ELSEVIER

Journal of Fluorine Chemistry 113 (2002) 55–63

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Unexpected selective monoadduct formation from 2-methyl-3-butyn-2-ol and α,ω-diiodoperfluorobutane

Claire Amato, Cathy Naud, Patrick Calas, Auguste Commeyras*

Laboratoire Organisation Moléculaire, Evolution et Matériaux Fluorés, UMR CNRS 5073, Université de Montpellier II,
F. 34095 Montpellier Cedex 05, France

Received 27 November 2000; accepted 24 July 2001

Abstract

Radical chain addition of α,ω-diiodoperfluorobutane to 2-methyl-3-buten-2-ol and 2-methyl-3-butyn-2-ol has been studied. The Huang sulfinatodehalogenation system, used as initiator, gave satisfactory conversion yields of the starting diiodide when compared to more classical initiators (AIBN, Fe, triethylborane). Addition to the alkenol yields classically the bis-adduct with variable amounts of the monoadduct. On the contrary the alkynol leads exclusively to the monoadduct formation, in high yield. Some considerations are proposed for interpreting this result. The monoadduct selectively obtained constitutes a powerful intermediate for synthesis. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: α,ω-Diiodoperfluorobutane; Monoadduct; Bis-adduct; Alkynol; Alkenol; Radical initiation

1. Introduction

Classically F-*n*-alkyl iodides add to alkenes and alkynes, preferably terminal ones, through a radical chain process [1]. A very large number of initiators have been used to perform such a reaction ([2] and references therein). In the case of α,ω-diiodoperfluoroalkanes I–$(CF_2)_n$–I similar reactions have been studied. However, the initiators used are more restricted: dibenzoyl [3] or di-terbutyl peroxides [4], metal carbonyl [5], cuprous halides [6], and sometimes thermal processes [7]. Various kinds of ethylenic compounds have been used as substrates yielding generally to the simultaneous formation of monoadducts and bis-adducts [6,7] or exclusively bis-adducts [5]. In the field of acetylenic substrates [4], the bis-adduct is observed for $n = 8, 10, 12$. For $n = 6$, the monoadduct or the bis-adduct can be obtained by varying the reaction time. A very complex mixture is observed for $n = 4$ and the monoadduct dominates for $n = 2$. Thus, these results are linked with drastic reaction conditions. We have investigated the addition of α,ω-diiodoperfluorobutane I–$(CF_2)_4$–I to 2-methyl-3-buten-2-ol and to 2-methyl-3-butyn-2-ol, chosen for future developments in synthesis [8–10]. We have withdrawn the use of peroxides as initiators as they are considered as drastic conditions and literature data exhibits poor selectivity towards monoadduct formation or complex results for ethylenic as well as for acetylenic substrates [4]. In our hands classical initiators (AIBN [11], Fe [12], triethylborane [13]) gave poor conversion yields (10–15% of the starting dihalide) contrary to the case of F-alkyl iodides F–$(CF_2)_n$–I. Thus, in recent work [14], the addition of α,ω-diiodoperfluorohexane to allyl alcohol has been performed in good yield using three successive additions of AIBN. We have found advantage in the use of the Huang system [15] which appeared as highly efficient and operates in very mild conditions. Generally used to perform sulfinatodehalogenation of F-alkyl iodides [16] and also of α,ω-diiodoperfluoroalkanes [17]. It is generally described as using stoichiometric amounts of halide and a $Na_2S_2O_4$/$NaHCO_3$ reagent system in a biphase CH_3CN/H_2O medium. When applied to α,ω-diiodoperfluoroalkane I–$(CF_2)_n$–I with a molar ratio diiodide/dithionite 1/2, perfluoroalkane-α,ω-bis-sulfinates are produced in good yield for $n = 3, 4, 6$ and readily converted to bis-sulfonyl chlorides. When using a ratio diiodide/dithionite 1/1, ω-iodoperfluoroalkanesulfinates are produced in poor yield (same *n* values) and easily converted to ω-iodoperfluoroalkanesulfonyl chlorides (Scheme 1) [17]. Thus, this system has also been used as initiator to perform addition of F-alkyl iodides to ethylenic [18,19], and to acetylenic compounds

---

* Corresponding author. Tel.: +33-4-67-14-48-37;
fax: +33-4-67-63-10-46.
E-mail address: patrick.calas@univ-montp2.fr (A. Commeyras).

