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ELECTROREDUCTIVE SYNTHESIS OF ORGANOMERCURIALS FROM n-PERFLUOROBUTYL-1,4-DIIODIDE

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SUMMARY

Electroreduction of the n-perfluorobutyl 1,4 diodide $I-(CF_2)_4-I$ is studied in dimethylformamide as a solvent. During the electrolysis their is intermediate production of $I-(CF_2)_4-H$ and of $H-(CF_2)_4-Hg-I$, the final product being the symmetrical mercurial $H-(CF_2)_4-Hg-(CF_2)_4-H$. The results are compared with previous studies on monoiodide $CF_3-(CF_2)_5-I$ and the dibromide $Br-(CH_2)_4-Br$.

INTRODUCTION

The previously reported study [1,2] of the electrochemical reduction of perfluoro-n-hexyl iodide $C_6F_{13}I$ at mercury in dimethyl formamide as a solvent, led us to show that two different routes are involved in the reduction process. The first consists in a two electron transfer yielding directly $C_6F_{13}H$, and, in the second, organometallic intermediates are produced ; the formation of the mercurial $C_6F_{13}HgI$ by mercury insertion is followed by reduction to $C_6F_{13}Hg^{\cdot}$ which dimerizes and yields $C_6F_{13}HgC_6F_{13}$ after disproportionation. This latter route was found very sensitive to the nature of the supporting salt. Thus, it is completely suppressed when LiCl is used, but is enhanced with $LiClO_4$. In this latter case, the mercurial $C_6F_{13}HgI$ is strongly adsorbed at the surface of the mercury.

TABLE : ^{19}F NMR *data in the solvents* Et_2O *and DMF.*
The chemical shifts are given in ppm relative to CCl_3F*, with* CF_3COOH *as an external reference* (CF_3COOH = 78, 5*ppm*/ $(CFCl_3)$ *and are counted positively with increasing field. The coupling constants are given in Hertz.* (EM 390 VARIAN *spectrometer, at* 90 MHz).

COMPOUNDS $\underset{a}{X-CF_2}-\underset{b}{CF_2}-\underset{c}{CF_2}-\underset{d}{CF_2}-Y$	δCF_2 *a*		δCF_2 *b*		δCF_2 *c*		δCF_2 *d*	
	Et_2O	DMF	Et_2O	DMF	Et_2O	DMF	Et_2O	DMF
(0) X = 1 Y = 1	59.9	62.9	112.7	112.3				
(1) X = HgI Y = H	101.7 $J_{F_a}Hg$= 1020.0	105.4	119.9 $J_{F_a}Hg$ = 150.0	120.1	132.4		137.7 $J_{F_d}H$ = 59.0	
(2) X = $Hg-(CF_2)_4H$ Y = H	$J_{F_a}Hg$ = 746.0	108.0	$J_{F_b}Hg$ = 148.0	121.9	132.4		137.7 $J_{F_d}H$ = 59.0	
(3) X = I Y = H	63.9		121.0		130.8		137.7 $J_{F_d}H$ = 59.0	

Casanova and Rogers have recently reported [3] an electroreductive synthesis of symmetrical organomercurials from perhydro-1, ω-dibromides $Br-(CH_2)_n-Br$. These authors compare their results with those found previously where no mercurials were obtained, and with previous work on monobromides.

We report in the present paper the results we have obtained on the electrochemical reduction of the perfluorobutyl diiodide $I-(CF_2)_4-I$. These results are compared with those obtained for the perfluorohexyl iodide [1,2], and with Casanova and Rogers work [3] on alkyl dibromides ; a mechanistic scheme is proposed.

RESULTS

PREPARATIONS

- *Controlled potential electrolysis.*

A small cell, (area of the mercury pool : 2 cm^2), with separated compartments was used. The anode was platinum gauze. Potential was controlled using a saturated calomel electrode. The solvent was DMF (0.15 M $LiClO_4$). Catholyte was 5 cm^3, anolyte 3 cm^3. The controlled potential was -0.750 V/SCE. 0.25 cm^3 $I(CF_2)_4I$ was added in most experiments (density 2.5).

