A new approach to the synthesis of 2,2-difluoro-1,3-dioxolanes

W. Navarrini *, L. Bragante, S. Fontana, V. Tortelli, A. Zedda

Ausimont, Research and Development Center, Viale Lombardia, 20, 20021 Bollate, Milan, Italy

Abstract

A direct and versatile way to prepare halogenated 2,2-difluoro-1,3-dioxolanes through the addition of bis-(fluoroxy)difluoromethane (BDM) to halogenated alkenes ($CF_2=CFCF_3$, $CF_2=CFOCF_2CF_3$, $CF_2=CHCF_3$, $CF_3CF=CFCF_3$, $CFCl=CFCl$, $CFBr=CFBr$, $CCl_2=CCl_2$, $CHCl=CCl_2$, $CHCl=CHCl$, $CH_2=CHCl$, $CF_2=CFCl$, $(CF_3)_2CFCF=CFCF_3$, $CF_2=CFBr$, $CF_2=CF_2$) has been discovered.

1. Introduction

Despite the fact that organic hypofluorites have been studied quite extensively during the past 30 years and many articles and reviews have appeared in the specialized literature [1], their behaviour towards unsaturated compounds is still a stimulating subject for investigation.

One of the first experiments by Cady [2] regarding the gas-phase addition of CF_3OF to ethylene suggested a free-radical reaction due to the need for activation by UV light at low reactant concentrations and to the uncontrollable nature of the reaction at higher concentration. Lately Barton et al. [3], in the 1960s, proposed an electrophilic pathway for the fluorination of electron-rich olefins with trifluoromethyl hypofluorite.

In the early 1980s, Johri and DesMarteau [4] suggested a free-radical mechanism for the addition of CF_3OF to substantially electron-poor olefins on the basis of wide experimental data. Also Santos Afonso and Schumacher [5] studied the kinetics of the free-radical reaction between trifluoromethyl hypofluorite and hexafluoropropene. More recently, Mukhametshin in his latest review [1c] observed that the majority of the contradictions regarding the reactivity of CF_3OF towards olefins could be readily solved by applying the one-electron-transfer theory, although no direct experimental evidence was available.

The majority of studies on fluoroxy compounds have been performed using trifluoromethyl hypofluorite as a model compound. Bis(fluoroxy)difluoromethane (BDM) has been much less studied since its synthesis in 1967 [6]. In 1968 Hohorst and Shreeve [7] found that BDM reacts with tetrafluoroethylene and *trans*-1,2-dichloroethylene giving bis-ethers of formula $(RO)_2CF_2$. Hence BDM was assumed to be substantially identical to CF_3OF in terms of its reactivity.

Its thermal decomposition was studied by Foss and Pitt in 1968 [8]. Later, in 1978, Toy and Stringham [9] described the thermal and photochemical reactions of BDM with 'Dewar hexafluorobenzene' underlining the more complex reactivity of BDM relative to CF_3OF. The reaction products were mainly complex copolymer mixtures and dioxolanic structures were isolated among the volatile by-products.

During the past 10 years halogenated 1,3-dioxolanes have been of continuous interest as inhalation anaesthetics [10], CFC substitutes and particularly as intermediates for the synthesis of halogenated dioxoles, a new family of monomers suitable for the preparation of both crystalline and amorphous polymers [11,12]. Descriptions have been given in the literature of the preparation of halogenated 2,2-difluoro-1,3-dioxolanes using multi-step processes but often with low or inconsistent yields [11b]. We now report the direct synthesis of 2,2-difluoro-1,3-dioxolanes [12] using a new one-step process involving the addition of BDM to ethylenic compounds.

* Corresponding author.

2. Results and discussion

The reaction can be carried out in the presence of halogenated inert solvents (CF_2Cl_2, $CFCl_3$ and perfluoropolyethers) as well as in the neat olefin. The results of the reactions tested are summarized in Table 1. The stoichiometry of the reaction is as depicted in Scheme 1.
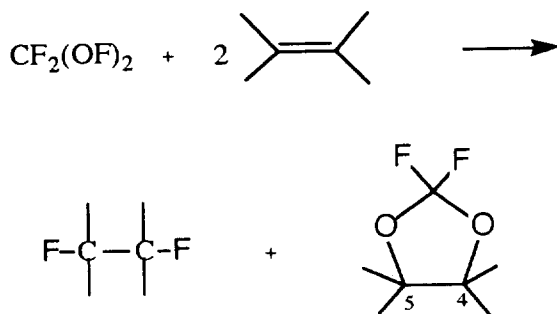
Scheme 1.

Substituents in positions 4 and 5 of the dioxolanic ring can be changed appropriately by choosing the right olefin without substantial modification of the stoichiometry of the reaction. Oligomeric or dimeric olefin

products can be also formed, but by using the appropriate experimental procedures these can easily be minimized to a few per cent.

