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Halofluorination of 1,2-difluoro-1,2-di(*p*-tolyl)ethene, 1,2,3,4-tetrafluoro-1,4-di(*p*-tolyl)butadiene and its nonfluorinated parent compounds

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Abstract

The reactions of (*E*)-1,2-difluoro-1,2-di(*p*-tolyl)ethene (**1**) with *N*-bromo- or *N*-chlorosuccinimide gave mainly the expected halofluorination products 1-bromo-1,2-di(*p*-tolyl)-1,2,2-trifluoroethane (**2**) or 1-chloro-1,2-di(*p*-tolyl)-1,2,2-trifluoroethane (**4**), respectively. As a side reaction halogenation of the double bond has been obtained. With (*E,E*)-1,4-di(*p*-tolyl)-1,2,3,4-tetrafluorobuta-1,3-diene (**6**) under the same conditions the products of 1,2- and 1,4-addition or its consecutive hydrolysis products were isolated. (*E*)-Stilbene (**19**) on bromofluorination gave solely *erythro*-1-bromo-2-fluoro-1,2-diphenylethane (**20**), while with 1,4-diphenylbuta-1,3-diene (**17**) mainly higher molecular weight products were formed.

Keywords: Halofluorination; Amine/HF reagents; Fluorinated and unfluorinated stilbenes and 1,4-diphenylbutadienes

1. Introduction

Halofluorinations of various alkenes using different methods have been described [1–3]. One of the most attractive procedures has proved the combination of a *N*-halosuccinimide (NXS) as the source of the halonium ion X^+ and triethylamine trishydrofluoride ($Et_3N \cdot 3HF$) as the fluoride source [4,5]. Application of this reagent in synthesis has been reviewed recently [6,7]. Several related halofluorination protocols have been subsequently used [8–16]. Halofluorinations of fluorinated aliphatic alkenes with IF, BrF or ClF [17–19] or with NBS/$Et_3N \cdot 3HF$ [20] have also been reported.

Halofluorinations of unsaturated compounds which have benzene rings on both sides of the double bond such as stilbene, or compounds with two conjugated double bonds such as 1,4-diphenylbuta-1,3-diene are unknown. There is only one report [21] on the interaction of stilbene with IF; but the overall result of this reaction is fluorination and 1,2-difluoro-1,2-diphenylethane was obtained. Halofluorinations of halogenated analogues of stilbene and 1,4-diphenylbuta-1,3-diene are not reported. We investigated the halofluorination of (*E*)-1,2-difluoro-1,2-di(*p*-tolyl)ethene, (*E,E*)-1,4-di(*p*-tolyl)-1,2,3,4-tetrafluorobuta-1,3-diene and its parent compounds, stilbene and (*E,E*)-1,4-diphenylbuta-1,3-diene as well as the reaction of 1,4-diphenylbuta-1,3-diine.

2. Results and discussion

Bromofluorination of (*E*)-1,2-difluoro-1,2-di(*p*-tolyl)ethene (**1**) with NBS and $Et_3N \cdot 3HF$ at room temperature gave mainly 1-bromo-1,2-di(*p*-tolyl)-1,2,2-trifluoroethane (**2**). In addition *meso* and racemic 1,2-dibromo-1,2-di(*p*-tolyl)-1,2-difluoroethane (**3**) were formed as minor products in a 1:1 ratio as demonstrated by GC. Some quantity of starting material was recovered (Scheme 1).

Chlorofluorination of **1** with NCS and $Et_3N \cdot 3HF$ under similar conditions gave higher yield of a mixture of 1-chloro-1,2-di(*p*-tolyl)-1,2,2-trifluoroethane (**4**), and *meso* and racemic 1,2-dichloro-1,2-di(*p*-tolyl)-1,2-difluoroethane (**5**) in approximately 2.5:1 ratio (GC).

The structural elucidation will be demonstrated by way of example for compound **4**. From mass spectrum (M^+, *m/z* = 298, 10%) and elemental analysis follows the molecular formula $C_{16}H_{14}ClF_3$. The ^{19}F spectrum shows the typical shape of an ABX-system of the CF_2-group at $\delta = -104.64$ ($^2J_{FF} = 249.8$ Hz, $^3J_{FF} = 7.6$ Hz). The doublet of a doublet for the CFCl-group is found at $\delta = -122.16$ ppm ($^3J_{FF} = 9.5$

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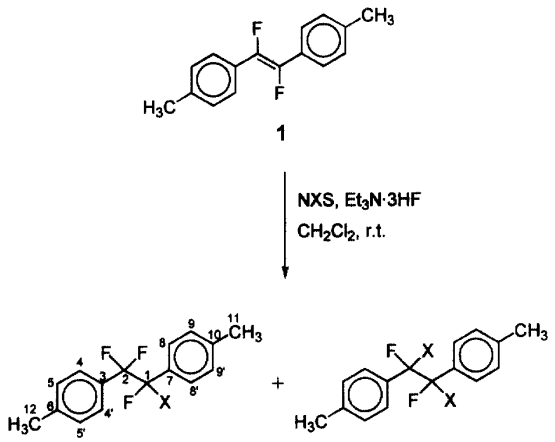


Scheme 1.

Hz or 7.6 Hz, respectively). The 600 MHz ^{1}H NMR spectrum shows the two different singlets of the methyl group at $\delta = 2.35$ (11-CH_3) or 2.36 (12-CH_3) ppm, respectively and four different quasi-doublets for the eight *o*- and *m*-protons of the different aromatic rings at $\delta = 7.12$ ppm (H_9 and $H_{9'}$, $^3J_{HH} = 8.4$ Hz), $\delta = 7.14$ ppm (H_5 and $H_{5'}$, $^3J_{HH} = 7.8$ Hz), $\delta = 7.19$ ppm (H_4 and $H_{4'}$, $^3J_{HH} = 7.8$ Hz), $\delta = 7.31$ ppm (H_8 and $H_{8'}$, $^3J_{HH} = 8.4$ Hz). The assignment of the different protons follows from GEMBC (gradient enhanced multibond correlation) and TOCSY experiments. These experiments and different CF-couplings were also used for the assignment of the signals in the 150 MHz ^{13}C NMR spectrum (cf. pre).

