,6,7,8,8,8-decafluoro-1–*iso*propylamino-oct-1-en-3-one, being characterized by X-ray structural analysis (triclinic, P-1, $a = 920.5(2)$, $b = 1027.9(3)$, $c = 1127.4(3)$ pm, $\alpha = 110.99$, $\beta = 105.68°$, $\gamma = 96.75°$).

Keywords: 2,3,3,4,4,5,5-Heptafluoro-1-trifluoromethyl-1,2-epoxycyclopentane; 2-*Iso*propyl-acetophenone imine; Intramolecular rearrangement; 4,4,5,5,6,6,7,8,8,8-Decafluoro-1–*iso*propylamino-1-phenyl-oct-1-en-3-one

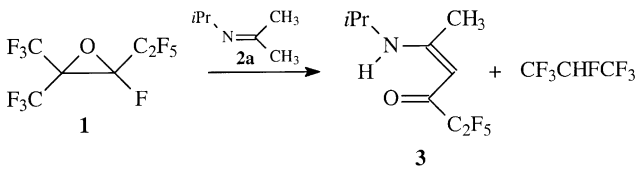
1. Introduction

Perfluorinated *terminal* epoxides may easily be converted by nucleophiles [1–3] to form perfluoroalkanoyl fluorides. With nucleophiles the respective *internal* epoxides give the corresponding ketones which, however, are not stable and undergo an alicyclic C–C bond cleavage (haloform reaction) [4–6]. We have recently studied reactions of several ketimines with perfluoroalkanoyl fluorides and obtained β-aminovinylketones or aminovinyldiketones in high yield, [7] useful precursors for the synthesis of new fluorinated diketones [8] and possible building blocks of pharmacologically important fluoroalkyl group-containing heterocycles [9,10].

2. Results and discussion

1,1,1,3,4,4,5,5,5-nonafluoro-2-trifluoromethyl-2,3-epoxypentane **1** [for the general method to synthesize perfluorinated oxides: see ref. 14] isomerizes in the presence of bases e.g. tertiary amines to give the corresponding ketone, [11] which is generated but not isolated in the case of using ketimine **2a** as a base. Compound **2a** and this ketone in its turn underwent a surprising C–C bond cleavage reaction accomponied by a hydrogen transfer yielding the already described enamino ketone **3** [7] and 1,1,1,2,3,3,3-heptafluoropropane (Scheme 1). Since an epoxide of a cyclic perfluoroolefin would offer the possibility for a ring opening reaction, 2,3,3,4,4,5,5-heptafluoro-1-trifluoromethyl-1,2-epoxycyclopentane **4** was synthesized which added ketimine **2b** under mild conditions to yield 2,3,3,4,4,5,5-heptafluoro-2-trifluoromethyl-1-(2′-*iso*propylimino-2′-phenylethane)cyclopentan-1-ol **5** product of a Stork enamine reaction [12] (Scheme 2).

In the cyclic β-iminoalcohol **5** the ring opens up to give the linear β-iminoketone **6** and finally its tautomer, 1-trifluoromethyl-1,2,2,3,3,4,4-heptafluoro-7-phenyl-7-isopropylamino-hept-6-en-5-one **7**. This reaction is the first example of a perfluorinated ring cleavage under nucleophilic conditions. In the intramolecular "haloform" reaction a secondary carbanion is probably produced which is stabilized by an intramolecular proton shift followed by an isomerization to form the final product **7**, whose molecular structure was confirmed by X-ray structure determination (Scheme 3, Fig. 1).



Scheme 1.