Coulombs consumed were measured by an electronic integrator and electrolysis was followed by direct ^{19}F NMR of the catholyte EM390 VARIAN spectrometer. During the electrolysis, iodine appeared in the anolyte ; coulometric data indicated 385. 4 coulombs for complete consumption of the starting material, corresponding to 2.9 faradays per mole. When the electrolysis was coupled the products were extracted with water/ether and separated and identified by ^{19}F NMR (see table) and mass spectrometry.

- *Products obtained.*

The following compounds, formed during the electrolysis, have been identified :

$H-(CF_2)_4-HgI$ (1)

$H-(CF_2)_4-Hg-(CF_2)_4-H$ (2)

$H-(CF_2)_4-I$ (3)

The only product isolated at the end of the reaction is (2), but the formation of the compound (1) in a higher concentration than (2) is observed throughout most of the electrolysis. This fact indicates that (1) is not adsorbed at the electrode. In some of the experiments the electrolysis was stopped when (1) was still present and it was characterized, after extraction, by mass spectrometry.

The concentration of compound (3) is always low and remains practically constant during the electrolysis : its molar fraction relative to other fluorinated compounds is about 0.1. This indicates that (3) may be an intermediate, probably produced in the first step of the reduction process. Consequently, the following mechanistic scheme can be proposed :

$$\begin{aligned}
&\text{I-(CF}_2)_4\text{-I} + 2e^- + \text{H}^+ &&\longrightarrow \text{H-(CF}_2)_4\text{-I} + \text{I}^- \\
&\text{H-(CF}_2)_4\text{-I} + \text{Hg} &&\longrightarrow \text{H-(CF}_2)_4\text{-Hg-I} \\
&\text{H(CF}_2)_4\text{-HgI} + e^- &&\longrightarrow \text{H-(CF}_2)_4\text{-Hg}^{\bullet} + \text{I}^- \\
&2|\text{H-(CF}_2)_4\text{-Hg}^{\bullet}| &&\longrightarrow \text{H-(CF}_2)_4\text{-Hg-Hg-(CF}_2)_4\text{-H} \\
&\text{H-(CF}_2)_4\text{-Hg-Hg-(CF}_2)_4\text{-H} &&\longrightarrow \text{Hg} + \text{H-(CF}_2)_4\text{-Hg-(CF}_2)_4\text{-H}
\end{aligned}$$

The possibility of the formation of the completely reduced product i.e. the perfluorobutyl-1,4-dihydride $H\text{-}R_F\text{-}H$, was studied by running the electrolysis at 5°C. No evidence was found for the formation of this volatile product, either by trapping experiments, or by NMR tests.

No other mercurials such as $I\text{-}Hg\text{-}R_F\text{-}Hg\text{-}I$ were observed. This result appears in agreement with the hypothesis of the production of $I\text{-}R_F\text{-}H$ in a first step. We comment further this point in the discussion.

^{19}F NMR spectrometric data for all compounds are reported in the Table. We note that the chemical shift of a CF_2 group attached to HgI is dependent on the nature of the solvent as is found for the $CF_2\text{-}I$ group [4] . This is shown clearly by $J_F\text{-}Hg$ compare with Table 1 in ref. 1.[7].

POLAROGRAPHY AND LINEAR SWEEP VOLTAMMETRY (LSV)

In the preparative experiments described in the above the concentration in electroactive compound was 0.27 Mole.ℓ^{-1}. A polarographic study at about 10^{-3} M probably does not give comparable results as compared with the preparative studies. However, it appears to be comparable with previous results [1] on the monoiodide $C_6F_{13}I$.

- Polarography of $H-(CF_2)_4-Hg-I$ (1) and of $H-(CF_2)_4-Hg-(CF_2)_4-H$ (2).

- In DMF $LiClO_4$, compound (2) exhibits a well developed wave at -1.450 V/SCE. This value has been found previously for the compound $(C_6F_{13})_2$ Hg. Reduction of (2) at this potential must correspond with the scheme :

$$(2) \quad + \quad 2e^- \xrightarrow{2H^+} \quad 2 \quad |H-(CF_2)_2-H| \quad + \quad Hg^\circ$$

We have not run the corresponding preparative electrolysis, considering that the similar experiment (1) on $C_6F_{13}-HgC_6F_{13}$ which yields $C_6F_{13}H$ at the same potential can be extended to the reduction of (2).

