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Perfluorocyclobutene and its dimers in Diels-Alder reaction with cyclopentadiene and furan. New data

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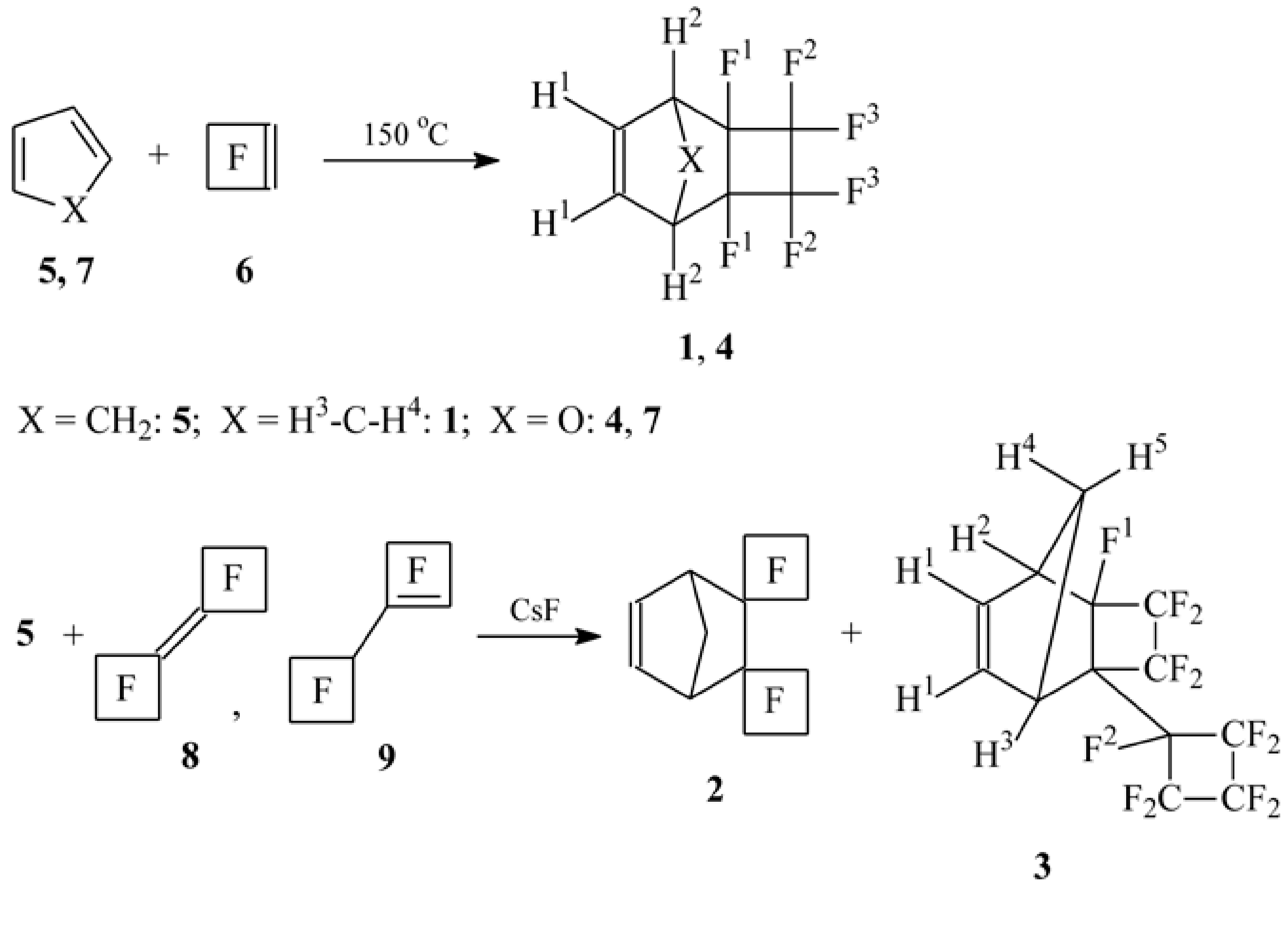
Abstract: *Fluorinated norbornenes and 7-oxanorbornene, containing perfluorocyclobutane fragments, were synthesized by Diels-Alder reaction from perfluorocyclobutene or perfluorocyclobutene dimers and cyclopentadiene or furan.*

Keywords: *perfluorocyclobutene, perfluorocyclobutene dimers, cyclopentadiene, furan, Diels-Alder reaction.*

Fluorinated polymers on the base of norbornene and its analogues were found to be promising materials for extreme UV lithography (see e.g. [1, 2]), and also for generation of gas-permeable [3] and ion-selective [4] membranes. In this work is given new data concerning synthesis of fluorinated norbornenes **(1-3)** and 7-oxanorbornene **(4)** (see scheme 1), which are prospective monomers for such polymersвЂ™ production.