The side products **3** and **5** should have been formed by formal addition of the respective halogen to starting material. However, only trace quantities of the halogen were present in the NXS. The phenomenon of simple halogenation of the substrate under the conditions of halofluorination (NXS, $Et_3N \cdot 3HF$) has been observed by us earlier in some cases but has not been explained [4,5]. Recently Camps et al. [22] investigated the halofluorination of double bonds with NXS and tetrabutylammonium hydrogendifluoride. They demonstrated the formation of a complex between NXS and tetrabutylammonium hydrogendifluoride which could produce the halogen in this system according to the following sequence.

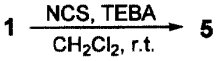
$$NBS + HF_2^- \rightleftarrows NS^- + [BrF] + HF$$

$$NS^- + NBS \rightleftarrows [NS^-NBS]$$

$$[NS^-NBS] \rightarrow 2NS^{\cdot} + Br^-$$

$$NBS + Br^- \rightleftarrows NS^- + Br_2$$

Presuming that $HF_2^{\ominus}$ is also the active fluoride source in $Alk_3N \cdot 3HF$, this process is probably acting in our system as well. In an additional experiment we demonstrated that the treatment of difluorostilbene **1** with NBS did not yield compound **3** in the absence of $Alk_3N \cdot 3HF$. On the other hand, the reaction of **1** with elemental bromine in dichloromethane gave a mixture (56:44) of *meso*- and racemic compound **3**. This compound did not give any depression of the melting point in the mixture with the product **3** obtained in the halofluorination reaction. This suggests the presence of elemental bromine in bromofluorination reaction mixtures. After several recrystallizations the main isomer (97% purity) has been isolated and a *meso*-structure can be assigned to this compound.



Scheme 2.

For comparison with the dichlorides **5** obtained as described above, synthesis of these compounds by an independent experiment was necessary. However, chlorination of difluorostilbene **1** with elemental chlorine occurred with substitution of hydrogen atoms in the methyl group even in the absence of light [23,24]. Therefore we synthesized compounds **5** by treatment of **1** with NCS as a source of chloronium ion and triethylbenzyl-ammonium chloride (TEBA) as a source of chloride ion (Scheme 2).

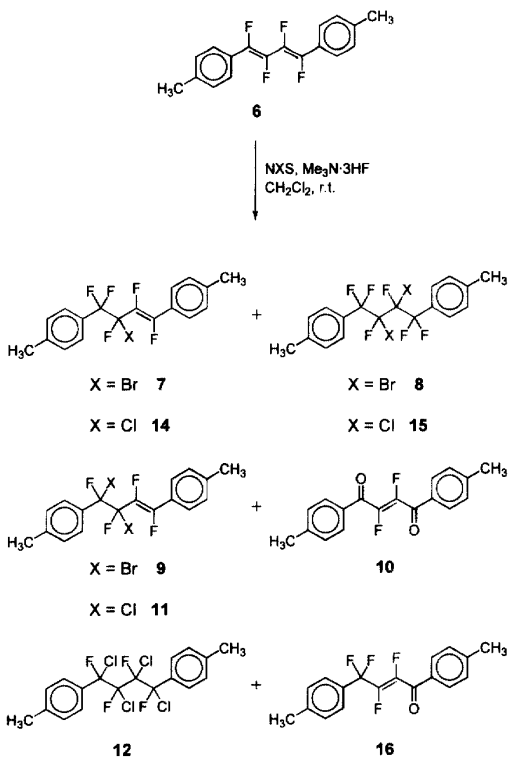
The product of this chlorination is also a mixture of *meso*-form and racemate of **5** in 2:1 ratio (GC). This dichloride does not give any depression of melting point in the mixture with the dichloride obtained in the halofluorination experiment.

Next the halofluorination of (*E,E*)-1,4-di(*p*-tolyl)-1,2,3,4-tetrafluorobuta-1,3-diene (**6**) was unsuccessfully tried with NBS and $Bu_3N \cdot 3HF$. However, the application of $Me_3N \cdot 3HF$ instead of $Bu_3N \cdot 3HF$ in a molar ratio of 1:2.2:5 (**6**/$Me_3N \cdot 3HF$/NBS) gave the products **7** and **8** of 1,2-bromofluorination of one or both double bonds, and the product of 1,2-dibromination **9**. Moreover, the diketone **10** was isolated in about 3% yield. Using less of $Me_3N \cdot 3HF$ and NBS (ratio to 1:1.1:2.5) to avoid reaction of both double bonds, besides the above-mentioned compounds in different ratio, mainly starting material was recovered (Scheme 3).

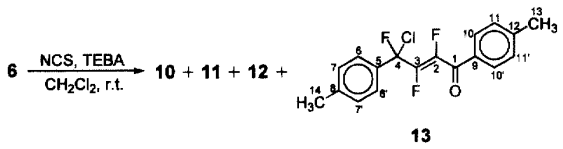
Formation of compound **10** can be explained by 1,4-bromination of the (*E,E*)-perfluorobutadiene fragment of **6** and fast hydrolysis under the basic conditions of work up procedure. The 1,4-dibromide was never isolated because of the easy hydrolysis which is due to the allylic and benzylic activation of the CFBr groups. Moreover, a stabilized conjugated system of a but-2-en-1,4-dione is formed in compound **10**. Compound **10** is a mixture of (*E*)- and (*Z*)-isomers in 93:7 ratio as demonstrated by ^{19}F NMR.

Compound **9** is a single isomer (X-ray) [25] and was obtained independently by direct bromination of perfluorobutadiene **6** in 75% yield.

Chlorination of tetrafluorobutadiene **6** with NCS and TEBA in dichloromethane gave a mixture of *erythro*- and *threo*-isomers of (*E*)-3,4-dichloro-1,4-di(*p*-tolyl)-tetrafluoro-1-butene (**11**) in 1:2 ratio, a mixture of the



Scheme 3.



Scheme 4.

diastereomeric 1,4-di(*p*-tolyl)-1,2,3,4-tetrachlorotetrafluorobutanes (**12**), the ketone **13** and the diketone **10**. The formation of **10** and **13** is again the result of hydrolysis or partial hydrolysis of the 1,4-addition product of chlorine to the perfluorobutadiene fragment. The 1,4-dichloride could not be isolated (Scheme 4).

