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OXIDATIVE FLUORINATION IN AMINE-HF MIXTURES

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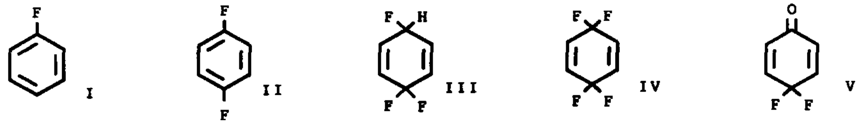
Abstract: The selective electrochemical fluorination of alkenes, phenanthroline, naphthalene and chlorobenzene in neat amine-HF mixtures is described, together with the chemistry of 4,4-difluorocyclohexadienone.

INTRODUCTION

Many methods exist for the preparation of fluorine-containing organic compounds. Perfluorinated products are mainly obtained by two processes: high-temperature reactions with high-valency metal fluorides[1] and the electrochemical Simons process[2]. Numerous methods have been developed for the preparation of selectively fluorinated compounds. Often, these consist of displacing a functional group by a fluoride. Methods for direct oxidative fluorination generally require the handling of elemental fluorine, either in a direct reaction with the substrate[3] or in the preparation of fluorinating agents, such as XeF_2[4], hypofluorites[5] or N-fluoro compounds[6]. Methods for selective oxidative fluorination that avoid the use of elemental fluorine include oxidation of the substrate with high-valency metals[7], photochemically[8] or anodically in the presence of a fluoride source. Selective electrochemical fluorination has been achieved by I.N.Rozhkov[9], who electrochemically oxidized benzene, substituted benzenes and naphthalene in solutions of tri- or tetraalkylammonium polyhydrogen fluorides in acetonitrile. For the fluorination of aromatics without electron-withdrawing substituents, however, the method yields fluorination only at low conversions and periodic current interruptions are required for the desorption of polymeric material formed on the electrode. Other groups have achieved the fluorination of aromatic side chains[10], anthracene[11] and pyrazole[12] derivatives using similar conditions. In the electrolyte the substrate is oxidized to give (radical) cations which subsequently react with a fluoride ion. The solvent acetonitrile may compete with the fluoride ion in the reaction with the intermediate cationic species formed. We have reported previously on a system that overcomes electrode passivation and solvent participation by oxidizing the substrate in neat amine-HF mixtures[13]. Benzene, electrochemically oxidized in these mixtures, reacted to give I-IV.



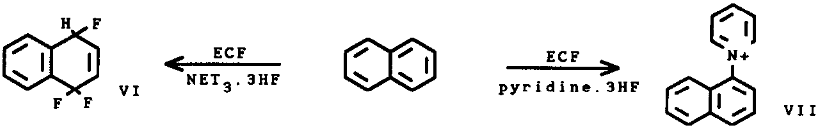
Scheme 1

Chemical oxidation of benzene and phenol in these mixtures with Pb(IV) compounds gave V. We now report on the extension of the use of these mixtures to selective electrochemical fluorination (ECF), and further on the related chemistry of fluorinated products.

RESULTS AND DISCUSSION

Electrochemical experiments were carried out by circulating the electrolyte through a plate cell operating at a constant current (3-6 mA/cm^2) using a platinum anode and a monel cathode. The electrolysis of benzene (1 mole/l) in pyridine.9HF resulted in a continuously growing black deposit on the anode without increase of cell voltage, indicating the formation of conductive poly-p-phenylene, as has also previously been observed in the electrochemical polymerization of benzene on the interface of pure HF[14]. Using pyridine.9HF the polymer is deposited from a homogeneous solution. Increasing the amount of pyridine inhibited polymer formation and, using pyridine.4HF, benzene was fluorinated to give I-IV in modest yields. Better results were obtained using $NEt_3.3HF$[13].

A pronounced amine effect was observed in the electrolysis of naphthalene.