Scheme 1

It should be noted, that there are some single reports about present compounds in the literature. Thus, the hexafluorotricyclononene **(1)** obtaining was declared in the publication [5], and its hydroformylation was reported about in the article [6]. But nowhere was given neither detailed description of the compound **(1)** synthesis, nor its characteristics.

We obtained tricyclononene **(1)** as the mixture of endo- and exo-isomers (16:1) by prolonged heating of cyclopentadiene (CPD) **(5)** with the excess of perfluorocyclobutene (PFCB) **(6)** in autoclave without solvent, and the yield amounted to 34%. Similarly, by the heating of furan **(7)** with the excess of PFCB **(6)** was synthesized also 9-oxatricyclononene **(4)**, isolated with the yield 23%. Low yield of products may be explained by necessity of end tricyclononene **(1)** deep purification from dicyclopentadiene (DCPD) impurity in the first case, and in the second case the reason was in the following [2+4]-cycloaddition reaction of compound **(4)** with furan **(7)** in this conditions (NMR and *GC-MS data were not given).*

The generation of 9-oxatricyclononene **(4)** by heating to 50-60 В°C of ether solution of furan **(7)** and PFCB **(6)** equimolar mixture is described in the literature [7]. We didnвЂ™t succeed in replaying this experiment: the reaction almost failed by the temperature 50-100 В°C and only about 150 В°C the conversion of furan **(7)** became approximately 10% after 19 hours. Although the melting point and parameters of ^{1}H and ^{19}F NMR spectra of our compound obtained are differing from literary data [7], the totality of its spectral characteristics (NMR, Raman, MS, see Tables 1-3) allows us to assign it the [2+4]-cycloadduct structure **(4)**.

The obtaining of dispironorbornene **(2)** by reaction of CPD **(5)** with PFCB dimer **(8)**, or with the mixture of PFCB dimers **(8/9)** in the CsF presence [8, 9] is also described in the literature. So the authors claimed perfluorobicyclobutylidene **(8)** only to be able to undergo the Diels-Alder reaction, whereas the olefin **(9)** stayed inert, and only its isomerisation to dimer **(8)** occurred in presence of CsF [9]. But we found in the result of more thorough purification and examination of reaction products, that heating of CPD **(5)** with the mixture of PFCB dimers **(8/9)*** in the CsF presence, led to [2+4]-cycloadducts from both olefins: dispironorbornene **(2)** and 2-nonafluorocyclobutyl substituted tricyclononene **(3)**, herewith the yield of dispironorbornene **(2)** beeing always higher at any ratio of starting dimers **(8/9)**. Besides this it appeared that pure dispironorbornene **(2)** was solid, but not liquid as was reported in [9]******.

Polymerization of synthesized fluorinated norbornenes **(1, 2)** and also 7-oxanorbornene **(4)** was investigated in Philipps-University, Marburg, (FRG), by Prof. Heitz group [10]**.**

Experimental

^{1}H, and ^{19}F (with CF_3COOH as the external standard) NMR spectra were recorded in $CDCl_3$ on Bruker WP-200SY spectrometer. Raman spectra were detected on Ramanor HG-2S spectrometer. Mass and GC-MS spectra were recorded on VG 7070E and Polaris/GCQ mass spectrometers (EI, 70 eV). Preparative GLC (PGLC) was performed at 150 В°C on QF1 on chromosorb column (l = 4 m, d =25 mm) or on FS1265 on chromosorb column (l = 3.6 m, d =25 mm).

CPD **(5)** and furan **(9)** were obtained by pyrolysis of DCPD and pyromucic acid, accordingly, and kept at -78 В°C. PFCB **(6)** [11] and PFCB dimers **(8/9)** with monohydrocycloalkane **(10**) impurity [12] were synthesized by known procedures, mixture ratio was evaluated according NMR spectra and GLC.

Synthesized compounds characteristics are represented in Tables 1-3.