Diketone **10** was separated from the mixture in 3.3% yield. The presence of the other compounds was demonstrated by ^{19}F NMR spectroscopy.

Chlorofluorination of tetrafluorobutadiene **6** is more complicated than bromofluorination and leads to the formation of a mixture of products of 1,2-addition of ClF (**14**, **15**), and by-products (**10–12**) in 41% overall yield. Ketone **16** was separated (10% yield) from this mixture by chromatography. This compound results from hydrolysis of the 1,4-addition product of ClF to the perfluorobutadiene fragment of **6**. The presence of compounds (**10**, **12**, **14**, **15**) and both isomers of product **11** was demonstrated by ^{19}F NMR spectroscopy. The products of 1,4-addition of halogens to compound **6** are not stable under the work up conditions. That is probably why they could not be separated in earlier investigations [26,27]. It is also possible that only the halogenation or halofluorination that uses *N*-halosuccinimides as source of halonium ions allows formation of the consecutive products of 1,4-addition. That would mean that the intermediate formation of a halogen is uncertain.

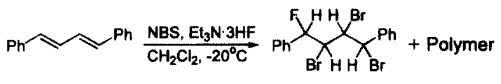
The reaction of 1,4-diphenyl-1,3-butadiyne with NBS and $Bu_3N \cdot 3HF$ or $Et_3N \cdot 3HF$ at room temperature was unsuccessful. In all cases starting material was recovered quantitatively. Chlorofluorination of 1,4-diphenyl-1,3-butadine with NCS and trimethyl trishydrofluoride at room temperature and 0°C gave only higher molecular weight products in 30% yield. On the other hand in this reaction at −25°C–−20°C all starting material were recovered. Also the treatment of 1,4-diphenyl-1,2,3,4-tetrachlorobuta-1,3-diene with $NCS/Me_3N \cdot 3HF$ for 60 h at room temperature failed, the starting material being recovered nearly quantitatively.

Reaction of (*E*,*E*)-1,4-diphenylbuta-1,3-diene (**17**) with $NBS/Bu_3N \cdot 3HF$ or $NBS/Et_3N \cdot 3HF$ at room temperature gave only oligomeric products in 90% yield. At low temperature (−20°C) this reaction gave a small amount of monomeric compound **18** (6% yield) and mainly higher molecular weight products. The monomer is a product of bromofluorination of one and bromination of the other double bond. When tributylamine or triethylamine was added to the reaction mixture to decrease the acidity of the fluorination agent ($Alk_3N \cdot 3HF/Alk_3N$ 1:1 or 1:0.5 molar ratio) the reaction did not occur (Scheme 5).

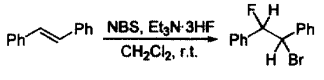
It is noteworthy that higher molecular weight material (not studied in detail) contains fluorine atoms as demonstrated by ^{19}F NMR spectroscopy. Probably, bromofluorination is the first step and then oligomerization occurs.

In contrast to the reaction of (*E*,*E*)-1,4-diphenylbuta-1,3-diene (**17**) the bromofluorination of (*E*)-stilbene (**19**) with $NBS/Et_3N \cdot 3HF$ gave *erythro*-1-bromo-2-fluoro-1,2-diphenylethane (**20**) as the sole product. Polymerization or bromination did not occur in noticeable quantities (Scheme 6).

It seems that halogenations competitive to halofluorinations occur only in cases when the reactivity of the unsaturated compound is low. Consequently, the reduction of NBS by HF_2^- should be a very slow process.



Scheme 5.



Scheme 6.

3. Experimental details

NMR spectra: ^{1}H (300 MHz), ^{13}C (75.5 MHz), ^{19}F (282.3 MHz): Bruker WM 300; ^{1}H (600 MHz), ^{13}C (150.8 MHz): Varian Unity Plus, TMS for ^{1}H and ^{13}C and $CFCl_3$ for ^{19}F as internal standard, ca. 15% solution in $CDCl_3$. Mass spectra (70 eV): GLC/MS coupling: Varian GC 3400/MAT 8230 and data system SS 300 using Finnigan/MAT. GLC: Hewlett-Packard 5890 II gas chromatograph, quartz capillary column 0.33 mm × 25 m, 0.52 μm HP-1, nitrogen as carrier gas, FID detector. Elemental analyses: Mikroanalytisches Laboratorium, OC, Universität Münster. Trialkylamine trishydrofluorides ($Me_3N \cdot 3HF$, $Et_3N \cdot 3HF$, $Bu_3N \cdot 3HF$) were provided by Hoechst/Frankfurt. (*E*)-1,2-Difluoro-1,2-di(*p*-tolyl)ethene, (*E,E*)-1,4-di(*p*-tolyl)-1,2,3,4-tetrafluorobuta-1,3-diene were obtained according to methods described in Refs. [26,27]. All other starting materials and applied reagents were obtained from Fluka or Jansen chemicals; dichloromethane was purified by distillation and dried by storage over molecular sieves (4 Å).

3.1. Halofluorination of (E)-1,2-difluoro-1,2-di(p-tolyl)-ethene (1)

A mixture of 1.22 g (5 mmol) of (*E*)-1,2-difluoro-1,2-di(*p*-tolyl)ethene (**1**) was treated with 2.5 ml (15.5 mmol) of triethylamine trishydrofluoride and 5.5 mmol of the respective *N*-halosuccinimide (NBS or NCS) in 15 ml of dichloromethane. This mixture was stirred at room temperature for 24 h. The solution was poured into 50 ml of ice water, neutralized with aq. ammonia and extracted twice with 30 ml of dichloromethane. The organic layer was washed with water and dried with magnesium sulfate. The solvent was evaporated in vacuum and the product mixture was separated by column chromatography (silica gel, cyclohexane). After chromatography the product was recrystallized.

