ELSEVIER

Journal of Fluorine Chemistry 81 (1997) 175–179

JOURNAL OF FLUORINE CHEMISTRY

Dehydrobromination of *trans*-3,4-dibromo-7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]nonane. A route to bicyclic fluoroalkenes and 7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]nona-2,4-diene

Ireneusz Nowak, Wojciech Dmowski *

Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

Received 28 March 1996; accepted 11 July 1996

Abstract

Dehydrobromination of *trans*-3,4-dibromo-7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]-nonane (**1**) was studied under a variety of conditions. In alkaline media, 3-bromo-7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]non-3-ene (**2**) and/or 1,3,3-trifluoro-1,3-dihydroisobenzofuran (**3**) were formed in ratios depending on the nature of the base and its concentration. Vacuum pyrolysis of **1** gave 7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]nona-2,4-diene (**7**) as the main product.

Keywords: Fluorobicycloalkanes; Dehydrobromination; Fluorobicycloalkenes; Fluorobicyclodiene; 3-Bromo-7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]-non-3-ene; 1,3,3-Trifluoro-1,3-dihydroisobenzofuran; 7,7,9,9-Tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]nona-2,4-diene

1. Introduction

Fluorine-containing unsaturated compounds have been widely used in various types of cycloaddition reactions, mostly as dienophiles and dipolarophiles [1,2]. However, only limited number of cyclisations with fluorinated dienes have been reported till now. Highly fluorinated dienes are better known for their [2+2] reactions, rather then Diels–Alder type condensations. Exceptions are perfluorocyclopentadiene [3] and a few trifluoromethylated dienes [4] and heterocycles [5]; the latter are particularly prone to inverse-electron-demand Diels–Alder reactions with electron rich dienophiles. Dienes with low fluorine contents, such as 2-fluoro-1,3- butadiene and 2-fluoro-3-methyl-1,3-butadiene were reported to readily undergo [4+2] cycloadditions [6] but they are available only with difficulty.

The aim of the present work was the synthesis of 7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]nona-2,4-diene (**7**) which we required as a Diels–Alder synthon for further studies. For this reason dehydrobromination of *trans*-3,4-dibromo-7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]-nonane (**1**) [7] was studied under various conditions. This study led also to the synthesis of new bicyclic fluoroalkenes and a discovery of interesting aromatisation proceeding with a hydrogen shift.

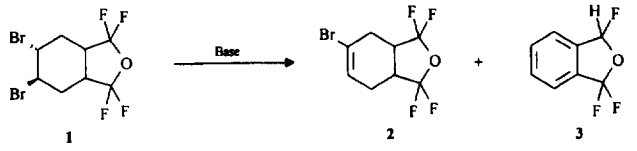
2. Results and discussion

Dehydrobromination of *trans*-1,2-dibromocyclohexane with various bases leads invariably to cyclohexadiene and constitutes the preparative method of its synthesis [8–10]. Dehydrobromination of *trans*-3,4-dibromo-8-thia-*cis*-bicyclo[4.3.0]nonane 8,8-dioxide, a structural analogue of compound **1**, with DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) was reported to give a mixture of isomeric dienes, but no alkenes were formed [11]. On the contrary, dehydrobromination of compound **1** under basic conditions does not lead to a diene. Instead, 3-bromo-7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]non-3-ene (**2**) and/or an aromatised and rearranged product, 1,3,3-trifluoro-1,3-dihydroisobenzofuran (**3**), were formed (Scheme 1).

Ratios of products **2** and **3** were found to be strongly dependent on the nature and amount of base used. With a little more than one molar equivalent of potassium carbonate in DMF, cycloalkene **2** was obtained in high yield and as the only product, but when a large excess of potassium carbonate was used a 2:1 mixture of compounds **2** and **3** was formed. With stronger bases, such as methanolic potassium hydroxide

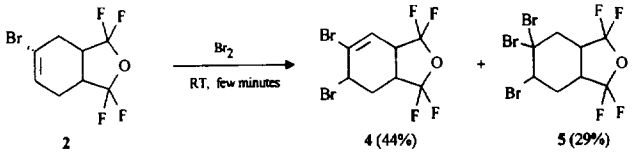
* Corresponding author.

