## FLUORINE-CONTAINING HETEROCUMULENES.

# 19.\* SYNTHESIS AND REACTIONS OF 2-PERFLUORO-tert-BUTYL-3,3-DIPHENYLOXAZIRIDINE

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With diazo compounds aliphatic and aromatic nitroso compounds, including the fluorinecontaining compounds, form nitrones or their decomposition products [2, 3]. It was found that 2-nitrosoperfluoroisobutane (I) gives the oxaziridine (II) with diphenyldiazomethane.

 $(CF_3)_3C - N = O + Ph_2CN_2 \xrightarrow{-N_2} (CF_3)_3C - N \xrightarrow{O} CPh_2$ (I)
(II)

In the IR spectrum of the oxaziridine (II) there is no absorption in the region for double bonds, and in the PMR spectrum there are two singlets from the phenyl groups, which indicate a high barrier to inversion at the nitrogen. In the case of the oxaziridine (II) it seemed of interest to compare the properties of fluorine-containing oxaziridines with their hydrocarbon analogs.<sup>†</sup> The oxaziridine (II) can be kept for a long time at 0°C but decomposes at 50°C. Like unfluorinated oxaziridines [5, 6], it is reduced by triphenylphosphine or lithium aluminum hydride to the imine (III) and also enters into cycloaddition reactions (see[7, 8]). Thus, at 50-60°C with perfluoropropyl isocyanate it forms the oxadiazolidinone (IV), and with hexafluoroacetone it forms the dioxazolidine (V).



The oxadiazolidinone (IV) does not change when boiled in toluene, alcohol, or alcoholic hydrochloric acid or when treated with concentrated sulfuric acid at  $\sim 20^{\circ}$ C but is reduced by lithium aluminum hydride to the substituted urea (VI) with substitution of the mobile fluorine atoms by hydrogen. In contrast to the oxadiazolidinone (IV), the dioxazolidine (V) decomposes at 100°C with the release of hexafluoroacetone. When (V) is heated in the presence of perfluoropropyl isocyanate, the oxadiazolidinone (IV) is formed in addition to hexafluoroacetone. When boiled in alcohol, compound (V) also eliminates hexafluoroacetone and gives the substituted hydroxylamine (VII), which is also formed in the reaction of the oxaziridine (II) with alcohol. Thus, compound (V) differs greatly in its properties from the fully fluorinated analog the extremely stable (both thermally and chemically) 2,3,3,5,5-pentakis(trifluoromethyl)-1,4,2-dioxazolidine [9].

\*For Communication 18, see [1].

<sup>†</sup>The first representative of fluorine-containing oxaziridines was recently obtained by oxidation of perfluoroazapropene [4], but its chemical properties were not investigated.

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The reaction of oxaziridine (II) with bis(trifluoromethyl)ketene was unexpected. In contrast to the presented reactions, in which (II) reacts as a 1,3-dipolar compound, with ketene it behaves formally as a donor of perfluoro-tert-butylnitrene (cf. [10]) and gives a good yield of N-perfluoro-tert-butyl-3,3-bis(trifluoromethyl)aziridinone (VIII) and benzo-phenone. The  $\alpha$ -lactam (VIII) is also formed when the dioxazolidine (V) is heated with bis-(trifluoromethyl)ketene.



It is not impossible that an unstable cyclic adduct, which decomposes into the  $\alpha$ -lactam and benzophenone, is formed in the reaction of (II) with ketene, as in the reactions with isocyanate, hexafluoroacetone, and isonitrile (see below). The formation of the  $\alpha$ -lactam was postulated in the reaction of unfluorinated oxaziridines with diphenylketene, but it could not be isolated on account of its ready reaction with a second molecule of the ketene [7]. Unlike the unstable unfluorinated  $\alpha$ -lactams [11] and the relatively stable N-tertbutyl-3-trifluoromethyl-3-phenylaziridinone [12], the  $\alpha$ -lactam (VIII) was surprisingly stable and did not change after prolonged boiling.

