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Journal of Fluorine Chemistry 110 (2001) 21–24
JOURNAL OF FLUORINE CHEMISTRY
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Synthesis and transformations of perfluoro-2-methyl-3-azido-2-pentene

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Received 27 July 2000; accepted 19 March 2001

Abstract

Reactions between perfluoro-2-methyl-2-pentene and NaN_3 in acetonitrile at −20°C provided perfluoro-2-methyl-3-azido-2-pentene stable only to 0°C, which decomposed in CCl_4 at 20°C to give 2,2-bis(trifluoromethyl)-3-pentafluoroethylaziridine or in EtOH at 20°C to 4,4-bis(trifluoromethyl)-5-ethoxy-5-pentafluoroethyl-1,2,3-triazoline, whose structure was confirmed by the X-ray crystallographic analysis. The routes of formation for these products have been discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Perfluoro-2-methylpent-2-ene; [1,2,3]triazoline and aziridine derivatives; 4,4-bis(trifluoromethyl)-5-ethoxy-5-pentafluoroethyl-1,2,3-triazoline; Nucleophilic addition; Cyclization

1. Introduction

[3 + 2] Cycloaddition of alkenes and alkynes with azide derivatives are known to lead to triazolines [1,2]. The presence of a N=N group in the latter facilitates the subsequent elimination of the N_2 molecule to give azirine derivatives. The introduction of fluorine atoms into alkene molecules does not change the direction of transformation of reaction products, but the direction is rather sensitive to the substituent at the 3-nitrogen atom. Thus, the reactions of octafluoroisobutylene [3] or perfluorobut-2-ene [4] with benzyl azide lead to the stable 1-benzyl-4,4-difluoro-5,5-bis(trifluoromethyl)-1,2,3-triazoline and 1-benzyl-4,5-difluoro-4,5-bis(trifluoromethyl)-1,2,3-triazoline, respectively, whereas the interaction between octafluoroisobutylene and phenyl azide yields 1-phenyl-2,2-difluoro-3,3-bis(trifluoromethyl)-aziridine [5].

In the case of the use of sodium azide, the structure of the initial alkene begins to play an important role. As a rule, the reaction leads to azirine derivatives in this case, e.g. the interaction of sodium azide with heptafluoroisobutylene derivatives [$(CF_3)_2C{=}CFR$, where R = OCH_3, F, NMe_2, $N(CH_2)_5$] yields 2,2-bis(trifluoromethyl)-3-fluoroazirine as a result of decomposition of the triazoline ring. Photolysis and thermolysis of 1,2,3-triazine derivatives is accompanied by N_2 elimination and leads to azete derivatives. Thus, photolyses of trifluoro-1,2,3-triazine and perfluoro-(4,6-diisopropyl)-1,2,3-triazine are known to give 2,3,4-trifluoroazete and perfluoro-2,4-diisopropylazete [6,7].

The reaction of sodium azide with perfluoroolefins begins with the addition of azide ion to the double bond. The presence of bromine leads to addition of bromide and azide ions to the double bond [8] and in the presence of CO_2 yields perfluorocarboxylic acids [9]. The presence of a fluorine atom on the carbon alpha to the azido group results in its elimination with formation of a double bond.

The azido group with a double bond leads to thermal instability of system. Perfluoroalkylazides are known to be thermally unstable [5], but the presence of the double bond, active towards nucleophilic reagents, makes the formation of 3- and 4-membered heterocycles possible.

The purpose of the present work is the investigation of the reaction between perfluoro-2-methyl-2-pentene (**1**) and NaN_3 and the factors determining the structure of the heterocycles obtained.

2. Results and discussion

The interaction of compound (**1**) with sodium azide in acetonitrile at −20°C gives perfluoro-2-methyl-3-azido-2-pentene (**2**), stable at this temperature (see Scheme 1).