The choice of a continuous, semi-continuous or batch procedure was determined mainly by the physicochemical properties of the olefin. The batch procedure, in which there was no temperature control and the solvent also acted as a heat sink, gave variable yields. Using this methodology, highly fluorinated olefins gave good to medium yields, while olefins substituted with a different halogen apart from fluorine on the double bond gave poor yields of the desired dioxolane. The semi-continuous procedure, where a stream of BDM diluted with an inert gas was added continuously to the total quantity of olefin, was successfully applied to halo olefins having a low tendency to oligomerize or polymerize. BDM reacted as soon as it was introduced into the reactor containing the olefin. The continuous method, where the two reagents were added simultaneously to the reactor, was adopted when it was necessary to have a low concentration of the olefin during the addition of BDM. Olefins with very low boiling points and a high tendency to oligomerize or polymerize (e.g. C_2F_4) or with a weak bond (e.g. $CF_2=CFBr$) were conveniently

Table 1
Addition of BDM to olefins

Entry	Alkene	Solvent	Temp. (°C)	Yield [d] (%)
1 [a]	$CF_2=CFCF_3$	CF_2Cl_2	−196 to 25	95
2 [a]	$CF_2=CFOCF_2CF_3$	CF_2Cl_2	−196 to 25	68
3 [a]	$CF_2=CHCF_3$	CF_2Cl_2	−196 to 25	48
4 [a]	$CF_3CF=CFCF_3$	–	−196 to 25	28
5 [b]	$CFCl=CFCl$ cis/trans = 1:1	CF_2Cl_2	−80	88 syn/anti = 1:4
6 [b]	$CFCl=CFCl$ cis/trans = 1:1	–	−65	78 syn/anti = 1:4
7 [b]	$CFBr=CFBr$ trans	CF_2Cl_2	−80	80 syn/anti = 1:9
8 [b]	$CCl_2=CCl_2$	$CFCl_3$	−60	75
9 [b]	$CHCl=CCl_2$	$CFCl_3$	−90	89
10 [b]	$CHCl=CHCl$ trans	$CFCl_3$	−95	63 syn/anti = 1:9
11 [b]	$CHCl=CHCl$ cis	$CFCl_3$	−95	66 syn/anti = 1:9
12 [b]	$CH_2=CHCl$	$CFCl_3$	−95	59
13 [b]	$CF_2=CFCl$	CF_2Cl_2	−75	65
14 [b*]	$(CF_3)_2CFCF=CFCF_3$	–	−61	43
15 [c]	$CF_2=CFBr$	CF_2Cl_2	−70	85
16 [c]	$CF_2=CF_2$	Galden [e]	−80	56

[a] Batch system.
[b] Semi-continuous system.
[b*] UV activation.
[c] Continuous system.
[d] Yield = mmol isolated dioxolane per mmol BDM.
[e] Trademark of Ausimont S.p.A. for perfluoro polyethers with low b.p. (range 70–270 °C).

converted to dioxolanes using this experimental approach.

Although a detailed mechanistic study has not yet been carried out, it seems likely that, under the experimental conditions selected, the addition of BDM to the olefin proceeds through a free-radical chain mechanism. The initiation, propagation and termination steps are shown in Scheme 2. Experimental evidence has been collected to support all the reaction steps.

In general, the reactions between BDM and olefins are auto-initiating. However, in the case of the internal perfluoro-olefins, the reactivity towards BDM decreases; at -80 °C, for example, no reaction was observed unless BDM containing traces of fluorine or UV light (Table 1, entry 14 [b]) were used as free-radical initiators.

The termination step is supported by the presence of typical radical coupling products (e.g. $(CF_2ClCFCl)_2$, $(CFHClCHCl)_2$) which were detected as traces by GLC/mass spectroscopy of the crude reaction mixtures. The intermediate adduct (1) has the right geometry and electronic configuration to behave as a β-peroxyalkyl radical [13] in the propagation step, where the oxygen lone pair is the site of attack in the homolytic ring closure to oxiranes. Sianesi et al. [14] have similarly explained the formation of cyclic perfluoropolyethers in the degradation of peroxide-containing perfluoropolyethers through intramolecular homolytic back-attack of a perfluoroalkyl radical on a peroxide bond in the polymer chain.

Initiation

Propagation
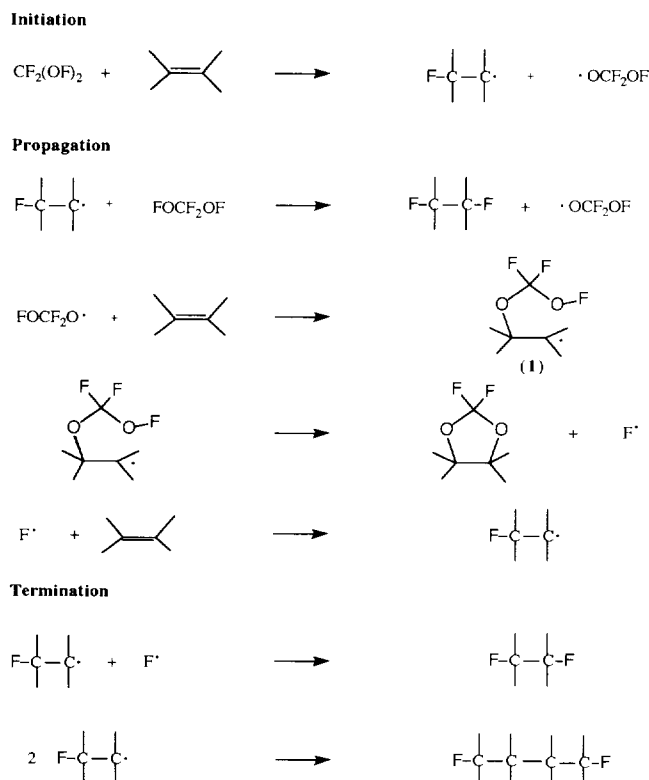
Termination

Scheme 2.

