Bis(polyfluoroalkyl)diazomethanes containing the 1-*H*-hexafluoroisopropyl group

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Abstract

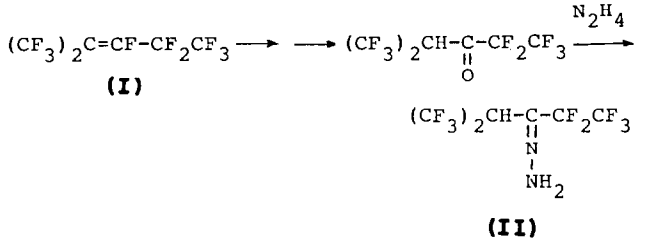
New bis(polyfluoroalkyl)diazomethanes have been obtained in high yield by the oxidation of polyfluorinated ketone hydrazones with bromine in water. A one-step preparative procedure for obtaining hexafluoroisopropylpentafluoroethylketone hydrazone from perfluoro-2-methyl-pent-2-ene and hydrazine hydrate has been worked out. Some reactions of the diazo compounds obtained, such as thermolysis, catalytic decomposition under the action of Et_3N and interaction with $P(OR)_3$ and PPh_3, have been studied.

Diazomethane with the 1-*H*-hexafluoroisopropyl group has been shown to be a suitable starting material for the preparation of the previously unobtainable perfluoro-1,2-dialkyl-substituted cyclopropene.

Introduction

This paper describes the synthesis of bis(polyfluoroalkyl)diazomethanes containing the 1-*H*-hexafluoroisopropyl group as one of the substituents, the latter imparting specific properties to such diazomethanes in contrast to known analogues.

The method of oxidation of unsubstituted polyfluoroalkylketone hydrazones with lead tetra-acetate in an organic solvent [1] is usually used for the preparation of bis(polyfluoroalkyl)diazomethanes. However, this method has disadvantages connected with the non-availability of unsubstituted hydrazones which are obtained, for example, via a multistep synthesis from perfluoro-olefin [2, 3]:



Results and discussion

We have worked out a one-step preparative method for obtaining the unsubstituted hydrazone **II** from perfluoro-2-methylpent-2-ene (**I**) and hydrazine hydrate.

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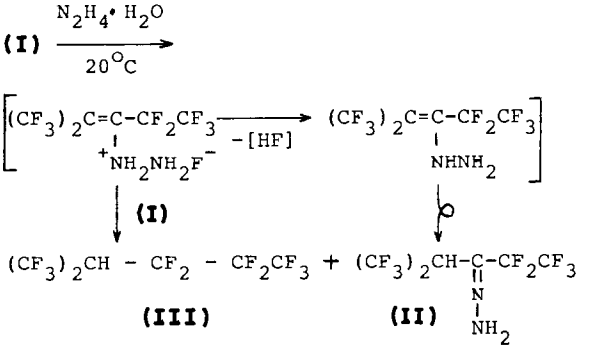
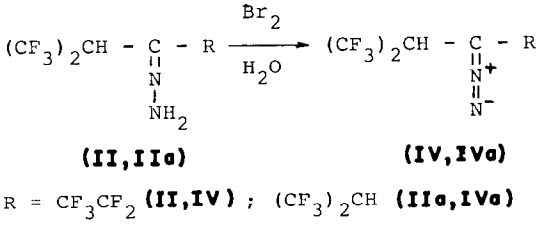


The mechanism of the formation of hydrazone **II** from olefin **I** involves two steps: nucleophilic substitution of the vinyl fluorine atom followed by isomerization of the intermediate hydrazino-substituted olefin. The hydrogen fluoride generated in this reaction reacts with the initial olefin to form 2-hydroperfluoro-2-methylpentane (**III**) with a 1:1 ratio of products **II** and **III**.

Hydrazone **II** proved to be easily oxidized by bromine in water [3] to give hexafluoroisopropylpentafluoroethyldiazomethane (**IV**) in high yield.