The oxaziridine (II) only reacts with the most electrophilic unsaturated organofluorine compounds. The less electrophilic benzoylimine of hexafluoroacetone, bis(trifluoromethyl)-ketene anil (cf. [13]), and methyl perfluoromethacrylate do not react with it under the same conditions as the weakly nucleophilic cyclohexene. However, the more nucleophilic cyclohexyl isocyanide reacts with (II) at 50-60°C, forming the cyclic adduct (IX), which partly decomposes into benzophenone and the carbodiimide (X) even during distillation under high vacuum. At 120°C this decomposition is complete after 30 min.



Thus, the oxaziridine (II) possesses the properties both of a weak electrophile and a weak nucleophile. It is interesting to note that in contrast to the unfluorinated analogs all the cycloaddition reactions of (II) are realized with cleavage of the C-N bond and lead to the formation of a series of organofluorine heterocycles, including the uniquely stable  $\alpha$ -lactam.

# **EXPERIMENTAL**

The <sup>13</sup>C NMR spectra were recorded on a Bruker HX-90 spectrometer at 22.635 MHz without a solvent at  $\sim 20^{\circ}$ C (external standard methylene chloride,  $\delta$  54.02 ppm). The chemical shifts are given with reference to TMS. The PMR spectra were recorded on a Perkin-Elmer R-12 instrument at 60 MHz. The <sup>19</sup>F NMR spectra were recorded on a Hitachi H-60 instrument at 56.46 MHz). The chemical shifts are given on the  $\delta$  scale in parts per million from TMS or from trifluoroacetic acid (external standards), respectively. The mass spectra were recorded on a Varian MAT instrument at 70 eV. The IR sepctra were recorded on a UR-20 instrument.

<u>2-Perfluoro-tert-butyl-3,3-diphenyloxaziridine (II)</u>. To a solution of 3.7 g of diphenyldiazomethane in 15 ml of absolute ether we added dropwise with cooling in ice a solution of 2-nitrosoperfluoroisobutane (I) in absolute ether until the red color of diphenyldiazomethane had disappeared. The residue after distillation of the ether was dissolved in hexane and cooled to -78°C. The precipitate was filtered off, and 3.6 g (46%) of (II) was obtained; mp 36-40°C (from hexane). Found %: C 49.41; H 2.48; F 41.29; N 3.55. Mol. wt. 415 (mass spectrometry).  $C_{17}H_{10}F_{9}NO$ . Calculated %: C 49.15; H 2.4; F 41.2; N 3.37. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1455. PMR spectrum (in carbon tetrachloride): 7.16 s and 7.26 s (Ph). F NMR spectrum (in carbon tetrachloride): -12.5 S [(CF<sub>3</sub>)<sub>3</sub>C].

<u>N-Perfluoro-tert-butylbenzophenone Imine (III).</u> a. To a suspension of 0.9 g of triphenylphosphine in 5 ml of absolute ether, while cooling, we added a solution of 1.4 g of the oxaziridine (II) in 5 ml of absolute ether. After 3 h the precipitated triphenylphosphine oxide was filtered off. From the filtrate we obtained 1 g (74%) of (III); bp 66-69°C (0.01 mm Hg). Found %: C 51.25; H 2.51; F 42.62; N 3.02.  $C_{17}H_{10}F_9N$ . Calculated %: C 51.13; H 2.50; F 42.85; N 3.25. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1640 (C=N). PMR spectrum (in carbon tetra-chloride): 7.2 s (Ph). <sup>19</sup>F NMR spectrum (in carbon tetrachloride): -10.8 s [(CF<sub>3</sub>)<sub>3</sub>C].

b. To a suspension of 0.5 g of lithium aluminum hydride in 30 ml of absolute ether we added a solution of 3 g of (II) in 20 ml of absolute ether. The mixture was boiled for 10 h and hydrolyzed with cooling. A 1.4-g yield (48%) of compound (III), identical with the sample obtained in expt. (a), was obtained.