PII: S0022-1139(01)00464-X

SULFINATODEHALOGENATION : overall reaction

$$R_FI + S_2O_4Na_2 \longrightarrow R_FSO_2Na + NaI + SO_2$$

$$IR_FI + 2\ S_2O_4Na_2 \longrightarrow NaSO_2R_FSO_2Na + 2\ NaI + 2\ S$$

$$IR_FI + S_2O_4Na_2 \longrightarrow IR_FSO_2Na + NaI + SO_2$$

SULFINATODEHALOGENATION : mechanism

$$S_2O_4^{2-} \rightleftharpoons 2\,SO_2^{-\bullet}$$

$$R_FI + SO_2^{-\bullet} \longrightarrow \boxed{R_F^{\bullet}} + SO_2 + I^-$$

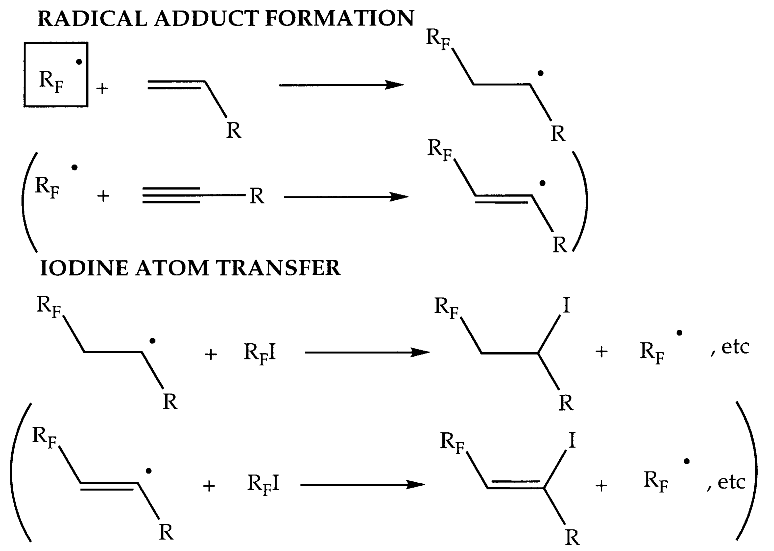
$$R_F^{\bullet} + SO_2^{-\bullet} \longrightarrow R_FSO_2^-$$

$$\text{or}\quad R_F^{\bullet} + S_2O_4^{2-} \longrightarrow R_FSO_2^- + SO_2^{-\bullet}$$

Scheme 1. Sulfinatodehalogenation of R_FI and IR_FI. Mechanism proposed for R_FI.

[19]. Effectively in the reaction mechanism postulated by Huang, F-alkyl radicals appear as transient species (Scheme 1) and in the presence of an unsaturated compound are able to initiate the classical radical chain reaction resulting in the addition compound (Scheme 2). In this way, the sulfinatodehalogenation reaction is completely suppressed to the advantage of the radical chain process. Similarly addition of diethyl iododifluoromethylphosphonate to acetylenic substrates went to completion in the presence of dithionite [20]. The addition of difluorodiiodomethane to ethylenic substrates [21] has been reported. In the case of dibromodifluoromethane, the Huang system is able to perform radical chain addition to olefins, even internal ones [22].

In order to evaluate the ability of the system to produce monoadduct or bis-adduct, we have conducted experiments varying the molar ratio diiodide/alkenol or alkynol and the relative amount of sodium dithionite/diiodide. Indeed when the Huang system is used as an initiator it appears of interest to test the efficiency of a low initiator molar ratio, particularly in order to limit sulfinate formation and possible further reaction of the initially formed monoadduct. Unexpectedly, we observed that although monoadduct and bis-adduct are obtained in the case of the alkenol, on the contrary monoadduct is selectively formed with the alkynol, satisfactory yields being noted in the two cases. Results are reported and discussed in the following section.



Scheme 2. Propagation steps occuring in the radical chain addition of R_FI ($F–(CF_2)_n–I$) to an alkene or an alkyne (in brackets).

Table 1
Product distribution when reacting α,ω-diiodoperfluorobutane with 2-methyl-3-buten-2-ol in the presence of various amounts of the sodium dithionite/sodium bicarbonate system in acetonitrile/water, at room temperature

Entry[a]	1	2	3	4
α,ω-Diiodoperfluorobutane (eq.)	1	1	1	1
2-Methyl-3-buten-2-ol (eq.)	2.4	1	1	0.5
Initiator ($Na_2S_2O_4$/$NaHCO_3$) (eq.)	1	1	0.2	0.2
Monoadduct (mol%)[b]	0	28	57	47
Bis-adduct (mol%)[b]	95	36	27	12
By-product (mol%)[b,c]	5	21	2	2
Remaining diiodide (mol%)[b]	0	15	14	39
Isolated yield (%)[d]	97	89	85	86

[a] Experiments on 0.02 mol of 1,4-diiodoperfluorobutane.

[b] On the basis of the ^{19}F NMR spectrum, see Section 5.

[c] Fluorinated compounds present in the NMR spectrum, partly in the organic phase and partly in the aqueous one, corresponding to mono or bis sulfinates and other compounds (see text and next footnote 'd').

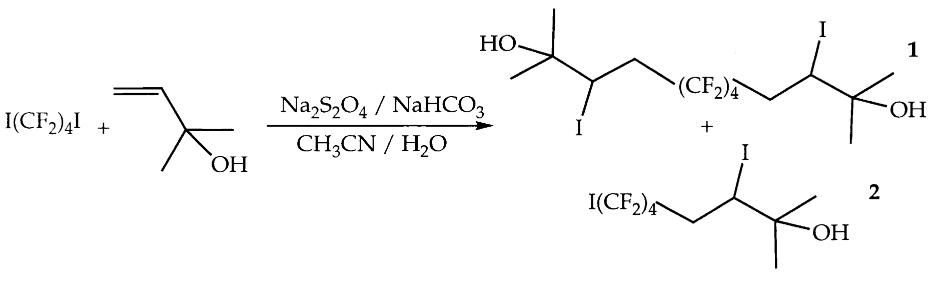
[d] For entries 1,3,4 (low by-product amounts): isolated yield = mass obtained after extraction/mass expected, this latter being calculated on the basis of the ^{19}F NMR repartition in remaining diiodide, mono and bis-adduct and the initial diiodide mass. For entry 2 by-products whose formulae are unknown are significant. Thus, the yield is deduced from the determination of the $(CF_2)_4$ chains recovered relatively to the ones introduced, on the basis of ^{19}F NMR comparison with a known amount of CF_3CH_2OH.