2,3,3,4,4,5-Hexafluorotricyclo[4.2.1.$0^{2,5}$]nonene-7 (1)

The mixture of 5.93 g (89.7 mmol) CPD **(5)**, 18.65 g (115.0 mmol) PFCB **(6)** and 0.2 g hydroquinone was heated at 150 В°C for 72 h in autoclave. After cooling all volatile compounds were distilled off, the residue was filtered and autoclave was washed by small amount of ether. 11.94 g (58%) of cycloadduct (**1**) was obtained by combined filtrates distillating , purity в‰Ґ 98%, DCPD impurity ~1.2% (NMR, GLC), b.p. 58-59 В°C (20 Torr). PGLC (QF1) of distilled product gave 6.89 g (34%) of tricyclononene **(1)** as colorless liquid, representing the mixture of endo/exo-isomers (16:1), purity в‰Ґ99.9%, DCPD content в‰¤0.01% (NMR, GLC).

5-Norbornene-2-spiro-1вЂ™-(2вЂ™,2вЂ™,3вЂ™,3вЂ™,4вЂ™,4вЂ™-hexafluorocyclobutane)-3-spiro-1вЂќ-(2вЂќ,2вЂќ,3вЂќ,3вЂќ,4вЂќ,4вЂќ-hexafluorocyclobutane) (2) and 2-heptafluorocyclobutyl-3,3,4,4,5-pentafluortricyclo[4.2.1.$0^{2,5}$]nonene-7 (3)

The mixture of 1.78 g (27.0 mmol) CPD **(5)**, 6.84 g PFCB dimers **(8/9)** with monohydrocycloalkane **(10)** [**(8)**/**(9)**/**(10)** = 1.0/0.51/0.15; 20.7 mmol calculating on C_8F_{12}] and 3.24 g (21.3 mmol) freshly calcined CsF were heated at 80 В°C for 16 h in periodically agitated sealed tube. After the reaction expired the supernatant liquid contained cycloadducts **(2)** and **(3)** in the ratio 4.4:1.0 (NMR, GLC).

Similarly, 3.19 g (48.3 mmol) CPD **(5)**, 11.11 g PFCB dimers **(8/9)** with monohydrocycloalkane **(10)** [**(8)**/**(9)**/**(10)** = 1.0/0.82/0.33; 33.7 mmol calculating on C_8F_{12}] and 7.37 g (48.5 mmol) CsF, and also 0.45g (6.82 mmol) CPD **(5)**, 1.49 g PFCB dimers **(8/9)** with monohydrocycloalkane **(10)** [**(8)**/**(9)**/**(10)** = 1.0/4.5/3.9; 4.39 mmol calculating on C_8F_{12}] and 1.18 g (7.76 mmol) CsF were heated for 6 h. The final solutions contained cycloadducts **(2)** Рё **(3)** in the ratio ~2:1 (NMR, GLC).

Reaction mixtures were filtered, the precipitate was washed with ether, combined filtrates were concentrated and distilled, the fraction with b.p. 61-66 В°C (5 Torr) was collected. Distilled product PGLC (FS1265) gave 12.83 g (56%) of cycloadduct **(2)** as white solid, with purity в‰Ґ99%, DCPD content в‰¤0.01% (NMR, GLC), and also 2.04 g (9%) cycloadduct **(3)** as white fusible solid, with purity в‰Ґ99% (NMR, GLC).

2,3,3,4,4,5-Hexafluoro-9-oxatricyclo[4.2.1.0^{2,5}]nonene-7 (4)

The mixture of 9.6 g (0.141 mol) furan **(7)** and 44.7 g (0.276 mol) PFCB **(6)** was heated at 150 В°C for 72 h in autoclave. After cooling all volatile compounds were distilled off, the residue was solved in ether and filtered. Similarly , the ether solution of cycloadduct **(4)** was obained from 4.4 g (0.065 mol) of furan **(7)** and 32.4 g (0.200 mol) PFCB **(6)**. The combined ether solutions were concentrated and the residue was distilled, given 11.0 g (23%)
9-oxatricyclononene **(4)** as colorless liquid, hardened to white crystalline substance with purity в‰Ґ99%.

Table 1. Boiling and melting points, Raman spectra, and elemental analysis data for the compounds obtained.

Compound	B.p./В°C (*p*/Torr) [m.p./В°C]	Raman, ОЅ/cmв€’1	Found (%) Calculated(%) C	H	F	Molecular formula
1	57.5 (20)	1569.0 vs (C=C)	47.3 47.4	2.50 2.65	50.2 50.0	$C_9H_6F_6$
2	71.5-72 (7) [52-53][a]	-	-	-	-	-
3	[31-33]	1569.2 m (C=C)	40.0 40.0	1.64 1.55	58.2 58.4	$C_{13}H_6F_{12}$
4	68-69 (20) [50-51.5][b]	1568.5 vs (C=C)	41.9 41.8	1.78 1.75	49.7 49.5	$C_8H_4F_6O$

[a] *Colorless liquid [9].* [b] *M.p. 59 В°C [7].*

Table 2. NMR spectra of the compounds obtained.