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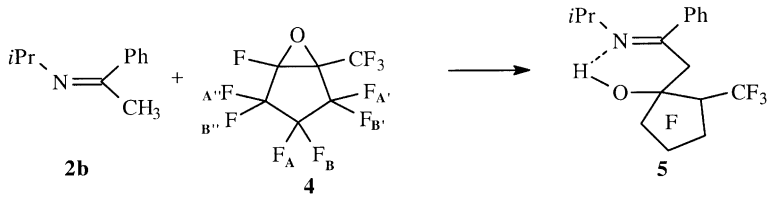
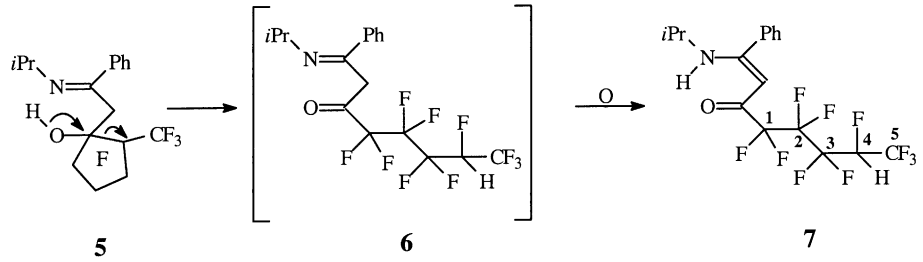


Scheme 2.



Scheme 3.

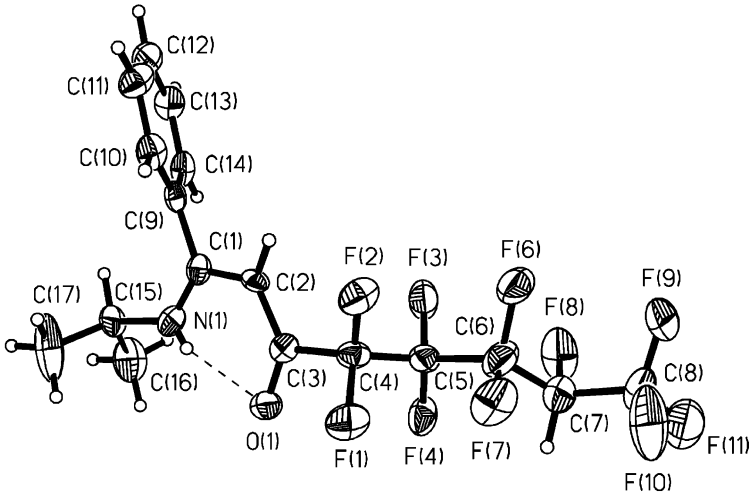


Fig. 1.

Two molecules were found in the unit cell of compound **7** with intramolecular hydrogen-bonding N(1)H–O(1) 270.5; the respective C–N and C–C distances in the aminovinyl ketone system of **7** are in between a single and a double bond indicating the expected delocalization with sp^2-hybridized carbon atoms; C(1)–N(1) 131.9(8), C(1)–C(2) 139.7(8). However, the C(3)–O(1) distance of 124.8(7) pm is common with a double bond [13] (Fig. 1).

Fig. 1: Molecular structure of **7** (thermal ellipsoids with 50% probability). Selected bond distances (pm) and angles(°): C(1)–N(1) 131.9(8), C(1)–C(2) 139.7(8), C(1)–C(9) 148.3(8), C(2)–C(3) 136.9(8), C(3)–O(1) 124.8(7), C(3)–C(4) 156.5(8), C(4)–F(2) 134.8(7), C(6)–F(7) 140.5(9), C(6)–C(7) 146.6(10), C(8)–F(9) 130.7(9), C(9)–C(10) 138.2(8), C(15)–N(1) 147.4(8), C(15)–C(17) 148.0(10), N(1)–C(1)–C(2) 121.7(6), C(3)–C(2)–C(1) 122.6(6), O(1)–C(3)–C(2) 128.3(5), O(1)–C(3)–C(4) 114.0(5), C(2)–C(3)–C(4) 117.6(5), C(5)–C(4)–C(3) 113.9(5), C(6)–C(7)–C(8) 115.2(7), C(10)–C(9)–C(14)118.1(6), N(1)–C(15)–C(17) 110.3(6), C(17)–C(15)–C(16) 112.4(6), C(1)–N(1)–C(15) 130.0(6).