2. Results

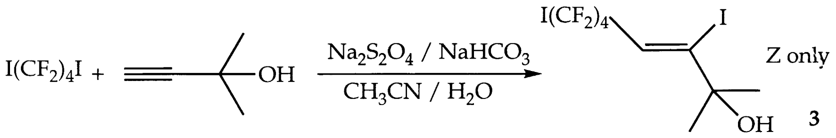
2.1. Formation of mono and bis-adduct from α,ω-diiodoperfluorobutane I–$(CF_2)_4$–I and 2-methyl-3-buten-2-ol

Results are summarised in Table 1. When used in a classical manner (Table 1, entry 1) with a molar ratio diiodide/dithionite 1 eq./1 eq. (similar result with 1 eq./2 eq.) and a relative excess of alkenol (2.4 eq.) a complete conversion of the diiodide is observed with a high yield of bis-adduct and only 5% of unknown fluorinated by-product. When limiting the alkenol amount to 1 eq. (Table 1, entry 2), in order to favour monoadduct formation, we observe, in spite of an acceptable conversion yield of the starting diiodide, that mono and bis-adduct are produced in similar amounts and that unidentified fluorinated compounds are formed significantly (21%). These exhibit signals in the ^{19}F NMR spectrum in the range −120 to −140 ppm and can be considered as compounds deriving from a sulfinatation of the monoadduct. However, they have not been completely identified. It seems reasonable to consider that the molar ratio between the diiodide and the alkene is favourable (Table 1, entry 2) to the monoadduct formation, but a too high concentration for the dithionite probably acts as a reactant towards the initially formed monoadduct. Consequently, experiments with a molar ratio diiodide/alkene favourable to the monoadduct formation (1 eq./1 eq.), but using a lower dithionite/diiodide ratio (0.2 eq./1 eq.) have been conducted (Table 1, entry 3). Then the conversion yield is acceptable, the yield in bis-adduct relatively unchanged, but the yield in monoadduct is remarkably increased (57%) with a drastic limitation of the formation of by-product. So these by-products again appear as possibly resulting from the action of the dithionite in excess on the monoadduct formed initially in a radical chain process in which the dithionite was acting as an initiator. However, if the lowering of by-product yield is satisfactory, we have to note that the monoadduct is not formed specifically, the yield in bis-adduct remaining significant. Looking for conditions favouring the selective formation of monoadduct, even at the price of an incomplete conversion of the starting diiodide, we have conducted experiments (Table 1, entry 4) with a ratio diiodide/alkene 1 eq./0.5 eq. In these conditions, the conversion yield falls dramatically, both monoadduct and bis-adduct are present even if the mono appears favoured relatively to the preceding conditions.

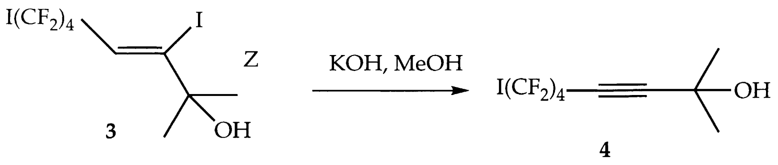
So when reacting α,ω-diiodoperfluorobutane with 2-methyl-3-buten-2-ol in the presence of various amounts of the sodium dithionite/sodium bicarbonate system in acetonitrile/water at room temperature, high yield selective formation of the bis-adduct is possible. The monoadduct can be obtained in a relatively significant yield, but only as a mixture with the bis-adduct. A low dithionite/diiodide ratio has to be used in order to limit by-product formation. We outline the fact (Table 1, entry 1) that the radical addition chain process largely overcomes the sulfinatodehalogenation reaction. In this entry, 1 eq. of dithionite is used (same result with 2 eq.). In these conditions, but in the absence of the alkenol mono or bis sulfinates (1 or 2 eq. of dithionite) are formed, as reported by Qiu and Burton [17] (a result we have verified with perfect accordance) (Scheme 3).



Scheme 3. Addition of the diiodide I–$(CF_2)_4$–I to 2-methyl-3-buten-2-ol, initiated by the Huang system.



Scheme 4. Selective monoadduct formation in the addition of the diiodide I–$(CF_2)_4$–I to 2-methyl-3-butyn-2-ol, initiated by the Huang system.



Scheme 5. Formation of the 2-methyl-4-(4-iodo-F-butyl)-but-3-yn-2-ol.

2.2. Selective formation of monoadduct from α,ω-diiodoperfluorobutane I–$(CF_2)_4$–I and 2-methyl-3-butyn-2-ol

Results are summarised in Table 2.

An experiment with a stoichiometry 1 eq./4.8 eq. for diiodide/alkynol and 1 eq./0.2 eq. for diiodide/dithionite (Table 2, entry 1), results in the total absence of the expected bis-adduct, monoadduct being formed in good yield. The amount of unreacted diiodide is significant (51%), by-product are not observed. Increasing the diiodide/dithionite ratio to 1 eq./0.5 eq. (Table 2, entry 2) results in a much better conversion of the diiodide (5% remaining), the monoadduct being formed in high yield. The bis-adduct is again absent and a given percentage of by-product is noted. A lowering of the alkynol excess (Table 2, entry 3) leads to similar results. An increase of the initiator ratio of diiodide/dithionite to 1 eq./1 eq. (Table 2, entry 4), results in increased by-product formation. Experiment with a stoichiometry 1 eq./2.4 eq. for diiodide/alkynol and 1 eq./2 eq. for diiodide/dithionite (Table 2, entry 5) results in a limited yield of monoadduct, unidentified by-product being dominant. By products, on the basis of the ^{19}F NMR spectra are always the same in Table 2 entry 2–5, only varying in relative abundance. They correspond to extremely complex signals in the ^{19}F NMR spectra (>50 signals between 103 and 139 ppm per CCl_3F). We have been unable to identify them clearly. It is possible that they correspond to oligomers, perhaps polysulfones (see Section 5).

