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ELECTROCHEMICAL INITIATION OF RADICAL CHAIN ADDITION OF F-n BUTYL IODIDE TO ACETYLENIC ALCOHOLS. CYCLIC VOLTAMMETRIC INVESTIGATION OF THE MECHANISM.

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SUMMARY

The initiation of the radical chain addition of F-n butyl iodide to alkynols through the cathodic reduction of the halide at a carbon cathode is presented. A simplified analysis, based on cyclic voltammetry affords an estimation of the ratio of the rate constants of the two propagation steps, addition of Rf° to alkynol and iodine atom transfer from the F-alkyl iodide to the resulting vinyl radical, involved in the radical chain mechanism.

INTRODUCTION

The addition of F-alkyl iodides to unsaturated compounds, an example of the Kharasch reaction, has been, in the past performed through a number of experimental conditions. Eméleus [1] and Haszeldine [2] developed photochemical initiation. Brace [3] has presented a wide variety of examples based on the use of azobisisobutyronitrile. More recently other authors have conducted similar reactions using different initiation methods : alkane sulfinates [4] iron powder [5], Raney nickel [6], magnesium [7], palladium [8,9] cadmium [10], complexes of rhodium [11], couples metallic tin-tin salts [12]; an enzymatic initiation has also been

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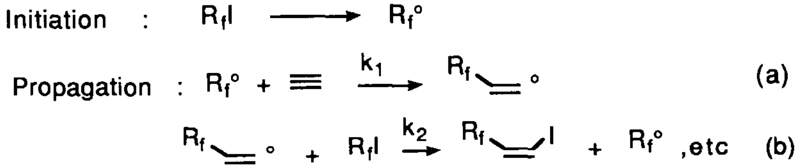
presented [13] . All these processes are commonly thought to involve a two step radical chain mechanism:



Step b) involves the abstraction of iodine of the starting compound by the vinyl radical produced at step a). Such a mechanism, is an example of free radical chain reactions processing through halogen atom transfer, a field recently reviewed by D.P.Curran [14]. The propagation process can be initiated by any reaction producing a radical Rf° from the starting halide.

As we have shown in a previous paper [15], the reduction of F-alkyl halides at a carbon cathode which affords quantitatively Rf° radicals is a possible route for this purpose.

In the past we have reported efficient conditions for the addition of such halides to alkenols and alkynols using electrolysis in aqueous emulsion [16].

In this paper we wish to present a simplified kinetic analysis of the radical chain mechanism as triggered electrochemically . For this purpose, cyclic voltammetry (CV) constitutes a powerful tool. However this method is best used under homogeneous conditions, for example when using DMF (dimethylformamide) as a solvent ; consequently we have completed a preparative electrochemical work in DMF as a solvent at a carbon cathode.The results thus obtained are a necessary background for the presentation of the following kinetic work, although we consider that the technique of electrolysis in emulsion is more efficient in terms of preparative macroscale experiments. This work is then divided in two parts, preparative experiments using DMF as a solvent, and kinetic study by CV, both with DMF as the solvent.

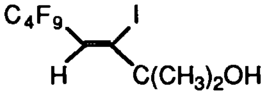
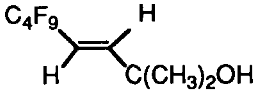
PREPARATIVE SCALE ELECTROLYSIS

The two-compartment electrochemical cell used, equipped with glassy carbon electrodes, is described in the experimental part. The cathodic compartment is filled with the halide C_4F_9I, the alkynol H-C≡C-C$(CH_3)_2$(OH) and the solvent DMF 0,2 M in LiCl.

A constant current is applied to the cell. The composition in the compartments is followed using ^{19}F n.m.r. Distribution of the observed compounds, as a function of the applied current, initial composition, and faradaic consumption is listed in Table 1.