In our BDM/olefin system, the carbon-centred radical (**1**), the key intermediate to the formation of dioxolane rings, undergoes a fast intramolecular radical substitution to the oxygen atom accompanied by elimination of a fluorine radical to yield the observed dioxolanes.
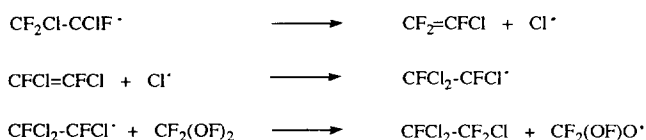
The radical nature of the intermediates involved in the reaction is supported by evidence of reaction inhibition when oxygen is present in the system: depending on the experimental conditions and the chosen olefin, the reaction may proceed to a more complex oligomeric and peroxidic structure [15]. We actually observed substantial inhibition of the reaction when N_2 containing 10% O_2 was used to dilute BDM during its addition to CFCl=CFCl in the same conditions as indicated in entry 5.

Perfluorocyclobutene, as other perfluorocyclo-olefins, does not react with BDM up to -30 °C; at room temperature, we observed extensive decomposition with perfluorocyclobutane as the main reaction product. Although perfluorocyclohexene and perfluorocyclopentene have been reported only to react with CF_3OF under UV light [16,17], perfluorocyclobutene reacts with CF_3OF at room temperature giving the simple addition product in good yield even in the absence of UV activation (see Experimental details). This behaviour represents a further difference between BDM and CF_3OF in their reaction with fluoro-olefins.

When the reaction between BDM and 1,2-dichlorodifluoroethylene was carried out in the presence of perfluorocyclobutene at -80 °C, the reaction proceeded smoothly and the products were perfluorocyclobutane, dioxolane and dichlorofluoroalkane, both of the latter deriving from 1,2-dichlorodifluoroethylene. This evidence indicates that the reaction proceeds through a free-radical chain mechanism. In fact, due to the considerable difference in reactivity between fluorine radicals and oxy radicals, the unreactive perfluorocyclobutene competes with the highly reactive 1,2-dichlorodifluoroethylene only in the fluorination step while the oxy radical reacts selectively with 1,2-dichlorodifluoroethylene to give the expected dioxolane.

Indirect evidence of a radical mechanism derives from an analysis of the by-products. When 1,2-dichlorodifluoroethylene was used, we always detected 1,1,2-trichlorotrifluoroethane in the final reaction mixture. On decreasing the reaction temperature to -100 °C and diluting BDM with an inert gas, the quantity of $CFCl_2CF_2Cl$ decreased to below 1%–2% of the overall products. In other words, with a better control of heat evolution we inhibited the formation of side-products deriving from β-scission of the carbon–chlorine bond of the radical intermediates (Scheme 3).

It has been recognized that the presence of 1,1,2-trichlorotrifluoroethane as a by-product in the addition of CF_3OF to 1,2-dichlorodifluoroethylene provides evidence of a free-radical pathway by analogy with the reaction of fluorine where the same by-products were isolated and explained via the same radical β-scission

$$CF_2Cl\text{-}CClF\cdot \longrightarrow CF_2{=}CFCl + Cl\cdot$$

$$CFCl{=}CFCl + Cl\cdot \longrightarrow CFCl_2\text{-}CFCl\cdot$$

$$CFCl_2\text{-}CFCl\cdot + CF_2(OF)_2 \longrightarrow CFCl_2\text{-}CF_2Cl + CF_2(OF)O\cdot$$

Scheme 3.

[1c]. The proposed mechanism also explains the stereochemical course of the reaction, which is independent of the cis/trans geometry of the starting olefin, as shown by the case of 1,2-dichloroethylene (Table 1, entries 10,11). Furthermore, in the case of 1,2-dichlorodifluoroethylene (1:1 cis/trans mixture), the two olefins were consumed at the same rate (as monitored by GLC) and the dioxolane obtained had a constant syn/anti ratio. From the above data, a concerted cycloaddition pathway is less likely than a step-by-step mechanism, where rotation of the radical intermediate can account for the isomeric end-product ratio.

A further mechanistic hypothesis can be envisaged where the difluorodioxirane is considered as a possible intermediate. However, it has been demonstrated that this compound reacts with fluoro-olefins as an epoxidating agent both in the condensed and gaseous phase [18]; although the oxy radical intermediate postulated in the dioxirane synthesis is $FOCF_2O\cdot$, we did not observe epoxidation of fluoro-olefins in the condensed-phase reaction with BDM. In contrast, in the gaseous phase, substantial epoxidation of perfluoropropene was observed. This could be ascribed to the formation of difluorodioxirane.