1-Bromo-1,2-di(*p*-tolyl)-1,2,2-trifluoroethane (**2**): Yield, 870 mg (51%), m.p. 102–104°C (methanol). ^{1}H NMR δ: 2.33 (s, 11-CH_3); 2.34 (s, 12-CH_3); 7.09 (quasi-d, 2H, arom. *meta*-H, H_9 and $H_{9'}$, $^3J_{HH}$ = 8.4 Hz); 7.11 (quasi-d, 2H, arom. *meta*-H, H_5 and $H_{5'}$, $^3J_{HH}$ = 8.4 Hz); 7.15 (quasi-d, 2H, arom. *ortho*-H, H_4 and $H_{4'}$, $^3J_{HH}$ = 8.4 Hz); 7.30 (quasi-d, 2H, arom. *ortho*-H, H_8 and $H_{8'}$, $^3J_{HH}$ = 8.4 Hz) ppm. ^{19}F NMR δ: −102.4 (d, CF_2 $^3J_{FF}$ = 11.4 Hz); −122.50 (dd, CFBr, $^3J_{FF}$ = 11.4 Hz) ppm. ^{13}C NMR δ: 21.21 (s, CH_3, C-11); 21.32 (s, CH_3, C-12); 106.4 (dt, CFBr, $^1J_{CF}$ = 259.6 Hz, $^2J_{CF}$ = 36.8 Hz); 117.87 (td, CF_2m $^1J_{CF}$ = 254.1 Hz, $^2J_{CF}$ = 30.4 Hz); 126.85 (d, C-8, C-8′, $^3J_{CF}$ = 8.3 Hz); 127.29 (t, C-4, C-4′, $^3J_{CF}$ = 5.6 Hz); 128.40 (s, C-9, C-9′); 128.57 (s, C-5, C-5′); 133.12 (t, C-3, $^2J_{CF}$ = 18.8 Hz); 133.25 (d, C-7, $^2J_{CF}$ = 20.3 Hz); 140.29 (s, C-10); 140.80 (s, C-6) ppm. GC/MS *m/z* (%): 343 (1) [M^+]; 263 (100) [M^+–Br]; 244 (12) [M^+–Br–F]; 201 (22) [$H_3CC_6H_4CFBr^+$]; 141 (100) [$H_3CC_6H_4CF_2^+$]; 122 (6) [$H_3CC_6H_4CF^+$]; 91 (4) [$H_3CC_6H_4^+$]. Analysis: $C_{16}H_{14}BrF_3$ (343.2) requires: C, 56.00; H, 4.11%. Found: C, 56.18; H, 4.00%.

1,2-Dibromo-1,2-difluoro-1,2-di(*p*-tolyl)ethanes (**3**): Yield, 180 mg (9%), m.p. 167–169°C (pentane). GC/MS *m/z* (%): 404 (1) [M^+]; 324 (10) [M^+–Br]; 244 (100) [M^+–2Br]; 201 (50) [$H_3CC_6H_4CFBr^+$]; 141 (100) [$H_3CC_6H_4CF_2^+$].

1-Chloro-1,2-di(*p*-tolyl)-trifluoroethane (**4**): Yield, 910 mg (61%), m.p. 123–125°C (methanol). ^{1}H NMR (600 MHz) δ: 2.35 (s, 11-CH_3); 2.36 (s, 12-CH_3); 7.12 (quasi-d, 2H, arom. *meta*-H, H_9 and $H_{9'}$, $^3J_{HH}$ = 8.4 Hz); 7.14 (quasi-d, 2H, arom. *meta*-H, H_5 and $H_{5'}$, $^3J_{HH}$ = 7.8 Hz); 7.19 (d, 2H, arom. *ortho*-H, H_4 and $H_{4'}$, $^3J_{HH}$ = 7.8 Hz); 7.31 (quasi-d, 2H, arom. *ortho*-H, H_8 and $H_{8'}$, $^3J_{HH}$ = 8.4 Hz) ppm. ^{19}F NMR δ: −106.64 (dd, CF_2, F^2, $^2J_{FF}$ = 249.8 Hz, $^3J_{FF}$ = 9.5 Hz); −104.64 (dd, CF_2, $F^{2'}$, $^2J_{FF}$ = 249.8 Hz, $^3J_{FF}$ = 7.6 Hz); −122.16 (dd, F^1, $^3J_{F^1F^2}$ = 9.5 Hz, $^3J_{F^1F^{2'}}$ = 7.6 Hz) ppm. ^{13}C NMR (150 MHz) δ: 21.22 (s, CH_3, C-11); 21.32 (s, CH_3, C-12); 110.84 (dt, CFCl, $^1J_{CF}$ = 251.3 Hz, $^2J_{CF}$ = 35.9 Hz); 117.9 (td, CF_2, $^1J_{CF}$ = 255.9 Hz, $^2J_{CF}$ = 32.2 Hz); 127.01 (d, C-8, C-8′, $^3J_{CF}$ = 7.4 Hz); 127.32 (t, C-4, C-4′, $^3J_{CF}$ = 5.4 Hz); 128.26 (t, C-3, $^2J_{CF}$ = 19.3 Hz); 128.39 (s, C-9, C-9′); 128.53 (s, C-5, C-5′); 131.85 (d, C-7, $^2J_{CF}$ = 22.9 Hz); 140.37 (s, C-10); 140.85 (s, C-6) ppm. GC/MS *m/z* (%): 298 (10) [M^+]; 263 (6) [M^+–Cl]; 244 (4) [M^+–Cl–F]; 206 (4) [M^+–Cl–3F]; 157 (52) [$H_3CC_6H_4CFCl^+$]; 141 (100) [$H_3CC_6H_4CF_2^+$]; 121 (6) [$H_3CC_6H_4CF^+$]; 91 (10) [$H_3CC_6H_4^+$]. Analysis: $C_{16}H_{14}ClF_3$ (298.7) requires: C, 64.33; H, 4.72%. Found: C, 63.80; H, 4.71%.