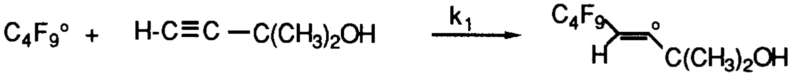
TABLE 1

Galvanostatic electrolysis at a glassy carbon electrode(40 mm in diameter). Catholyte : C_4F_9I 4 cm3 (0,02 M) ; acetylenic alcohol 4 cm3 (0,04 M); DMF, LiCl 0,1M : 2 cm3. Anolyte : DMF , LiCl 0,1M : 10cm3. Imposed curent: 70 mA. Moles formed for 100 moles of starting C_4F_9I introduced. Approximate ohmic drop in the cell :10 volts.

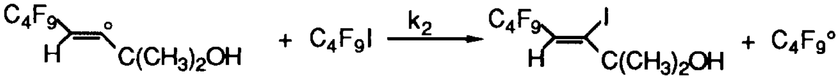
Time (hours)	0	1.5	4.5	9
Faradays/Mole of starting R_fI	0	0.2	0.6	1.15
C_4F_9I catholyte	100	16	2	6
anolyte	0	26	34	19
total	100	42	36	25
C_4F_9H	0	0	traces	traces
	0	36	20	8.5
	0	18	40	41
C_4F_9-C ≡C-$C(CH_3)_2OH$	0	1	2	4
% of F compunds in the cell balance including anolyte and catholyte.	100	97	96	78.5

The formation of the addition compound is clearly shown to occur electrochemically, resulting from the initiation of the radical chain process through the production of radicals $C_4F_9°$ at the carbon cathode. The formation of the different products detected in the medium, can be rationalised by the following scheme:

$$C_4F_9I + e^- \longrightarrow C_4F_9^\circ + I^- \qquad (1)$$

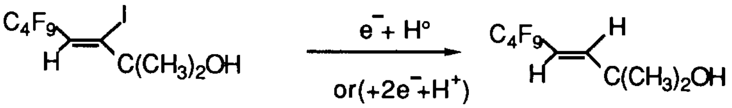


(2)

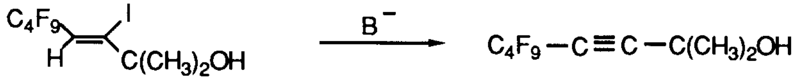


(3)

possibly followed by:



(4)



(5)

at more cathodic potentials.

Equation(1) represents the initiation step, equations (2) and (3) are the propagation steps producing the expected addition compound; equation (4) corresponds to the reduction of the vinyl iodide wich occurs partially at high current densities. The partial production of the acetylenic compound in equation (5), is interpreted as resulting from dehydrohalogenation of the vinyl iodide by electrogenerated bases, due to possible discharge of the solvent/supporting electrolyte system, and/or possible two electron reductions of C4F9I and/or vinyl iodide at high current densities.

Under the conditions of high concentrations used in our preparative experiments, diffusion of the starting halide from the catholyte towards the anolyte occurs significantly (compare 3rd and 4th rows in Table 1). This point constitutes the main limitation of the process but is easily overcome by using particular conditions of electrolysis, viz. in emulsions as outlined above.

In the first phase of the electrolysis, the process appears as being catalytic from a faradaic point of view. It is noticeable that only addition compounds with I and H in trans positions are formed. As we have previously reported [16] the other isomer is obtained partly (70/30) when using a secondary or primary alkynol H-C≡C-CHR(OH) (R = H or CH_3). This result is interpreted by considering steric effects in the formation of the intermediate vinyl radical and its possible equilibration before the iodine atom transfer step.

The electroinitiation for the addition of C_4F_9I to alkynols at a carbon cathode, in DMF as a solvent, appears consequently as an operating method, provided the problem of diffusion between compartments is solved. Potentiostatic conditions, instead of the described intentiostatic ones, could be used in order to prevent reduction of the produced vinyl iodide. However we did not attempt to optimize the process since, as explained above, the preparative aspect was not the main purpose of this work. On the basis of the preparative results, we present a voltametric technique applied to the kinetic analysis of the radical chain mechanism involved in the reaction.