Compound **2** was separated by treatment of the reaction mixture with water at 0°C. Its structure was confirmed by NMR and IR spectroscopy at −20°C. The reaction of compound **1** with sodium azide in acetonitrile at room

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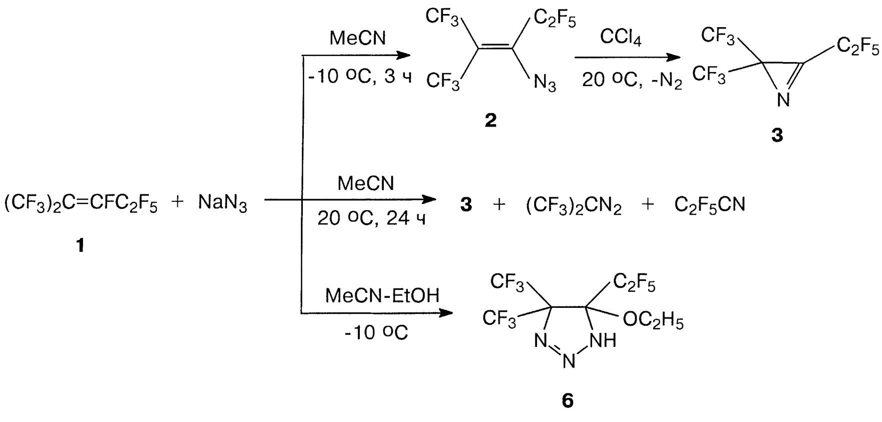
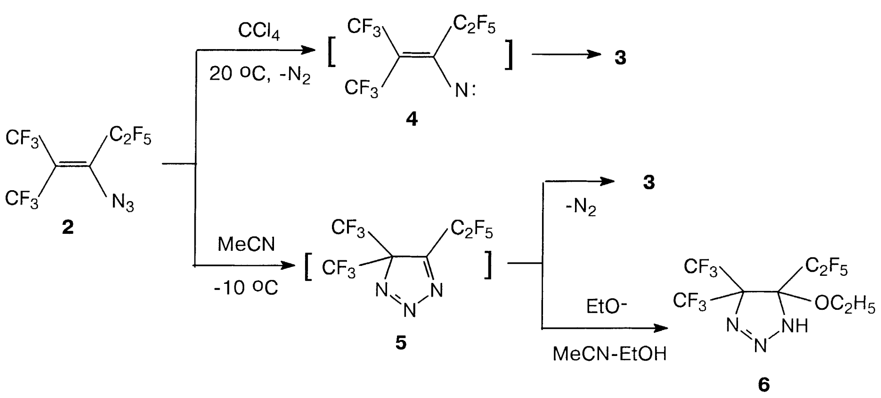
0022-1139/01/$ – see front matter
PII: S0022-1139(01)00395-5



Scheme 1.



Scheme 2.

temperature leads to a mixture of products, including, in particular, compound **3**, bis(trifluoromethyl)diazomethane and the nitrile of perfluoropropionic acid.

Holding of compound **2** in CCl_4 at 20°C was found to lead to its decomposition, being accompanied by N_2 elimination and formation of 2,2-bis(trifluoromethyl)-3-pentafluoroethyl-2H-azirine (**3**). The structure of latter was confirmed spectroscopically. Compound **3** can be easily decomposed under UV irradiation (mercury lamp) in hexane or CCl_4. The formation of compound **3** can be explained either via generation of a corresponding nitrene (**4**), or by decomposition of thermally unstable 1,2,3-triazoline (**5**) (see Scheme 2).

Nitrene (**4**) could participate in intramolecular cyclization to give **3**. The intermediate formation of compound **5**, also seems to be real. Thus, the reaction of compound **1** with sodium azide in MeCN–EtOH (1:2) at −10°C (2 h) has been found to yield stable 4,4-bis(trifluoromethyl)-5-ethoxy-5-pentafluoroethyl-1,2,3-triazoline (**6**). The formation of the latter compound can be explained by nucleophilic attack of ethoxy anion on the C=N bond of the 1,2,3-triazoline ring.

To confirm the structure of compound **6**, an X-ray structure was carried out. The structure and bond lengths of **6** are given in Fig. 1. The triazoline ring in molecule **6** has the "envelope" form; atom C5 is out of double bond plane with a deviation equal to −0.381(5) Å. The Cambridge data bank has only two recorded structures of compounds with similar triazoline fragments [10,11] and both of them have the same "envelope" conformation. Such lengthening of the C4–C5 bond can be explained by mutual repulsion of the CF_3 and CF_2 groups bonded to the C4 and C5 atoms. The bond length in the other fragments of molecule **6** are close to typical values [12].