- Compound (1) exhibits a very complicated polarogram with a very high and extremely sharp maximum at -0.900 V/SCE. This has also been found [1] for $C_6F_{13}HgI$. It has been clearly shown in preparative experiments on $C_6F_{13}HgI$ that reduction at -0.9 V produces $C_6F_{13}-Hg-C_6F_{13}$. Moreover no wave is present at -1.450 V in the polarogram of $C_6F_{13}HgI$ nor in that for $H(CF_2)_4HgI$.

From the fact that there is no wave at -1.450 V/SCE in the polarogram of (1), we believe that the dimerization of $H-(CF_2)_4-Hg^\bullet$, and/or the following disproportionation in (2) must be slow. Moreover inhibition phenomena present in the polarogram of (1) after -0.9 V indicate that radicals $H-(CF_2)_4-Hg^\bullet$ and/or their dimeric form are adsorbed at the electrode as in the case of $C_6F_{13}HgI$ |1,2|.

Polarography and linear sweep voltammetry (LSV) of $I-(CF_2)_4-I$

- Polarograms were recorded at 5.10^{-4} M and $1.4.10^{-3}$ M the capillary flow rate being m = 0.115 mg s^{-1}. With a drop time of 1 second, two waves are detected at -0.520 and -0.730 V/SCE. In LSV, at a scan rate of 1 V s^{-1}, two peaks are detected at corresponding potentials. When using short drop times (e.g. 0.1s), only the wave at -0.730 V is visible polarographically with a single peak in LSV at a scan rate of 10 V s^{-1}.

- When using a long drop time (e.g. : 5s), (ivst) curves for each drop in polarography become abnormal, exhibiting one or two maxima ; this phenomenon starts at -0.9 V and is present until the discharge of the supporting salt is reached (-2.2 V). This inhibition phenomenon perharps denotes the presence of organomercurials with disturb the main wave which is found pure when using short drop times. It seems reasonable to consider that the diffusion wave at -0.730 V corresponds with the direct reduction :

$$I\text{-}(CF_2)_4\text{-}I \;+\; 2e^- \;+\; H^+ \longrightarrow I\text{-}(CF_2)_4\text{-}H \;+\; I^-$$

- Working with $C_6F_{13}I$ we have shown [1] that when starting from -0.4 V/SCE LSV shows a very sharp peak corresponding to the reduction of adsorbed $C_6F_{13}HgI$, this compound being produced from $C_6F_{13}I$ at polarized mercury [1,2] . It is remarkable that in the case of the diiodide this characteristic is not observed and that there is just a little hump at -0.9 V on the main peak at -0.8 V (scan rate 10 V s^{-1}).

We believe that H-$(CF_2)_4$-Hg-I is either produced very slowly or is not adsorbed. This appears in accord with the fact that this compound is found in solution during the preparative experiments.

DISCUSSION

The study of the electrochemical reduction of the perfluoromonoiodide $C_6F_{13}I$ led us to conclude [1,2] that two different routes are competing for the reduction process as in the following scheme :

i) $C_6F_{13}I + 2e \longrightarrow C_6F_{13}^- + I^-$ (around -0.6 V/SCE)

$C_6F_{13}^- + H^+ \longrightarrow C_6F_{13}H$ (proton abstracted from the solvent)

or $C_6F_{13}^- + CO_2 \longrightarrow C_6F_{13}CO_2^-$ (CO_2 being added-see ref.[2])

ii) $C_6F_{13}I + Hg \longrightarrow C_6F_{13}HgI$ (at polarized mercury between -0.3 and -0.5 V/SCE)

$C_6F_{13}HgI + e^- \longrightarrow C_6F_{13}Hg^{\cdot} + I^-$ (-0.850 V/SCE)

$2C_6F_{13}Hg^{\cdot} \longrightarrow C_6F_{13}HgC_6F_{13} + Hg^{\cdot}$(slow disprotionation)

$C_6F_{13}HgC_6F_{13} + 2e^- + 2H^+ \longrightarrow 2C_6F_{13}H + Hg^{\cdot}$ (-1.450 V/SCE).