STUDY OF THE PROPAGATING SEQUENCE BY CYCLIC VOLTAMMETRY (CV)

A vitreous carbon disk (3 mm in diameter) immersed in DMF, 0.05 M TBAF (tetrabutylammonium tetrafluoroborate) electrolyte, is polarised at a given potential referenced to a standard calomel electrode, using a classical three electrodes apparatus (cf experimental part).

CV in the absence of alkynol

Figures 1 and 2 report the voltammograms observed for the reduction of C_4F_9I and of the vinyl iodide $C_4F_9\text{-}CH{=}CI\text{-}C(CH_3)_2OH$ studied alone (peak potential -1,3 and -2 V respectively/SCE).

On Figure 1 a second cycle is performed immediately after the first one; the reduction peak of the halide is smaller than the one observed during the first scan. This fact reveals that after the first cathodic sweep the average concentration of the halide in the immediate vicinity of the electrode is lowered with respect to its initial value. This is observed because diffusion of C_4F_9I from the bulk solution is not sufficiently efficient to renew the concentration of the halide in the diffusion layer because of the short delay between the two scans.

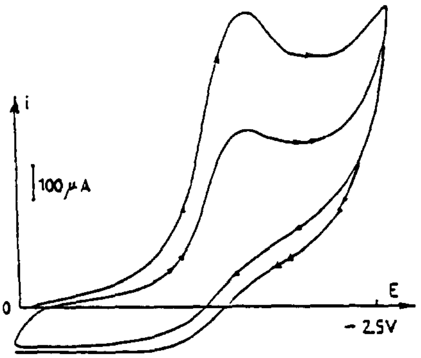


Fig. 1 . Cyclic Voltammetry of C_4F_9I ; program of potential: 0;-2.5;0;-2.5;0 volts applied to the glassy carbon disk (3mm in diameter) vs a SCE reference. Scan rate :1Volt/sec. First scan (-->),second scan (-->>). 10 cc of DMF, 0.05 M in TBAF, 10 microliters of C_4F_9I added. Atmosphere of Argon. Auxiliary electrode in platinum.

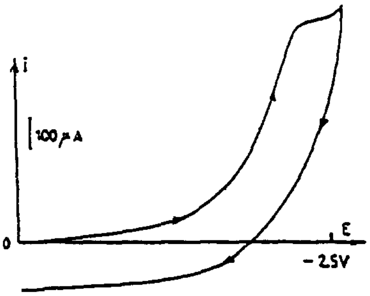
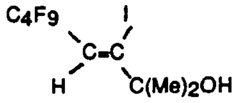


Fig. 2 . Cyclic Voltammetry of the vinylic iodide : Scan rate 1 V/sec. Cathodic scan from 0 to -2.5 V/ECS and back to zero . Electrodes as in figure 1 .



CV in the presence of alkynol

Program of potential used: the initial potential is controlled at 0 V/SCE and linearly varied through two successives cathodic explorations : 0 to -2,5 V; -2,5 to 0 V; 0 to -2,5 V; -2,5 to 0 V/SCE.

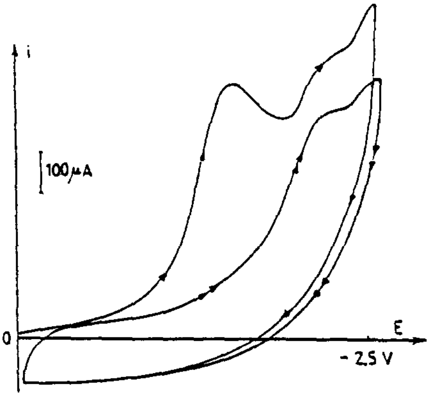


Fig. 3 . Conditions as in Figure 1, except 250 microliters of alkynol $H\text{-}C{\equiv}C\text{-}CMe_2OH$ added.

The CV obtained is reprèsenting the value of the observed currents as a function of the potential. A typical one is shown in Figure 3.

