1,1-Bis(trifluoromethyl)butadiene-1,3—A new fluorinated building block

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Abstract

Although 1,1-bis(trifluoromethyl)butadiene-1,3 (**1**) reacts with dimethylamine with selective formation of 1,4-adduct [*trans*-$(CF_3)_2CHCH=CHCH_2N(CH_3)_2$], halogenation of **1** proceeds with predominant formation (>92%) of 1,2-adducts $(CF_3)_2C=CHCHXCH_2X$ (X = Cl or Br). Electrophilic conjugated addition of ''ClF'' or ''BrF'' to **1** proceeds exclusively with the formation of 1,2-adducts $(CF_3)_2C=CHCHFCH_2X$ (major) and $(CF_3)_2C=CHCHXCH_2F$ (X = Cl or Br). Difluorocarbene adds selectively to $-CH=CH_2$ moiety of **1** forming thermally stable vinylcyclopropane. In Diels-Alder reaction with linear or cyclic dienes (butadienes, cyclopentadiene, cyclohexadiene-1,3) and quadricyclane compound **1** behaves as dienophile providing for the reaction electron-deficient $-CH=CH_2$ bond. The relative rate of cycloaddition of **1** and other fluoroolefins to quadricyclane, measured by high temperature NMR, indicates that $(CF_3)_2C=CH-$ acts as very strong electron-withdrawing substituent. Synthetic utility of products based on **1** was also demonstrated.
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Keywords: 1,1-Bis(trifluoromethyl)butadiene-1,3; Chlorination; Bromination; Electrophilic chlorofluorination; Bromofluorination; Reaction with difluorocarbene; Cycloaddition to butadienes; Diels-Alder reactions

1. Introduction

At present the chemistry of polyfluorinated dienes is represented mostly by transformations of hexafluorobutadiene-1,3 (HFB). The regiochemistry of the reactions of HFB with nucleophilic, electrophilic and radical agents is well studied and in most cases reactions proceed with the formation of 1,4-adducts. For example, the bromination of HFB in the dark (in sulfolane as solvent, 30 °C, 120 h) was reported to give exclusively 1,4-adduct in 96% yield [1]. Similarly, the conjugated addition of ''ClF'' or ''BrF'' [*N*-chlorosuccinimide (NCS) or *N*-bromosuccinimide (NBS)/anhydrous HF system] to 2-chloropentafluorobutadiene-1,3 (CPB) results in the exclusive formation of the corresponding 1,4-adducts.

Cycloaddition reactions of HFB are less definitive, since it can participate in both [4 + 2] and [2 + 2] processes. For example, the thermal reaction of HFB with butadiene (125 °C, 8 h) was reported to produce a mixture of 2 + 2 and 4 + 2 adducts in ratio 56:41 along with smaller amount of other byproducts [2]. Interestingly, the [4 + 2] process proceeds as a Diels-Alder cycloaddition with the reverse electronic demand resulting in formation of vinylcyclohexene, containing a fluorinated double bond in the cycle [2].

The reliable synthesis of 1,1-bis(trifluoromethyl)butadiene-1,3 (**1**) was reported in 1970 [4]. It is based on the dehydration of $CH_2=CHC(CF_3)_2OH$ by H_2SO_4. Despite the fact that **1** has been known for over 30 years, its chemistry is limited to only a few transformations, including radical [5,6] and anionic [7–9] polymerization; hydrogenation and the reaction with butyl lithium [4].

The presence of two electron-withdrawing trifluoromethyl groups should significantly affect the reactivity of 1,1-bis(trifluoromethyl)-butadiene-1,3 (**1**), thus creating a positive charge on the CH_2 end of the molecule. On the other hand, two bulky groups (the CF_3-substituent has been estimated to be approximately the same size as a *sec*-butyl group [3]) connected to the terminal carbon should also significantly distort the cisoid conformation of diene, due to the repulsion between CF_3- and H-substituents connected to C-1 and C-4, and affect the ability of **1** to participate as diene in Diels-Alder reactions.
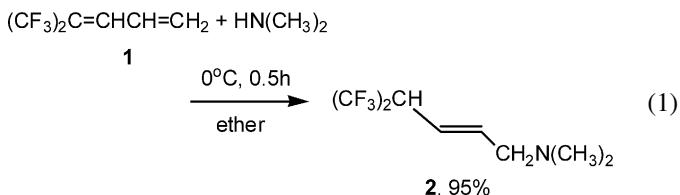
The present study is the first attempt of the systematic investigation of the chemical behavior of **1** in nucleophilic, radical, electrophilic and cycloaddition reactions.

2. Results and discussion

2.1. Reactions with nucleophiles

Similar to butyllithium [4], dimethylamine (DMA) attacks 1,1-bis(trifluoromethyl)butadiene-1,3 (**1**) regioselectively on the CH$_2$-group giving exclusively the 1,4-adduct **2**.

$$(CF_3)_2C=CHCH=CH_2 + HN(CH_3)_2$$
$$\mathbf{1}$$

$$\xrightarrow[\text{ether}]{0\,^\circ C,\,0.5h} (CF_3)_2CH$$
$$\diagdown CH_2N(CH_3)_2$$
$$\mathbf{2},\,95\% \qquad (1)$$

The reaction of **1** and DMA was very fast even at 0 °C (100% conversion of **1** in 15 min), leading to selective, high yield formation of the *trans*-isomer of **2**. The regioselectivity of the addition is similar to that observed in the reaction of hexafluorobutadiene (HFB), which predominantly gives 1,4-adducts in its reaction with HN(C$_2$H$_5$)$_3$ and alcohols/N(C$_2$H$_5$)$_3$ [10].
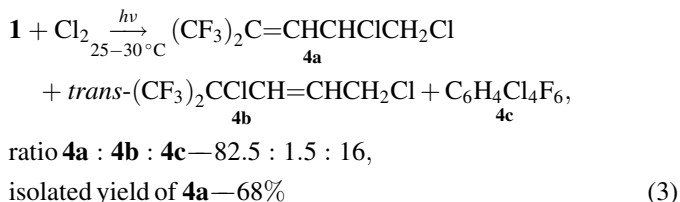
2.2. Halogenation reactions

2.2.1. Chlorination and bromination

Bromination of **1** rapidly proceeds without irradiation upon the addition of bromine to **1**, but in sharp contrast to the reaction with nucleophiles, only a *1,2-adduct* **3** forms in this reaction.

$$\mathbf{1} + Br_2 \xrightarrow{\text{exothermic}} (CF_3)_2C=CHCHBrCH_2Br \qquad (2)$$
$$\mathbf{3}, 68\%$$

When the reaction was carried out under irradiation (sun lamp), it resulted in the same product, isolated in 75% yield. It should be pointed out that the isomeric 1,4-adduct – (CF$_3$)$_2$CBrCH=CHCH$_2$Br – was not detected (NMR) in either reaction.