PII S0022-1139(96)03525-7



Conditions	Yield (mol%)	
1.3 mol K_2CO_3, DMF, 130°C, 3 h	82	0
6.5 mol K_2CO_3, DMF, 130°C, 2 h	51	30
3.5 mol DBU, DMF, 120°C, 1 min	6.5	60
4 mol KOH, MeOH, reflux, 0.5 h	3	41
6 mol t-BuOK, THF, reflux, 2.5 h	0	41

Scheme 1.



Scheme 2.

or DBU, double dehydrobromination, dehydrofluorination and a hydrogen shift occurred to give aromatic compound **3** as the main product. Compound **3** was obtained as the only product when **1** was treated with an excess of potassium tert-butoxide in THF.

Selective monodebromination of **1** with K_2CO_3 is a useful reaction leading to synthetically interesting bromocycloalkene **2**. Prior to this work, selective dehalogenation of the 1,2-dihalocyclohexane ring to give 1-halocycloalkenes was achieved only by using a complex base, $NaNH_2$–tert-BuONa [12,13]. The structure of **2** has been confirmed by the presence of one vinylic hydrogen signal in the ^1H NMR spectrum and two signals in the ^{13}C NMR spectrum within the range typical for vinylic carbon atoms. Additionally, it has been found that compound **2** readily adds bromine to give a mixture of tribromoderivative **5** and a product of partial dehydrobromination of the latter, 3,4-dibromo-7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]non-2-ene (**4**) (Scheme 2).

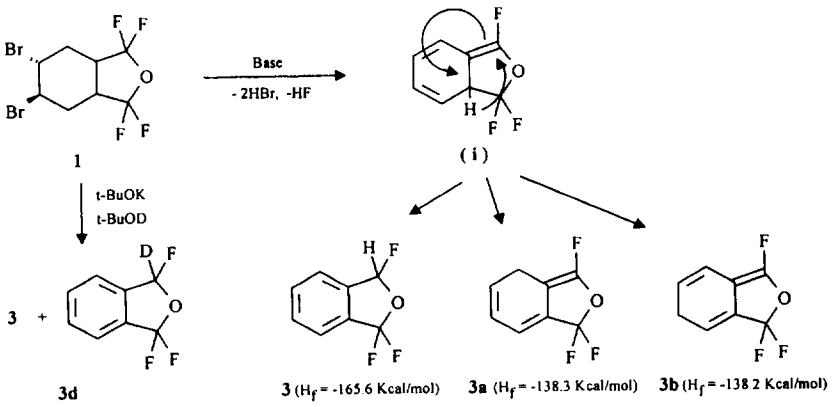
Spectral investigations gave satisfactory evidence for the structure of compound **3**. The MS spectrum exhibited a strong peak of molecular ion (m/z 174) and the ^1H, ^{19}F NMR and ^{13}C NMR spectra revealed signals of the CHF group as doublets with typical geminal hydrogen-to-fluorine (^2J= 66.2 Hz) and carbon-to-fluorine (^1J=220 Hz) coupling constants.

It seems rational that a mechanism of the dehydrohalogenation of **1** to aromatic compound **3** by strong bases should involve, at first, fast double dehydrobromination and dehydrofluorination to form intermediate bicyclotriene (**i**) (Scheme 3). Semiempirical calculations (AM1, MOPAC 6.0 package) have shown that the heat of formation of triene (**i**) is extremely high (the programme tries to shift tertiary hydrogen and then suspends), such that it could not exist and must rapidly isomerise. From amongst three isomeric final products **3**, **3a** and **3b** which could form, compound **3** is energetically favourable by ca. 27 kcal mol^{-1} over the two latter. The isomerisation of (**i**) to **3** should involve a base promoted (via a carbanionic species) [1,3] sigmatropic migration of hydrogen. When the reaction was carried in deuterated tert-butanol a mixture of **3** and its deuterated analogue **3d** was obtained. It is well known that a structural analogue of (**i**), 5-methylene-1,3-cyclohexadiene, "is stable at the dry ice temperature and in diluted solutions but in the pure liquid it isomerises to toluene at a moderately rapid rate at room temperature" [14].