During the first cathodic scan the peak reduction of the halide C_4F_9I (-1,3 V/SCE) is observed. A second peak, which is not present in the absence of alkynol, is also detected around -2 V/SCE. This latter corresponds exactly in position to the reduction of the vinyl iodide $C_4F_9\text{-}CH{=}CI\text{-}C(CH_3)_2OH$ studied alone (displayed on the Figure 2). During the second cathodic scan, we observed a partial or complete disparition of the peak of reduction of the halide C_4F_9I , depending on the concentrations of the halide and of the alkynol. Note that the depletion of the first peak on the second scan , is more important than the one observed during the study of the C_4F_9I alone.

These patterns are interpreted as follows: during the first scan, the reduction of the C_4F_9I produce radicals $C_4F_9°$ which initiate the radical chain addition of the halide to the alkynol. This chain still propagates during the completion of the first scan, resulting in the nearly complete disappearance of C_4F_9I from the solution immediately adjacent to the electrode, because of its consumption by the radical chain process. The produced vinyl halide is detected at the end of the first scan. During the second scan the starting compound C_4F_9I has disappeared in the solution layer adjacent to the electrode, a result of his consumption in the radical chain process (compare Figure 4). The vinyl iodide is thus detected again at the end of the

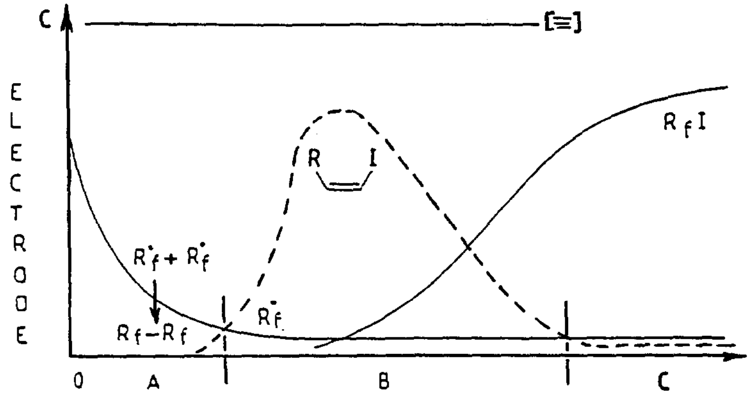


Fig. 4 . Schematic representation of the concentration profiles of the concerned species in the diffusion layer adjacent to the electrode (x=0) after the first cathodic scan (0 to -2.5 V/ECS) , in the conditions reported for the Figure 3.

second scan. The decrease in height of the first peak around -1,3 V is thus clearly related to the efficiency of the chain process.

Consequently we have conducted systematic experiments varying the concentrations of the starting halide and of the alkynol. Results are presented in the Figure 5, under the form of the ratio R of the height of the reduction peak of RfI during the second cathodic scan, in the presence and in the absence of alkynol, as a function of the concentration of the alkynol, and this for a number of initial concentrations of the halide. A noticeable depletion of the peak of reduction of RfI on the first scan is also observed and reported on Figure 6. This situation is attributed to a significant consumption of the halide through the radical chain process which is initiated during the first cathodic scan.

We propose a simplified mathematical analysis of the results. On the Figure 4 are schematized the concentration profiles in the vicinity of the cathode at the end of the first sweep.We assume that even if the essential part of the radicals Rf° produced at the cathode may have been consumed by a dimerisation process, owing to their large production flux at the electrode, a small number of radicals initiate the chain process.