Moreover, an important feature is the nature of the supporting salt :

. when LiCl is used, only route i) is involved ;

. when $LiClO_4$ is used, the two routes i) and ii) are competing at low concentrations (10^{-3} M), but, at a preparative scale (10^{-1} M), route ii) is the main process. In this case the mercurial $C_6F_{13}HgI$, produced at polarized mercury is adsorbed at the electrode and directly reduced in $(C_6F_{13})_2Hg$. Consequently, it is not found in the bulk of the catholyte.

On the contrary, during the preparative electrolysis of the diiodide, $I-(CF_2)_4-I$, the mercurial $H-(CF_2)_4-Hg-I$, produced at polarized mercury is found in high concentration in the bulk of the solution. This indicates that it is not, or not strongly, adsorbed at the working electrode. This fact is confirmed in LSV by the absence of a sharp peak at -0.9 V for the diiodide.

- Compounds produced during the electrolysis of the diiodide, result from similar mechanisms to routes i) and ii). These two routes are involved in the production of (1) and of (2).

The first step may be a bielectronic transfer according to route i), yeilding the compound $H-(CF_2)_4-I$, and followed by an insertion of mercury (route ii)) giving the mercurial $H-(CF_2)_4-HgI$; this compound is then desorbed from the cathode and reduced to the symmetrical mercurial $H(CF_2)_4-Hg-(CF_2)_4-H$.

The electrolysis described were run using $LiClO_4$ as supporting salt. Complementary work with LiCl gave identical results. Change in the mechanism when varying the supporting salt, particularly clear when working on the monoiodide $C_6F_{13}I$, is not present with the diiodide. The products detected result from both routes i) and ii) as defined for the monoiodide.

Casanova and Rogers [3] have pointed out the high efficiency of the production of organomercurials when using a dibromide as compared with a monobromide. However, they suggest that for a given molecule the first reaction is the insertion of one mercury atom, followed by reduction, dimerization and disproportionation in the electric field of the double layer, the molecule being caught in the vicinity of the metallic surface by terminal bromides. In our studies, although we obtain the same high yield of the corresponding compound, we have observed details which do not agree with their proposed. Effectively, we have evidence for the very large desorption of $H-(CF_2)_4-HgI$, and so for the very probable production of $H-(CF_2)_4-I$ in a first step. We do agree with the strong adsorption of the radical $H(CF_2)_4-Hg^\bullet$, and of its dimer.

CONCLUSION

Generally, the electrochemical reduction of monohalides has been shown to result from two main processes, corresponding with a direct bielectronic transfer to yield a carbanion, or with an organomercuric route [5] .
(for references see complete bibliographic study in ref. [1] and ref. [3]. The results obtained depend upon the working potential used but also the concentration of the supporting salt [6].

We have shown that the electroreduction of perfluoromonoiodides results from two possible routes, varying the nature of the supporting salt [2] . From the diiodide, we obtain compounds which result from these two main processes, acting selectively at the two extremities of a given molecule.

EXPERIMENTAL

- DMF FLUKA puriss was distillated under vacuo.
- Polarograms and voltammograms recorded under nitrogen-$LiClO_4$, LiCl, from Smith Chemical Co and Rhône Poulenc respectively are used as received.
- The diiodide $I(CF_2)_4I$ was a generous gift from PUK Company.
- Potentiostat was a PRT 40 (40 volts one ampere). Integrator IGSN.
- Polarographic unit PRG5 and GSTP3 for LSV. All from TACUSSEL.

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7 In table 1 of ref. [1], the values of J_{F-Hg} must be read as following :

$(C_6F_{13})_2Hg$ $J_{^{19}F_{\alpha}-Hg} = 790.0$ Hz, $J_{^{19}F_{\beta}-Hg} = 150.0$ Hz

$C_6F_{13}HgI$ $J_{^{19}F_{\alpha}-Hg} = 1090.0$ Hz, $J_{^{19}F_{\beta}-Hg} = 140.0$ Hz