3. Conclusion

We were able to perform a novel alicyclic ring opening of a new type of a haloform reaction. Other perfluorinated cycloalkenes of epoxides are to be investigated.

4. 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 and 188.31 MHz for ^{19}F. MS spectra were

obtained on a Varian MAT CH7A instrument at 70 eV. All reactions and manipulations were conducted under atmosphere of dry nitrogen. The X-ray structural study was carried out on a Siemens P4 diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 71.073$ pm). Crystal data for **6**, colorless crystals, $C_{17}H_{15}F_{10}NO$, $M = 439.30$, triclinic, P-1, $a = 920.5(2)$, $b = 1027.9(3)$, $c = 1127.4(3)$ pm, $\alpha = 110.99$, $\beta = 105.68°$, $\gamma = 96.75°$, $V = 0.9312(4)$ nm^3; final R values [$I > 2\sigma(I)$], $R_1 = 0.0755$, $wR_2 = 0.1928$; R values (all reflections), $R_1 = 0.1141$, $wR_2 = 0.2187$; 0.5 mm × 0.4 mm × 0.3 mm with $Z = 2$, reflections measured 2913, unique reflections 2344 ($R_{int} = 0.0351$). CCDC deposit number 160015. See http://www.rsc.org/suppdata/

*4.1. 1,1,1,3,4,4,5,5,5-nonafluoro-2-trifluoromethyl-2,3-epoxypentane (**1**) and 2-isopropyliminopropane (**2a**)*

2-*Iso*propyliminopropane (**2a**) (1.5 g, 15 mmol) and 4.8 g (15 mmol) compound **1** in 20 ml Et_2O at 22 °C for 24 h gave 1.8 g (4.3 mmol) (29%) enamino ketone **3** [7] and 1,1,1,2,3,3,3-hexafluoropropane.

*4.2. 2,3,3,4,4,5,5-Heptafluoro-1-trifluoromethyl-cyclopent-1-ene oxide (**4**)*

1-Trifluoromethyl-2,3,3,4,4,5,5-heptafluoro-cyclopentene (26.0 g, 100 mmol) were added dropwise to an aqueous NaOCl solution at room temperature (cf. ref. [14]). The mixture was stirred for 2 h, the lower layer separated, washed with water and dried over $MgSO_4$. Distillation gave 24.1 g (87 mmol) (87%) of the epoxide **4**. The bp 52 °C. ^{19}F NMR($CDCl_3$): −72.6 (CF_3, 3F, s); −185.6 (CF, 1F, d, $^2J_{FFA''}$ 15.4); −127.9 (CF_2, 2F, AB-system, J_{AB} 268.6); −131.3 (CF_2, 2F, AB-system, $J_{A'B'}$ 246.7); −134.6 (CF_2, 2F, ABX-system, $J_{A''B''}$ 250.6). MS: *m/z* (%): 278 (M^+, 6), 259 ($M^+ - F$, 17), 209 ($M^+ - CF_3$, 65), 15i9 ($M^+ - C_2F_5$, 39), 131 ($C_3F_5^+$, 86), 109 ($C_3F_3O^+$, 30), 109 ($C_2F_4^+$, 69), 93 ($C_3F_3^+$, 45), 69 (CF_3^+, 100), 47 (CFO^+, 25). Anal. calc. for $C_6F_{10}O$ (278.00): C, 25.90; F, 68.35. Found: C, 25.84; F, 68.37%.