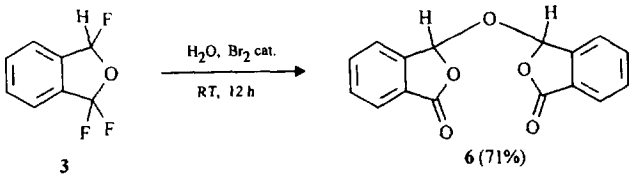
Compound **3** is unstable and undergoes hydrolytic dimerisation, slowly by the action of atmospheric moisture and fast in the presence of a catalytic amount of bromine, to the known dimeric product, 3,3′-oxidiphthalide (**6**) [15,16] (Scheme 4).

The required diene **7**, together with bromoalkene **2**, cycloalkene **8** and tetrafluorophthalide **9**, was obtained by a vacuum gas-phase pyrolysis of **1** at 550 °C. As found by the GC–MS analysis, a liquid mixture of products contained ca. 50% of **7** and three other minor components. This mixture is unstable at ambient temperature; the initially transparent reddish liquid readily turns brown and hydrogen fluoride is slowly released (Scheme 5).

The instability of the pyrolizate prevented isolation of particular components **2**, **7**, **8** and **9**. The last three compounds



Scheme 3.



Scheme 4.

have been identified only by GC–MS but the identity of diene **7** has been confirmed by its reaction with maleic anhydride, which gave a 2:1 cycloadduct **10** in over 70% isolated yield. This result has shown that diene **7**, when used as a raw pyrolizate, may be successfully applied for Diels–Alder reactions (Scheme 6).

3. Experimental details

Melting points were determined in capillaries and are uncorrected. ^1H, ^{19}F and ^{13}C NMR spectra were recorded in $CDCl_3$ or in DMSO, as indicated, with a Varian Gemini 200 spectrometer at 200, 188 and 50 MHz, respectively. Chemical shifts are quoted in ppm from internal TMS for ^1H and ^{13}C (positive downfield) and from internal $CFCl_3$ for ^{19}F (positive upfield). GC–MS analyses were performed with a Hewlett-Packard 5890 apparatus (70 eV) using a 30 m capillary column coated with a HP5 oil.