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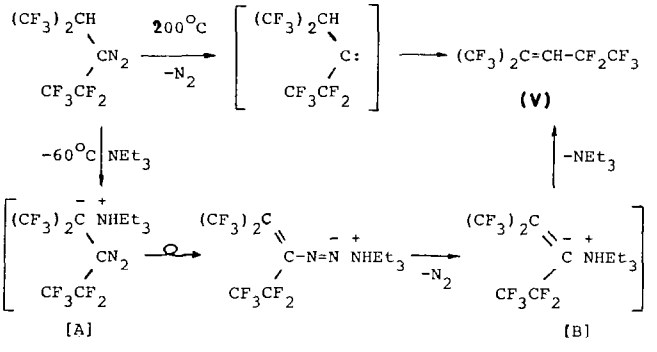
Symmetrical bis(hexafluoroisopropylpentafluoroethyl)diazomethane (**IVa**) was obtained in a similar fashion by oxidation of bis(hexafluoroisopropyl)ketone hydrazone (**IIa**) prepared by a procedure described previously [4].

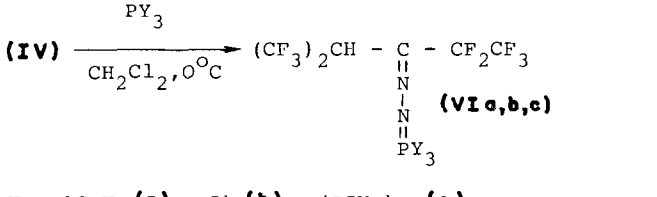
The diazomethanes obtained are yellowish-green liquid materials which are stable under normal conditions; they can be distilled and stored for long periods.

Diazomethane **IV** is stable on heating in a Carius tube up to 180 °C, but converts entirely to 3-*H*-perfluoropent-2-ene (**V**) at 200 °C for 10 h [5]; evidently, this conversion proceeds via formation of the intermediate dialkylcarbene (cf. ref. 1).

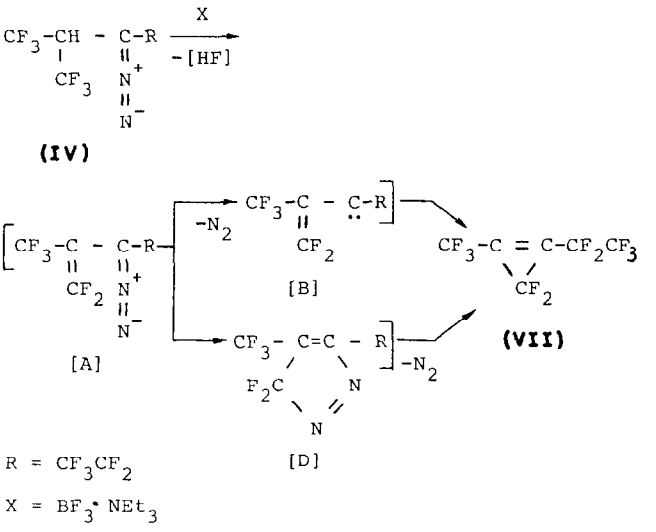


Unexpectedly, diazomethane reacted with triethylamine under mild conditions leading to a similar result. In this case, the reaction appears to proceed via the intermediate formation of the triethylammonium salt of carbanion A and then of carbanion B.

We have shown that diazomethane **IV**, like bis(trifluoromethyl)diazomethane [6], reacts readily with organic derivatives of trivalent phosphorus under mild conditions to form phosphine azines. For example, the interaction of diazomethane **IV** with triethylmethyl phosphite and triphenylphosphine gives the triethoxy- (**VIa**), trimethoxy- (**VIb**) and triphenyl- (**VIc**) phosphinazines of hexafluoroisopropylpentafluoroethylketone, respectively.



The dehydrofluorination reaction of diazomethane **IV** proved to be interesting, in that it results in the generation of perfluoro-1-methyl-2-ethylcyclopropene (**VII**) in *c.* 80% yield. This reaction is readily carried out by boiling **IV** with the $BF_3 \cdot NEt_3$ complex [7].