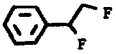
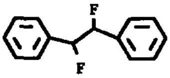
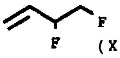
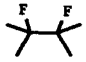
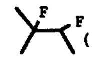
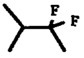
Scheme 2

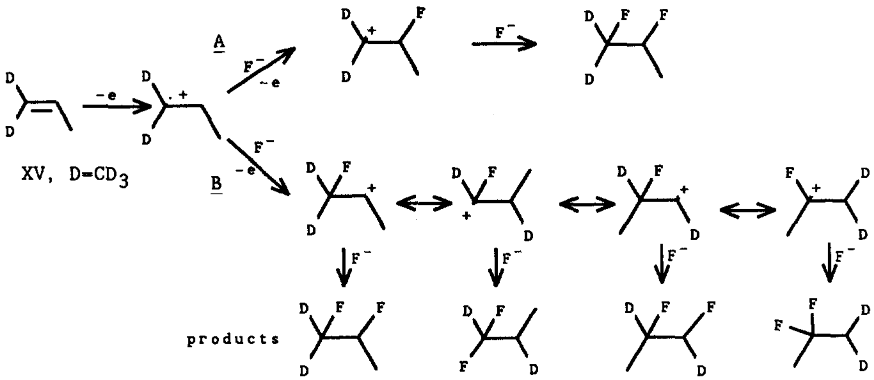
Using pyridine.3HF not even traces of fluoronaphthalenes were formed. The reaction afforded a pyridinium salt (VII) which was isolated in 50% yield. Using $NEt_3.3HF$ the electrolysis afforded VI (18%) together with 1-fluoronaphthalene (6%). In the reaction naphthalene was oxidized to give a radical cation. In $NEt_3.3HF$ it reacted with fluoride. Subsequent oxidation followed by the release of a proton yielded fluoronaphthalene, which was further oxidized to give VI. In pyridine.3HF the radical cation of naphthalene reacted exclusively with pyridine.

The electrochemical oxidation of olefins in $NEt_3.3HF$ led to 1,2-addition of fluorine to the double bond (see Table 1). In the case of butadiene 1,4-addition also took place. ECF of cyclopentene and α-pinene gave complex reaction mixtures, containing fluorinated products. ^{19}F-NMR showed that geminal difluoro compounds were also formed in these reactions.

The ECF of 2-methylbutene-2 gave only one major by-product (XIV). The formation of this geminal difluoro compound was investigated by ECF of labelled 2-methylbutene-2 (XV) prepared by a Wittig reaction with hexadeuteroacetone. Due to the basic conditions of this reaction, XV contained also vinylic deuterium. Surprisingly, NMR analysis of the fluorinated reaction mixture of XV showed a complete scrambling of CD_3 groups in the products, which may be explained by the sequence depicted in Scheme 3. Anodic oxidation of XV resulted in the formation of a radical cation. Fluoride addition may take place either at the secondary (path A) or the tertiary carbon atom (path B). Subsequent release of an electron gives a tertiary or a secondary carbenium ion respectively. From the absence of geminal difluoro compounds in the fluorination of dimethylbutene-2 involving only tertiary carbenium ions, we conclude that path B is preferred and a secondary carbenium ion is formed. In this unstable species a 1,2-methyl shift takes place.

TABLE 1: ECF of olefins in $NEt_3.3HF$

styrene	$\xrightarrow{2F/mole}$		(VIII,51%)
stilbene	$\xrightarrow{2F/mole}$		threo (IXa,20%) erythreo(IXb,12%)
butadiene	$\longrightarrow$	 (X)  (XI)	(ratio 1:2)
2,3-dimethylbutene-2	$\xrightarrow{2F/mole}$		(XII,22%)
2-methylbutene-2	$\xrightarrow{2F/mole}$	 (XIII,23%) 	(XIV,11%)
octene-1	$\longrightarrow$	solvent degradation	
cyclopentene, α-pinene	$\longrightarrow$	complex mixture of fluorinated products	