*4.3. 2,3,3,4,4,5,5-Heptafluoro-1-trifluoromethyl-1-(2′-isopropyliminopropane) cyclopentan-1-ol (**5**)*

To compound **2b** (1.6 g, 10 mmol) in 20 ml diethylether 2.8 g (10 mmol) epoxide **4** was added dropwise and stirred for 12 h. All volatiles were removed under reduced pressure and the remaining yellow compound **5** distilled. The bp 94 °C (10^{-2} hPa). ^{1}H NMR ($CDCl_3$): 1.2 (*i*Pr, 6H, d, $^3J_{HH}$ 6.2), 2.4 (CH_2, 2H, AB-System, J_{AB} 25.5), 3.6 (*i*Pr, 1H, sep, $^3J_{HH}$ 6.2), 7.3 (Ph, 5H, m), 7.8 (OH, 1H, s). ^{19}F NMR ($CDCl_3$): −74.3 (CF_3, 3F, dt, $^3J_{FF}$ 11.8, $^4J_{FF}$ 6.0), −125.8 (CF_2, 2F, AB-system, J_{AB} 261.1), −126.3 (CF_2, 2F, AB-system, $J_{A'B'}$ 242.5), −128.5 (CF_2, 2F, AB-system, $J_{A''B''}$ 253.6), −186.5 (CF, 1F, m). MS: *m/e* (%) = 439(M^+, 100), 424 ($M^+ - CH_3$, 62), 370 ($M^+ - CF_3$, 12), 104 ($PhCO^+$, 58). Yield: 2.0 g = 4.6 mmol (46%). HRMS for $C_{17}H_{15}F_{10}NO$: calc: 439.09940, found: 439.09974.

*4.4. 1-Trifluoromethyl-1,2,2,3,3,4,4,-heptafluoro-7-phenyl-7-isopropylamino-hept-6-en-5-one (**7**)*

Compound **5** (1.5 g, 3.4 mmol) was allowed to stand for 2 weeks in a sealed tube at room temperature. The colorless crystals obtained were recrystallized from *n*-hexane. The mp 79 °C. ^{1}H NMR ($CDCl_3$): 1.2 (*i*Pr, 6H, d, $^3J_{HH}$ 6.5), 3.7 (*i*Pr, 1H, qq, $^3J_{HH}$ 6.4 Hz, 6.5), 5.4 (=CH, 1H, s), 5.5 (CHF, 1H, dtq, $^2J_{HF}$ 37.4, $^3J_{HF}$ 21.2, $^3J_{HF}$ 11.0), 7.5 (Ph, 5H, m), 11.3 (NH, 1H, brs). ^{19}F NMR ($CDCl_3$): −74.3 (CF_3(5), 3F, ddt, $^3J_{FF}$ 11.1, $^4J_{FF}$ 3.1), −120.2 (CF_2(2), 2F, m), 124.5 (CF_2(1), 2F, m), 124.8 (CF_2(3), 2F, ABMX-system, J_{AB} 295.1), 216.2 (CF(4), 1F, dqt, $^3J_{FF}$ 4.1). ^{13}C NMR ($CDCl_3$): 24.2 ($2CH_3$, s), 47.6 (CH, s), 83.1 (CFH, dqt, $^1J_{CF}$ 201.2, $^2J_{CF}$ 34.3, $^2J_{CF}$ 34.7), 92.1 (=CH, s), 110.6 ($C(1)F_2$, tt, $^1J_{CF}$ 264.8, $^2J_{CF}$ 30.3), 111.5 ($C(2)F_2$, tqu, $^1J_{CF}$ 268.3, $^2J_{CF}$ 31.2), 112.7 ($C(3)F_2$, ttd, $^1J_{CF}$ 281.0, $^2J_{CF}$31.6, $^2J_{CF}$ 24.1), 120.4 (CF_3, qd, $^1J_{CF}$ 281.8, $^2J_{CF}$ 25.6), 127.5 (*m*-Ph, s), 129.3 (*o*-Ph, s), 130.8 (*p*-Ph, s), 134.5 (*i*-Ph, s), 169.8 (=C–N, s), 177.2 (C=O, t, $^2J_{CF}$ 23.7). MS: *m/e* (%) = 439 (M^+, 40), 420 ($M^+ - F$, 9), 378 ($M^+ - F$, *i*Pr), $C_{17}H_{15}F_{10}NO$ (439.10) C, 46.48; H, 3.44; F, 43.25. Found: C, 46.40; H, 3.40; F, 44.05%.

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