Warning: Although it has been found that $CF_2(OF)_2$ has a high thermal stability [6], safety precautions must be taken in handling BDM [8]. Because of its high energy content, high reactivity and oxidizing properties, fires and explosions can occur on contact with organic reagents. The thermal decomposition of BDM [6] proceeds mainly to carbonyl difluoride, fluorine and oxygen (Eq. (1)).

$$CF_2(OF)_2 \longrightarrow COF_2 + F_2 + 0.5O_2$$

$$\Delta H^\circ = -16.8 \text{ kcal mol}^{-1} \tag{1}$$
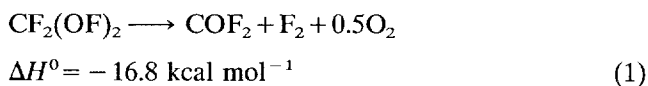
Explosive decomposition of BDM at a pressure of 100 Torr [8] gives a more complex product distribution including fluoroxytrifluoromethane, oxygen, perfluoromethylperoxide, carbonyl difluoride and carbon tetrafluoride in low quantity. The decomposition of BDM to carbon tetrafluoride and oxygen (Eq. (2)) exhibits the greatest enthalpy change relative to all the other possible decomposition reactions.

$$CF_2(OF)_2 \longrightarrow CF_4 + O_2$$

$$\Delta H^\circ = -85.6 \text{ kcal mol}^{-1} \tag{2}$$
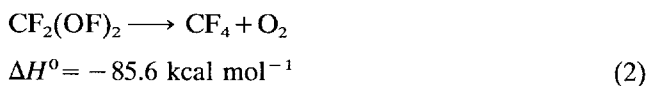
We have observed almost complete decomposition to carbon tetrafluoride and oxygen in a BDM sample autodecomposed by contact with unpassivated SS 316 at atmospheric pressure (different experimental conditions from those reported in the literature).

The above reported enthalpies were calculated from heats of formation available in the literature [8].

3. Experimental details

Volatile compounds were handled in glass and/or stainless-steel vacuum systems equipped with glass-PTFE or stainless-steel valves. Pressures were measured with a Druck PDCR 110/W differential pressure gauge. Amounts of gaseous reactants and products were measured from known volumes assuming ideal gas behaviour. ^{19}F NMR spectra and ^1H NMR spectra were recorded respectively on a Varian 200 MHz spectrometer and a Varian 300 MHz instrument with $CDCl_3$ as solvent and employing $CFCl_3$ or TMS as internal standards. GLC analyses were performed with a HRGC 5300 Carlo Erba instrument equipped with thermoconductivity detectors. IR spectra were recorded on a Perkin-Elmer 1600 series FT-IR instrument. GLC/MS spectra were performed on a Varian Mat CH7-A at 700 eV in the electron impact mode. All boiling points are uncorrected.

Bis(fluoroxy)difluoromethane was prepared according to standard methods described in the literature [6,19]. Fluorine was obtained from Prax Air and was passed through a sodium fluoride scrubber before use. Caesium fluoride was activated by melting in a platinum crucible followed by powdering in a ball mill under anhydrous conditions. Olefins and other chemicals were obtained from commercial sources and were purified appropriately as required.

3.1. Syntheses of 2,2-difluoro-1,3-dioxolanes

General procedure for the batch system

Reactions were carried out under the mildest possible conditions following literature procedures [4]. A stainless-steel passivated reactor was usually charged at liquid nitrogen temperature with 3.3 mmol of the olefin and approximately 15 mmol of solvent. The contents were then warmed to room temperature to obtain a homogeneous solution. Then, again at liquid nitrogen temperature, 1.5 mmol of $CF_2(OF)_2$ were condensed into the reactor. The reactor was then allowed to reach room temperature over a period of 24 h. The reaction mixture was then distilled in a trap-to-trap fashion using a conventional vacuum line equipped with glass-PTFE valves.

General procedure for the semi-continuous system

A glass reactor equipped with a mechanical stirrer, reflux condenser, thermocouple, inner plunging pipes,

maintained at the temperatures reported in Table 1, was charged with a 0.2–5 M solution (50–300 ml) of the olefin in $CFCl_3$, CF_2Cl_2 Galden® or with the pure olefin. A flow of bis(fluoroxy)difluoromethane (usually $1\ 1\ h^{-1}$ flow rate) diluted with He in a 1:5 ratio was then fed into the reactor until 90% of the olefin had been converted. At the end of the addition, helium was bubbled through the reaction mixture to remove traces of unreacted $CF_2(OF)_2$. The dioxolanes were isolated via fractional distillation using an HMS 500 C Spaltrohr Fischer apparatus.

General procedure for the continuous system

Bis(fluoroxy)difluoromethane at a flow rate of 0.4 l h^{-1}, diluted with He ($2\ 1\ h^{-1}$) and the olefin (36 mmol h^{-1}) were simultaneously but separately fed, at the temperatures shown in Table 1, into a multi-neck glass reactor containing a 10^{-1} to 10^{-2} M solution of the olefin and equipped with a magnetic entrainment mechanical stirrer, reflux cooler, thermocouple and inner plunging pipes. After feeding the reagents for 4 h, helium was bubbled through the reaction mixture to remove traces of unreacted $CF_2(OF)_2$. The reaction mixture was purified by fractional distillation.

Using one or other of the above procedures, the following olefins were reacted with the results indicated.

$CF_2=CFCF_3$: The reaction products were separated through traps cooled to -80, -100, -120 and -196 °C, respectively. Further distillation of the mixture collected at -120 °C through traps cooled to -105, -112, -120 and -196 °C, respectively, led to collection of the pure dioxolane in the -112 °C trap.