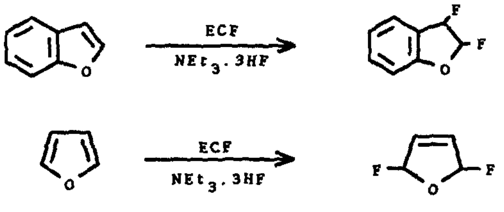


XV, $D=CD_3$

Scheme 3

In this particular case the shift is reversible and rapid, and fluoride traps a scrambled intermediate. The experiment shows that stabilization by fluorine located on the positive carbon atom is of the same order as stabilization by hydrogen. Furthermore, cation stabilization of fluorine in the α-position is negligible, in contrast to that of the well-known bromonium ions. It may be clear that, in this particular case only, wandering alkyl groups afford only two products and stabilization of intermediate carbenium ions is required for selective fluorination.

Unstable products were obtained in the electrochemical fluorination of benzofuran and furan in $NEt_3.3HF$ (Scheme 4). In the case of furan, 1,4-addition of fluorine takes place



cis and trans (XVIa,b)

cis and trans (XVIIa,b)

Scheme 4

to give cis- and trans-2,5-difluoro-2,5-dihydrofuran (XVII). The compound proved to be extremely labile when separated from the electrolyte and its structure could only be assigned on the basis of ^1H-NMR showing two AA'BB'XX' spin systems with the characteristic large geminal FH coupling (see Fig. 1).

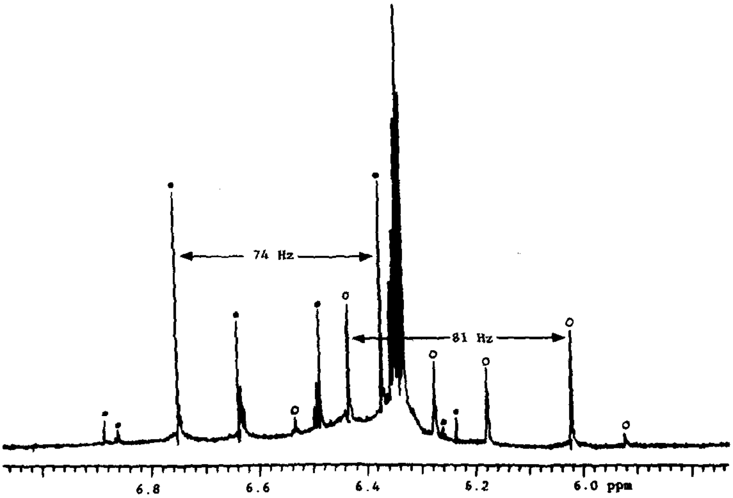
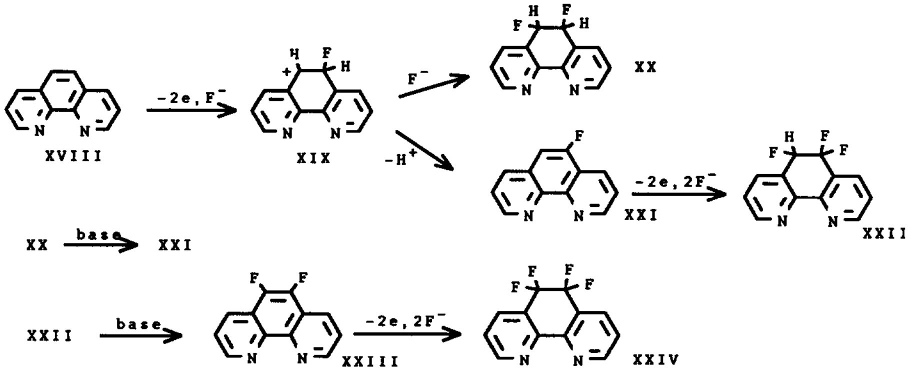


Fig 1: ^1H-NMR (200 MHz) of XVIIa (•) and XVIIb (o)