Evidently, unsaturated diazo compound A is formed in this case and this converts into cyclopropene via the alkenylcarbene B in a similar manner to the non-fluorinated tosylhydrazones [8]. Transformation of A into cyclopropene via 3-*H*-pyrazole D should be excluded.

The synthesis of perfluoroalkylcyclopropenes has been achieved previously by the addition of difluorocarbene to fluoroacetylenes in the gas phase [9], but the addition of the second CF_2 group complicates the reaction.

The reaction studied is the first example of a new approach to the synthesis of the previously unobtainable perfluorinated alkyl-substituted cyclopropenes.

Experimental

NMR spectra were obtained with a Perkin-Elmer 32 spectrometer [^1H (90 MHz), ^{19}F (84.6 MHz)], Me_4Si or CF_3COOH being used as external standards. Chemical shifts are quoted in parts per million relative to external standards. IR spectra were recorded on a UR-20 instrument. Mass spectroscopic data were obtained with a VG 7070E instrument at 70 eV [*m/z*, tentative assignment, intensity (%) listed].

Preparation of hexafluoroisopropylpentafluoroethylketone hydrazone (II)

Method 1

To a solution of $N_2H_4 \cdot H_2O$ (10.0 g, 200 mmol) in monoglyme (80 ml) was added CF_3COOH (22.8 g, 200 mmol) at −50 °C with stirring; the reaction mixture was then warmed to room temperature and perfluoro-2-methylpent-2-ene (**I**) (60.0 g, 100 mmol) was added slowly dropwise. The solution was stirred until it was homogeneous, and then poured into water; the organic layer was separated, washed several times with water

with shaking, dried over $MgSO_4$ and distilled. The products **III** (30.0 g, 94%, b.p. 60–62 °C), identified by comparison of the ^{19}F NMR spectra with those of an authentic sample [10], and **II** (29.0 g, 93%, b.p. 130–132 °C) were obtained as a mixture of *syn–anti* isomers. Analysis: Found: C, 22.97; H, 0.96%. $C_6H_3F_{11}N_2$ requires: C, 23.07; H, 0.96%. IR (ν, cm^{-1}, KBr): 1610 (s) (C=N); 2990 (C–H); 3390 and 3490 (NH_2). ^{19}F NMR δ: −14.7 and −11.2 (d, 6F); 5.5 and 7.6 (m, 3F); 35.0 and 41.0 (m, 2F, $J[(CF_3)_2C-H]=10$ Hz) ppm. ^1H NMR δ: 6.95 and 6.80 (br s, 2H); 3.82 (hept., 1H, $J[H-C(CF_3)_2]=10$ Hz) ppm. MS: 312 (M^+).

Method 2

To a solution of olefin **I** (30.0 g, 50 mmol) in monoglyme (50 ml) was added $N_2H_4 \cdot H_2O$ (5.0 g, 100 mmol) dropwise with stirring. The solution was stirred until it was homogeneous when it was treated in the same manner as above (see Method 1). The products **III** (14.0 g, 87%, b.p. 60–65 °C), **II** (11.0 g, 70%) and the residual 3-pentafluoroethyl-4-fluoromethyl-5-fluoropyrazole (3.0 g) [11] were obtained (according to ^{19}F NMR data).

Preparation of hexafluoroisopropylpentafluoroethyldiazomethane (IV)

Bromine (33.0 g, 208 mmol) was added dropwise with stirring to a solution of hydrazone **II** (50.0 g, 160 mmol) in 50 ml H_2O. The mixture was stirred until the release of HBr had ceased, when the organic layer was separated, washed with 1% $Na_2S_2O_3 \cdot 5H_2O$ solution and with water, dried over $MgSO_4$ and distilled. The products **IV** (38.0 g, 79%, b.p. 74–75 °C) and **II** (residue, 5.0 g) were obtained. Compound **IV**: IR (ν, cm^{-1}, KBr): 2130 (s) ($\bar{C}-\overset{+}{N}\equiv N$); 3000 (w) (C–H). Analysis: Found: C, 23.44; H, 0.43; F, 66.45%. $C_6HF_{11}N_2$ requires: C, 23.22; H, 0.32; F, 67.41%. ^{19}F NMR δ: −9.1 (d, 6F, $J[(CF_3)_2C-H]=7$ Hz); 9.1 (m, 3F); 35.2 (m, 2F) ppm. MS: 310 (M^+) 23.9; 263 (M^+-F) 1.9.