$CF_3{}^FCF^E-O-CF_2{}^{AB}-O-CF_2{}^{CD}$: ^{19}F NMR δ: AB = -54.5 ppm (1F, dm) and -58.3 ppm (1F, dm) AB pattern, $J_{A-B}=64$ Hz, $J_{A-C}=J_{B-D}=8$ Hz; CD = -81.7 ppm (1F, dm) and -86.5 ppm (1F, dd) AB pattern, $J_{C-D}=134$ Hz, $J_{C-E}=5$ Hz; E = -128.6 ppm (1F, m); F = -81.1 ppm (3F, m). MS m/z (rel. int.): 213 (M⁺ − F, 2.1); 147 ($C_3F_5O^+$, 8.4); 119 ($C_2F_5{}^+$, 41.6); 97 ($C_2F_3O^+$, 45.71); 69 ($CF_3{}^+$, 100).

$CF_2=CFOCF_2CF_3$: The products were separated through traps cooled to -50, -100, -120 and -196 °C, respectively. Further purification of the mixture collected at -100 °C through traps cooled to -60 and -100 °C, respectively, led to collection of the pure dioxolane in the -100 °C trap.

$CF_3{}^HCF_2{}^{FG}O-CF^E-O-CF_2{}^{AB}-O-CF_2{}^{CD}$: colourless liquid. ^{19}F NMR δ: AB = -56.2 ppm (1F, dd) and -57.4 ppm (1F, dt) AB pattern, $J_{A-B}=65$ Hz, $J_{A-C}=8$ Hz, $J_{B-C}=J_{B-D}=7.5$ Hz; CD = -83.4 ppm (1F, dm) and -88.9 ppm (1F, dm) AB pattern, $J_{C-D}=124$ Hz; E = -85.5 ppm (1F, m); H = -87.1 ppm (3F, s); FG = -87.9 ppm (1F, dm) and -89.3 ppm (1F, dm) AB pattern, $J_{F-G}=147$ Hz. MS m/z (rel. int.): 163 ($C_3F_5O_2{}^+$, 11.2); 135 ($C_2F_5O^+$, 3.3); 119 ($C_2F_5{}^+$, 100);

116 ($C_2F_4O^+$, 31.5); 97 ($C_2F_3O^+$, 51.3); 69 ($CF_3{}^+$, 78). IR (KCl) (cm⁻¹): 1248; 1209; 1153; 1103; 1023.

$CF_2=CHCF_3$: The products were separated through traps cooled to -50, -75, -90 and -196 °C, respectively. The pure dioxolane was collected in the trap cooled to -75 °C.

$CF_3{}^DCH-O-CF_2{}^A-O-CF_2{}^{BC}$: colourless liquid. ^{19}F NMR δ: A = -56 ppm (2F, s); BC = -67 ppm (1F, dd) and -84.3 ppm (1F, dq) AB pattern, $J_{B-C}=140$ Hz, $J_{C-D}=7$ Hz, $J_{C-H}=20$ Hz, C = -76.6 ppm (3F, dm). ^1H NMR δ: 5.03 ppm (m, 1H). MS m/z (rel. int.): 175 ($C_4F_5O_2{}^+$, 12.7); 167 ($C_3HF_6O^+$, 9.6); 148 ($C_3HF_5O^+$, 20.8); 145 (M⁺ − CF_3, 29.9); 129 ($C_3HF_4O^+$, 10.7), 101 ($C_2HF_4O^+$, 22.1); 69 ($CF_3{}^+$, 100). IR (KCl) (cm⁻¹): 2992; 1396; 1327; 1252; 1213; 1128.

$CF_3CF=CFCF_3$: The products were separated through traps cooled to -95, -105 and -196 °C, respectively. A 46:54 mixture of the *syn/anti* dioxolanes was collected in the trap cooled at -95 °C.

$CF_3{}^FCF^D-O-CF_2{}^{AB}-O-CF^CCF_3{}^E$: colourless liquid. ^{19}F NMR δ: *syn* Isomer: AB = -52.1 ppm (1F, d) and -60.6 ppm (1F, dt) AB pattern, $J_{A-B}=64$ Hz, $J_{A-C}=7$Hz; E = F = -80.3 ppm (6F, s); C = D = -127.1 ppm (2F, d). *anti* Isomer: A = B = -55.5 ppm (2F, t), $J_{A-C}=J_{B-D}=5$ Hz; E = F = -80.3 ppm (6F, d), $J_{E-D}=J_{F-C}=13$ Hz; C = D = -128.3 ppm (2F, tm). MS m/z (rel. int.): 263 (M⁺ − F, 24.5); 213 (M⁺ − CF_3, 12.1); 197 ($C_4F_7O^+$, 18.1); 166 ($C_3F_6O^+$, 16.8); 147 ($C_3F_5O^+$, 26.5); 131 ($C_3F_5{}^+$, 6.7); 119 ($C_2F_5{}^+$, 100); 100 ($C_2F_4{}^+$, 38.9); 97 ($C_2F_3O^+$, 92.6); 69 ($CF_3{}^+$, 96).

$CFCl=CFCl$ (1:1 mixture of *cis/trans* isomers): The reaction was undertaken under a variety of conditions to investigate the influence of temperature and dilution on the product ratio. The obtained dioxolane was always a 78:22 mixture of the *anti/syn* isomers.