Compound	Оґ (J/Hz)

	^{1}H	^{19}F
1 endo-isomer	1.71 (dtt, 1H, H(4), $^{2}J_{H(4),H(3)}$ = 11.6, $^{4}J_{H(4),F(1)}$ = 6.8, $^{5}J_{H(4),F(2\ or\ 3)}$ = 2.1); 1.89 (br.d, 1H, H(3), $^{2}J_{H(3),H(4)}$ = 11.6); H(3),H(4) вЂ“ AB-system; 3.38 (s, 2H, H(2)); 6.54 (s, 2H, H(1))	-112.5 (br.dt, 2F, F(1), $^{4}J_{F(1),H(4)}$ в‰€ $^{3}J_{F(1),F(2\ or\ 3)}$ в‰€ 6.5); -51.3 and -50.4 (both dm, both 2F, F(2) and F(3), AB-system, J_{AB} = 225)
1 exo-isomer	2.24 (br.d, 1H, H(3), $^{2}J_{H(3),H(4)}$ = 9.8); 2.39 (br.dm, 1H, H(4), $^{2}J_{H(4),H(3)}$ = 9.8); H(3),H(4) вЂ“ AB-system; 3.22 (br.m, 2H, H(2)); 6.18 (br.m, 2H, H(1))	-110.2 m, 2F, F(1)); -49.7and -47.8 (both dm, both 2F, F(2) Pё F(3), AB-system, J_{AB} = 225)
3	1.72 (br.dm, 1H, H(5), $^{2}J_{H(5),H(4)}$ = 11.6); 2.16 (br.d, 1H, H(4), $^{2}J_{H(4),H(5)}$ = 11.6); H(4),H(5) вЂ“ AB-system; 3.47 Pё 3.56 (both br.s, both 1H, H(2) Pё H(3)); 6.63 (br.s, 2H, H(1))	-101.5 (br.d.d, 1F, F(1), J_d = 51.5, J_d = 28.6); -94.8 (br.s, 1F, F(2)); -55.5 - -39.9 (m, 10F, five CF_2-groups)
4	5.28 (br.s, 2H, H(2)); 6.84 (br.s, 2H, H(1))P°	-114.5 (m, 2F, F(1)); -52.5 (m, 4F, F(2, 3))P°

P° For the ^{1}H Pё ^{19}F NMR spectra, cf. Ref. [7].

Table 3. Mass spectra of the compounds obtained.

Compound	*m/z* ($I_{rel.}$ (%))
1 endo-isomer	228 $[M]^+$ (8.7); 209 [M вЂ“ F]$^+$ (0.6); 189 $[C_9H_5F_4$ and/or $C_6H_3F_6]^+$ (1.7); 169 $[C_6H_2F_5]^+$ (2.6); 163 $[C_7H_3F_4]^+$ (3.0); 145 $[C_7H_4F_3]^+$ (3.5); 128 [M вЂ“ $C_2F_4]^+$ (8.7); 127 [M вЂ“ $C_2HF_4]^+$ (19.6); 109 $[C_7H_6F]^+$ (5.2); 69 $[CF_3]^+$ (6.5); 66 $[C_5H_6]^+$ (100); 57 $[C_3H_2F]^+$ (6.5); 51 $[CHF_2]^+$ (6.5); 39 $[C_3H_3]^+$ (8.7)
1 exo-isomer	228 $[M]^+$ (15.7); 209 [M вЂ“ F]$^+$ (1.1); 189 $[C_9H_5F_4$ and/or $C_6H_3F_6]^+$ (2.4); 177 [M вЂ“ $CHF_2]^+$ (4.8); 169 $[C_6H_2F_5]^+$ (4.1); 163 $[C_7H_3F_4]^+$ (4.3); 159 $[C_8H_6F_3]^+$ (4.8); 145 $[C_7H_4F_3]^+$ (8.9); 133 $[C_6H_4F_3]^+$ (7.8); 128 [M вЂ“ $C_2F_4]^+$ (17.8); 127 [M вЂ“ $C_2HF_4]^+$ (43.0); 109 $[C_7H_6F]^+$ (8.7); 77 $[C_3H_3F_2]^+$ (8.5); 69 $[CF_3]^+$ (8.7); 66 $[C_5H_6]^+$ (100); 57 $[C_3H_2F]^+$ (7.4); 51 $[CHF_2]^+$ (7.4); 39 $[C_3H_3]^+$ (8.7)
2	390 $[M]^+$ (2.3); 351 $[C_{13}H_5F_{10}$ and/or $C_{10}H_3F_{12}]^+$ (3.2); 331 $[C_{13}H_4F_9$ and/or $C_{10}H_2F_{11}]^+$ (5.6); 311 $[C_{13}H_3F_8$ and/or $C_{10}HF_{10}]^+$ (6.6); 290 [M вЂ“ $C_2F_4]^+$ (22.8); 289 [M вЂ“ $C_2HF_4]^+$ (25.4); 275 $[C_7HF_{10}]^+$ (16.4); 269 $[C_{11}H_4F_7]^+$ (23.2);