3.1. Dehydrobromination of 1 with bases

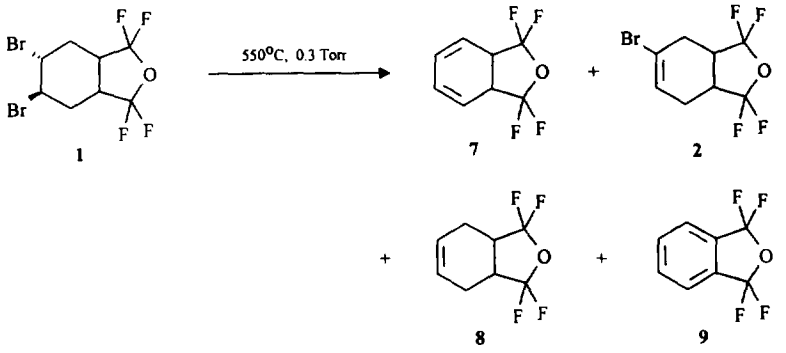
3.1.1. With K_2CO_3

Dibromoalkane **1** (1 g, 2.8 mmol), solid potassium carbonate (0.5 g, 3.7 mmol) and dry DMF (2.5 ml) were heated at 130 °C for 3 h on an oil bath. The reaction mixture was poured into water (15 ml), the organic material was extracted with $CHCl_3$ (3×2 ml) and the extract was dried over $MgSO_4$. The solvent was removed on a rotary evaporator and the residue was vacuum distilled. A fraction collected at 113–116 °C/40 Torr (0.64 g, 2.3 mmol) was identified as 3-bromo-7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]non-3-ene (**2**); yield: 82%. Analysis. Found: C, 34.36; H, 2.55; Br, 29.42; F, 27.43%. $C_8H_7BrF_4O$ requires: C, 34.94; H, 2.57; Br, 29.05; F, 27.63%. ^1H NMR (in $CDCl_3$) δ: 2.33–2.47 (m, 2H, CH_2); 2.65–2.70 (m, 2H, CH_2); 2.80–3.15 (broad m, 2H, 2 CH); 6.08–6.14 (m, 1H, =CH). ^{19}F NMR (in $CDCl_3$); two AB systems δ: 70.9 (ddd, $^2J_{FF}=140.8$ Hz, $^4J_{FF}=10.2$ Hz, $^4J_{FF}=8.8$ Hz, 1F); 71.7 (dt, $^2J_{FF}=140.8$ Hz, $^4J_{FF}=8.8$ Hz, 1F); 80.2 (dt, $^2J_{FF}=141.2$ Hz, $^4J_{FF}=10.2$ Hz, 1F); 81.5 (dt, $^2J_{FF}=141.2$ Hz, $^4J_{FF}=8.8$ Hz, 1F). ^{13}C NMR (in $CDCl_3$) δ: 22.4 (s, CH_2); 28.8 (d, $^3J_{CF}=3.4$ Hz, CH_2); 37.4 (dd, $^2J_{CF}=23.9$ and 27.4 Hz, CH); 41.2 (dd, $^2J_{CF}=23.8$ and 27.3 Hz, CH); 117.7 and 124.8 (s, =CH and =CBr); 129 (2×t, $^1J_{CF}=269$ Hz, 2 CF_2). GC–MS (*m/z*): 276,274 [25%, M^+]; 256,254 [21, $(M-HF)^+$]; 167 [100, $(C_7H_7F_4)^+$]; 147 [60, $(C_7H_6F_3)^+$]; 127 [95, $(C_7H_5F_2)^+$]; 77 [35, $(C_6H_5)^+$].

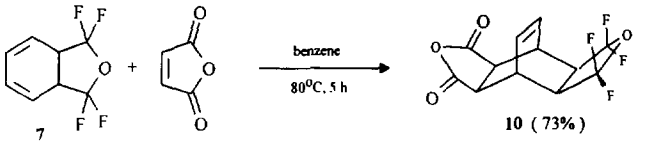
The reaction of **1** with an excess of potassium carbonate (2.5 g, 18 mmol in 7.5 ml of DMF), under the above conditions, gave a mixture of two products (0.55 g) which were identified by GC–MS as alkene **2** (71%) and 1,3,3-tetrafluoro-1,3-dihydroisobenzofuran (**3**) (27%) (spectral data below); yield: ca. 51 and 30%, respectively.