$CF^CCl-O-CF_2{}^{AB}-O-CF^CCl$: colourless liquid, b.p. 47 °C. ^{19}F NMR δ: *syn* Isomer: AB = -54.1 ppm (1F, d) and -58 ppm (1F, dt) AB pattern, $J_{A-B}=68$ Hz, $J_{B-C}=9$ Hz; C = -69.9 ppm (2F, d). *anti* Isomer: A = B = -55.5 ppm (2F, t), $J_{A-C}=4.7$ Hz; C = 57.8 ppm (2F, t). MS m/z (rel. int.): 179 ((M⁺ − Cl, 30.3); 132/134 ($C_2ClF_3O^+$, 33.9/13.2); 113/115 ($C_2ClF_2O^+$, 100/57.8); 85/87 ($CClF_2{}^+$, 63.7/23.8); 68 ($CF_3{}^+$, 26.6), IR (KCl) (cm⁻¹); 1305; 1214; 1089; 1013; 945; 901; 747. Analysis: Calc. for $C_3Cl_2F_4O_2$: C, 16.77; F, 35.36%. Found: C, 16.69; F, 35.29%.

trans-CFBr=CFBr: The reaction mixture was purified by fractional distillation and the fraction boiling at 81 °C was a 1:9 mixture of *syn/anti*-perfluoro-4,5-dibromo-1,3-dioxolane.

$CF^CBr-O-CF_2{}^{AB}-O-CF^CBr$: colourless liquid. ^{19}F NMR δ: *syn* Isomer: AB = -54.2 ppm (1F, d) and -59.5 ppm (1F, dt) AB pattern, $J_{A-B}=67$ Hz, $J_{B-C}=9$ Hz; C = -66.4 ppm (2F, d). *anti* Isomer: A = B = -56 ppm (2F, t), $J_{A-C}=4.7$ Hz; C = -50.3 ppm (2F, t). MS m/z (rel. int.): 236/238/240 (M⁺ − 66, 1.27/2.7/1.2); 223/225 (M⁺ − Br, 30.1/30); 189/191/193 (CBr_2F^+, 5.6/11.2/5.5); 157/159 ($C_2BrF_2O^+$, 100/99); 129/131 ($CBrF_2{}^+$,

42.3/42.5); 110/112 (CBrF$^+$, 17.8/17.6); 91/93 (CBr$^+$, 2.5/2.3). IR (KCl) (cm^{-1}): 1294; 1200; 1105; 1040; 914; 887. Analysis: Calc. for C$_3$Br$_2$F$_4$O$_2$: C, 11.86; F, 25.01%. Found: C, 11.81; F, 25.13%.

CCl$_2$=CCl$_2$: The reaction mixture was purified by fractional distillation. The fraction having a boiling point of 80 °C at 280 mm Hg was the pure dioxolane.

CCl$_2$–O–CF$_2^A$–O–CCl$_2$: colourless liquid, b.p. 80 °C/280 mmHg. ^{19}F NMR δ: A = –56.5 ppm (2F, s). MS m/z (rel. int.): 211/213/215 (M$^+$ –Cl, 25.5/25/9); 145/147/149 (C$_2$Cl$_3$O$^+$, 83.3/81.3/31.1); 117/119/121 (CCl$_3^+$, 81.7/79/30.8); 82/84 (CCl$_2^+$, 100/70). IR (KCl) (cm^{-1}): 1260; 1213; 1189; 1174; 1074; 1053; 1027; 921; 766. Analysis: Calc. for C$_3$F$_2$Cl$_4$O$_2$: C, 14.54; F, 15.33%. Found: C, 14.53; F, 14.22%.

CHCl=CCl$_2$: The reaction products were purified by fractional distillation.

CHCl–O–CF$_2^{AB}$–O–CCl$_2$: colourless liquid, b.p. 34 °C/80 mbar. ^{19}F NMR δ: AB = –53.5 ppm (1F, dd) and –57.7 ppm (1F, d), AB pattern, J_{A-B} = 74 Hz, J_{A-H} = 5 Hz. ^{1}H NMR δ: 6.5 ppm (1H, d). MS m/z (rel. int.): 177/179/181 (M$^+$ –Cl, 23.9/16.2/2.3); 149/151/153 (C$_2$HCl$_2$F$_2$O, 9.2/5.8/0.8); 114/116 (C$_2$HClF$_2$O$^+$, 57/20); 83/85 (CHCl$_2^+$, 100/72); 82/84 (CCl$_2^+$, 28/20); 48 (31.8). IR (KCl) (cm^{-1}): 3041; 1315; 1282; 1245; 1195; 1152; 1084; 1034; 889. Analysis: Calc. for C$_3$HCl$_3$F$_2$O$_2$: C, 16.89; H, 0.47; F, 17.81%. Found: C, 16.75; H, 0.43, F, 17.88%.

CHCl=CHCl: The reaction mixture was purified by fractional distillation.

CHCl–O–CF$_2^{AB}$–O–CHCl: colourless liquid, b.p. 100 °C. ^{19}F NMR δ: syn Isomer: AB = –55.3 ppm (1F, dt) and –58.8 ppm (1F, d) AB pattern, J_{A-B} = 81 Hz, J_{A-H} = 3 Hz. anti Isomer: A = B = –55.5 ppm (2F, t), J_{A-H} = J_{B-H} = 5 Hz. ^{1}H NMR δ: syn Isomer: 6.4 ppm (2H, d). anti Isomer: 6.29 ppm (2H, t). MS m/z (rel. int.): 178/180 (M$^+$, 1.2/0.8); 143/145 (M$^+$ –Cl, 85/31.9); 114/116 (C$_2$HClF$_2$O$^+$, 100/36.9); 77 (35.3). IR (KCl) (cm^{-1}): 3043; 1341; 1290; 1240; 1181; 1099; 1038; 974; 839. Analysis: Calc. for C$_3$H$_2$Cl$_2$F$_2$O$_2$: C, 20.14; H, 1.13; F, 21.23%. Found: C, 19.95; H, 1.26; F, 21.15%.