The reaction of **1** with Cl$_2$ in a closed system (Hastelloy reactor, acetonitrile as solvent, 16 h, 20 °C) resulted in the recovery ~60% of starting diene. Under UV irradiation, however, the chlorination rapidly proceeds under mild conditions with predominant formation of 1,2-adduct (**4a**), along with a smaller amount of the 1,4-adduct (**4b**) (ratio **4a**:**4b**—92:8 at 90% conversion of **1**, after 15 min of irradiation at 25–30 °C).

$$\mathbf{1} + Cl_2 \xrightarrow[25-30\,^\circ C]{h\nu} (CF_3)_2C=CHCHClCH_2Cl$$
$$\mathbf{4a}$$

$$+ \textit{trans-}(CF_3)_2CClCH=CHCH_2Cl + C_6H_4Cl_4F_6,$$
$$\mathbf{4b} \qquad\qquad\qquad \mathbf{4c}$$

ratio **4a** : **4b** : **4c**—82.5 : 1.5 : 16,

isolated yield of **4a**—68% (3)

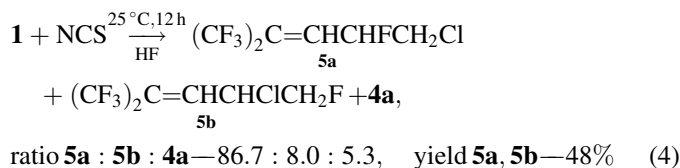Interestingly, the final product isolated after 2 h of irradiation contained only a trace (1.5%) of **4b**, along with a substantial amount of the tetrachloride **4c** (see Table 2). Pure **4a** (>99%) was isolated in 68% yield by simple distillation, due to substantial difference in boiling points of **4a** and **4c**.

It should be pointed out that the radical halogenation of HFB proceeds with preferential formation of 1,4-adducts (ratio 1,4-/1,2-adducts: Cl$_2$—58:42, Br$_2$—78:28) [11]. The regiochemistry of the radical halogenation of **1** correlates surprisingly well with the regioselectivity of the radical polymerization, reported to proceed mostly as 1,2-addition and involving nonfluorinated double bond of **1** [4]. On the other hand, the radical polymerization of HFB proceeds mostly as a 1,4-addition [1].
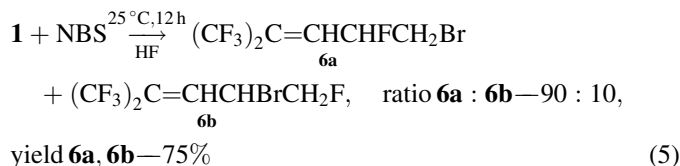
2.2.2. Conjugate electrophilic halofluorination

The solution of *N*-halogen compounds in anhydrous HF is known to be an effective reagent for electrophilic conjugate halofluorination of polyfluorinated olefins and dienes [12–14]. For example, the halofluorination of 2-chloropentafluorobutadiene-1,3 (CPB) using the solution of *N*-chlorosuccinimides or *N*-bromosuccinimides in HF, results in conjugated addition of "ClF" or "BrF", with exclusive formation of 1,4-adducts [15]. These results are also in a good agreement with the regiochemistry of electrophilic halogenation of HFB, which predominantly produces 1,4-adducts [11].

The electrophilic halofluorination of **1** was found to be highly regioselective. The regioselectivity of this process, however, was opposite to that observed in reactions of CPB and HFB. The reaction of **1** with NCS in anhydrous HF led to the selective formation of the *1,2-adduct*—**5a,b**, along with a small amount of the dichloride **4a**

$$\mathbf{1} + NCS \xrightarrow[HF]{25\,^\circ C,12\,h} (CF_3)_2C=CHCHFCH_2Cl$$
$$\mathbf{5a}$$

$$+ (CF_3)_2C=CHCHClCH_2F + \mathbf{4a},$$
$$\mathbf{5b}$$

ratio **5a** : **5b** : **4a**—86.7 : 8.0 : 5.3, yield **5a**, **5b**—48% (4)

Similarly, the interaction of **1** with NBS/HF mixture results in exclusive formation of two isomeric 1,2-adducts **6a,b**.

$$\mathbf{1} + NBS \xrightarrow[HF]{25\,^\circ C,12\,h} (CF_3)_2C=CHCHFCH_2Br$$
$$\mathbf{6a}$$

$$+ (CF_3)_2C=CHCHBrCH_2F, \quad \text{ratio } \mathbf{6a} : \mathbf{6b}—90 : 10,$$
$$\mathbf{6b}$$

yield **6a**, **6b**—75% (5)

It should be pointed out that in both reactions involving diene **1** the corresponding 1,4-adducts were not detectable in the crude product (NMR). The formation of two isomers in both reactions is the likely result of a ring opening reaction of the intermediate halonium cation **A** by a counter anion (Scheme 1).

The difference in the regiochemistry of electrophilic halofluorination of **1** versus HFB or CPB can be explained in terms of the relative stability of the intermediates—allylic (**B** and **C**) versus halonium (**A** and **D**) cations (Scheme 2).

The presence of two electron-withdrawing CF$_3$-groups connected to the carbon of allylic system bearing positive charge leads to significant destabilization of cation **B** compared to the halonium cation **A** (Scheme 1). The steric shielding of the
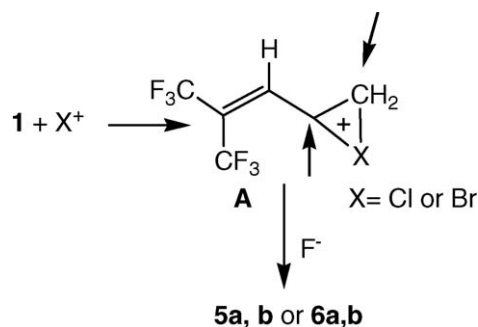
Scheme 1.