Table 2
Product distribution when reacting α,ω-diiodoperfluorobutane with 2-methyl-3-butyn-2-ol in the presence of various amounts of the sodium dithionite/sodium bicarbonate system in acetonitrile/water, at room temperature

Entry[a]	1[a,b]	2	3	4	5
α,ω-Diiodoperfluorobutane (eq.)	1	1	1	1	1
2-Methyl-3-butyn-2-ol (eq.)	4.8	4.8	2.4	2.4	2.4
Initiator ($Na_2S_2O_4$/$NaHCO_3$) (eq.)	0.2	0.5	0.5	1	2
Monoadduct (mol%)[c]	49	77	74	58	14
Bis-adduct (mol%)[c]	0	0	0	0	0
By-product (mol%)[c,d]	0	18	18	39	86
Remaining diiodide (mol%)[c]	51	5	8	3	0
Isolated yield (%)[e]	92	86	88	85	91

[a] Experiments on 0.02 mol of 1,4-diiodoperfluorobutane.

[b] For entry 1, a more precise mass balance has been deduced from a large scale experiment starting from 30 g (0.066 mol, 12 ml) of diiodide (see Section 5.3).

[c] On the basis of the NMR spectrum, see Section 5.

[d] Fluorinated compounds present in the NMR spectrum, partly in the organic phase and partly in the aqueous one, corresponding to unidentified compounds (see text).

[e] For entry 1: isolated yield = mass obtained after extraction/mass expected, this latter being calculated on the basis of the ^{19}F NMR repartition in remaining diiodide, mono and bis-adduct and the initial diiodide mass, see also above footnote 'b'. For entry 2–5, by-product whose formulae are unknown are significant or dominating. Thus, the yield is deduced from the determination of the $(CF_2)_4$ chains recovered, on the basis of ^{19}F NMR comparison with a known amount of CF_3CH_2OH.

So when reacting α,ω-diiodoperfluorobutane with 2-methyl-3-butyn-2-ol in the presence of the sodium dithionite/sodium bicarbonate system in acetonitrile/water at room temperature, the bis-adduct has never been observed and it has been possible to define conditions where the monoadduct is obtained free of by-product and in good yield. A complete mass balance relative to a large scale experiment as Table 2, entry 1 is reported in the Section 5, including unreacted diiodide recovery.

2.3. H,I trans-elimination on the 3-iodo-2-methyl-4-(4-iodo-F-butyl)-but-3-en-2-ol

The vinyl iodide (compound **3**, Scheme 4) monoadduct, selectively obtained and only in the *Z* form[1] when reacting the diiodide and the alkynol is readily converted into the corresponding acetylenic compound (see Section 5). This compound obtained in good yield and in the pure state constitutes a powerful synthon for synthesis [8–10] Scheme 5.

---

[1] F–$(CF_2)_n$–I adds to alkynols H–C≡C–CR_1R_2OH yielding F–$(CF_2)_n$–CH=CI–CR_1R_2OH only in the *Z* form for $R_1 = CH_3$ and $R_2 = CH_3$ or C_2H_5, but yields $E/Z \sim 2$ for R_1 = H and R_2 = H, CH_3 or C_2H_5. See for example [8–10]. IH transelimination in a basic medium is possible only on the *Z* form.

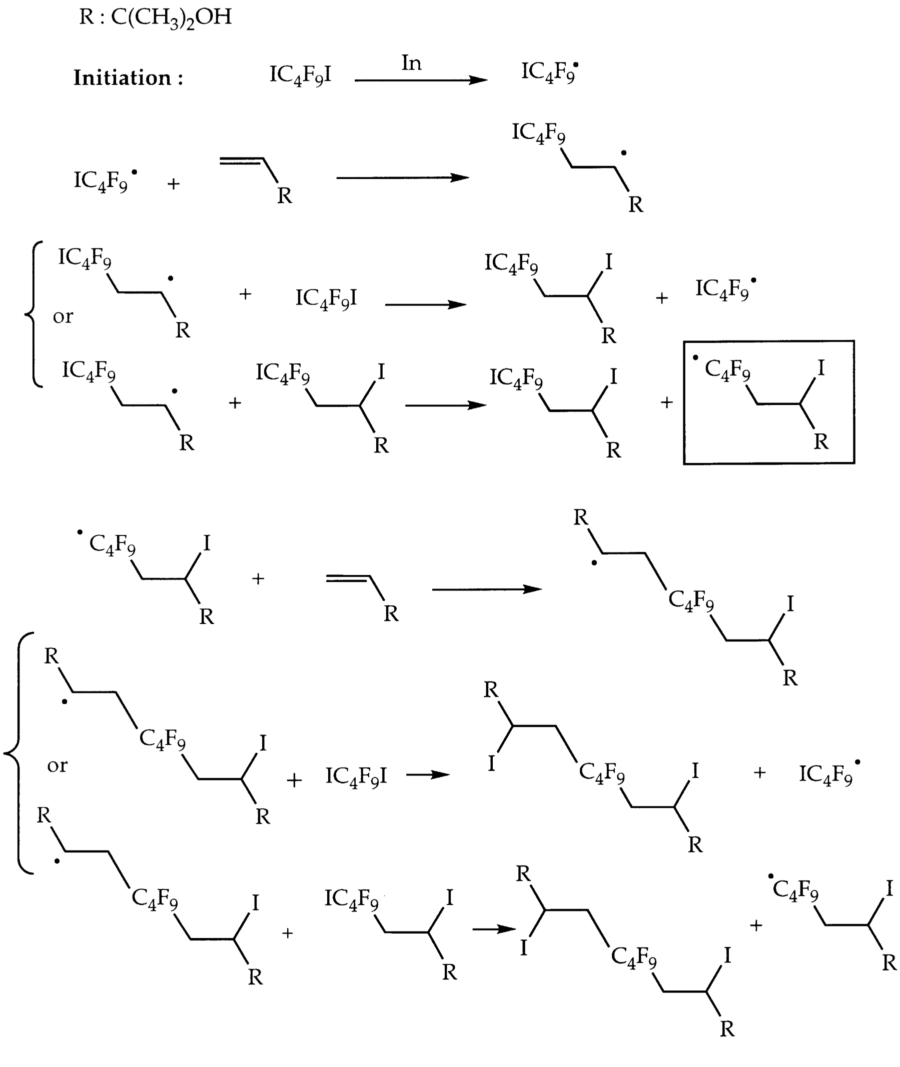
3. Discussion

An important point in the results reported consists in the unexpected difference between the diiodide addition to the alkenol and alkynol. Such a situation may not derive from differences in the reactivity of the fluorinated radicals towards the two kinds of unsaturated alcohols studied. Indeed in previous work on the addition of F-alkyl iodides to alkenols and alkynols, we have shown that the kinetic parameters involved in the propagation steps of the addition radical chain process do not differ significantly [23].