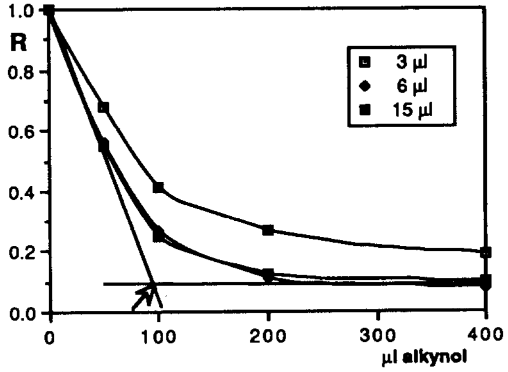


FIG. 5 : Data from linear sweep voltammetry. Vertical axis, values of $R = iP_x/iP_0$ peaks current observed for the reduction of R_fI during <u>the second cathodic scan</u> (see Fig 1); iP_x being the current value in the presence of x µl (50 to 400) of the studied acetylenic alcohol and iP_0 the same parameter in the absence of this alcohol. Horizontal axis, amounts of $H\text{-}C{\equiv}C\text{-}CMe_2OH$ in microliters added to the medium (density 0.868). Total volume 10 cc of DMF 0.05 M in TBAF. Three curves are reported, corresponding to different quantities of R_fI added: 3, 6 and 15 microliters (density value 2).

The dashed curves correspond to each limiting kinetic behaviour for the overall chain (see text); the arrow indicates the threshold value of the alkynol concentration corresponding to the shift from one limiting behaviour to the other.

A front of reaction is thus created in which the halide R_FI diffusing towards the electrode is converted in the addition compound.

In the chain reaction zone we can write:

$$d(Rf^\circ)/dt = -k_1\,(Rf^\circ)\,(\equiv) + k_2\,(RfCH{=}C^\circ R)\,(RfI)$$

where $(\equiv)$ represents the concentration of the alkynol used.

Since concentration of the radicals Rf° will remain very low in the chain reaction zone, we can apply to these species the quasi-

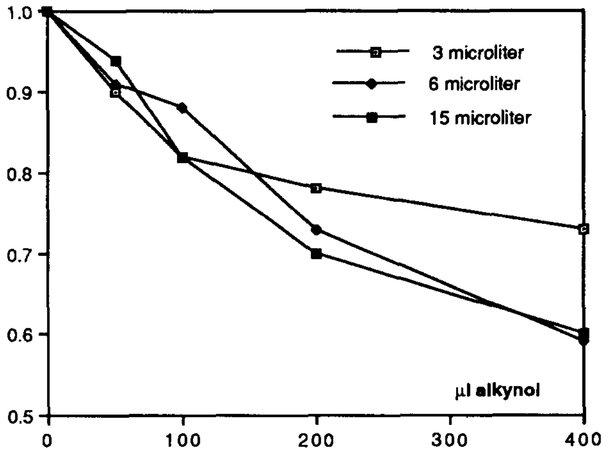


FIG. 6 : Data from linear sweep voltammetry.

Vertical axis, values of $R = iP_x/iP_o$ peaks current observed for the reduction of RfI during <u>the first cathodic scan</u> (see Fig 1); iP_x being the current value in the presence of x µl (50 to 400) of the studied acetylenic alcohol and iP_o the same parameter in the absence of this alcohol.

Horizontal axis, amounts of $H\text{-}C{\equiv}C\text{-}CMe_2OH$ in microliters added to the medium (density 0.868). Total volume 10 cc of DMF 0.05 M in TBAF.

Three curves are reported, corresponding to different quantities of RfI added: 3, 6 and 15 microliters (density value 2). Cathode : glassy carbon disk 3 mm in diameter.

steady state principle , viz. $d(Rf°)/dt=0$. Introducing the total concentration in radicals $C° = (RfCH{=}C°R) + (Rf°)$, leads to

$d(RfI)/dt = - k_2\ (RfCH{=}C°R)\ (RfI)$

as :

$d(RfI)/dt = - C°\ k_1\ k_2\ (\equiv)\ (RfI)\ /\ \{\ k_1\ (\equiv) + k_2\ (RfI)\ \}$

This equation has two limiting forms :

$k_1\ (\equiv) << k_2\ (RfI) \longrightarrow d(RfI)/dt = - C°\ k_1\ (\equiv)$

$k_1\ (\equiv) >> k_2\ (RfI) \longrightarrow d(RfI)/dt = - C°\ k_2\ (RfI)$ ·

On Figure 5 one can identify two zones, in agreement with these limiting cases. Indeed, in the CV experiments the height of the reduction peak of the C_4F_9I during the second cathodic scan is related to the value of d(RfI/dt) in the chain reaction zone.