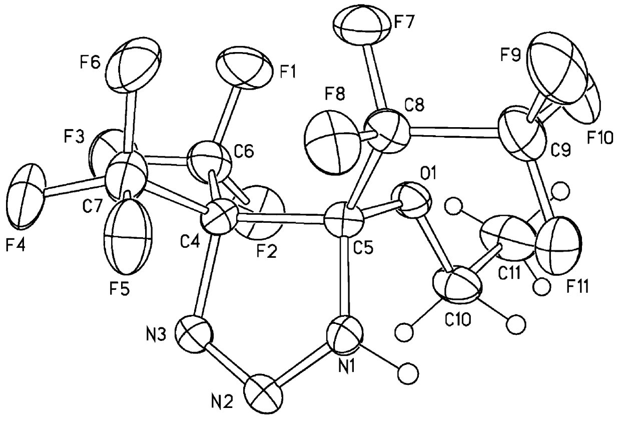


Fig. 1. The molecular geometry of the to 4,4-bis(trifluoromethyl)-5-ethoxy-5-pentafluoroethyl-1,2,3-triazoline (**6**) (ORTEP diagram).

The molecules of compound **6** are connected in infinite chains along the axis *b* because of shortened Van der Waals contacts of N···H and F···F type (N3···H1 2.469 Å, F4···F11 2.874 Å). These chains, in turn, contain dimer pairs of molecules due to shortened intermolecular contacts of F···N type (F4···N2 2.933 Å).

Thus, the route for stabilization of unstable heterocyclic systems is revealed. It consists in their transfer into thermodynamically more stable heterocycles by the interaction with nucleophilic reagents.

3. Experimental

^{19}F NMR spectra were recorded in ppm downfield from internal standard C_6F_6 in $CDCl_3$ using a Bruker WP 200SY spectrometer operating at 188.324 MHz. ^{13}C NMR Spectra were recorded in ppm downfield from the internal standard (Me_4Si, δ 0.00) using a Bruker AM 400 spectrometer operating at 100.614 MHz in $CDCl_3$ (J_{CH} were not recorded). Infrared (IR) spectra were recorded on Bruker IFS66 spectrometers (5% in CCl_4). GC-MS spectra were obtained using a Finnigan MAT model 8200 spectrometer at 70 eV in the electron impact mode and are reported as *m/z* (relative intensity). Mass spectra were determined with a gas chromatograph electron ionization detector (Hewlett Packard G 1800A GCD system), 30 mm capillary column 0.25 mm with 0.25 μk film of co-polymer 5% diphenyl–95% dimethylsilicate (HP-5), gas: helium, 1 ml min^{-1}, *T* of column 280°C. X-ray structure analysis was carried out on a "Bruker P4" diffractometer (λ Mo Kα graphite monochromator, $\theta/2\theta$-scan, $2\theta < 140°$) and a crystal sample sealed in a polyethylene capillary.

Crystallographic data for **6**: monoclinic, space group $P2_1/c$, $a = 10.4361(7)$, $b = 9.1628(4)$, $c = 14.4475(4)$ Å, $\beta = 107.893(7)°$, $V = 776.7(2)$ Å^3, $C_8H_6F_{11}N_3O$, $M = 369$. $Z = 4$, $D_c = 1.130$ g cm^{-3}, $m = 0.618$ mm^{-1}. Intensities of 1526 reflections were measured using a $\theta/2\theta$-scan mode, $2\theta < 45°$. Crystal size 0.61 mm × 0.34 mm × 0.30 mm. The structure was solved by direct methods (SHELXS-86 program) and refined by a full matrix least squares technique (SHELXL-97 program) in anisotropic–isotropic (for H-atoms) approximation to $wR_2 = 0.1114$, $S = 1.060$ ($R = 0.0426$ for 1096 $F > 4\sigma$) using all F^2. H-atom positions were found from a D-map. Nonhydrogen atom coordinates are shown in Table 1.

All reactions were monitored routinely with the aid of ^{19}F NMR spectroscopy.

3.1. Reaction of perfluoro-2-methyl-2-pentene (1) with sodium azide

3.1.1. Preparation of perfluoro-2-methyl-3-azido-2-pentene (2)

To a stirred suspension of NaN_3 (6.5 g, 0.1 mol) in anhydrous MeCN (50 ml) was added **1** (30 g, 0.1 mol) dropwise at −20°C for 15 min. Stirring was continued at −10°C for 3.5 h. The resulting solution was poured into water (100 ml). The organic extracts were washed with 5% hydrochloric acid (50 ml), brine (70 ml) and dried over Na_2SO_4 at −20°C.