Scheme 2.

carbon by bulky CF$_3$-groups also may hinder the addition of the counter anion on this end of cation **A**. On the other hand, in electrophilic reactions of HFB and CPB intermediate **C** should be more stable compared to halonium cation **D**, due to pronounced ability of fluorine substituents adjacent to carbons of allylic system bearing positive charge (C-1 and C-3) to stabilize carbocationic center by back-donation of unshared electron pare [13,16].
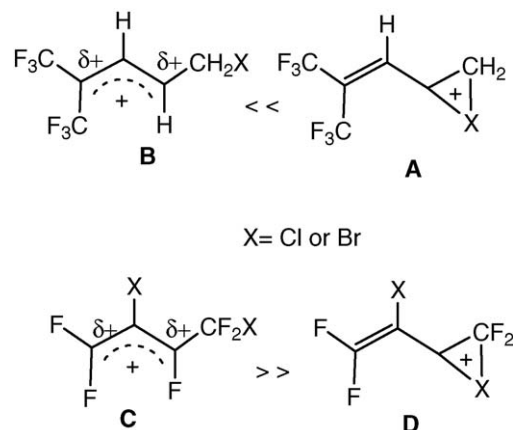
2.3. Cycloaddition reactions

2.3.1. Reaction with difluorocarbene

The reaction of **1** and hexafluoropropene oxide (HFPO) as a difluorocarbene source rapidly proceeds at 200 °C, thus leading to the selective formation of vinylcyclopropane **7**.

(6)
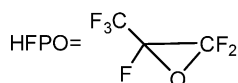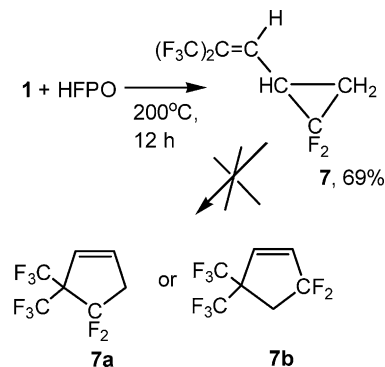
Compound **7**, which was contaminated by a trace of a bypro-duct (∼2%, possibly, the product of double addition of CF$_2$ to **1**) was isolated in 69% yield through distillation. Despite of high reaction temperatures, products of ring expansion of **7** – cyclopentenes **7a** or **7b** – were not detected (NMR) in the crude reaction product.

It should pointed out that the introduction of fluorine into cyclopropane rings effectively reduces thermal stability of vinyl cyclopropanes [17–19]. This is the reason why the addition of difluorocarbene at elevated temperature to CF$_2$=CFCF=CF$_2$ [20], CF$_2$=CFCCl=CF$_2$ and CF$_3$CF=CFCF=CF$_2$ [21] results in high yield formation of the corresponding fluorinated cyclo-

pentenes, since thermally less stable vinylcyclopropanes undergo isomerization under the reaction conditions [19,20].
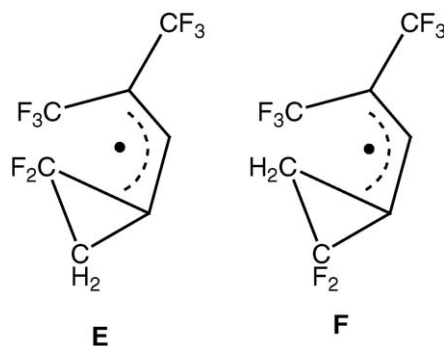
The unusually high thermal stability of **7** is the likely result of unfavorable steric repulsions between the cyclopropane ring and the CF$_3$-group in intermediate radicals **E** or **F**, which in turn inhibits the ring expansion process to form cyclo-pentenes **7a,b** under the reaction conditions (Scheme 3).

Significantly slower thermal isomerization of *Z*- versus *E*-1-propenylpentafluoro-cyclopropanes ($t_{1/2}$ = 3.6 h and 38 min at 110 °C, respectively) was explained as the result of repulsion between *syn*-methyl group and cyclopropane ring in the corresponding radical intermediate derived from the *Z*-isomer [19].
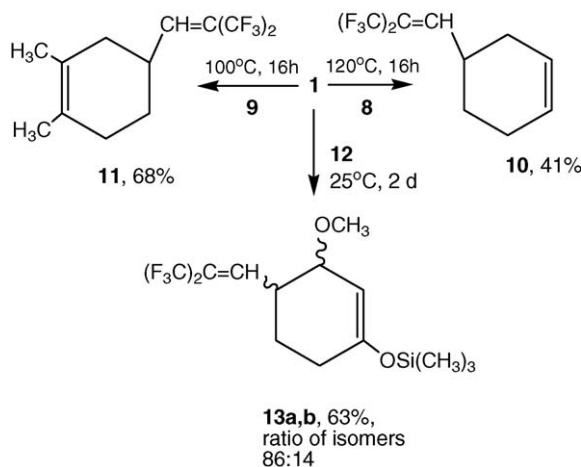
2.3.2. Diels-Alder reactions

Although 1,1-bis(trifluoromethyl)-3-methylbutadiene-1,3 has been reported to produce 1-methyl-3,3-bis(trifluoro-methyl)cyclohexene-1 in reaction with ethylene at 275 °C [22], the corresponding cycloadduct of diene **1** and ethylene was not detected after heating the mixture for 16 h at 250 °C (NMR).

Interestingly, in reaction with electron-rich dienes, com-pound **1** behaves as an activated dienophile, providing electron-deficient, unsubstituted double bond for the reaction. The Diels-Alder reaction of **1** with butadiene-1,3 (**8**) or 2,3-dimethylbu-tadiene (**9**) proceeds under relatively mild conditions (100–120 °C, 16 h), resulting in the formation of the corresponding [2 + 4] cycloadducts **10** or **11** (Scheme 4).

Scheme 3.

Scheme 4.

Scheme 5.

Table 1
Rate constants and relative reactivities for the cycloaddition of selected fluoroolefins [23] and **1**[a] to **18** at 109 °C[b]

Fluoroolefin	Pseudo-first-order rate constant (h^{-1})	Relative reactivity
$CF_3CF=CF_2$	0.021 ± 0.003	1
cis-$CF_3CF=CFCF_3$	0.026 ± 0.003	1.2
$trans$-$CF_3CF=CFCF_3$	0.039 ± 0.003	1.9
$(CF_3)_2C=C(CF_3)_2$	0.085 ± 0.003	4.0
$(CF_3)_2C=CH_2$	0.27 ± 0.01	13
$(CF_3)_2C=CHCH=CH_2$ (**1**)	0.60 ± 0.01	29
$(CF_3)_2C=CFCF_2CF_3$	2.94 ± 0.01	138

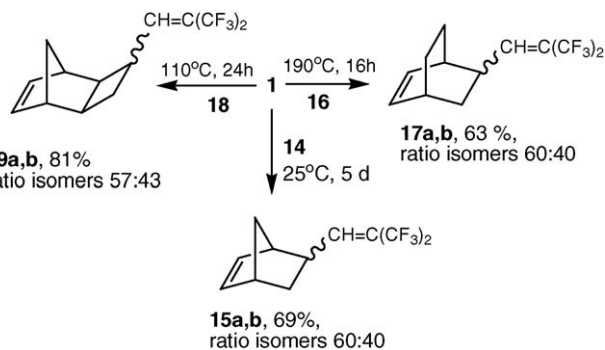[a] This work.
[b] 0.15 mol L^{-1} in neat quadricyclane.