 $\frac{2-\text{Perfluoro-tert-butyl-4-perfluoropropyl-5,5-diphenyl-1,2,4-oxadiazolidin-3-one (IV)}{\text{a. A mixture of 4.2 g of (II) and 4.3 g of perfluoropropyl isocyanate in a sealed tube was heated at 50-60°C for 10 h. After distillation of the unreacted isocyanate, 4.5 g (72%) of (IV) was obtained; mp 72-74°C (from hexane, alcohol). Found %: C 39.70; H 1.72; F 48.88; N 4.63. Mol. wt. 626 (mass spectrometry). C<sub>21</sub>H<sub>10</sub>F<sub>16</sub>N<sub>2</sub>O<sub>2</sub>. Calculated %: C 40.25; H 1.59; F 48.56; N 4.47. IR spectrum (<math>\nu$ , cm<sup>-1</sup>): **1790** (C=0). PMR spectrum (in carbon tetrachloride): 7.23 s (Ph). <sup>19</sup>F NMR spectrum (in carbon tetrachloride): -13.9 s [(CF<sub>3</sub>)<sub>3</sub>C], +2.63 t (CF<sub>3</sub>), +11.05 qm (CF<sub>2</sub>N), +44.3 m (CF<sub>2</sub>), JF-F = 9.9 Hz.

b. A mixture of 1.5 g of the dioxazolidine (V) and 1 g of perfluoropropyl isocyanate in a sealed tube was heated at 95°C for 6 h. After distillation of the volatile substances we obtained 1.4 g (88%) of (IV); mp 72-74°C.

<u>N-Perfluoro-tert-butyl-N'- $\alpha$ , $\alpha$ -dihydropentafluoropropylurea (VI)</u>. To a suspension of 0.7 g of lithium aluminum hydride in 20 ml of absolute ether we added dropwise a solution of 2 g of (IV) in 10 ml of absolute ether. The mixture was stirred at  $\sim$ 20°C for 6 h and hydro-lyzed with cooling. The residue after distillation of the ether was washed with bexane. We obtained 0.3 g (23%) of (VI); mp 230-232°C (from benzene). Found %: C 24.25; H 1.18; F 65.17. C<sub>8</sub>H<sub>4</sub>F<sub>14</sub>N<sub>2</sub>O. Calculated %: C 23.41; H 0.97; F 64.87. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1585, 1680, 1690 (C=O), 3260, 3320-3410 (NH). PMR spectrum (in acetonitrile): 4.95 dt (CH<sub>2</sub>), J<sub>H-F</sub> = 15.8, J<sub>H-H</sub> = 7 Hz, 6.04 m and 6.34 m (NH). <sup>19</sup>F NMR spectrum (in acetonitrile): -8.55 s [(CF<sub>3</sub>)<sub>3</sub>C], +6.98 s (CF<sub>3</sub>), +43.5 t (CF<sub>2</sub>), J<sub>H-F</sub> = 15.4 Hz.

<u>N-Perfluoro-tert-butyl-O-( $\alpha$ -ethoxy)benzhydrylhydroxylamine (VII).</u> A 0.5-g sample of (V) in 5 ml of absolute alcohol was boiled for 3 h. After distillation of the alcohol we obtained 0.35 g (87%) of (VII); mp 64-66°C (from 75% alcohol). Found %: C 49.39; H 3.34; F 36.25; N 3.11. C<sub>19</sub>H<sub>16</sub>F<sub>9</sub>NO<sub>2</sub>. Calculated %: C 49.45; H 3.47; F 37.09; N 3.03. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 3235, 3280 (NH). PMR spectrum (in carbon tetrachloride): 1.18 t (Me), 3.24 q (OCH<sub>2</sub>), J<sub>HCCH</sub> = 7.35 Hz, 5.42 s (NH), 6.8-7.35 m (aromatic). F NMR spectrum (in carbon tetrachloride): -10 s [(CF<sub>3</sub>)<sub>3</sub>C].