1,2-Dichloro-1,2-difluoro-1,2-di(*p*-tolyl)ethanes (**5**): Yield, 330 mg (21%), m.p. 158–160°C (pentane). GC/MS *m/z* (%): 315 (2) [M^+]; 279 (6) [M^+–Cl]; 244 (12) [M^+–2Cl]; 157 (100) [$H_3CC_6H_4CFCl^+$]; 121 (4) [$H_3CC_6H_4CF^+$].

meso-1,2-Dibromo-1,2-difluoro-1,2-di(*p*-tolyl)ethane (**3**). A mixture of 1.22 g (5 mmol) of difluorostilbene **1**, 2.40 g (15 mmol) bromine and 10 ml of dichloromethane was stirred at room temperature for 4 h. The reaction mixture was washed with an aqueous solution of $Na_2S_2O_3$, water and dried with magnesium sulfate. The solvent was evaporated in vacuum and the product was crystallized. Yield, 1.5 g (84%, mixture of diastereoisomers of **3**). After several recrystallizations pure *meso*-isomer was obtained, m.p. 171–173°C (pentane). ^{1}H NMR δ: 2.38 (s, 6H, CH_3); 7.19 (d, 4H, arom. H); 7.53 (d, 4H, arom. H, $^3J_{HH}$ = 8.1 Hz) ppm. ^{19}F NMR δ: −115.09 ppm. ^{13}C NMR δ: 21.27 (s, CH_3); 110.30 (d, *C*FBr, $^1J_{CF}$ = 135.8 Hz); 127.46 (t, C-2, C-6, $^3J_{CF}$ = 5.1 Hz); 128.36 (s, C-3, C-5); 135.03 (m, C-1); 140.22 (s, C-4) ppm. Analysis: $C_{16}H_{14}Br_2F_2$ (404.1) requires: C, 47.56; H, 3.49%. Found: C, 47.65; H, 3.48%.

meso-1,2-Dichloro-1,2-difluoro-1,2-di(*p*-tolyl)ethane (**5**). A mixture of 1.22 g (5 mmol) of difluorostilbene **1**, 2.00 g (15 mmol) of *N*-chlorosuccinimide, 3.41 g (15 mmol) of triethylbenzylammonium chloride and 15 ml of dichloromethane was stirred at room temperature for 60 h. The reac-

tion mixture was washed with aqueous $Na_2S_2O_3$ and water. After drying with $MgSO_4$ the solvent was evaporated in vacuum and the product was purified by chromatography (silica gel cyclohexane/ethyl acetate, 20:1). Yield, 0.81 g (51%), m.p. 160–161°C (pentane). ^{1}H NMR δ: 2.38 (s, 6H, CH_3); 7.16 (d, 4H, arom. H, $^3J_{HH}$ = 8.1 Hz); 7.38 (d, 4H, arom. H, $^3J_{HH}$ = 8.1 Hz) ppm. ^{19}F NMR δ: −115.44 (s, CFCl, *meso*, 94%); −113.86 (s, CFCl, *dl*, 6%) ppm. ^{13}C NMR δ: 21.23 (s, CH_3); 127.69 (m, C-2, C-6, $^3J_{CF}$ = 5.1 Hz); 128.29 (s, C-3, C-5); 132.44 (m, C-1); 140.35 (s, C-4) ppm. Analysis: $C_{16}H_{14}Cl_2F_2$ (315.2) requires: C, 60.97; H, 4.48%. Found: C, 60.87; H, 4.32%.

3.2. Halofluorination of 1,4-di(p-tolyl)tetrafluorobuta-1,3-diene (6)

A mixture of 1.53 g (5 mmol) of the tetrafluorobutadiene **6** was treated with 2.88 g (25 mmol) of trimethylamine trishydrofluoride and 11 mmol of NBS or NCS in 20 ml of dichloromethane. This mixture was stirred at room temperature for 24 h. After the solution was poured into 50 ml of ice water, neutralized with aq. ammonia and extracted twice with 30 ml of dichloromethane. The organic layer was washed with water and dried with magnesium sulfate. The solvent was evaporated in vacuum and the product was purified by column chromatography (silica gel, pentane).

3.2.1. Products of bromofluorination

After chromatography the main product was crystallized to give a 1:2 mixture of 3-bromo-1,4-di(*p*-tolyl)-1,2,3,4,4-pentafluorobut-1-ene (**7**) and 2,3-dibromo-1,4-di(*p*-tolyl)hexafluorobutane (**8**): Yield, 0.60 g (61%), m.p. 111–113°C (methanol).

3-Bromo-1,4-di(*p*-tolyl)-1,2,3,4,4-pentafluorobut-1-ene (**7**). ^{1}H NMR δ: 2.36 (s, CH_3); 7.24 (d, 4H, arom. H, $^3J_{HH}$ = 6.2 Hz); 7.49 (d, 4H, arom. H, $^3J_{HH}$ = 6.2 Hz) ppm. ^{19}F NMR δ: −143.15 (m, F^1, $^3J_{F^1F^2}$ = 127.8 Hz, $^4J_{F^1F^3}$ = 57.2 Hz, $^5J_{F^1F^4}$ = 3.8 Hz); −152.14 (m, F^2, $^3J_{F^2F^1}$ = 127.8 Hz); −131.42 (m, F^3, $^4J_{F^3F^1}$ = 57.2 Hz, $^3J_{F^3F^2}$ = 26.1 Hz, $^3J_{F^3F^{4'}}$ = 9.5 Hz); −102.15 (dt, F^4, CF_2, $^1J_{F^4F^{4'}}$ = 253.6 Hz, $^5J_{F^4F^1}$ = 3.8 Hz); −104.13 (dt, $F^{4'}$, CF_2, $J_{F^{4'}F^4}$ = 253.6 Hz, $^3J_{F^{4'}F^3}$ = 9.5 Hz) ppm. MS *m/z* (%): 405 (0.6) [M^+]; 325 (6) [M^+–Br]; 203 (16) [$H_3CC_6H_4CF_2CFCF^+$]; 141 (100) [$H_3CC_6H_4CF_2^+$]; 91 (15) [$H_3CC_6H_4^+$].

2,3-Dibromo-1,4-di(*p*-tolyl)hexafluorobutane (**8**). ^{1}H NMR δ: 2.40 (s, CH_3); 7.42 (d, 4H, arom. H, $^3J_{HH}$ = 8.3 Hz); 7.65 (d, 4H, arom. H, $^3J_{HH}$ = 8.3 Hz) ppm. ^{19}F NMR δ: −98.68 (d, CF_2, $^3J_{FF}$ = 9.5 Hz); −156.41 (t, $F^{2,3}$, $^3J_{FF}$ = 9.5 Hz) ppm. ^{13}C NMR δ: 21.75 (s, CH_3); 125.64 (s, C-2, C-6); 128.98 (s, C-3, C-5); 137.40 (s, C-1); 140.38 (s, C-4) ppm. MS *m/z* (%): 422 (0.1) [M^+–Br]; 344 (70) [M^+–2Br].