CH$_2$=CHCl: The products of the reaction were separated through traps cooled to –40, –80, –120 and –196 °C, respectively. The pure dioxolane was obtained through preparative GLC of the contents of the –80 °C trap.

CH$_2^{DE}$–O–CF$_2^{AB}$–O–CH^{C}Cl: colourless liquid. ^{19}F NMR δ: AB = –58.1 ppm (1F, dt) and –58.7 ppm (1F, dd) AB pattern, J_{A-B} = 88 Hz, J_{A-C} = J_{A-D} = 4 Hz, J_{B-E} = 3Hz. ^{1}H NMR δ: C = 6.32 ppm (1H, t), J_{C-D} = J_{C-A} = 4 Hz; DE = 4.7 ppm (1H, dt) and 4.5 ppm (1H, dd) AB pattern, J_{D-E} = 11 Hz. MS m/z (rel. int.): 109 (M$^+$ –Cl, 87.7); 80 (C$_2$H$_2$F$_2$O$^+$, 100); 61/63 (C$_2$H$_2$Cl$^+$, 12.8/5.5); 43 (C$_2$H$_3$O$^+$, 59.2).

CF$_2$=CFCl: The products of the reaction were separated through traps cooled to –40, –80, –120 and –196 °C, respectively. The pure dioxolane was collected in the trap cooled to –80 °C.

CF$_2^{DE}$–O–CF$_2^{AB}$–O–CF^{C}Cl: colourless liquid. ^{19}F NMR δ: AB = –55.6 ppm (1F, dd) and –58 ppm (1F, dt) AB pattern, J_{A-B} = 72 Hz, J_{A-C} = J_{B-C} = 5.8 Hz; C = –69.9 ppm (1F, m); DE = –76 ppm (1F, dm) and –90.8 ppm (1F, dm) AB pattern, J_{D-E} = 120 Hz. MS m/z (rel. int.): 179 (M$^+$ –F, 1); 163 (M$^+$ –Cl, 92); 132/134 (C$_2$ClF$_3$O$^+$, 38/12.1); 116 (C$_2$F$_4$O$^+$, 68), 97 (C$_2$F$_3$O$^+$, 100); 69 (CF$_3^+$, 86); 66/68 (CClF$^+$, 82/26.9).

(CF$_3$)$_2$CFCF=CFCF$_3$: The reaction was carried out following the general procedure for the semi-continuous system with irradiation by a TQ 125 W high-pressure mercury lamp, located in a quartz double-walled refrigerated jacket, immersed in the middle of the reactor.

CF$_3^E$CF^D–O–CF$_2^{AB}$–O–CF^C–CF^F(CF$_3$)$_2^G$: colourless liquid, b.p. 82 °C. ^{19}F NMR δ: (only anti isomer in two rotational conformations): AB = –56.2 ppm (dd) and –58.6 ppm (dd) AB pattern, J_{A-B} = 67 Hz, J_{A-C} = J_{B-D} = 8 Hz; C = –117.9 ppm (m); D = –126.4 ppm (m); E = –81.4 ppm (dd, 3F), J_{E-C} = 20 Hz, J_{E-F} = 9 Hz; F = –186.4 ppm and –186.6 ppm (both multiplet); G = –73.7 ppm and –74.7 ppm (both multiplet). MS m/z (rel. int.): 363 (M$^+$ –F, 59.1); 297 (C$_6$F$_{11}$O$^+$, 74.7); 219 (C$_4$F$_9^+$, 76.6); 181 (C$_4$F$_7^+$, 63.4); 147 (C$_3$F$_5$O$^+$, 76.6); 119 (C$_2$F$_5^+$, 77.7); 69 (CF$_3^+$, 100). IR (KCl) (cm^{-1}): 1256; 1212; 1156; 1090; 1018; 982. Analysis: Calc. for C$_7$F$_{14}$O$_2$: C, 22.01; F, 69.62%. Found: C, 22.13; F, 69.58%.

CF$_2$=CFBr: The products were separated through traps cooled to –40, –75, –120 and –196 °C, respectively. The pure dioxolane was obtained by preparative GLC of the contents of the –75 °C trap.

CF$_2^{DE}$–O–CF$_2^{AB}$–O–CF^{C}Br: colourless liquid. ^{19}F NMR δ: AB = –55.3 ppm (1F, dd) and –58.2 ppm (1F, dt) AB pattern, J_{A-B} = 67 Hz, J_{A-C} = J_{A-D} = J_{B-E} = 9 Hz; C = –63.7 ppm (1F, m); DE = –72.1 ppm (1F dt) and –91 ppm (1F, dt) AB pattern, J_{D-E} = 125 Hz. MS m/z (rel. int.): 163 (M$^+$ –Br, 100); 135 (C$_2$F$_5$O$^+$, 2.2); 129/131 (CBrF$_2^+$, 11.4/10.4); 110/112 (CBrF$^+$, 12.3/10.8); 97 (C$_2$F$_3$O$^+$, 63.4); 69 (CF$_3^+$, 48.7).