	239 [M вЂ“ C_3HF_6]$^+$ (28.0); 231 $[C_8H_2F_7]^+$ (22.7); 221 [M вЂ“ C_3F_7]$^+$ (26.6); 219 $[C_{10}H_4F_5]^+$ (41.4); 201 $[C_{10}H_5F_4]^+$ (49.4); 200 $[C_{10}H_4F_4]^+$ (33.9); 190 $[C_9H_6F_4]^+$ (30.9); 189 $[C_9H_5F_4]^+$ (36.4); 170 $[C_6H_3F_5]^+$ (43.0); 169 $[C_6H_2F_5]^+$ (50.9); 151 $[C_6H_3F_4]^+$ (40.1); 66 $[C_5H_6]^+$ (100); 65 $[C_5H_5]^+$ (39.4)[a]
3	390 $[M]^+$ (6.1); 371 [M вЂ“ F]$^+$ (2.5); 351 [$C_{13}H_5F_{10}$ and/or $C_{10}H_3F_{12}$]$^+$ (4.6); 331 [$C_{13}H_4F_9$ and/or $C_{10}H_2F_{11}$]$^+$ (5.8); 311 [$C_{13}H_3F_8$ and/or $C_{10}HF_{10}$]$^+$ (6.1); 301 $[C_{12}H_5F_8]^+$ (6.8); 290 [M вЂ“ C_2F_4]$^+$ (17.2); 289 [M вЂ“ C_2HF_4]$^+$ (27.6); 269 $[C_{11}H_4F_7]^+$ (20.2); 239 [M вЂ“ C_3HF_6]$^+$ (25.9); 219 $[C_{10}H_4F_5]^+$ (39.7); 201 $[C_{10}H_5F_4]^+$ (44.0); 200 $[C_{10}H_4F_4]^+$ (32.7); 189 $[C_6H_3F_6]^+$ (25.6); 170 $[C_6H_3F_5]^+$ (46.0); 169 $[C_6H_2F_5]^+$ (46.6); 151 $[C_6H_3F_4]^+$ (31.6); 115 $[C_6H_5F_2]^+$ (37.9); 66 $[C_5H_6]^+$ (100); 65 $[C_5H_5]^+$ (44.8)
4	191 [$C_8H_3F_4O$ and/or C_5HF_6O]$^+$ (0.2); 181 $[C_7H_2F_5]^+$ (0.6); 163 $[C_4HF_6]^+$ (3.4); 132 $[C_3HF_5]^+$ (4.3); 114 $[C_3H_2F_4]^+$ (3.0); 101 $[C_2HF_4]^+$ (4.8); 93 $[C_3F_3]^+$ (3.6); 75 $[C_3HF_2]^+$ (4.8); 68 $[C_4H_4O]^+$ (100); 57 $[C_3H_2F]^+$ (3.4); 51 $[CHF_2]^+$ (3.4); 40 $[C_3H_4]^+$ (6.1); 39 $[C_3H_3]^+$ (8.7); 31 $[CF]^+$ (5.5); 29 $[CHO]^+$ (6.9)

[a] *For the mass spectrum, cf. Ref. [9].*

The mixture of PFCB dimers (8/9) used in this work contained some amount of hydrofluorination product вЂ“ 1-hydro-1-nonafluorcyclobutyl-2,2,3,3,4,4-hexafluorocyclobutane (10), which quantatively underwent dehydrofluorination in presence of CsF to fluoroolefins (8/9) in situ

****Parameters of ^{1}H and ^{19}F NMR spectra of dispironorbornene (2) obtained here virtually coincide with literary data [9].***

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