Danishefsky's diene (**12**), which is activated by two electron donating groups, reacts with **1** at ambient temperature, selectively affording adduct **13a,b** as a mixture of *trans-/cis-* isomers, with significant predominance of one of them, probably the *trans*-isomer.

Freshly prepared cyclopentadiene (**14**) also reacts with **1** at ambient temperature to afford a mixture of two isomeric norbornenes **15a,b** (Scheme 5).

The interaction of **1** with cyclohexadiene-1,3 (**16**) at high temperature leads to the mixture of two isomeric cycloadducts **17a,b**. Quadricyclane (**18**) reacts with diene **1** at high temperature forming a mixture of isomeric tricyclononenes **19a,b**. Interestingly, the reaction of **18** with $(CF_3)_2CFCH=CH_2$ under similar conditions (110 °C, 20 h) is significantly slower, thus resulting in the formation of only trace of the corresponding cycloadduct. An amazingly high reactivity of **1** towards **18** was confirmed by measuring the relative rate of this cycloaddition in a high temperature kinetic NMR experiment [23]. It was found that the rate of addition of **1** to **18** was 29 and 2 times higher compared to that of hexafluoropropene and $CH_2=C(CF_3)_2$, respectively. Relative rates of cycloaddition to **18** of selected olefins [23] and **1** (measured in this work[2]) are given in Table 1.

Judging from the relative rates of cycloaddition to **18**, the $(CF_3)_2C=CH–$ substituent in diene **1** acts as an extremely strong electron-withdrawing group, actually more powerful than the $(CF_3)_2CF—$or even two CF_3 substituents.

The fact that diene **1** participates in Diels-Alder reactions as dienophile rather than as diene, is likely to be the result of the destabilization of the cisoid conformation of **1** due to repulsion between bulky CF_3- and CH_2-groups in *s-cis-* conformation. This argument was previously used to explain the formation of ene—rather than the expected Diels-Alder adduct in the reaction of 2,5-dimethylhexadiene-1,3 with benzyne [24].

2.4. Synthetic utility of products based on 1

Compounds containing the $–CH=C(CF_3)_2$ fragment are relatively rare materials, due to the absence of general method of preparation. Most synthesis are based either on dehydration of $(CF_3)_2C(OH)R$ [25], $CF_3[(CR'_2)OH]=CF_2$ [26], or on Wittig reactions, of either $(CF_3)_2C=PR_3$ with hydrocarbon carbonyl compounds [27–29] or nonfluorinated phosphorous ylides with hexafluoroacetone [22,29,30].

The ability of diene **1** to participate in halogenation and cycloaddition reactions with the conservation of a fluorinated double bond makes it an interesting fluorinated building block and offers an alternative methodology for the introduction of the $–CH=C(CF_3)_2$ fragment into organic molecules. Materials synthesized using **1** are valuable intermediates for the synthesis of other products. For example, dehydrohalogenation of olefins **3** and **6a,b** results in the formation of the corresponding dienes **20** and **21**.

(7)
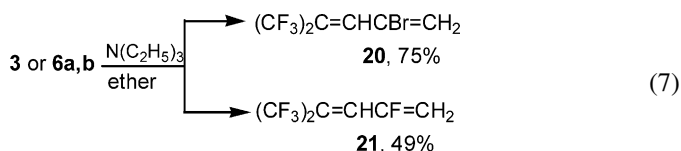
Being reactive towards nucleophiles, diene **1** can be oxidized by sodium hypochlorite. The reaction of diene **1** with NaOCl proceeds at elevated temperature resulting in

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[2] The measurement was carried out by A. Marchione.

formation of bis-epoxide **22** along with small amount of mono-epoxide **22a**.

$$\tag{8}$$

PTC= $(C_4H_9)_4N^+HSO_4^-$

ratio **22:22a** - 90:10;
yield **22** - 41%
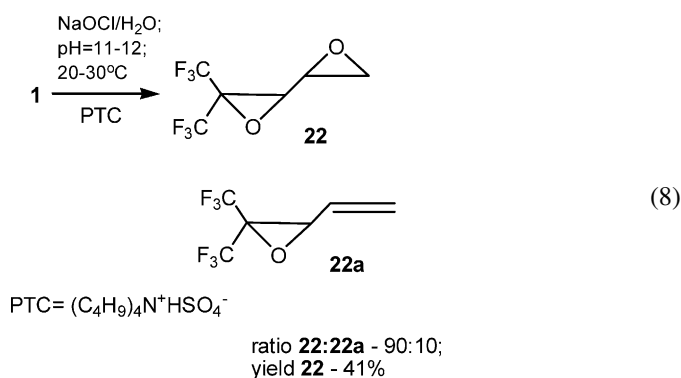
In contrast to the epoxidation of CH_2=$C(CF_3)_2$ [31], which rapidly proceeds at 0–5 °C and pH 14, the oxidation of **1** seems to be sensitive to both the temperature and the pH of the reaction medium. At ambient temperature, oxidation was slow, but compound **22** was prepared in moderate yield at elevated temperature. The oxidation at pH 14 (freshly prepared NaOCl) was found to be very slow at 25 °C. However, when it was carried out at pH 11–12 (commercially available NaOCl, Aldrich) and elevated temperature, the reaction resulted in a moderate yield of **22** along with byproduct **22a**. The formation of **22a** seems to be the result of an independent rather than a subsequent reaction. However, mechanistic studies and yield optimization were not carried out in this study. Pure **22** was isolated as a mixture of two diastereomers after removal of byproduct **22a** by fractionation (see Section 3.6.1). Since unambiguous assignment of the structure could not be made based on the data of NMR spectroscopy, additional proof of the correctness of the structure was obtained through conversion of **22** into the known diol **23** [32] by reaction with $LiAlH_4$

$$\mathbf{22} + LiAlH_4 \xrightarrow[THF]{0-10\,°C} \underset{\mathbf{23}, 75\%}{(CF_3)_2C(OH)CH_2CH(OH)CH_3} \tag{9}$$
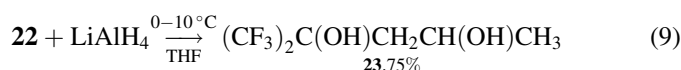
Bis-epoxide **22** is the second known example of polyfluorinated oxides of conjugated dienes. The first representative of diepoxide of perfluoro-3,4-dimethylhexadiene-2,4 was reported in 1995 by Chambers et al. [33,34].