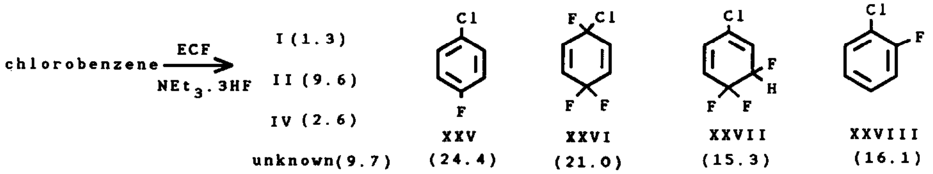
At ambient temperature a solution of XV in $CDCl_3$ decomposed within 30 min to give a black resinous product, accompanied by the emission of HF fumes. The oxidation of furan in $NEt_3.3HF$ with bromine resulted in the formation of a complex reaction mixture. However, product XVII was also formed, which may open the possibility of using a mediator to achieve fluorination, similarly to the bromine-mediated electrochemical methoxylation of furan[15].

The electrolysis of 1,10-phenanthroline (XVIII) in $NEt_3.3HF$ resulted in the degradation of the electrolyte. Increasing the amount of HF to $NEt_3.6HF$ raised the anodic limit of the electrolyte, so that complete oxidation of XVIII could take place. This resulted in the formation of equal amounts of XX and XXII (Scheme 5). Dehydrofluorination with base gave a mixture of XXI and XXIII respectively. In a second electrolysis this mixture gave XXII and XXIV. Repeating the base/electrolysis sequence afforded the tetrafluoro compound (XXIV) in 34% isolated yield based on intake of phenanthroline. In this case the substrate may replace the amine and ECF of phenanthroline in HF (50% w/w) operated for 72 h without anode passivation. The simultaneous formation of both XX and XXII may be explained by a twisted pyridine-pyridine bond in the Wheland intermediate XIX. This places the α-proton in either an axial or an equatorial position. In the first case elimination of this proton is favourable and gives XXI. The unfavourable elimination of the equatorial proton does not take place and subsequent reaction of XIX with fluoride gives only one isomer of XX, which is further oxidized to give XXII. The introduction of fluorine in the aromatic nucleus apparently lowers its oxidation potential with respect to the parent molecule. No data is available on the oxidation potentials of phenanthroline or 5-fluorophenanthroline, but similar behaviour has been observed in the anodic fluorination reactions of naphthalene, phenol and benzene[13]. Comparison of the Ionization Potential (IP) of the latter (9.25 eV) with that of fluorobenzene (9.21 eV) and 1,4-difluorobenzene (9.15 eV) may indicate that selective monofluorination of aromatic compounds is difficult to achieve at high conversions.



Scheme 5

Absence of selective monofluorination was also observed in the ECF of chlorobenzene. Conversion after 2 F/mole was 67% and gave 43% of fluorinated products. In Scheme 6 relative amounts of products are given.



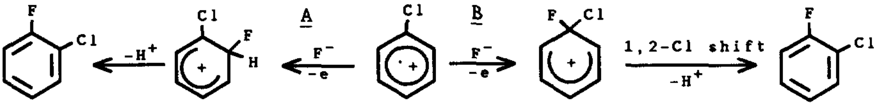
Scheme 6

In the reaction the radical cation of chlorobenzene reacts with fluoride. Rozhkov observed that the regioselectivity of the attack of fluoride to aromatic radical cations is determined by charge distribution in the intermediate[9]. Charge density distribution together with coefficients of SOMO and LUMO of the radical cation of chlorobenzene were calculated using MNDO[15] (Table 2).