CF$_2$=CF$_2$: The products were distilled from the solvent and collected in a –78 °C trap. The contents of the –78 °C were distilled in a trap-to-trap fashion through traps cooled to –110 –130 and –196 °C, respectively. The dioxolane collected in the –130 °C trap.

CF$_2^B$–O–CF$_2^A$–O–CF$_2^B$: ^{19}F NMR δ: A = –57.7 ppm (2F, quintet); B = –88 ppm (4F, t). MS m/z (rel. int.): 163 (M$^+$ –F, 1); 119 (C$_2$F$_5^+$, 11); 116 (C$_2$F$_4$O$^+$, 17); 97 (C$_2$F$_3$O$^+$, 15); 69 (CF$_3^+$, 22). IR (KCl) (cm^{-1}): 1265; 1205; 1029; 975.

3.2. Reaction of CF$_3$OF with perfluorocyclobutene

The reaction was carried out following the general procedure for the batch system. The reaction mixture

was separated through traps cooled to -80, -97, -105 and -196 °C, respectively. The perfluoromethoxycyclobutane collected in the -97 °C trap.

$CF_3{}^A O-CF^B-CF_2{}^{CD}-CF_2{}^{CD}-CF_2{}^E$: ^{19}F NMR δ: $A = -56.9$ ppm (3F, s); $B = -141.8$ ppm (1F, s); $CD = -130.8$ ppm (2F, d) and -133.7 ppm (2F, d) AB pattern, $J_{C-D} = 230$ Hz, $E = -131.4$ ppm (2F, s). MS m/z (rel. int.): 247 ($M^+ - F$, 0.9); 181 ($M^+ - OCF_3$, 8.5); 150 ($C_3F_6{}^+$, 9.1); 131 ($C_3F_5{}^+$, 50.8); 100 ($C_2F_4{}^+$, 17.6); 69 ($CF_3{}^+$, 100).

Acknowledgements

References

[1] (a) F.M. Mukhametshin, *Russ. Chem. Rev.*, *49* (1980) 668; (b) J.M. Shreeve, *Adv. Inorg. Chem. Radiochem.*, *26* (1983) 119; (c) F.M. Mukhametshin, in L. German and S. Zemskov (eds.), *New Fluorinating Agents in Organic Synthesis*, Springer-Verlag, Berlin, 1989, p. 69, and literature reported therein.

[2] J.A.C. Alison and G.H. Cady, *J. Am. Chem. Soc.*, *81* (1959) 1089.

[3] D.H.R. Barton, L.S. Godinho, R.H. Hesse and M.M. Pechet, *Chem. Commun.*, (1968) 804.

[4] K.K. Johri and D.D. DesMarteau, *J. Org. Chem.*, *48* (1983) 242.

[5] M. dos Santos Afonso and H.J. Schumacher, *Int. J. Chem. Kinet.*, *16* (1984) 103.

[6] (a) R.L. Cauble and G.H. Cady, *J. Am. Chem. Soc.*, *89* (1967) 1962; (b) F.A. Hohorst and J.M. Shreeve, *J. Am. Chem. Soc.*, *89* (1967) 1809; (c) P.G. Thompson, *J. Am. Chem. Soc.*, *89* (1967) 1811.

[7] F.A. Hohorst and J.M. Shreeve, *Inorg. Chem.*, *7* (1968) 624.

[8] G.D. Foss and D.A. Pitt, *J. Phys. Chem.*, *72* (1968) 3512.

[9] M.S. Toy and R.S. Stringham, *J. Fluorine Chem.*, *12* (1978) 23.

[10] (a) R.D. Bagnal, W. Bell, K. Person and A. Jeater, *J. Fluorine Chem.*, *13* (1979) 123; (b) G.L. Moore and R.C. Terrell, US Patent 4 017 519, 1977.

[11] (a) Ming-H. Hung, *Macromolecules*, *26* (1993) 5829; (b) E.N. Squire, US Patent 4 399 264, 1983; (c) P.R. Resnick, US Patent 3 978 030, 1976.

[12] (a) W. Navarrini, S. Fontana and V. Montanari, US Patent 5 225 576, 1993; (b) W. Navarrini and S. Fontana, US Patent 5 296 617, 1994.

[13] (a) A.J. Bloodworth, A.G. Davies, I.M. Griffin, B. Muggleton and B.P. Roberts, *J. Am. Chem. Soc.*, *96* (1974) 7599; (b) A.L.J. Beckwith and K.U. Ingold, in *Rearrangements in Ground and Excited States*, Academic Press, New York, 1980, Vol. 1, p. 161, and literature reported therein.

[14] D. Sianesi, A. Pasetti, R. Fontanelli, G.C. Bernardi and G. Caporiccio, *Chim. Ind. Milan*, *55* (1973) 208.

[15] D. Sianesi, A. Marraccini and G. Marchionni, US Patent 5 258 110, 1993.

[16] R.S. Porter and G.H. Cady, *J. Am. Chem. Soc.*, *79* (1957) 5625.

[17] M.S. Toy and R.S. Stringham, *J. Fluorine Chem.*, *5* (1975) 481.

[18] A. Russo and D.D. DesMarteau, *Angew. Chem., Int. Ed. Engl.*, *32* (1993) 905.

[19] M.J. Fifolt, US Patent 4 499 024, 1985.