Interestingly, the oxidation of dienes containing a halogen substituent in adjacent to C-3 results in selective oxidation of the $(CF_3)_2C$=CH– fragment.

$$\tag{10}$$

PTC= $(C_4H_9)_4N^+HSO_4^-$

24, X=Br, 50%
25, X=F, 68%
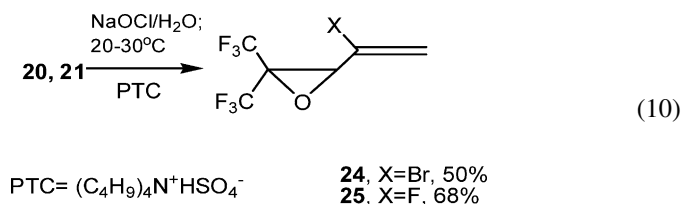
Using a recently developed procedure for the oxidation of polyfluorinated 1,1-dihydro-olefins by NaOCl under phase-transfer catalysis conditions [31], materials containing a moiety that is reactive towards nucleophiles $(CF_3)_2C$=CH– were

converted into the corresponding epoxides. For example, the oxidation of olefins **7** and **19a,b** carried out at ambient temperature resulted in formation of epoxides **26** and **27a,b**, respectively.

$$\tag{11}$$

PTC= $(C_4H_9)_4N^+HSO_4^-$

26, 64%, R=
27a,b, 72%, R=
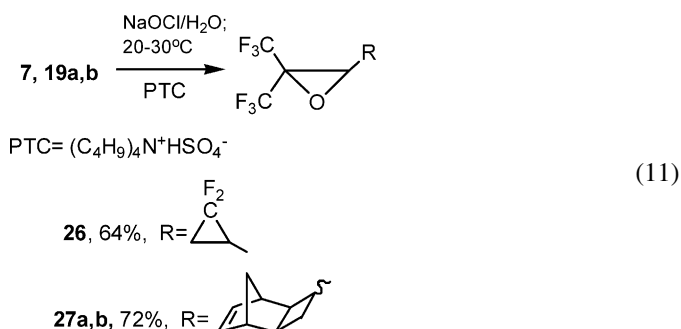
3. Experimental

^1H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker DRX 400 (400.5524, 100.8642 and 376.8485 MHz) using internal $CFCl_3$, TMS as standards and $CDCl_3$ as a lock solvent. IR spectra were recorded on a Perkin-Elmer 1600 FT spectrometer as liquid films (KCl plates). Moisture sensitive materials were handled in a glove box. GC and GC/MS analysis were carried out on HP-6890 instrument, using HP FFAP capillary column and either TCD (GC) or mass selective detector (GS/MS), respectively.

Dimethylamine, NCS, NBS, dienes **8**, **9**, **12**, **16** (Aldrich), the solution of NaOCl (12% of active chlorine, Aldrich), HF, HFPO, CH_2=$CHCH_2C(CF_3)_2OH$ (DuPont) were used without further purification. Quadricyclane (**18**) was prepared by photochemical isomerization of norbornadiene [35] using *t*-butyl methyl ether as a solvent. Compound **1** was prepared according literature procedure [4]. All other chemicals and solvents were obtained commercially and used as received. Oxidation of olefins and dienes using NaOCl was carried out using published procedure [31]. Compound **23** [32] was identified by comparison with authentic sample (NMR,GC).

Caution: Anhydrous HF is toxic and corrosive material that should be handled properly and by trained personnel only. Despite the fact that sodium hypochlorite is a stable material at pH 14, its stability is limited at lower pH. In reactions using sodium hypochlorite the pH should be monitored during the process to avoid rapid decomposition of NaOCl.

3.1. Halogenation of 1

(a) Bromine (10 g, 0.056 mol) was slowly added with stirring to 10 g (0.05 mol) of **1** at a rate that allowed to maintain the internal reaction temperature <35 °C. The reaction mixture was stirred for 1 h at ambient temperature, washed with the solution of sodium thiosulfate; the organic layer was separated, dried over $MgSO_4$ and distilled. It was isolated 12.5 (68%) of **3**, bp 82 °C/46 mmHg.

(b) The same reaction was carried on 0.3 mol scale out under irradiation with a sun lamp at 25–35 °C. Compound **3**