In the right hand side of Figure 5 , which corresponds to large values of the concentration of the alkynol, the value of R tend to be independent of the concentration of the alkynol.

In the left hand side, i.e. at low (≡) values, the R value is depending on the alkynol concentration. The shift between one limiting behaviour to the other is then observed for :

k_1 (≡) = k_2 (R_fI)

In this relation the concentration in alkynol to be considered is the one corresponding to the limit between the two parts of the curve on the Figure 5 (see dashed lines and arrow); the concentration of the halide is the one remaining in the chain reaction zone and considered to be equal to the product of the bulk concentration by the value of R at this point.

This allows us to evaluate an approximate value for the ratio of the rate constants of the two steps of the propagation process. For example from the Figure 5 (curve obtained for 6 microliters of C_4F_9I in 10 ml DMF) , at the intersection point:

(≡) = 0.103 mol/l (100 microliters in 10 cc)
(C_4F_9I) = 3.47 10^{-3} mol/l (6 microliters in 10 cc)
R= 0.11
It then follows that : k_2/k_1 = 270.

Such a result shows that the atom transfer step is faster, by more than two orders of magnitude, than the step involving radical attack of $C_4F_9°$ on the alkynol. Moreover on the basis of a remark from Newcomb (references 8 and 9 in [14,d]) we can consider that k_2 is close to the diffusion limit, i.e. 10^8-10^9 $M^{-1}s^{-1}$; Hence k_1 must consequently have a value of ca. 10^6-10^7 $M^{-1}s^{-1}$.

It appears that F-Butyl halide is an excellent donor of iodine atom [14,a-c]. This point is in accordance with the absence, in the Fpreparative experiments, of products resulting from possible evolution of the intermediary vinyl radical (dimerisation, protonation, telomerisation).

CONCLUSION

Electrochemical reduction of F-alkyl iodides can be considered as an efficient source of F-alkyl radicals. In the presence of an acetylenic derivative, these radicals are able to initiate an efficient chain mechanism . Preparative scale electrochemistry thus appears as a convenient route to perform the addition of F-alkyl halides to unsaturated compounds, and particularly to alkynols which affords interesting Synthons [17]. In addition we wish to emphasize that cyclic voltammetry constitutes a particularly attractive method for a rapid diagnostic and kinetic investigation of the mechanism involved .

Electrochemistry is by nature an heterogeneous process. Consequently the possibility of producing a controlled flux of radicals from a plane (the electrode), and to analyse after a given time the evolution of the front of reaction thus created, through the selective detection of reactant and reaction products, is an interesting alternative to classical kinetic studies in homogeneous conditions. Mathematical tools necessary for a complete analysis of the recorded data are not simple, but accessible.We wish to apply this kind of experiment to a number of unsaturated compounds in order to obtain numerical data in the field of radical chain processes involving halogen atom transfer.

EXPERIMENTAL

Compounds used: F-nButyl iodide was a generous gift from ATOCHEM Cie. DMF and the alkynol have been purchased from FLUKA. TBAF was prepared in our laboratory. Densities of the studied compounds : 0.868 for the alkynol and 2.0 for the F-Butyl Halide.

Voltammetry - Electrodes and electrochemical apparatus: glassy carbon disk from Tacussel; Potentiostat and program potential generator were home made. Data were recorded through a numerical oscilloscope (Nicolet).

Preparative experiments - The cell used for preparative experiments was in PTFE. The cell has a cylindrical geometry with an horizontal axis. The electrodes consist in two discs of vitreous carbon (Carbone Lorraine France) 40 mm in diameter, connected through small carbon rods to the external electrical circuit. Cathodic and anodic compartments are cylindrical, 40 mm in diameter, width 9mm (volume 10cc each). They are separated by a fritted glass, diameter 40 mm, porosity 3 from Prolabo. The cathodic compartment is continuously stirred by a magnetic bar, turning on an horizontal axis, sustained by the magnetic field of a classical magnetic stirrer disposed in a vertical position. This cell realises perfect geometrical conditions in order to assume that electrical conditions are the same in all points of the cathodic surface. Small amounts of Loctite B 504411 are used in order to perfect the sealing of the fritted glass. Galvanostat was a PRT 30 Volts, 2 Amps from Tacussel (France).