TABLE 2: MNDO of the radical cation of chlorobenzene

	Cl	C_1	C_2	C_3	C_4	C_5	C_6
Charge	0.124	0.150	-0.008	-0.046	0.190	-0.050	-0.007
SOMO	0.320	-0.571	-0.278	0.242	0.547	0.238	-0.283
LUMO	-0.146	0.589	-0.311	-0.228	0.578	-0.224	-0.318

From the absence of a positive charge in the 2-position, Rozhkov proposed that the formation of 2-fluorochlorobenzene (XXVIII) was the result of IPSO attack by fluoride, followed by migration of chlorine in the subsequent cation[9] (path B in Scheme 7).



Scheme 7

Verification of this mechanism by ECF of 2,3,5,6-tetradeuterochlorobenzene and NMR analysis of XXVIII showed a J_{HF} of 5.0 Hz, which is consistent with *m*-coupling as the value of the *p*-coupling would have been 0.85 Hz[16]. Thus XXVIII is formed via path A by direct addition of fluoride at C_2, despite the absence of a positive charge on this atom. Products I, II, IV and XXV-XXVII (ca. 80%) are formed via addition of fluoride at C_1 and C_4, giving fluorobenzene (I) and XXV respectively. In view of the formation of XVIII we considered that a frontier orbital term may play a role as well, and coefficients of the half-vacant orbital SOMO and LUMO are given in Table 2. Simulating the approach of fluoride to C_1, MNDO shows an increase of charge on chlorine and to a minor extent on C_2, and a decrease of charge on C_1, while coefficients of both SOMO and LUMO on C_2 increase. This now indicates that the addition of fluoride at C_2 is the result of polarization of the substituent. For example, ortho-fluorination has been observed in tert-butylbenzene[9] and chlorobenzene but not in fluorobenzene[9,13]. Calculated SOMO and LUMO energy levels are respectively -12.0 and -5.97 eV. Comparison with the experimental value of the SOMO of the radical cation of benzene (-16.4 eV)[17] indicates a significant error using MNDO (ca. 4 eV) although, being gas-phase figures, the very low values may suggest that interaction of the HOMO of fluoride (-12 eV) with the SOMO or even with the LUMO of the radical cation of chlorobenzene is feasible. The introduction of an electron in the antibonding orbital of a carbon-halogen bond generally leads to bond cleavage. This and the preferential addition of fluoride at the tertiary carbon atom in Scheme 3 may be arguments in favour of a HOMO-LUMO interaction. The susceptibility of radical cations to fluoride addition may now be related to their energy levels. Although SOMO-LUMO energies are not directly related to the HOMO energies it is illustrative that, when using pyridine.3HF, electrolysis of benzene (IP = 9.23 eV) gives fluorinated products whereas naphthalene (IP = 8.12 eV) reacts to give a pyridinium salt (HOMO of nitrogen of pyridine = 10.5 eV).

It should be noted that direct attack of fluoride on aromatic radical cations has been the subject of discussions[18-21]. According to Eberson[18,21] the transition state, by analogy with the reaction of a carbene and a double bond, involves attack by fluoride perpendicular to the π-system at the mid-point between two centres and hence should be forbidden according to the Dewar-Zimmermann rules. In our opinion the addition of fluoride at a radical cation is not a chelotropic reaction. Addition of fluoride, a nucleophile, takes place at a centre, like the Michael addition, and hence the Dewar-Zimmermann rules are not applicable in this case.