Preparation of bis-(hexafluoroisopropyl)diazomethane (IVa)

Product **IVa** (0.9 g, 60%) was prepared from hydrazone **IIa** (the synthesis of **IIa** has been reported in ref. 4) (1.5 g, 43 mmol) and Br_2 (0.9 g, 56 mmol) in 10 ml H_2O in a similar manner: b.p. 95–96 °C. IR (ν cm^{-1}): 2110 (s) ($\bar{C}-\overset{+}{N}\equiv N$); 2980 (w) (C–H). Analysis: Found: N, 7.58%. $C_7H_2F_{12}N_2$ requires: N, 8.18%. ^{19}F NMR δ: −10.2 (d m, 12F, $J[(CF_3)_2C-H]=7$ Hz) ppm. ^1H NMR δ: 3.7 (hept., $J[H-C(CF_3)_2]=7$ Hz) ppm. MS: 344 (M^+) 28.0; 325 (M^+-F) 9.2; 304 (M^+-2HF) 11.4; 285 (M^+-F,HF) 10.6; 193 ($M^+-(CF_3)_2CH$) 73.3; 69 (CF_3^+) 40.0.

Preparation of 3-H-perfluoro-2-methylpentene (V)

Method 1

The diazo compound **IV** (1 g) was heated in a Carius tube placed in a steel autoclave at 200 °C for 10 h. Product **V** (0.8 g, 90%, b.p. 52–53 °C) was obtained. ^{19}F NMR spectra were identical to those of an authentic sample [12].

Method 2

Triethylamine (1.4 g, 14 mmol) in CH_3CN (4 ml) was added dropwise to **IV** (7.0 g, 23 mmol) in CH_3CN (10 ml) at −70 °C with stirring. Evolution of N_2 began at −60 °C. The reaction mixture was gradually warmed to 20 °C and diluted with water over a period of 20 min; the organic layer was separated, washed with water, 10% HCl and water, dried over $MgSO_4$ and distilled. Product **V** (4.8 g, 75%, b.p. 52–54 °C) was obtained and was identical to an authentic sample according to IR, ^1H and ^{19}F NMR spectral data.

Preparation of hexafluoroisopropylpentafluoroketone triethoxyphosphazine (VIa)

Triethyl phosphite (14.2 g, 86 mmol) in CH_2Cl_2 (20 ml) was added to diazomethane **IV** (28.2 g, 91 mmol) in CH_2Cl_2 (40 ml) with stirring at 0 °C, the reaction mixture allowed to stand at 0 °C for 2 h and at 20 °C for 5 h, and then the solvent and excess diazomethane removed *in vacuo*; the residue was distilled. Product **VIa** (36.0 g, 87%, b.p. 80–82 °C/1 mmHg, colourless liquid) was obtained. Analysis: Found: N, 5.89; P, 6.80%. $C_{12}H_{16}F_{11}O_3N_2P$ requires: N, 5.88; P, 6.51%. IR (ν, cm^{-1}): 1560 (m) (C=N). ^{31}P NMR δ: 18.9 [$(C_2H_5)_2O$] ppm. ^{19}F NMR (mixture of *syn–anti* isomers) δ: −14.4 and −12.4 (d m, 6F); 3.2 and 3.7 (m, 3F); 31.4 and 35.0 (m, 2F, $J[(CF_3)_2C-H]=9$ Hz) ppm. ^1H NMR δ: 1.27 (t, 3H); 4.19 (q, 2H); 6.45 (h, 1H, $J[H-(CF_3)_2C]=9$ Hz) ppm. MS: 476 (M^+) 61; 457 (M^+-F) 13; 357 ($M^+-C_2F_5$) 10; 166 [$M^+-P(OEt_3)$] 100; 93 ($C_3F_3^+$) 10.6; 69 (CF_3^+).