3.1.2. With potassium tert-butoxide

A solution of potassium tert-butoxide (1 g, 9 mmol) in anhydrous THF (5 ml) was added dropwise to a vigorously stirred solution of **1** (0.5 g, 1.4 mmol) in THF (3 ml) at ambient temperature and the reaction mixture was refluxed for 2.5 h. The solvent was removed on a rotary evaporator, the residue was acidified with dilute hydrochloric acid and steam distilled. The distillate was extracted with $CHCl_3$ and dried over $MgSO_4$. A liquid residue obtained after removal of the solvent under atmospheric pressure (0.1 g, 0.57 mmol) was identified as 1,3,3-trifluoro-1,3-dihydroisobenzofuran (**3**); yield, 41%. Analysis. Found: C, 54.86; H, 2.67; F, 32.37%. $C_8H_5F_3O$ requires: C, 55.18; H, 2.89; F, 32.73%. ^1H NMR (in $CDCl_3$) δ: 6.8 (dd, $^2J_{HF}=66.2$ Hz, $^4J_{HF}=10.2$Hz, CHF); 7.5–7.7 (m, $4H_{arom}$). ^{19}F NMR (in $CDCl_3$) δ: 60.6 (ddd, $^2J_{FF}=158.6$ Hz, $^4J_{FF}=9.7$ Hz, $^4J_{HF}=10.2$ Hz,1F, CF_2); 71.6 (dd, $^2J_{FF}=158.6$ Hz, $^4J_{FF}=12.1$ Hz, 1F, CF_2); 114.6 (dt, $^2J_{HF}=66.2$ Hz, 2×$^4J_{FF}$ = average 10.9 Hz, 1F, CHF). ^{13}C NMR (in $CDCl_3$) δ: 109.4 (ddd, $^1J_{CF}=219.7$ Hz, $^3J_{CF}=6.7$ and 3.2 Hz, CHF); 122.4 and 123.4 (s, C-6 and C-7); 129.3 (ddd, $^1J_{CF}=258.4$ and 250.8 Hz, $^3J_{CF}=2.3$ Hz, CF_2); 131.9 (d, $^3J_{CF}=2.5$ Hz, C-5); 132.3 (dt, $^2J_{CF}=33.9$ Hz, $^3J_{CF}=2.5$ Hz, C-9); 132.6 (s, C-8); 136.1 (dt, $^2J_{CF}=18.9$ Hz, $^3J_{CF}=2.9$ Hz, C-4). GC–MS (*m/z*): 174



Scheme 5.



Scheme 6.

[40%, M^+]; 155 [20, $(M-F)^+$]; 127 [100, $(C_6H_5CF_2)^+$]; 145 [45, $(M-CHO)^+$].

3.1.3. With potassium tert-butoxide in $(CH_3)_3COD$

A solution of **1** (0.2 g, 0.56 mmol) and potassium tert-butoxide (0.3 g, 2.7 mmol) in 3 ml of deuterated tert-butanol (70% tert-BuOD) was refluxed for 0.5 h. The GC–MS and ^{19}F NMR investigations revealed the presence of compounds **2**, **3** and its deuterated analogue **3d** in a 1:6:4 ratio (total conversion 11%).

1-Deutero-1,3,3-trifluoro-1,3-dihydroisobenzofuran (**3d**): ^{19}F NMR (in $CDCl_3$) δ: 60.4 (dd, $^2J_{FF}=159.8$ Hz, $^4J_{FF}=9.5$ Hz, 1F, CF_2); 74.4 (dd, $^2J_{FF}=159.8$ Hz; $^4J_{FF}=12.0$ Hz, 1F, CF_2); 115.2 (m, 1F, CDF). GC–MS (*m/z*): 175 [70%, M^+]; 145 [60, $(C_7H_4F_3)^+$]; 128 [100, $(C_7H_4DF_2)^+$]; 156 [20, $(M-F)^+$].

3.1.4. With methanolic KOH

A solution of potassium hydroxide (0.6 g, 11 mmol) in methanol (5 ml) was added dropwise to a vigorously stirred solution of **1** (1 g, 2.8 mmol) in methanol (5 ml) at ambient temperature. A precipitate of KBr immediately formed. The reaction mixture was refluxed for 0.5 h, poured into water (50 ml) and an oily organic layer was separated (0.45 g) and shown by GC–MS to consist of compounds **2** (5%) and **3** (44%). Yields: ca. 3 and 41%, respectively.

3.1.5. With DBU

A mixture of **1** (1 g, 2.8 mmol) and DBU (1.5 g, 10 mmol) was heated at 120 °C for one minute then water (20 ml) was added and the products were steam distilled to give an oil (0.36 g) consisting of compounds **2** (14%) and **3** (81%)(GC–MS analysis). Yields: ca. 6.5 and 60%, respectively.