THE ELECTROLYTE: AMINE-HF MIXTURES

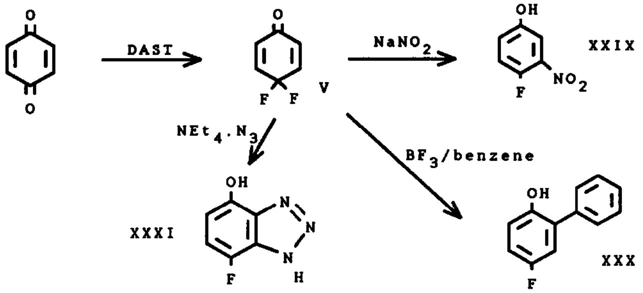
The use of pure amine-HF mixtures as electrolytes enables electrochemical fluorination to be carried out on a continuous basis without electrode passivation, and conversions of up to 100% can be achieved. Product selectivities differ from those when acetonitrile is used as a co-solvent. In the present study we mainly used $NEt_3.3HF$. In the presence of organic substrates the complex is neutral, which is illustrated by the stability of compounds such as VI, XVI and XIX in $NEt_3.3HF$. The anodic limit permits oxidation of benzene without serious degradation of the electrolyte. Attempts to fluorinate substrates which are more difficult to oxidize, such as octene-1 and XVII, resulted in the degradation of electrolyte. Volatile degradation products found were acetaldehyde, acetyl fluoride and fluoroethane. The oxygen-containing products indicate the presence of small amounts of water in the electrolyte. The anodic range of the electrolyte can be increased by additional amounts of HF. Using $NEt_3.6HF$, phenanthroline was fluorinated. Electrolytes with a high anodic range and with a low HF content may consist of tetraalkylammonium fluorides and HF. For example, $NEt_4F.3HF$ was used for the fluorination of benzene[13]. In pyridine-HF-containing electrolytes, pyridine may compete with fluoride as a nucleophile, as observed in the fluorination of naphthalene.

It will be clear that a variety of amine-HF complexes can be used in a reaction. HF content as well as the size and number of alkyl groups in the amine may be adjusted for a particular conversion.

The use of HF complexes as electrolytes provides a very convenient counter-electrode reaction, eg hydrogen evolution, which in most cases allows the use of a very simple cell design. Only when easily reducible products as V or substrates are present may a divided cell be required. Electrode materials which were found to be stable using $NEt_3.3HF$ in the electrofluorination of benzene were vitreous carbon, platinum and platinum deposited on a copper base. Vitreous carbon rapidly degrades when polarized in electrolytes with a higher HF content. Lifetimes of graphite electrodes did not exceed 10 min. Chemical oxidants such as PbO_2[7b,13] and bromine may behave as electron oxidants in the fluorination reactions. The fixed potential of these chemical oxidants may prevent selective oxidation of the substrate. Furthermore, these reagents introduce additional nucleophiles such as reaction water or bromide, which limits their applicability.

4,4-DIFLUOROCYCLOHEXADIENONE

Oxidative fluorination may lead to the formation and accessibility of interesting compounds with unexplored chemistry such as 4,4-difluorocyclohexadienone (V). The compound has been prepared by the anodic fluorination of 4-fluorophenyl ethers[22]. We have previously reported[13] that V is also formed by oxidative fluorination of phenol in amine-HF mixtures and have described reactions of V with methanol, cyanide and hydrogen. An additional method we have found for the preparation of V consists of refluxing equal amounts of p-benzoquinone and dimethylaminosulphur trifluoride (DAST) in hexane, which gave V in 50% yield. Novel conversions of V in yields >60% are depicted in Scheme 8. Similar to the reaction of V with cyanide is the reaction with sodium nitrite in DMSO at 80°C, which gives XXIX. In the presence of small amounts of water V is reduced by nitrite to give 4-fluorophenol.



Scheme 8

An intermediate in the formation of 4,4-difluorocyclohexadienone is the 4-fluorocyclohexadienonyl cation, which is formed by oxidation of 4-fluorophenol in amine-HF mixtures. In these mixtures the cation reacts at the 4-position with fluoride to give V. The reverse reaction takes place in a reaction of V with BF_3/ether in benzene and the 4-fluorocyclohexadienonyl cation reacts with benzene, yielding XXX. In DMF a curious reaction of V with azide in DMF takes place, which affords the triazole compound XXXI.

EXPERIMENTAL

CAUTION! Hydrogen fluoride is toxic and if in contact with skin causes serious burns. Amine/HF compositions are much less aggressive. However, proper safety precautions should be taken at all times[23]. Fluorocyclohexadienones are strongly lachrymatory. Care should be taken with compounds that contain monofluorinated sp3 carbon atoms. They may spontaneously decompose, giving off HF fumes. With VI and XVII spontaneous and exothermic reactions with emission of HF took place.