Table 1
Atomic coordinates (10^4) and equivalent isotropic displacement parameters (Å × 10^3) for 4,4-bis(trifluoromethyl)-5-ethoxy-5-pentafluoroethyl-1,2,3-triazoline (U(eq)) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

A	*x*	*y*	*z*	*U*(eq)
O(1)	2072(2)	738(3)	1462(2)	49(1)
N(1)	4431(3)	1013(4)	1691(2)	46(1)
N(2)	4975(3)	2044(4)	2354(2)	54(1)
N(3)	4324(3)	3216(3)	2209(2)	51(1)
C(4)	3161(4)	3069(4)	1299(2)	43(1)
C(5)	3065(4)	1356(4)	1131(2)	41(1)
C(6)	1911(5)	3724(5)	1478(3)	66(1)
C(7)	3614(6)	3986(5)	557(3)	66(1)
C(8)	2714(4)	763(5)	75(3)	56(1)
C(9)	2540(6)	−894(5)	−22(4)	75(1)
C(10)	2409(5)	56(7)	2413(3)	67(1)
C(11)	1137(7)	−425(11)	2558(5)	101(2)
F(1)	806(2)	3438(3)	764(2)	91(1)
F(2)	1753(3)	3228(3)	2297(2)	91(1)
F(3)	1999(3)	5164(3)	1576(2)	99(1)
F(4)	3877(3)	5352(3)	861(2)	90(1)
F(5)	4749(3)	3459(3)	461(2)	87(1)
F(6)	2695(3)	4018(3)	−297(2)	100(1)
F(7)	1537(3)	1363(3)	−464(2)	78(1)
F(8)	3655(3)	1126(3)	−339(2)	76(1)
F(9)	2583(4)	−1309(3)	−886(2)	110(1)
F(10)	1400(3)	−1350(3)	68(2)	108(1)
F(11)	3547(3)	−1542(3)	640(2)	91(1)

Perfluoro-2-methyl-3-azido-2-pentene (**2**), 24 g (74%). IR 1300–1100 (C–F), 1680 (C=C), 2150 cm^{-1} (N_3); ^{19}F NMR ($(CD_3)_2CO$) δ_F 107.0 (F^1), 103.7 (F^6), 81.6 (F^5), 53.4 (F^4); ^{13}C NMR (CD_2Cl_2) δ_C 141.0 (C^3, J^2_{C-F} 29 Hz), 120.4 (C^1, J^1_{C-F} 316.2 Hz), 120.3 (C^6, J^1_{C-F} 273.4 Hz), 117.7 (C^5, J^1_{C-F} 287 Hz, J^2_{C-F} 35.2 Hz), 115.6 (C^2, J^2_{C-F} 35 Hz), 110.6 (C^4, J^1_{C-F} 261 Hz, J^2_{C-F} 35.2 Hz).

3.1.2. Preparation of 4,4-bis(trifluoromethyl)-5-ethoxy-5-pentafluoroethyl-1,2,3-triazoline (6)

To a stirred suspension of NaN_3 (3.25 g, 0.05 mol) in anhydrous MeCN–EtOH (45 ml, 2.5:2) was added compound **1** (15 g, 0.05 mol) dropwise at −20°C 15 min. Stirring was continued at −10°C for 2.5 h. The resulting solution was poured into water (100 ml). The organic extracts were washed with 5% hydrochloric acid (50 ml), brine (70 ml) and dried over Na_2SO_4 at room temperature 24 h. The remaining solid was recrystallized from petroleum ether (70–100°C). 4,4-Bis(trifluoromethyl)-5-ethoxy-5-pentafluoroethyl-1,2,3-triazoline (**6**), 7.5 g, mp 84.5–85.5°C. IR 3410, 3400 (N–H), 3000 (C–H), 2900 (C–H), 1100–1300 (C–F); ^{1}H NMR δ 11.08 (NH), 3.59 d.q. (CH), 3.14 d.q. (CH) and 1.12 t (CH_3); ^{19}F NMR ($(CD_3)_2CO$) δ_F 99.3 (F^8), 84.9 (F^7), 51.1 and 44.8 (F^6) (AB-system, J_{FF} 280.4 Hz); ^{13}C NMR (CD_2Cl_2) δ_C 120.6 (C^8, J^1_{C-F} 282.7 Hz), 120.2 (C^9, J^1_{C-F} 287.1 Hz), 118.6 (C^7, J^1_{C-F} 287.6 Hz; J^2_{C-F} 36.1 Hz), 111.8 (C^6, J^1_{C-F} 270.0 Hz; J^2_{C-F} 36.6 Hz), 94.2 (C^4, J^2_{C-F} 31.4 Hz), 92.2 (C^5, J^2_{C-F} 21.1 Hz), 62.4 (C^{10}), 12.9 (C^{11}). Found M^+ 369. $C_8H_6F_{11}N_3O$. Found (%): C 25.94, 26.07; H 1.68, 1.58; F 57.25, 57.12; N 10.84. Calcd. (%): C 26.01; H 1.63; F 56.64; N 11.38.