3.2. Bromination of compound 2

Bromine (0.4 g, 2.5 mmol) was added in one portion to compound **2** (0.5 g, 1.8 mmol) placed in a small glass vial and pre-cooled to −78 °C. The vial was shaken for a while and left at ambient temperature for few minutes, after which the contents solidified. The solid (0.6 g) was shown by GC–MS to consist of compounds **4** (47%) and **5** (38%). Yields: 44 and 29%, respectively. Analytical samples were isolated by column chromatography on silica gel with benzene as an eluent.

3,4-Dibromo-7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]-non-2-ene (**4**): m.p. 123–124 °C. Analysis. Found: C, 27.13; H, 2.06, Br, 44.98; F, 21.60%. $C_8H_6Br_2F_4O$ requires: C, 27.15; H, 1.71; Br, 45.15; F, 21.47%. ^1H NMR (in $CDCl_3$) δ: 2.29 and 2.48 (AB system, $^2J_{HH}=14.2$ Hz, 2H, CH_2); 3.25–3.63 (m, 2H, CH); 4.76 (ddd, $^3J_{HH}=3.8$ and 2.4 Hz, $^4J_{HH}=1.8$ Hz, 1H, CHBr); 6.16 (dd, $^3J_{HH}=4.7$ Hz, $^4J_{HH}=1.8$ Hz, 1H, =CH). ^{19}F NMR (in $CDCl_3$) two AB systems δ: 62.9 (dt, $^2J_{FF}=143.8$ Hz, $J=10.9$ Hz, 1F); 64.8 (dt, $^2J_{FF}=138.9$ Hz, $J=13.5$ Hz, 1F); 72.3 (dt, $^2J_{FF}=138.9$ Hz, $J=7.8$ Hz, 1F); 83.7 (dd, $^2J_{FF}=143.8$ Hz, $J=5.8$ Hz, 1F). ^{13}C NMR (in $CDCl_3$) δ: 29.9 (t, $^3J_{CF}=4.7$ Hz, CH_2); 37.3 (dd, $^2J_{CF}=31.5$ and 22.5 Hz, CH); 44.7 (t, $^2J_{FF}=26.5$ Hz, CH); 47.7 (s, CHBr); 121.5 (s, =CH); 126.7 (tm, $^1J_{CF}=267.5$ Hz, CF_2); 127.5 (s, CBr); 128.5 (tm, $^1J_{FF}=262.8$ Hz, CF_2). GC–MS (*m/z*): 356,354,352 [10,20,10%, M^+]; 275,273 [50, $(M-Br)^+$]; 247, 245 [10, $(M-Br-C_2H_4)^+$]; 227,225 [20, $(M-Br-HF-C_2H_2)^+$]; 165 [70, $(C_7H_5F_4)^+$]; 127 [100, $(C_7H_5F_2)^+$].

3,3,4-Tribromo-7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]-nonane (**5**) (contaminated with 10% of **4**): ^1H NMR (in $CDCl_3$) δ: 2.47–2.57 (m, 2H, CH_2); 2.60–2.75 and 2.90–3.15 (m, 2H, CH_2); 3.15–3.3.35 (m, 2H, CH); 4.42 (dd, $^3J_{HH}=10.9$ and 6.3 Hz, CHBr). ^{19}F NMR (in $CDCl_3$) two AB systems δ: 64.9 (ddd, $^2J_{FF}=143.0$ Hz, $J=13.9$ and 7.5 Hz, 1F); 68.1 (ddd, $^2J_{FF}=144.3$, $J=18.6$ and 14.3 Hz, 1F); 74.7 (ddd, $^2J_{FF}=144.3$ Hz, $J=8.6$ and 6.4 Hz, 1F); 85.8 (dd, $^2J_{FF}=143.0$ Hz, $J=6.4$ Hz, 1F). ^{13}C NMR (in $CDCl_3$) δ: 30.6 (s, CH_2); 41.5 (t, $^2J_{CF}=25.8$ Hz, CH); 41.8 (dddd, $^2J_{CF}=31.1$ and 21.3 Hz, $^3J_{CF}=3.9$ and 2.0 Hz, CH), 43.5 (t, $^3J_{CF}=4.5$ Hz, CH_2); 57.5 (d, $^4J_{CF}=5.3$ Hz, CHBr); 66.9 (d, $^4J_{CF}=1.8$ Hz, CBr_2); 127.8 (tdd, $^1J_{CF}=264.8$ Hz, $^3J_{CF}=5.6$ and 2.0 Hz, CF_2); 128.7 (tdd, $^1J_{CF}=264.5$ Hz, $^3J_{CF}=5.7$ and 2.0 Hz, CF_2). GC–MS (*m/z*): 357,355,353 [30,60,30% $(M-Br)^+$]; 275,273 [35, $(M-Br-HBr)^+$]; 225,223 [30, $(M-2HBr-COF)^+$]; 165 [100, $C_7H_5F_4^+$].