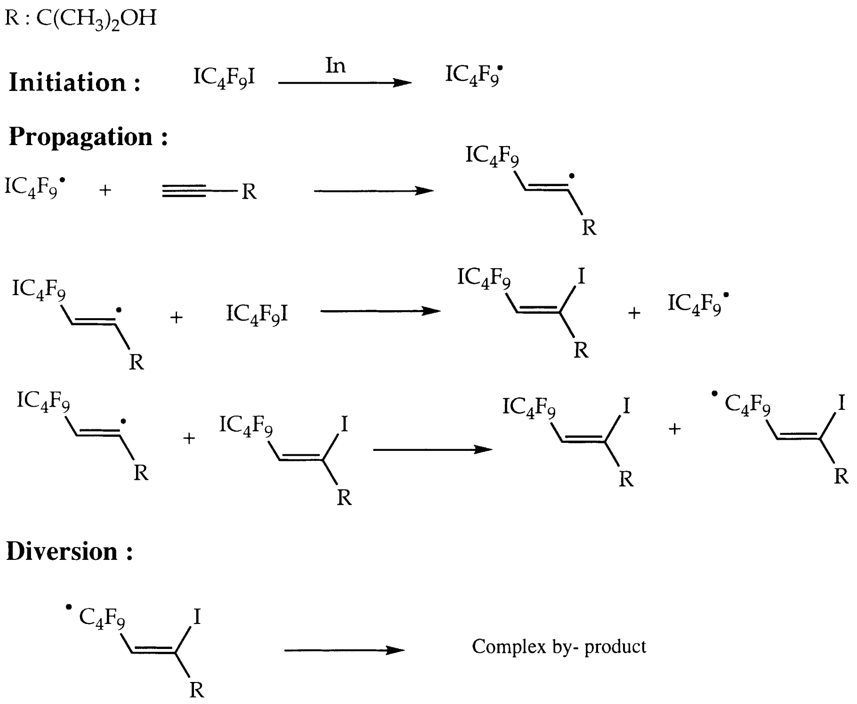
In the case of the alkenol, the initially formed σ-alkyl monoadduct (Scheme 6) is able to abstract an iodine atom from the starting diiodide (monoadduct formation, main path at the beginning of the process) or from, the thus formed monoadduct (main path when the starting diiodide concentration has been reduced). A new F-alkyl radical (in a frame on Scheme 6) is produced. It is able to participate in the bis-adduct formation. Such a radical can also be produced by direct reaction of the monoadduct with the dithionite (this is not displayed on Scheme 6). The overall process results in both mono and bis-adduct formation, the ratio of these two species depending on the olefin equivalent used. Selective formation appears possible for the bis-adduct but not for the monoadduct (Table 1).

The failure to achieve bis-addition when starting from the alkynol, can be interpreted in different ways.

This situation can arise from the fact that the σ-vinyl radical formed in the initial propagation step (Scheme 7), although it is able to efficiently remove an iodine atom from the starting diiodide, is unable to abstract an iodine atom from the first formed monoadduct compound (Scheme 7). In other words in the monoadduct, the remaining CF_2–I bond has been deactivated by the presence of a double bond at the opposite end of the fluorinated segment. Consequently, the iodine atom present in the terminal CF_2–I group cannot be transferred to the σ-vinyl radical, thus, disrupting the chain process and bis-adduct formation. We plan to return to this question in a separate paper based on electrochemical



Scheme 6. Radical chain mechanism for monoadduct and bis-adduct formation starting from I–$(CF_2)_4$–I and 2-methyl-3-buten-2-ol.



Scheme 7. Radical chain mechanism for monoadduct formation starting from I–$(CF_2)_4$–I and 2-methyl-3-butyn-2-ol.

studies of the monoadducts involved in order to support this possible interpretation.

The radical $^\bullet(CF_2)_4$–CH=CI–CMe_2OH could be engaged in a competitive very fast reaction, thus, hindering the radical addition chain process. Such a reaction could be an intramolecular cyclisation on the remaining double bond (vinyl iodide), followed by subsequent reactions in this complex medium that yield the complex by-product observed. Clearly such a diversion of the radical species to a pathway different from the intermolecular addition to the starting alkynol is not possible when working with the alkenol, the corresponding radical $^\bullet(CF_2)_4$–CH_2–CHI–CMe_2OH containing no unsaturation. Yet compound **3** studied in the pure state in similar conditions (in the presence of the alkynol or of the alkenol and in the medium dithionite/bicarbonate ACN/water), undergoes no reaction. These complementary experiments apparently rule out such a process. On the contrary under these conditions compound **4** yields interesting cyclic compounds [24].

So the fact that the use of large stoichiometric ratios in dithionite yields complex (and probably telomeric) by-product is perhaps not related to a reaction on **3**, but to an initial conversion of the two iodide bonds of the starting diiodide in the presence of sulfinates before the radical addition process takes place. This calls for further study.