Table 2
Reaction conditions, yields, IR and MS data for new compounds

Reactants (mol)	Temperature (°C) (time, h)	Product (yield, %)	bp (°C/mmHg)	Purity[a]	IR (cm^{-1})[b]	MS (m/z)[c]
DMA (0.15), **1** (0.1)	0 (0.5)	**2** (95)	43/15	99.8	2950, 2780, 1462, 1358, 1271, 1142, 1094, 979, 956, 912, 860, 788, 730, 678	236[(M + 1), $C_8H_{12}F_6N^+$], 235 (M^+, $C_8H_{11}F_6N^+$), 166 [(M-CF$_3$)$^+$, $C_7H_{11}F_3N^+$]
1 (0.3), Br$_2$ (0.32)[d]	25–30 (2)	**3** (75)	82/46	>99	1680, 1398, 1356, 1298, 1246, 1181, 1152, 1026, 948, 925, 664, 723	269 (M-Br, $C_6H_4BrF_6^+$, 100%)
1 (0.05), Cl$_2$ (0.08)[d]	25–30 (2)	**4a,b** (68)	134–136	99.5	1685, 1396, 1355, 1302, 1242, 1172, 1099, 1046, 954, 925, 727, 706	260 (M^+, $C_6H_4Cl_2F_6^+$)
–	–	**4b**[e]	–	–	–	260 (M^+, $C_6H_4Cl_2F_6^+$)
1 (0.05), NCS (0.06), HF (5)	25 (12)	**5a,b**[f] (48)	106–108	95	1689, 1396, 1360, 1294, 1236, 1179, 1105, 1045, 946, 718, 665	246, 244 (M^+, $C_6H_4ClF_7^+$)
1 (0.18), NCS (0.2), HF (7.5)	25 (12)	**6a,b**[g] (49)	127–128	>99	1689, 1395, 1358, 1288, 1236, 1170, 1104, 1028, 1007, 941, 718, 696	288, 290 (M^+, $C_6H_4BrF_7^+$)
1 (0.15), HFPO (0.21)	200 (12)	**7** (69)	105–108	98[h]	1677, 1474, 1414, 1380, 1327, 1296, 1250, 1167, 1073, 1017, 969, 904, 849, 717	240 (M^+, $C_7H_4F_8^+$)
1 (0.1), **8** (0.2)	150 (20)	**10** (41)	57–58.5/26	>99[i]	3033, 2922, 2845, 1676 (1645 sh), 1401, 1372, 1327, 1235, 1155, 11.02, 1094, 957, 745, 710	244 (M^+, $C_{10}H_{10}F_6^+$)
1 (0.1), **9** (0.22)	150 (20)	**11** (68)	84–85/18	>99	2917, 1675 (1640 sh), 1401, 1328, 1289, 1235, 1165, 1094, 1052, 958, 715, 663	272 (M^+, $C_{12}H_{14}F_6^+$)
1 (0.03), **9** (0.03)	25 (2d)	**13a,b**[j] (63)	65–67/02	>99	2959, 1723 (sh), 1696 (sh), 1678, 1399, 1338, 1150, 1094, 960, 925, 846	273 [(M-C$_3H_{10}$OSi)$^+$, $C_{11}H_{11}F_6O^+$]
1 (0.1), **14** (0.1)	25 (5d)	**15a,b**[k] (69)[l]	60–68/27	95	3050, 2946, 2871, 1669, 1398, 1360, 1286, 1243, 1154, 1111, 956, 933, 705	256 (M^+, $C_{11}H_{10}F_6^+$)
1 (0.13), **14** (0.18)	190 (16)	**17a,b** (63)	80–82/0.26	>99[m]	3050, 2946, 2871, 1669, 1398, 1360, 1286, 1243, 1154, 1111, 956, 933, 705	270 (M^+, $C_{12}H_{12}F_6^+$)
1 (0.13), **14** (0.18)	190 (16)	**19a,b** (81)	98–102/23	>99[n]	2971, 1667, 1403, 1297, 1243, 1215, 1157, 1111, 973, 948, 698	282 (M^+, $C_{13}H_{12}F_6^+$)
3 (0.05), N(C$_2$H$_5$)$_3$ (0.1), ether 100 mL	25 (16)	**20** (75)	102–104	99	1670, 1619, 1392, 1256, 1254, 11159, 1000, 939, 915, 740	268, 270 (M^+, $C_6H_3BrF_6^+$)
6a,b (0.09), N(C$_2$H$_5$)$_3$ (0.1), ether 100 mL	25 (12)	**21**[o] (49)[p]	76–82	75	1666, 1622, 1404, 1367, 1325, 1289, 1274, 1227, 1165, 978, 923, 888, 731, 655	208 (M^+, $C_6H_3F_7^+$)
1 (0.1), NaOCl (200 mL), (C$_4$H$_9$)$_4$N$^+$ HSO$_4^-$ (0.2 g)	25–35 (12)	**22**[q] (41)	54–55/100	>99	1492 (sh), 1467, 1357, 1305, 1202, 1118, 1007, 952, 835, 758, 716, 656	223 (M + 1, $C_6H_5F_6O_2^+$)
–	–	**22a**[r]	–	–	1661 (w), 1457 (?)	205 (M-1$^+$, $C_6H_3F_6O^+$), 137 (M-CF$_3^+$, 100%)
20 (0.02), NaOCl (80 mL), (C$_4$H$_9$)$_4$N$^+$ HSO$_4^-$ (0.2 g)	25–35 (6)	**24** (50)[p]	–[s]	>95	1643, 1440, 1359, 1200, 1102, 1105, 959, 936, 872	284, 286 (M^+, $C_6H_3BrF_6O^+$)
21 (0.05), NaOCl (150 mL), (C$_4$H$_9$)$_4$N$^+$ HSO$_4^-$ (0.2 g)	0–25 (20)	**25** (68)[p]	–[s]	75	1687, 1451, 1359, 1317, 1112–1170, 1108, 1005, 969, 934, 882, 723, 651	224 (M^+, $C_6H_3F_7O^+$)

7 (0.03), NaOCl (100 mL), (C$_4$H$_9$)$_4$N$^+$ HSO$_4^-$ (0.1 g)	20 (16)	**26** (64)^q	40–41.5/270	98	1491, 1453, 1368, 1330, 1300, 1204, 1120, 1089, 1025, 999, 964, 908, 879, 758, 730, 706, 661	240 [(*M*$^+$-O), C$_7$H$_4$F$_8$$^+$)]
19a,b (0.04), NaOCl (250 mL), ether 30, (C$_4$H$_9$)$_4$N$^+$ HSO$_4^-$ (0.1 g)	20 (16)	**27a,b** (72)	49/0.1	>99	–	282 (*M*$^+$-O, C$_{13}$H$_{12}$F$_6$)
22 (0.01) LiAlH$_4$^{t}	0–10 (2)	**23** (75)				

[a] GC or NMR.
[b] KCl, liquid, major peaks.
[c] GC/MS; electron ionization.
[d] Under UV irradiation.
[e] In mixture with **4a**, ratio **4a**:**4b** 92:8 at 90% conversion of **1**.
[f] Mixture of **5a,b** and **4a**, ratio 86.7:8.0:5.3.
[g] Mixture of **6a** and **6b**, ratio 90:10.
[h] Isolated material contained trace (∼2%) of impurity, possibly the product of double addition of CF$_2$.
[i] Calc.: C, 49.19; H, 4.13; F, 46.68. C$_{10}$H$_{10}$F$_6$. Found: C, 49.46; H, 4.18; F, 46.84.
[j] Mixture of *trans*- and *cis*-isomers, ratio 86:14.
[k] Purity 95%, the remainder is dimer of cyclopentadiene; mixture of two isomers, ratio 67:33.
[l] Calculated yield on pure **15a,b**.
[m] Mixture of isomers, ratio 70:30; Calc.: C, 53.34; H, 4.48; F, 42.19. C$_{12}$H$_{12}$F$_6$. Found: C, 53.33; H, 4.62; F, 42.02.
[n] Mixture of isomers, ratio 57:43; Calc.: C, 55.32; H, 4.29; F, 40.39. C$_{13}$H$_{12}$F$_6$. Found: C, 55.10; H, 4.51; F, 39.88.
[o] Isolated product contained 25% ether.
[p] Calculated yield.
[q] Mixture of diastereomers, ∼1:1.
[r] Isolated by distillation as the mixture with **22**, ratio **22a**:**22**—40:60.
[s] Isolated by vacuum transfer into cold (−78 °C) trap.
[t] 1 M solution in THF.