3.3. Hydrolysis of 1,3,3-trifluoro-1,3-dihydroisobenzofuran (3)

A mixture of compound **3** (0.15 g, 0.9 mmol) and wet bromine (0.2 g, 1.25 mmol) was left overnight in an open vessel. A yellow solid formed which was vacuum sublimed (0.4 Torr) at 200 °C to give 3,3′-oxididiphthalide (**6**) as colourless crystals (0.09 g, 0.32 mmol); yield, 71%. An analytical sample was obtained by recrystallization from toluene: m.p. 232–234 °C (lit. [15] 234–236 °C]. Analysis. Found: C, 67.69; H, 3.19%. $C_{16}H_{10}O_5$ requires: C, 68.09; H, 3.57%. ^1H NMR (DMSO-d_6) δ: 7.14 (s, 2H, CH); 7.7–8.0 (m, 8H, H_{arom}). ^{13}C NMR (DMSO-d_6) δ: 101.4; 124.4; 124.8; 125.9; 131.4; 135.0; 144.6; 167.8 (C=O). MS (*m/z*): 282 [15%, M^+]; 238 [20, $(M-CO_2)^+$]; 209 [30, $(M-CO_2-CHO)^+$]; 194 [60, $(M-2CO_2)^+$]; 149 [20, $C_8H_5O_2^+$]; 133 [100, $C_8H_5O^+$]; 105 [20, $C_7H_5O^+$]; 77 [25, $C_6H_5^+$].

3.4. Pyrolysis of 1

Dibromide **1** (18 g, 50.6 mmol) was evaporated at 0.3 Torr and the vapours were passed for 1 h through a 40 cm long quartz tube heated at 550 °C. Products were condensed in two cold-fingers immersed in an acetone–dry ice bath and the non-condensed hydrogen bromine was absorbed on pellets of KOH. An initially transparent reddish liquid obtained was collected (10 g) which at room temperature readily turned brown. The GC–MS analysis revealed that the liquid consisted of 7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]-nona-2,4-diene (**7**) as the main product (ca.50%), 3-bromo-7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]non-3-ene (**2**) (ca.10%), 7,7,9,9-tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]non-3-ene (**8**) (ca.10%) and 1,1,3,3-tetrafluoro-1,3-dihydroisobenzofuran (**9**) (ca.20%).

7,7,9,9-Tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]nona-2,4-diene (**7**): yield: ca. 51%. GC–MS (*m/z*): 194 [25%, M^+]; 127 [100, $C_7H_4F_2^+$]; 78 [45, $C_6H_6^+$].

7,7,9,9-Tetrafluoro-8-oxa-*cis*-bicyclo[4.3.0]non-3-ene (**8**): mass spectrum in accord with the reported data [7].

1,1,3,3-Tetrafluoro-1,3-dihydroisobenzofuran (**9**): MS (*m/z*): 192 [40%, M^+]; 173 [20, $(M-F)^+$]; 145 [100. $(C_7H_3F_3)^+$].