Finally, the mechanism involved in the by-product formation does not appear clearly. A consequence of the diversion from the radical chain addition process is that the diversion of **3** towards complex by-product requires stoichiometric dithionite amounts (Table 2, entry 5). Clean reactions are easily performed when using catalytic amounts of dithionite. This is clear from Table 2, entry 1.

4. Conclusion

Starting from α,ω-diiodoperfluorobutane it has been possible to define experimental conditions in order to produce selectively the bis-adduct with 2-methyl-3-buten-2-ol and the monoadduct with 2-methyl-3-butyn-2-ol. In this latter case, the monoadduct has been converted to 2-methyl-4-(4-iodo-F-butyl)-but-3-yn-2-ol, a powerful synthon obtained in high yield and in the pure state.

5. Experimental

5.1. General comments

1,4-Diiodoperfluorobutane was kindly supplied by Daikin Co.; 2-methyl-3-buten-2-ol and 2-methyl-3-butyn-2-ol were purchased from Avocado.

The products were characterised by ^1H and ^{19}F NMR spectroscopy, all undertaken at room temperature and recorded in $CDCl_3$ on a Brucker AC 250 spectrometer (250 MHz). All chemical shifts are reported in ppm downfield of the standard (TMS and CCl_3F). The letters s, d, t, q, kv, and m designated singlet, doublet, triplet, quadruplet, quintuplet and multiplet, respectively. Infrared spectra were recorded on a Brucker IFS 25 instrument in the transmittance mode. Frequencies are given in cm^{-1}. Mass spectra were recorded on a Jeol DX 300 spectrometer. Refractive indices were recorded on a Mettler Toledo RE40 refractometer.

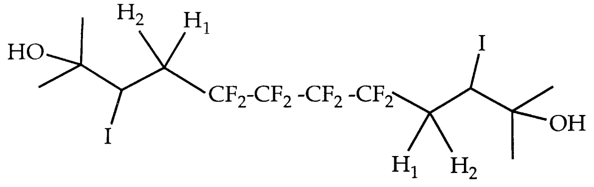
5.2. General procedure for the radical addition of 1,4-diiodoperfluorobutane to alkene and alkyne initiated by the sulfinatodehalogenation system

The sulfinatodehalogenation system is a mixture of a stoichiometric molar amounts of sodium dithionite and sodium bicarbonate. Water/acetonitrile were used as solvents in a volume ratio 1/2.5. The volume of water was calculated relative to the amount of initiator used: 25 ml of water were necessary to dissolve 0.02 mol of sodium dithionite. The ratios diiodide/initiator and diiodide/2-methyl-3-buten-2-ol or 2-methyl-3-butyn-2-ol were varied in the different experiments which are reported in Tables 1 and 2. All experiments have been conducted starting from 0.02 mol of 1,4-diiodoperfluorobutane.

To a mixture of sulfinatodehalogenation system, solvents and unsaturated compound, diiodide was added at a temperature between 20 and 24 °C. The addition completed, the mixture was stirred at room temperature for 4 h. The biphasic reaction mixture of volume *v* was extracted with water (*v*/2) and ether (3 × *v*/2). The ethereal layers were separated, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated at 30 °C under vacuum to give a yellow oil (viscous oil in the case of **1**). This oil contained monoadduct and/or bis-adduct in a variable ratio, and in some cases unreacted starting diiodide and by-product.

Compounds **1**, **2** and **3** were obtained following this typical procedure: **1** and **3** in the pure state (Table 1, entry 1 and Table 2, entry 1), **2** as a mixture with **1** (Table 1, entry 3). Compounds **1** (colorless viscous oil) and **2** (colorless oil) were isolated in the pure state by column chromatography (silica gel; petroleum ether/ethyl acetate 95/5). Compounds **1**, **2** and **3** were characterised by ^{1}H and ^{19}F NMR through comparison to known equivalent compounds obtained previously when starting from the monoiodide $F–(CF_2)_4–I$ [23] and also from a direct study: IR data, MS, HRMS or elemental analysis, refractive index and specific weight are reported below.

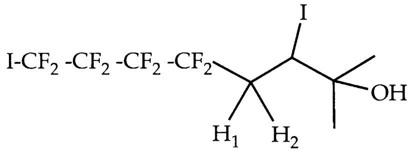
In the case of Table 2, entry 5 by-product are dominating and after the ethereal/aqueous extraction are present in the ethereal and in the aqueous layers. After removal of Et_2O or H_2O, their NMR study is as follows. For the ethereal part over 51 signals in the range 103–139 ppm (^{19}F NMR, DMSO D_6) and no signal in ^{1}H NMR. For the aqueous part four major equal signals at 125, 125.5, 125.6, 126.8, ppm (^{19}F NMR, D_2O) corresponding to 45% of the total integration and again multiple signals in the range 103–139 ppm (55% of the total integration); in ^{1}H NMR, D_2O complex signals (over 18 peaks) in the range 1.7–2.7 ppm. Mass ratio for the ethereal/aqueous residues is 1.5/1. Overall yield as indicated in Table 2. We have not succeeded in a clear identification of these by-products .



1

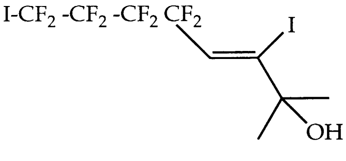
Assignments for 5,5,6,6,7,7,8,8-octafluoro-3,10-diiodo-2,11-dimethyl-dodecan-2,11-diol (**1**) are as follows: ^{19}F NMR ($CDCl_3$) δ: A from AB − 114.5, B from AB− 116.1 (AB system, $^{2}J_{FF} = 1.15$ Hz, $CH_2\mathbf{CF_2}$, 4F); −124 (d, $CH_2CF_2\mathbf{CF_2}$, 4F). ^{1}H NMR ($CDCl_3$) δ: 4.25 (q, $^{3}J_{HH1} = 1.8$ Hz, $^{3}J_{HH2} = 9.15$ Hz, C**H**I, 2H); 3.1 (m, 2H, C**H**H); 2.75 (m, CH**H**, 2H); 1.95 (s, O**H**, 2H); 1.45 (s, $C\mathbf{H_3}$, 6H); 1.4 (s, $C\mathbf{H_3}$, 6H). IR (KBr) ν_{max}: 3397 (O–H); 2980, 1378 (CH_3); 1113 (C–F). MS (FAB+, matrix NBA) *m/z*: 609 $(M + H - H_2O)^+$. Refractive index: $n^{20} = 1.4690$. In addition, the ratio H/F has been verified by comparison with an added sample of CF_3CH_2OH.