From 2 g of (II) in 10 ml of absolute alcohol under similar conditions we obtained 2 g (91%) of (VII); mp 62-64°C (from 75% alcohol).

N-Perfluoro-tert-butyl-3,3-bis(trifluoromethyl)aziridinone (VIII). a. A mixture of 7 g of (II) and 7 ml of bis(trifluoromethyl)ketene in a sealed tube was heated at 50-60°C for 10 h. After distillation of the unreacted ketone the liquid was decanted and distilled. A 5.6-g yield (79%) of (VIII) was obtained; bp 100-101°C. Found %: C 23.56; F 69.81; N 3.64. Mol. wt. 411 (mass spectrometry).  $C_8F_{15}NO$ . Calculated %: C 23.35; F 69.34; N 3.40. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 1860, 1940, 1975, 2085 (C=0). <sup>19</sup>F NMR spectrum: -7.4 h [(CF<sub>3</sub>)<sub>3</sub>C], -8.3 dec [(CF<sub>3</sub>)<sub>2</sub>C], J<sub>F-F</sub> = 3.3 Hz. <sup>13</sup>C NMR spectrum: 54.05 h (C<sup>3</sup>), J<sub>C<sub>3</sub>-CF</sub> = 37.87 Hz, 68.26 dec (C<sup>1</sup>), J<sub>C<sub>1</sub>-CF</sub> = 32.26 Hz, 130.27 s (C=0), 118.8 q (CF<sub>3</sub>), J<sub>C-F</sub> = 290.7 Hz, 118.64 q, J<sub>C-F</sub> = 285.3 Hz.

From the residue after decantation of (VIII) we obtained 2.7 g of a compound (mp 46-49°C) identical with benzophenone.

b. A mixture of 1.5 g of (V) and 1 ml of bis(trifluoromethyl)ketene in a sealed tube was heated at 95°C for 6 h. After distillation of the volatile substances the liquid was

decanted and distilled. A 0.8-g yield (75%) of (VIII) was obtained; bp 102°C. In the residue we obtained 0.55 g of benzophenone.

During the action of heat  $(50-60^{\circ}C, \sim 10 \text{ h})$  in a sealed tube on a mixture of equimolar amounts of (II) with N-benzoylhexafluoroacetone imine, N-phenylbis(trifluoromethyl)ketene imine, methyl perfluoromethacrylate, or cyclohexene the latter remained unchanged (GLC, <sup>19</sup>F NMR spectra).

<u>N-Perfluoro-tert-butyl-N'-cyclohexylcarbodiimide (X)</u>. A mixture of 4.2 g of (II) and 1.5 g of cyclohexyl isocyanide in a sealed tube was heated at 50-60°C for 10 h. In the residue after distillation of the unreacted isocyanide we identified the cyclic adduct (IX). IR spectrum: 1740 cm<sup>-</sup>. F NMR spectrum: -12.1 s. The reaction mixture was then heated at 120°C for 30 min and distilled. A 3-g yield (86%) of (X) was obtained; bp 75-76°C (10 mm Hg). Found %: C 38.42; H 3.36; F 50.05; N 8.16.  $C_{11}H_{11}F_{9}N_{2}$ . Calculated %: C 38.59; H 3.21; F 50.00; N 8.18. IR spectrum ( $\nu$ , cm<sup>-1</sup>): 2180 (N=C=N). F NMR spectrum: -5.53 s [(CF<sub>3</sub>)<sub>3</sub>C].

By distillation from the residue after distillation of (X) we obtained 1.5 g of benzo-phenone.

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#### CONCLUSIONS

A method is proposed for the production of N-perfluoro-tert-butyldiphenyloxaziridine. Its cycloaddition to electrophilic and nucleophilic **dipolarophiles**, leading to the synthesis of fluorine-containing **oxadiazolidinones**, dioxazolidine, and a uniquely stable aziridinone, was investigated.

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