Preparation of hexafluoroisopropylpentafluoroethylketone trimethoxyphosphinoazine (VIb)

Product **VIb** (2.5 g, 86%, b.p. 58–60 °C/1 mmHg) was obtained from diazomethane **VI** (2.5 g, 8 mmol) and $P(OMe)_3$ (0.8 g, 6 mmol) by a procedure similar to that used in the previous experiment. Analysis: Found: C, 25.03; H, 2.32; F, 48.86%. $C_9H_{10}N_2O_3PF_{11}$ requires: C, 24.89; H, 2.30; F, 48.16%. ^{19}F NMR (mixture of *syn–anti* isomers) δ: −13.4 (dd, 6F, $J=10$ Hz) and −11.5 (d m, 6F); 3.9 and 4.4 (br s, 3F); 3.2 (dq, 2F, $J=10$ Hz) and 35.6 (m, 2F) ppm. ^1H NMR δ: 3.6 (d, 9H, $J=10$ Hz); 3.9 and 6.2 (h, 1H, $J=10$ Hz) ppm. IR (ν, cm^{-1}): 1560 (m) (C=N). MS: 434 (M^+) 23.1: 415 (M^+-F) 13.8; 124 [$P(OCH_3)_3$] 100; 93 [$P(OCH_3)_2$].

Preparation of hexafluoroisopropylpentafluoroethylketone triphenylphosphinoazine (VIc)

Product **VIc** (8.3 g, 85%) was obtained from diazomethane **IV** (6.5 g, 20 mmol) in CH_2Cl_2 (30 ml) and PPh_3 (4.5 g, 17 mmol) by the previous procedure. Compound **VIc** was an oil, which then converted into a white powder. Analysis: Found: C, 51.29; H, 2.92; F, 5.73%. $C_{24}H_{16}F_{11}N_2P$ requires: C, 50.35; H, 2.80; P, 5.42%. ^{19}F NMR (CH_2Cl_2) δ: −15.4 (m, 3F); −11.5 (d m 6F); 5.7 (m, 3F); 39.2 (m, 2F) ppm. IR (ν, cm^{-1}): 1650–1660 (m) (C=N). MS: 572 (M^+) 3.7; 553 ($M^+ - F$) 4.7; 262 (PPh_3^+) 100; 193 ($C_2F_7^+$) 19; 143 ($C_4F_5^+$) 3.6; 131 ($C_3F_5^+$) 6; 124 ($C_4F_4^+$) 3; 119 ($C_2F_5^+$) 4; 69 (CF_3^+) 24.8.

Preparation of perfluoro-1-methyl-2-pentafluoroethyl-cyclopropene (VII)

Diazomethane **IV** (10 g, 38 mmol) and $BF_3 \cdot NEt_3$ (9.6 g, 57 mmol) were refluxed until the evolution of N_2 was over, then the liquid was distilled *in vacuo* (1 mmHg) (at room temperature and on heating with a water bath) into a trap cooled to −100 °C. This liquid was then distilled under atmospheric pressure. Product **VII** (6.7 g, 80%, b.p. 29–31 °C) was obtained. Analysis: Found: C, 27.34; F, 72.11%. C_6F_{10} requires: C, 27.48; F, 72.51%. ^{19}F NMR δ: −14.0 (m, 3F); 10.0 (m, 3F); 29.6 (m, 2F); 39.0 (m, 2F) ppm. IR (ν, cm^{-1}): 1830 (m) (C=C). MS: 262 (M^+) 1.5; 243 ($M^+ - F$) 13.0; 193 ($M^+ - CF_3$) 14.5; 74 ($C_3F_2^+$) 15.3; 50 (CF_2^+) 13.9.

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