3.5. Reaction of diene 7 with maleic anhydride

A solution of maleic anhydride (3 g, 30.6 mmol) in benzene (5 ml) was added to raw pyrolizate (11 g) containing ca. 50% of diene **7** (28 mmol). The mixture was heated on a water bath at 80 °C for 5 h. After cooling, the resulting solid was filtered off and recrystallized from a 10:1 mixture of toluene and DMF to give cycloadduct **10** (6 g, 20.5 mmol) as colourless prisms. Yield: 73%. M.p. 260–261 °C. Analysis. Found: C, 49.31; H, 2.59; F, 25.88%. $C_{12}H_8F_4O_4$ requires: C, 49.33; H, 2.76; F, 26.01%. ^{1}H NMR (DMSO-d_6) δ: 3.45 (d, $^3J_{HH}$ = 1.1 Hz, 2H, CHCO); 3.48 (broad m, 2H, $CHCF_2$); 3.60 (dm, $^3J_{HF}$ = 4.5 Hz, 2H, bridgehead CH); 6.31 (m, 2H, CH=CH). ^{19}F NMR (DMSO-d_6) δ: 52.3 and 76.6 (AM system, dm, $^2J_{FF}$ = 144.9 Hz, 4F, CF_2). ^{13}C NMR (DMSO-d_6) δ: 31.1 (t, $^3J_{CF}$ = 4.5 Hz, bridgehead C); 42.7 (s, C–CO); 46.3 (dd, $^2J_{CF}$ = 31.6 and 21.3 Hz, C–CF_2); 128.8 (dt, $^1J_{CF}$ = 261.6 Hz, $^3J_{CF}$ = 7.6 Hz, CF_2); 131.3 (s, =C); 172.4 (s, CO). MS (*m/z*): 292 [7%, M^+]; 248 [5, $(M-CO_2)^+$]; 220 [50, $(M-CO-CO_2)^+$]; 78 [100, $C_6H_6^+$].

References

[1] D.R.A. Perry, *Fluorine Chem. Rev., 1* (1967) 253–313.

[2] B.E. Smart, in M. Hudlický and A. Pavlath (eds.), *Chemistry of OrganicFluorine Compounds II. A critical Review*, ACS Monograph 187, ACS, Washington, DC, 1995, pp. 767–839.

[3] R.E. Banks, *Fluorocarbons and their Derivatives*, MacDonald, London, 1970, pp. 51–52.

[4] T. Nagai, Y. Nasu, T. Shimada, H. Shoda, M. Koyama, A. Ando, T. Miki and H. Kumadaki, *J. Fluorine Chem., 57* (1992) 245.

[5] B.E. Smart, in M. Hudlický and A. Pavlath (eds.), *Chemistry of OrganicFluorine Compounds II. A critical Review*, ACS Monograph 187, ACS, Washington, DC, 1995, pp. 832–833.

[6] A.A. Petrov and A.V. Tumanova, *Zh. Obshch. Khim., 26* (1956) 2744, 2991, 2995.

[7] W. Dmowski, I. Nowak, P.G. Jones and H. Thönnessen, *J. Fluorine Chem., 78* (1996) 193–194.

[8] J.P. Schaefer and L. Endres, *Organic Synthesis, Coll. Vol., 5* (1973) 285.

[9] J. Hine, J.A. Brown, L.H. Zalkow, W.E. Gardner and M. Hine, *J. Am. Chem. Soc., 77* (1955) 594.

[10] N.A. Domnin and A.S. Beletskaya, *Zh. Obshch. Khim., 24* (1954) 1636.

[11] R.A. Aitken, J.I.G. Cadogan, I. Gosney and S.F. Newlands, *J. Chem. Soc. Perkin Trans.*, (1994) 2301.

[12] P. Caubere, *Acc. Chem. Res., 7* (1974) 301.

[13] J.G. Lee and R.A. Bartsch, *J. Am. Chem. Soc., 101* (1979) 228.

[14] W.J. Bailey and R.A. Baylouny, *J. Org. Chem., 27* (1962) 3476.

[15] J.O. Hawthorne and M.H. Wilt, *J. Org. Chem., 25* (1960) 2215.

[16] I. Yamamoto, S. Yanagi, A. Mamba and H. Gotoh, *J. Org. Chem., 39* (1974) 3924.