3.2. Reaction compound 2

A solution of **2** (16.1 g, 0.05 mol) and CCl_4 (benzene, toluene, pentane, DMF) (50 ml) was stirred at 20°C (under irradiation UV lamp). The liberated gas was collected in a balloon. The mixture was left overnight and cooled to −20°C. On warming to room temperature, the mixture clearly divided into layers. The upper layer was separated and distilled, a fraction with bp 15–20°C to give heptafluoro-2-diazopropane; ^{19}F NMR spectrum: δ_F 106.6 ppm (CF_3); IR (5% solution in CCl_4): 1100–1300 (C–F), 2140 (C=N=N). A fraction bp 37–38°C to give 2,2-bis(trifluoromethyl)-3-pentafluoroethyl-aziridine **3**, 11.7 g (80%). IR 1300–1100 (C–F) and 1700 cm^{-1} (C=N); ^{19}F NMR ($(CD_3)_2CO$) δ_F 96.0 ($F^{1,6}$) and 44.8 (F^4); ^{13}C NMR (CD_2Cl_2) δ_C 158.9 (C^3, J^2_{C-F} 40 Hz), 120.1 ($C^{1,6}$, J^1_{C-F} 276.4 Hz), 117.2 (C^5, J^1_{C-F} 285.3 Hz; J^2_{C-F} 33.3 Hz), 108.1 (C^4, J^1_{C-F} 260.3 Hz; J^2_{C-F} 33.3 Hz), 42.0 (C^2, J^2_{C-F} 42.5 Hz). Calcd. (%): C 24.41; F 70.85; N 4.75. *M* 295 for $C_6F_{11}N$, Found (%): C 24.35, 24.45; F 70.67, 70.45; N 4.65; *M* 295.

References

[1] R. Huisgen, Angew. Chem. Int. Ed. (1963) 565, 633.

[2] R. Huisgen, G. Szeimies, L. Moebins, Chem. Ber. 100 (1967) 2494.

[3] W. Carpenter, A. Haymaker, D.W. Noore, J. Org. Chem. 31 (1966) 789.

[4] C.G. Krespan, J. Org. Chem. 34 (1969) 1278.

[5] Yu.V. Zeifman, V.V. Tuleneva, A.P. Pleshkova, R.G. Kospyakovskii, I.L. Knunyants, Izv. Akad. Nauk SSSR. Ser. Khim., 1975, p. 2732.

[6] R.D. Chambers, T. Shepherd, M. Tamura, H. Hoare, J. Chem. Soc., Perkin Trans. I (1990) 983.

[7] R.D. Chambers, M. Tamura, T. Shepherd, C.J. Ludman, J. Chem. Soc., Chem. Commun. (1987) 1699.

[8] S.A. Pospovoy, Yu.V. Zeifman, I.L. Knunyants, Izv. Akad. Nauk SSSR. Ser. Khim. (1986) 1306.

[9] C.G. Krespan, F.A. Van-Catledge, B.E. Smart, J. Am. Chem. Soc. 106 (1984) 5544.

[10] R.L. Eagan, M.A. Ogliaruso, J.P. Springer, J. Org. Chem. 51 (1986) 1544.

[11] O. Caruga, F. Clerici, D. Pocar, Tetrahedron 49 (1993) 9117.

[12] F.H. Allen, O. Kennard, D.G. Watson, L. Bramer, G. Orpen, R. Taylor, J. Chem. Soc., Perkin Trans. II (1987) 1.