3,4-Dibromo-1,4-di(*p*-tolyl)-1,2,3,4-tetrafluorobut-1-ene (**9**) was isolated as a byproduct by chromatography and crystallization: Yield, 0.71 g (31%), m.p. 127–129°C (pentane). This compound did not give depression of melting point in the mixture with a specimen obtained by direct bromination of tetrafluorobutadiene **6** (see the experiment described below).

2,3-Difluoro-1,4-di(*p*-tolyl)but-2-ene-1,4-dione (**10**) was isolated by chromatography and crystallization as a 97:3 mixture of *E*/*Z*-isomers: Yield, 0.05 g (3.3%), m.p. 125–126°C (methanol). ^{1}H NMR (*E*-isomer) δ: 2.45 (s, CH_3); 7.32 (d, 4H, arom. H, $^3J_{HH}$ = 8.3 Hz); 7.86 (d, 4H, arom. H, $^3J_{HH}$ = 8.3 Hz); (*Z*-isomer) δ: 2.41 (s, CH_3); 7.26 (d, 4H, arom. H, $^3J_{HH}$ = 8.3 Hz); 7.81 (d, 4H, arom. H, $^3J_{HH}$ = 8.3 Hz) ppm. ^{19}F NMR (*E*-isomer) δ: −143.44 (s, CF=CF); (*Z*)-isomer δ: −130.20 (s, CF=CF) ppm. ^{13}C NMR (*E*-isomer) δ: 22.25 (s, CH_3); 129.98 (s, C-2, C-6); 130.05 (s, C-3, C-5); 144.16 (s, C-1); 146.46 (s, C-4); 148.10 (dd, CF, $^1J_{CF}$ = 292.5 Hz, $^2J_{CF}$ = 12.7 Hz); 185.20 (d, CO, $^2J_{CF}$ = 20.0 Hz) ppm. IR (KBr): ν_{CO} = 1662.4; $\nu_{C=C}$ = 1605.5 cm^{-1}. MS *m/z* (%): 300 (70) [M^+]; 282 (4) [M^+–F]; 209 (12) [M^+–$H_3CC_6H_4$], 150 (4) [$H_3CC_6H_4COCF^+$]; 119 (96) [$H_3CC_6H_4CO^+$]; 91 (100) [$H_3CC_6H_4^+$]. Analysis: $C_{18}H_{14}F_2O_2$ (300.3) requires: C, 71.98; H, 4.70%. Found: C, 72.01; H, 4.38%.

3.2.2. Products of chlorofluorination

Mixture of compounds (**10–12**, **14**, **15**): Yield, 0.55 g (41%). The ^{19}F NMR spectra of compounds **10–12** in this mixture are identical with those given above or below, respectively for the pure compounds. Tetrafluoro-1,3-butadiene (**6**) was recovered from the reaction mixture (0.53 g, 35%).

(*E*)-3-Chloro-1,4-di(*p*-tolyl)-1,2,3,4,4-pentafluorobut-1-ene (**14**). ^{1}H NMR δ: 2.55 (s, CH_3); 7.35–7.83 (m, 8H, arom. H) ppm. ^{19}F NMR δ: −143.26 (ddd, F^1, $^3J_{F^1F^2}$ = 129.6 Hz, $^4J_{F^1F^3}$ = 51.5 Hz, $^5J_{F^1F^4}$ = 5.7 Hz); −154.62 (ddd, F^2, $^3J_{F^2F^1}$ = 129.6 Hz, $^3J_{F^2F^3}$ = 28.6 Hz, $^4J_{F^2F^4}$ = 9.5 Hz, $^4J_{F^2F^{4'}}$ = 9.5 Hz); −129.47 (ddt, F^3, $^4J_{F^3F^1}$ = 51.5 Hz, $^3J_{F^1F^2}$ = 28.6 Hz, $^3J_{F^3F^4}$ = 9.5 Hz, $^3J_{F^3F^{4'}}$ = 9.5 Hz); −107.80 (dt, CF_2, F^4, $^2J_{FF}$ = 251.3 Hz, $^3J_{F^4F^3}$ = 9.5 Hz, $^4J_{F^4F^2}$ = 9.5 Hz, $^5J_{F^4F^1}$ = 5.7 Hz); −104.84 (dt, CF_2, $F^{4'}$, $^2J_{FF}$ = 251.3 Hz, $^3J_{F^{4'}F^3}$ = 9.5 Hz, $^4J_{F^{4'}F^2}$ = 9.5 Hz) ppm.

1,4-Di(*p*-tolyl)-2,3-dichlorohexafluorobutane (**15**). ^{1}H NMR δ: 2.53 (s, CH_3); 7.35–7.83 (m, 8H, arom. H). ^{19}F NMR δ: −100.51 (m, CF_2, $^3J_{FF}$ = 15.3 Hz); −124.20 (m, $F^{2,3}$, $^3J_{FF}$ = 153.3 Hz).

(*E*)-1,4-Di(*p*-tolyl)-2,3,4,4-tetrafluorobut-2-ene-1-one (**16**), 0.1 g (10%), m.p. 72–74°C (pentane). ^{1}H NMR δ: 2.31 (s, CH_3); 2.32 (s, CH_3); 7.18 (d, 2H, *meta*-arom. H at C-7, $^3J_{HH}$ = 8.3 Hz); 7.19 (d, 2H, *meta*-arom. H at C-11, $^3J_{HH}$ = 8.1 Hz); 7.40 (d, 2H, *ortho*-arom. H at C-10, $^3J_{HH}$ = 8.1 Hz); 7.57 (d, 2H, *ortho*-arom. H at C-6, $^3J_{HH}$ = 8.3 Hz) ppm. ^{19}F NMR δ: −103.59 (dd, CF_2, $^3J_{FF}$ = 19.1 Hz, $^4J_{FF^2}$ = 5.7 Hz); −129.52 (dt, F^2, $^3J_{F^2F^3}$ = 123.9 Hz, $^4J_{F^2F^4}$ = 5.7 Hz); −165.54 (dt, F^3, $^3J_{F^2F^3}$ = 123.9 Hz, $^4J_{F^3F^4}$ = 19.1 Hz) ppm. IR (KBr): ν_{CO} = 1715.4 cm^{-1}. MS *m/z* (%): 322 (50) [M^+]; 181 (100) [$H_3CC_6H_4ClCF$=CF^+], 141 (100) [$H_3CC_6H_4CF_2^+$]; 116 (26) [$H_3CC_6H_4CO^+$]; 91 (10 [$H_3CC_6H_4^+$]. Analysis:

$C_{18}H_{14}F_4O$ (322.3) requires: C, 67.08; H, 4.38%. Found: C, 67.18; H, 4.54.