Assignments for 5,5,6,6,7,7,8,8-octafluoro-3,8-diiodo-2-methyl-octan-2-ol (**2**) are as follows: ^{19}F NMR ($CDCl_3$) δ: −59 (t, $I\mathbf{CF_2}$, 2F); A from AB − 12.8, B from AB − 113.4 (AB system, $^{2}J_{FF} = 1.3$ Hz, $\mathbf{CF_2}CF_2CH_2$, 2F); A from AB − 114.5, B from AB − 116.1 (AB system, $^{2}J_{FF} =$ 1.15 Hz, $\mathbf{CF_2}CH_2$, 2F); −123.1 (t, $ICF_2\mathbf{CF_2}$, 2F). ^{1}H NMR ($CDCl_3$) δ: 4.25 (q, $^{3}J_{HH1} = 1.8$ Hz, $^{3}J_{HH2} =$ 9.15 Hz, C**H**I, 1H); 3.1 (m, C**H**H, 1H); 2.75 (m, CH**H**, 1H); 1.95 (s, O**H**, 1H); 1.45 (s, $C\mathbf{H_3}$, 3H); 1.4 (s, $C\mathbf{H_3}$, 3H). IR (KBr) ν_{max}: 3409 (O–H); 2978, 1378 (CH_3); 1000–1200 (C–F). MS (FAB+) *m/z*: 540 $(M)^+$. HRMS calculated for $C_9H_{10}OF_8I_2$: 539.8693 $(M)^+$, found 539.8644. Refractive index: $n^{20} = 1.4597$. Specific weight: 1.98 g ml^{-1} .



2

Assignments for (Z)-5,5,6,6,7,7,8,8-octafluoro-3,8-diiodo-2-methyl-oct-3-en-2-ol (**3**) are as follows: ^{19}F NMR ($CDCl_3$) δ: −59.1 (t, $I\mathbf{CF_2}$, 2F); −108.9 (q, $\mathbf{CF_2}CH{=}CI$, 2F); −113 (kv, $ICF_2\mathbf{CF_2}$, 2F); −122.7 (t, $\mathbf{CF_2}CF_2CH{=}CI$, 2F). ^{1}H NMR ($CDCl_3$) δ: 6.8 (t, $^{3}J_{HF} = 13.44$ Hz, **H**C=CI, 1H); 2,9 (s, O**H**, 1H); 1.5 (m, $C\mathbf{H_3}$, 6H). IR (NaCl) ν_{max}: 3395 (O–H); 2985, 1367 (CH_3); 1000–1200 (C–F); 1633.8 (C=C). MS (FAB+) *m/z*: 538 $(M)^+$.



3

5.3. Large scale experiment devoted to monoadduct formation from 1,4-diiodoperfluorobutane and 2-methyl-3-butyn-2-ol

This experiment corresponded to that described in Table 2, entry 1. It has been performed on a large scale in order to prepare the corresponding monoadduct for further work. It is described in detail in order to clearly assess the yields obtained as well as to establish the best way to obtain the monoadduct in the pure state and to recover unreacted starting diiodide.

Diiodide 30 g (0.066 mol, 12 ml) was added dropwise at a temperature between 20 and 24 °C into a mixture of sulfinatodehalogenation system ($Na_2S_2O_4$ 2.3 g (0.013 mol), $NaHCO_3$ 1.11 g (0.013 mol)) solvents (water 20 ml, acetonitrile 50 ml) and 2-methyl-3-butyn-2-ol 26.64 g (0.317 mol, 30.7 ml). The addition completed, the mixture was stirred at room temperature for 4 h. A biphasic reaction mixture (organic phase 92 ml, aqueous phase 22 ml (upper layer)) was obtained. The organic layer was analysed as follows: 31 μl (0.43 mmol) of pure CF_3CH_2OH ($d = 1.39$) was added to an aliquot (0.6 ml) of the organic layer. ^{19}F NMR showed the presence in the organic phase of unchanged diiodide 0.034 mol and monoadduct 0.032 mol. In this way, it was clearly established that the starting diiodide (0.066 mol) is selectively converted to monoadduct and that formation of other compounds as sulfinates lost in the aqueous phase or any others do not occur. The aqueous phase analysed in a similar manner was found free of fluorinated compounds, in accordance with the preceding mass balance, with the exception of a small amount of probably deiodosulfinato monoadduct.

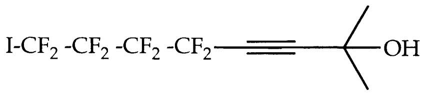
The organic phase was washed with water (40 ml) in order to remove excess starting alkynol and then distilled at atmospheric pressure in order to eliminate acetonitrile and water as an azeotrope. We observed that the remaining unreacted diiodide also distilled (60–78 °C). This appeared a possible way for the recovery of the unreacted starting diiodide. The monoadduct $I–(CF_2)_4–CH=CI–CMe_2OH$ **3** (*Z* only, see footnote 1) was, thus, obtained in a relatively pure state (^{19}F NMR 96%), but still containing some of the starting alkynol. Further washing with water/diethylether led to 17.3 g of an orange oil containing 1.6 g of starting alkynol and 15.6 g of the expected monoadduct. Yield relative to the starting diiodide: 43.9 mol%. Yield relative to the consumed diiodide: 90.6 mol%. Characterisation of compound **3** has been reported above.