Table 3
NMR spectra of new materials

Compound no.	¹H NMR[a] (δ, ppm; J, Hz)	¹⁹F NMR[a] (δ, ppm; J, Hz)	¹³C NMR[b,c] (δ, ppm; J, Hz)
2	2.4 (6H, s), 2.9 (2H, dd, J = 6.4, 1.5), 3.5 (1H, sept. J = 9.5), 5.5 (1H, ddt, J = 15.6, 9.5, 1.5), 6.0 (1H, dt, J = 15.1, 6.4)	−68.00 (d, J = 8.0)	44.9, 52.3 (sept., J = 30), 61.4, 117.2, 123.6 (q, J = 280), 141.7
3	3.63 (1H, t, J = 10.4), 3.88 (1H, dd, J = 10.4, 4.5), 5.15 (1H, td, J = 11.3, 4.5), 6.70 (1H, dm, J = 11.3, 1.2)	−58.92 (3F, q, J = 6.9), −65.27 (3F, q, J = 6.9)	
4a	3.75 (1H, dd, J = 11.6, 8.2), 3.93 (1H, dd, J = 11.6, 4.2), 5.12 (1H, ddd, J = 10.7, 8.2, 4.6), 6.72 (1H, dm, J = 10.7, 1.2)	−58.71 (3F, q, J = 6.7), −65.40 (3F, q, J = 6.7)	
4b	4.24 (2H, dd, J = 6.1, 1.8), 6.10 (1H, dm, J = 15.0), 6.63 (1H, dt, J = 15.0, 6.1)	−73.30 (s)	
5a	3.75 (2H, m, 5.12 (1H, ddd, J = 10.7, 8.2, 4.6)), 5.68 (1H, dm, J = 47.2), 6.83 (1H, dd, J = 14.6, 7.6)	−59.10 (3F, quint., J = 7.3), −65.43 (3F, q, J = 7.3), −179.88 (1F, dm, J = 47.2)	
5b	3.70 (2H), 4.60 (1H, dm, J = 46.6), 4.96 (1H, m), 6.75 (1H, d, J = 10.0)	−58.60 (3F, q, J = 7.2), −65.30 (3F, q, J = 7.2), −219.79 (1F, tdq, J = 46.6, 14.4, 1.8)	
6a	3.55 (1H, m), 3.63 (1H, m), 5.70 (1H, d, J = 47.9), 6.85 (1H, dd, J = 14.0, 7.6)	−59.12 (3F, quint., J = 6.0), −65.30 (3F, q, J = 6.9), −175.55 (1F, dm, J = 47.9)	
6b	4.60 (1H, ddd, J = 47.3, 10.0, 7.3), 4.70 (1H, ddd, J = 47.3, 10.0, 4.0), 5.1 (1H, m), 6.85 (1H)	−58.88 (3F, q, J = 6.9), −65.28 (3F, q, J = 6.9), −210.40 (1F, tdq, J = 47.3, 13.2, 1.5)	
7	1.7 (1H, m), 2.1 (1H, m), 2.8 (1H, m), 6.4 (1H, d, J = 9.9)	−59.28 (3F, q, J = 6.8), −64.93 (3F, q, J = 6.8), −128.0 (1F, dtd, J = 159.9, 11.2, 4.4), −139.1 (1F, dddd, J = 159.9, 13.1, 5.9, 1.2)	19.0 (t, J = 11.0), 21.64 (tq, J = 13.1, 1.9), 112.3 (t, 285.0), 120.50 (qq, J = 270.3, 1.9), 120.90 (q, J = 273.2), 123.30 (sept., J = 32.9), 139.64 (m)
10	1.45 (1H, m), 1.70 (1H, m), 1.65 (1H, s), 1.85 (1H, m), 2.10 (2H, m), 2.93 (1H, m), 5.60 (1H, m), 5.68 (1H, m), 6.56 (1H, dm, J = 11.2, 1.3)	−58.50 (3F, q, J = 7.2), −64.75 (3F, q, J = 7.2)	23.40, 27.64, 29.94, 33.75, 121.47 (qq, J = 272.0, 2.9), 121.47 (sept., J = 31.0), 121.58 Z(q, J = 274.0), 124.15, 127.00, 151.10 (m)
11	1.47 (1H, m), 1.65 (1H, s), 1.7–2.2 (3H, m), 2.93 (1H, q, J = 11.3), 6.60 (1H, d, J = 11.3)	−58.40 (3F, q, J = 7.5), −64.73 (3F, qt, J = 7.5, 1.3)	20.77, 20.91, 30.48, 32.04, 36.60, 38.32, 123.22 (q, J = 272.0), 123.29 (sept, J = 32.0), 123.34 (q, J = 274.0), 124.92, 127.59, 153.22 (m)
13a,b[d]	0.26 (s), 1.7 (m), 2.0 (m), 2.98 (t, J = 10.5), 3.06 (m), 3.33 (m), 3.80 (t, t, J = 4.4), 5.01 (dt, 3.4, J = 1.3), 5.13 (dt, J = 4.8, 1.3), 6.70 (1H, d, J = 10.9), 7.05 (dm, J = 10.7, 1.3)	Major: −58.45 (3F, q, J = 7.3), −64.65 (3F, q, J = 7.3); minor: −58.70 (3F, q, J = 7.3), −64.80 (3F, q, J = 7.3)	
15a,b[e]	0.8–2.8 (7.4H), 3.6 (0.6H), 5.96 (2H, m), 6.93 (0.6H, d, J = 8.0), 6.98 (0.4H, d, J = 10.7)	Major: −58.80 (3F, dq, J = 6.9, 2.3), −64.35 (3F, qt, J = 6.9, 1.7); minor: −58.75 (3F, m), −64.56 (3F, m)	
17a,b[e]	1.0–2.0 (6H), 2.4–3.0 (3H), 5.6–6.9 (3H)	−58.3 (m), −64.6 (m)	
19a,b[e]	0.8–2.8 (7.4H), 3.6 (0.6H, t), 5.96 (2H, m), 6.93 (0.6H, d, J = 8.0), 6.98 (0.4H, d, J = 10.7)	Major: −59.80 (3F, qd, J = 6.9, 2.3), −64.35 (3F, qt, J = 6.9, 1.7); minor: −58.72 (3F, m), −64.53 (3F, m)	
20	5.94 (1H, dd, J = 2.8, 1.2), 6.02 (1H, t, J = 1.2), 7.07 (1H, m)	−58.41 (3F, q, J = 6.9), −65.27 (3F, qd, J = 6.9, 1.5)	116.91, 119.53 (q, J = 273.2), 119.90 (q, J = 273.2), 122.25 (sept., J = 31.0), 122.59, 139.67 (m)
21	5.10 (1H, dd, J = 42.7, 3.0), 5.25 (1H, dd, J = 13.7, 3.0), 6.27 (1H, dq, J = 25.9, 1.5)	−58.35 (3F, dq, J = 31.6, 7.5), −65.10 (3F, q, J = 7.5), −105.53 (1F, m)	107.20 (d, J = 20.3), 120.30 (q, J = 274.2), 121.02 (sept., m, J = 34.9, 3.9), 121.1 (q, J = 271.3), 132.40 (dm, J = 26.2), 157.05 (d, J = 258.7)