3,4-Dibromo-1,4-di(*p*-tolyl)-1,2,3,4-tetrafluorobut-1-ene (**9**). A mixture of 0.61 g (2 mmol) of tetrafluorobutadiene **6** 0.64 g (4 mmol) of bromine and 10 ml of dichloromethane was stirred at room temperature for 4 h. The reaction mixture was washed with an aqueous solution of $Na_2S_2O_3$, water and dried with magnesium sulfate. The solvent was evaporated in vacuum. Yield: 0.7 g (75%), m.p. 130–131°C (pentane). ^{1}H NMR δ: 2.40 (brs, 6H, 2×, CH_3); 2.21–2.28 (m, 4H, arom. H); 7.47–7.72 (m, 4H, arom. H) ppm. ^{19}F NMR δ: −142.06 (ddd, F^1, $^3J_{F^1F^2}$ = 127.8 Hz, $^4J_{F^1F^3}$ = 66.1 Hz, $^5J_{F^1F^4}$ = 5.7 Hz); −150.31 (dd, F^2, $^3J_{F^1F^2}$ = 127.8 Hz, $^3J_{F^2F^3}$ = 26.7 Hz, $^4J_{F^2F^4}$ = 24.8 Hz); −123.73 (dt, F^3, $^4J_{F^3F^1}$ = 66.7 Hz, $^3J_{F^3F^2}$ = 26.7 Hz, $^3J_{F^3F^4}$ = 26.7 Hz); −114.95 (ddd, F^4, $^3J_{F^4F^3}$ = 26.7 Hz, $^4J_{F^4F^2}$ = 24.8 Hz, $^5J_{F^4F^1}$ = 5.7 Hz) ppm. ^{13}C NMR (150 MHz) δ: 21.30 (d, C-14, $^6J_{CF}$ = 1.6 Hz); 21.50 (s, C-9); 103.27 (ddd, C-4, $^1J_{CF}$ = 265.8 Hz, $^2J_{CF}$ = 30.8 Hz, $^3J_{CF}$ = 4.3 Hz); 106.92 (ddd, C-3, $^1J_{CF}$ = 264.7 Hz, $^2J_{CF}$ = 30.8 Hz, $^2J_{CF}$ = 30.2 Hz); 126.61 (t, C-11, $^3J_{CF}$ = 8.1 Hz, $^4J_{CF}$ = 8.1 Hz); 127.66 (dd, C-12, $^4J_{CF}$ = 8.6 Hz, $^5J_{CF}$ = 2.7 Hz); 128.57 (s, C-6); 129.33 (s, C-7); 133.66 (d, C-10, $^2J_{CF}$ = 21.2 Hz); 133.79 (d, C-5, $^2J_{CF}$ = 21.1 Hz); 140.77 (s, C-8); 140.96 (d, C-13, $^5J_{CF}$ = 1.6 Hz); 141.82 (ddd, C-2, $^1J_{CF}$ = 243.1 Hz, $^2J_{CF}$ = 44.0 Hz, $^3J_{CF}$ = 28.1 Hz); 149.76 (dd, C-1, $^1J_{CF}$ = 260.1 Hz, $^2J_{CF}$ = 41.6 Hz) ppm. MS *m/z* (%): 466 (4) [M^+]; 385 (3.5) [M^+–Br]; 306 (100) [M^+–2Br]; 214 (60) [$H_3CC_6H_4CFCBr^+$]. Analysis: $C_{18}H_{14}Br_2F_4$ (466.1) requires: C, 46.38; H, 3.03%. Found: C, 46.20; H, 3.19%.

Chlorination of 1,4-di(*p*-tolyl)tetrafluorobuta-1,3-diene (**6**). A mixture of 0.92 g (3 mmol) of tetrafluoro-1,3-butadiene **6**, 2.67 g (20 mmol) of *N*-chlorosuccinimide, 4.50 g (20 mmol) of triethylbenzyl ammonium chloride and 15 ml of dichloromethane was stirred at room temperature for 70 h. The mixture was washed with an aqueous $Na_2S_2O_3$ solution and water. After drying with $MgSO_4$ the solvent was evaporated in vacuum and the product was purified by chromatography (silica gel, cyclohexane). Besides 0.47 g (51%) of starting material 0.21 (31%) of a mixture of **11**, **12** and **13** and 0.05 g (11%) of **10** were isolated.

2,3-Difluoro-1,4-di(*p*-tolyl)but-2-ene-1,4-dione (**10**): m.p. 124–126°C (methanol). This compound did not give depression of melting point in the mixture with a specimen obtained as described above.