5.4. Procedure for H,I trans-elimination from (Z)-5,5,6,6,7,7,8,8-octafluoro-3,8-diiodo-2-methyl-oct-3-en-2-ol

A mixture of monoadduct/alkynol (0.022 mol/0.015 mol, 13.4 g) resulting from the experiment on diiodide/2-methyl-3-butyn-2-ol (cf. Section 5.3), was dissolved in methanol (40 ml). Then 50 ml of methanol containing 3.76 g of KOH pellets (a 85%) were added dropwise at room temperature. The solution was kept for 2 h with mixing. A water/diethylether extraction was performed. After separation the ethereal phase was concentrated under vacuum. A yellow oil (8.83 g) was obtained. Yield from the starting monoadduct: 87%.

Product **4** was obtained following this typical procedure and was characterised by ^1H, ^{19}F NMR, IR, mass spectrometry and elemental analysis.

Assignments for 5,5,6,6,7,7,8,8-octafluoro-8-iodo-2-methyl-oct-3-yn-2-ol (**4**) are as follows: ^{19}F NMR ($CDCl_3$) δ: −59.1 (q, $IC\mathbf{F}_2$, 2F); −98.7 (t, $C\mathbf{F}_2CC$, 2F); −112.8 (q, $ICF_2C\mathbf{F}_2$, 2F); −122.2 (kv, $C\mathbf{F}_2CF_2CC$, 2F). ^1H NMR ($CDCl_3$) δ: 2.6 (s, O**H**, 1H); 1.6 (d, C**H**$_3$, 6H). IR (KBr) ν_{max}: 3357 (O–H); 2990, 1374 (CH_3); 2260 (C≡C); 1000–1200 (C–F). MS (FAB+) *m/z*: 411 $(M + H)^+$, 393 $(M + H - H_2O)^+$. Elemental analysis: calculated for $C_9H_7F_8IO$: 26.34; H: 1.71; O: 3.90; F: 37.07; I: 30.98; found: C: 26.09; H: 1.60; F: 36.48; I: 30.87%. Refractive index: $n^{20} = 1.4116$. Specific weight: 1.93 g ml^{-1} .



4

Acknowledgements

We are grateful to the DAIKIN INDUSTRIES, Ltd., through Kazuaki OBATA for providing α,ω-diiodoperfluorobutane used as starting compound and to the European Commission, TMR Research Networks, Contract Number: ERBFMRXCT 970120 for financial support.

References

[1] N.O. Brace, J. Fluorine Chem. 93 (1999) 1–25.
[2] A.-R. Li, Q.-Y. Chen, Synthesis 12 (1997) 1481–1488.
[3] V. Cirka, B. Améduri, B. Boutevin, J. Kvicala, O. Paleta, J. Fluorine Chem. 74 (1995) 97–105.
[4] K. Baum, C.D. Bedford, R.J. Hunadi, J. Org. Chem. 47 (1982) 2251–2257.
[5] H. Urata, Y. Kinoshita, T. Asanuma, O. Kosukegawa, T. Fuchikami, J. Org. Chem. 56 (1991) 4996–4999.
[6] A. Manseri, B. Améduri, B. Boutevin, M. Kotora, M. Hajek, G. Caporricio, J. Fluorine Chem. 73 (1999) 151–158.
[7] D. Boulahia, A. Manseri, B. Améduri, B. Boutevin, G. Caporricio, J. Fluorine Chem. 94 (1999) 175–182.
[8] P. Calas, P. Moreau, A. Commeyras, J.C.S. Chem. Commun. (1982) 433–434.
[9] H. Collet, P. Calas, A. Commeyras, J.C.S. Chem. Commun. (1984) 1152–1153.
[10] L. Gomez, P. Calas, A. Commeyras, J.C.S. Chem. Commun. (1985) 1493–1494.
[11] N.O. Brace, J. Org. Chem. 28 (1963) 3093–3102.
[12] Q.Y. Chen, Y.B. He, Z.Y. Yang, J. Fluorine Chem. 34 (1986) 255–258.
[13] Y. Takeyama, Y. Ichinose, K. Oshima, K. Utimoto, Tetrahedron Lett. 30 (1989) 3159–3162.
[14] D. Lahiouel, B. Ameduri, B. Boutevin, J. Fluorine Chem. 107 (2001) 81–88.
[15] W.-Y. Huang, J. Fluorine Chem. 58 (1992) 1–8.

[16] W.-Y. Huang, B.-N. Huang, C.-M. Hu, J. Fluorine Chem. 23 (1983) 193–204.
[17] W. Qiu, D.J. Burton, J. Fluorine Chem. 60 (1993) 93–100.
[18] X.-C. Guo, Q.-Y. Chen, J. Fluorine Chem. 93 (1999) 81–86.
[19] G.-B. Rong, R. Keese, Tetrahedron Lett. 31 (1990) 5615–5616.
[20] A.-R. Li, Q.-Y. Chen, Synthesis 5 (1996) 606–608.
[21] A.-R. Li, Q.-Y. Chen, J. Fluorine Chem. 82 (1997) 151–155.
[22] F.-H. Wu, B.-N. Huang, L. Lu, W.-Y. Huang, J. Fluorine Chem. 80 (1996) 91–94.
[23] C. Dapremont-Avignon, P. Calas, C. Amatore, A. Commeyras, J. Fluorine Chem. 56 (1992) 249–258.
[24] C. Amato, P. Calas, A. Commeyras, to be published.