Compound	^{13}C NMR	^{19}F NMR	^1H NMR
22[d]	42.42, 44.70, 45.35 (q), 45.88 (q), 58.40 (m), 58.56 (q), 60.45 (q), 122.50 (q, $J = 279$), 122.80 (q, $J = 279$)	Major: −66.99 (3F, q, $J = 6.9$), −73.33 (3F, q, $J = 6.9$); minor: −67.26 (3F, q, $J = 6.9$), −73.33 (3F, q, $J = 6.9$)	2.84 (dd), 2.91 (dd), 3.0 (m), 3.12 (m), 3.20 (m), 3.40 (d)
22a		−66.73 (3F, q $J = 7.3$), −73.45 (3F, q, $J = 7.3$)	3.87 (1H, d, $J = 5.0$), 5.6 (1H, m), 5.73 (2H, m)
24	59.42 (q, $J = 3.9$), 60.50 (sept, $J = 37.8$), 117.17 (s), 119.90 (q, $J = 281$), 120.10 (q, $J = 281$), 120.17 (q, $J = 1.9$), 120.18 (q, $J = 281$)	−65.95 (3F, qd, $J = 7.5$, 1.1), −73.25 (3F, q, $J = 7.5$)	4.10 (1H, s), 5.90 (1H, dd, $J = 1.2$, 2.8), 6.15 (1H, m)
25	107.20 (d, $J = 20.3$), 120.30 (q, $J = 274.2$), 121.02 (sept., m, $J = 34.9$, 3.9), 121.1 (q, $J = 271.3$), 132.40 (dm, $J = 26.2$), 157.05 (d, $J = 258.7$)	−66.17 (3F, quint., $J = 7.5$), −73.40 (3F, q, $J = 7.5$), −110.53 (1F, ddq, $J = 46.7$, 16.0, 4.6)	4.03 (1H, s), 4.88 (1H, dd, $J = 46.7$, 4.0), 5.1 (1H, dd, $J = 15.9$, 3.3)
26		Major: −67.06 (3F, q, 7.5), −73.43 (3F, q, 7.5), −131.3 (1F, dtd, 164.1, 11.5, 4.6), −143.10 (1F, ddd, 164.1, 13.8, 3.7); minor: −67.17 (3F, q, 6.9), −73.55 (3F, q, 6.9), −130.5 (1F, dtd, 163.5, 11.5, 4.6), −141.8 (1F, ddd, 163.5, 13.8, 6.3)	1.3–2.0 (m), 3.3 (d, $J = 7.3$), 3.5 (d, $J = 5.8$)
27a,b[e]		−66.03 (q), −66.36 (q), −67.21 (q), −67.82 (q), −73.39 (m)	1.2–2.2 (m), 2.5–3.0 (m), 3.50 (dd), 5.9 (m)

a In CDCl$_3$ unless stated otherwise.
b $^{13}C\{^1H\}$.
c Neat.
d Mixture of diastereomers.
e Mixture of isomers.

was isolated in 75% yield. Reaction conditions, reagents ratio and spectroscopic data of **3** are given in Tables 2 and 3.

(c) A solution of 10 g of **1** in 100 mL of acetonitrile was loaded in a 240 mL Hastelloy reactor. It was cooled down, evacuated and charged with 10 g of chlorine gas. The reaction mixture was stirred for 16 h at ambient temperature, the reactor was unloaded and the mixture was worked up as in example (a). Six grams of **1** were recovered.

(d) Chlorine gas (6 g, 0.08 mol) was slowly introduced and irradiated with a sun lamp into a three-neck round bottom flask equipped with a dry-ice condenser and containing 10 g (0.05 mol) of **1** at a rate that allowed to maintain the internal temperature <35 °C. In the sample of crude reaction mixture taken ∼15 min after beginning of chlorine addition it was found by NMR that conversion of **1** was 90% and the reaction mixture contained a mixture of **4a** and **4b** in the ratio 92:8, along with a trace of **4c**. The reaction mixture was stirred under irradiation for 2 h and was worked up as in example (a). Reaction conditions, ratio reagents and spectroscopic data of **4a,b** are given in Tables 2 and 3.

3.2. Halofluorination reactions

A mixture of *N*-halosuccinimide, diene **1** and HF was stirred in 400 mL Hastelloy reactor at ambient temperature. Water (100 mL) was injected into the reactor and it was unloaded. The organic layer was separated, washed with water, dried over MgSO$_4$ and distilled. Reaction conditions, reagents ratio and spectroscopic data of the products are given in Tables 2 and 3.

3.3. Reaction with HFPO

A mixture of 28 g (0.15 mol) of **1** and 35 g (0.21 mol) of HFPO was stirred in a Hastelloy reactor for 12 h at 200 °C. The reactor was unloaded and the product was distilled to give 25 g (69%) of compound **7**, bp 105–108 °C. The spectroscopic data of **7** are given in Tables 2 and 3.

3.4. Cycloaddition reactions

3.4.1. Compounds 8, 9, 16 and 18

A mixture of **1** and the corresponding diene was stirred in a Hastelloy reactor for 12–16 h at ambient temperature. The reactor was unloaded and the product was distilled. Reaction conditions, ratio of reagents and spectroscopic data of the products are given in Tables 2 and 3.

3.4.2. Compounds 12 and 14

A mixture of **1** and the corresponding diene was stirred in round bottom flask equipped with water condenser and thermocouple for 2–5 days at ambient temperature. The reactor was unloaded and the product was distilled. Reaction conditions, ratio of reagents and spectroscopic data of products are given in Tables 2 and 3.

3.5. Preparation of dienes 20 and 21

To a solution of triethylamine in dry ether, compounds **3** or **6a,b** were added and the reaction mixture was stirred at ambient temperature for 12–16 h. It was washed with water; the organic layer was dried over MgSO$_4$ and distilled. Reaction conditions, ratio of reagents and spectroscopic data of products are given in Tables 2 and 3.

3.6. Oxidation using NaOCl

3.6.1. Oxidation of 1 (typical procedure)

Diene **1** (19 g, 0.1 mol) was added at 0 °C to an stirred mixture of 200 mL of sodium hypochlorite and 0.2 g of $(C_4H_9)_4N^+ HSO_4^-$ and the mixture was allowed to warm up slowly; the temperature of the exothermic reaction was kept at ~35 °C with a cooling bath. The mixture was stirred overnight, diluted with water (500 mL), the organic layer was separated, dried over MgSO$_4$, the crude material was vacuum-transferred into a cold trap to separate the product from catalyst and distilled at reduced pressure to give 5 g of mixture **22** and **22a** (bp 50–54/100 mmHg; ratio 60:40, respectively) and 9.1 g (41%) pure **22**, bp 54–55/100 mmHg, as a mixture of two diastereomers. Spectroscopic data of the products are given in Tables 2 and 3.

The oxidation of compounds **7**, **19a,b**, **20** and **21** was carried out similarly, but at ambient temperature; ether was used as solvent for the oxidation of **19a,b**.

Acknowledgements

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