(*E*)-3,4-Dichloro-1,4-di(*p*-tolyl)tetrafluorobut-2-ene (**11**). ^{1}H NMR (threo) δ: 2.37 (s, CH_3); 7.2–7.5 (m, 8H, arom. H); (erythro) δ: 2.43 (s, CH_3); 7.2–7.5 (m, 8H, arom. H) ppm. ^{19}F NMR (threo) δ: −141.45 (ddd, F^1, $^3J_{F^1F^2}$ = 124.0 Hz, $^4J_{F^1F^3}$ = 51.5 Hz, $^5J_{F^1F^4}$ = 7.6 Hz); −151.59 (ddd, F^2, $^3J_{F^1F^2}$ = 124.0 Hz, $^3J_{F^2F^3}$ = 19.1 Hz, $^4J_{F^2F^4}$ = 15.2 Hz); −121.58 (dt, F^3, $^4J_{F^3F^1}$ = 51.5 Hz, $^3J_{F^3F^2}$ = 19.1 Hz, $^3J_{F^3F^4}$ = 19.1 Hz); −114.51 (ddd, F^4, $^3J_{F^4F^3}$ = 19.1 Hz, $^4J_{F^4F^2}$ = 15.2 Hz, $^5J_{F^4F^1}$ = 7.6 Hz); (eyrthro) δ: −142.22 (ddd, F^1, $^3J_{F^1F^2}$ = 129.7 Hz, $^3J_{F^2F^3}$ = 17.2 Hz, $^4J_{F^2F^4}$ = 15.2 Hz); −152.14 (ddd, F^2, $^3J_{F^2F^1}$ = 129.7 Hz, $^3J_{F^2F^3}$ = 17.2 Hz, $^4J_{F^2F^4}$ = 15.2 Hz); −123.26 (dd, F^3, $^4J_{F^3F^1}$ = 53.4 Hz, $^3J_{F^3F^2}$ = 17.2 Hz, $^4J_{F^2F^4}$ = 15.2 Hz); −116.63 (dt, F^4, $^3J_{F^3F^4}$ = 15.2 Hz, $^4J_{F^4F^2}$ = 15.2 Hz, $^5J_{F^4F^1}$ = 5.7 Hz) ppm.

1,4-Di(*p*-tolyl)-1,2,3,4-tetrachlorotetrafluorobutane (**12**). ^{1}H NMR δ: 2.39 (s,CH_3); 7.2–7.5 (m, 8H, arom. H) ppm. ^{19}F NMR (*meso*) δ: −119.12 (s, $F^{1,4}$); −147.36 (s, $F^{2,3}$); (*dl*) δ: −119.57 (s, $F^{1,4}$); −147.80 (s, $F^{2,3}$) ppm.

(*E*)-4-Chloro-1,4-di(*p*-tolyl)trifluorobut-2-en-1-one (**13**). ^{1}H NMR δ: 2.39 (s, CH_3), 7.2–7.3 (m, 2H, *meta*-arom. H); 7.51 (d, 4H, *ortho*-arom. H at C-10, $^3J_{HH}$ = 8.3 Hz); 7.64 (d, 2H, *ortho*-arom. H, at C-6, $^3J_{HH}$ = 8.3 Hz) ppm. ^{19}F NMR δ: −128.93 (dd, F^2, $^3J_{F^3F^2}$ = 125.9 Hz, $^3J_{F^3F^4}$ = 19.1 Hz); −161.50 (dd, F^3, $^3J_{F^2F^3}$ = 125.9 Hz, $^3J_{F^3F^4}$ = 19.1 Hz); −108.11 (dd, F^4, $^3J_{F^4F^3}$ = 19.1 Hz, $^4J_{F^4F^2}$ = 3.8 Hz) ppm.

1,4-Diphenyl-4-fluoro-1,2,3-tribromobutane (**18**). A mixture of 1.03 g (5 mmol) of the (*E*,*E*)-1,4-diphenylbuta-1,3-diene (**17**) was treated with 5 ml (25 mmol) of triethylamine trishydrofluoride, 2.00 g NBS (11 mmol) in 20 ml dichloromethane at −25°C. This mixture was stirred at −25°C for 10 h and then was slowly allowed to warm up to room temperature for 12 h under stirring. The solution has been poured into 50 ml of ice water, neutralized with aq. ammonia and extracted twice with 30 ml of dichloromethane. The organic layer was washed with water and dried with magnesium sulfate. The solvent was evaporated in vacuum and the product was purified by column chromatography (silica gel, pentane). Yield: 0.13 g (5.6%), m.p. 193–194°C (methanol). MS *m/z* (%): 465 (1) [M^+], 385 (10) [M^+–Br], 305 (36) [M^+–2Br], 202 (10) [$PhCHFCHBr^+$], 109 (100) [$PhCHF^+$]. Analysis: $C_{16}H_{14}Br_3F$ (465.0) requires: C, 41.33; H, 3.03%. Found: C, 41.27; H, 3.01%.

Erythro-1-bromo-2-fluoro-1,2-diphenylethane (**20**). A mixture of 0.9 g (5 mmol) of (*E*)-stilbene (**19**) was treated with 2.5 ml (15.5 mmol) of triethylamine trishydrofluoride and 2.00 g (11 mmol) of NBS in 20 ml dichloromethane. This mixture was stirred at room temperature for 26 h. After the solution has been poured into 50 ml of ice water, it was neutralized with aq. ammonia and extracted twice with 30 ml of dichloromethane. The organic layer was washed with water and dried with magnesium sulfate. The solvent was evaporated in vacuum and the product was separated from starting material by column chromatography (silica gel, cyclohexane:ethylacetate 20:1): Yield, 0.61 g (44%), m.p. 108–109°C (methanol). ^{1}H NMR δ: 5.13 (dd, 1H, CHBr, $^3J_{HF}$ = 15.0 Hz, $^3J_{HH}$ = 6.7 Hz); 5.34 (dd, 1H, CHF, $^2J_{HF}$ = 46.0 Hz, $^3J_{HH}$ = 6.7 Hz); 7.23–7.40 (m, 10H, arom. H) ppm. ^{19}F NMR δ: −169.82 (dd, CHF, $^2J_{HF}$ = 46.0 Hz, $^3J_{HF}$ = 15.0 Hz) ppm. ^{13}C NMR δ: 57.42 (d, CHBr, $^3J_{CF}$ = 28.0 Hz); 98.28 (d, CHF, $^2J_{CF}$ = 183.1 Hz); 129.61 (d, C-4, C-4′; $^3J_{CF}$ = 5.1 Hz); 131.03 (s, C-6); 131.20 (s, C-5, C-5′); 131.51 and 131.64 (2×s, C-8, C-8′, C-9, C-9′); 131.91 (s, C-10). Analysis: $C_{14}H_{12}BrF$ (279.2) requires: C, 60.24; H, 4.33%. Found: C, 60.11; H, 4.30%.

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