Composition of the catholyte and anolyte was followed continuously using ^{19}F n.m.r . Through the addition of known amounts of C_6F_6 to the samples this technique furnished the composition of the medium and the total quantity of fluorinated compounds present in the cell. Some C_4F_9H was lost in the small stream of nitrogen passing in the upper part of the compartments. This compound was quantitatively determined by trapping in cold Et_2O .

At the end of the electrolysis, catholyte and anolyte were mixed together, and an equal volume of water was added. The fluorinated heavy phase was separated and extracted with water/Et_2O . The organic phase was dried over sodium sulfate and Et_2O removed by slow distillation at atmospheric pressure. The resulting oil was then distilled . The trans position for I and H on the produced vinyl iodide $C_4F_9\text{-}CH{=}CI\text{-}CMe_2OH$ was established by deshydroiodination in MeOH/KOH at the ambient temperature, yielding the acetylenic compound. For the reduced compound $C_4F_9\text{-}CH{=}CH\text{-}CMe_2OH$ the trans position of the ethylenic H atoms was derived from a comparative study of the electrochemical reduction of $C_4F_9\text{-}CH{=}CI\text{-}CHMeOH$ having I and H in the cis position. This compound was obtained (see text) during the electrochemical addition of nC_4F_9I to the alkynol $H\text{-}C{\equiv}C\text{-}CHMeOH$ (70% I and H cis, 30% trans. The two isomers were separated by deshydroiodination of the trans in MeOH/KOH, followed by distillation). Reduction of the cis $C_4F_9\text{-}CH{=}CI\text{-}CHMeOH$ compound (stable in MeOH/KOH) yields the two possible isomers (again 70% cis, 30% trans) .

N M R Data

^1H n.m.r spectra are referenced to Me_4Si and ^{19}F n.m.r spectra to CCl_3F, measured with C_6F_6 as internal reference (Chemical Shifts are given in ppm). Solvent CCl_4.

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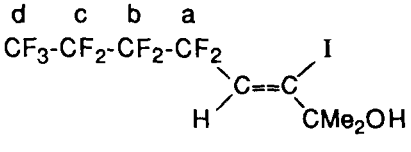

^1H n.m.r δ 6.89 (t,1H) J_{FH} 15Hz, 2.88 (s,1H), 1.55 (s,6H) .
^{19}F n.m.r δ $(CF_2)a$ -109.1, b -124.1, c -126.1, d -81.5 .

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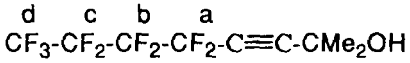
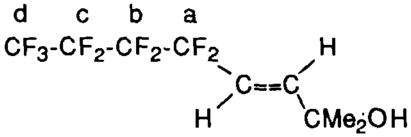


$$\overset{d}{CF_3}\text{-}\overset{c}{CF_2}\text{-}\overset{b}{CF_2}\text{-}\overset{a}{CF_2}\text{-}C{\equiv}C\text{-}CMe_2OH$$

^1H n.m.r δ 4.6 (s,1H), 1.63 (s,6H) .
^{19}F n.m.r δ $(CF_2)a$ -98.5, b -123, c -126, d -81.5 .
i.r 2280 cm^{-1}



^1H n.m.r δ AB (2H) {A of AB 5.92, B of AB 6.48, J_{AB} 20Hz, J_{FH_A} 13.5 Hz, J_{FH_B} 1.6 Hz}, 3.6 (s,1H), 1.53 (s,3H), 1.34 (s,3H) .
^{19}F n.m.r δ $(CF_2)a$ -111.5, b -125.1, c -126.1, d -81.5 .

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