The plate cell (Electroprep cell^{TM}) was assembled from a flat platinum anode (18.5 x 5.0 cm) and a monel cathode (18.5 x 5.0 cm) separated by a 0.5-2 mm thick teflon gasket of the same size with an excision of 17.0 x 3.0 cm. The electrolyte was circulated through the cell and an open reservoir at a rate of ca. 50 ml/min using a peristaltic pump. The minimum hold-up of the loop was 7 ml. The electrolyses were carried out at ambient temperature (20-25°C) and 2 F/mole were passed. Concentrations of the substrates varied from 50-250 g/l. Current was maintained constant (3-6 mA/cm^2) using a potentiostat (PAR, model 173). $NEt_3.3HF$ (ex Fluka), pyridine.9HF (ex Merck) and chemicals were used as received. Other amine/HF mixtures were prepared by condensation of HF in a polyethylene bottle containing the amine (ca. -30°C, highly exothermic!!). The Pt electrode consisted of 0.1 mm platinum foil glued on a copper base. The Pt/Cu electrode consisted of a electrodeposited layer of platinum on copper (2% $(NH_4)_2.PtCl_6/NH_3$, ca. 60°C, 1 mA/cm^2, 3 h)[24]. The 2,3,5,6-tetradeuterochlorobenzene was prepared by deuteration of 4-chlorobromobenzene with D_2SO_4[25] followed by selective reduction[26]. The experiment described below is illustrative of electrochemical fluorination in amine-HF mixtures.

Phenanthroline (13.5 g, 0.075 mole) in 40 ml of $NEt_3.6HF$ was electrolysed in the cell (3 mA/cm^2, 3.5 F/mole) for 49 h. Then 200 ml of water and 100 ml of CH_2Cl_2 were added. The mixture was neutralized to pH 9 with K_2CO_3. The organic layer was filtered over silica gel and evaporated to give XX and XXII. This mixture was dehydrofluorinated by stirring at 60°C for 1.5 h with 200 ml of 10% K_2CO_3 solution. Extraction with 200 ml of CH_2Cl_2 and evaporation of the solvent dried with $MgSO_4$ gave 11.3 g of a mixture of XXI and XXIII. This sequence was repeated twice, passing 2.1 F/mole for the second electrolysis and 0.5 F/mole (based on intake of XVIII) for the third electrolysis, giving 8.7 g of impure XXIV. This was dissolved in 100 ml of CH_2Cl_2 and 10% HCl was added until XXIV started to dissolve in the aqueous phase. Then the organic solvent was dried over $MgSO_4$, evaporated and the residue distilled (170°C/0.5 mm Hg) to give 6.5 g of pure XXIV. Mp 102.6°C. ^{1}H-NMR:7.50, 8.13 and 8.98 ppm. ^{13}C-NMR:112.5, 124.6, 125.2, 133.3, 149.3 and 153.6 ppm.

4,4-Difluorocyclohexadienone (V): A mixture of p-benzoquinone (10.8 g, 0.1 m) and DAST (16.1 g, 0.12 m) was stirred at 60°C for 7 h. After cooling, dichloromethane was added (50 ml). Excess DAST was decomposed by careful addition of water. Then the mixture was extracted with water and dried over magnesium sulfate. The solvent was distilled off and the residue sublimated (80 - 120°C). Recrystallization of the sublimate from hexane gave V (6.5 g, 50%).

^{19}F-NMR (Varian XL200) in $CDCl_3$ ($CFCl_3$=0ppm). Coupling constants with nuclei in Hz (d=doublet, t=triplet q=quartet). Separations of major lines into patterns that are not first order are given in Hz.

VI	-77.2(dF=306.8), -87.0(dF=306.8), -172.1(dH=46.8)
VIII	-222.5(dF=16.2, tH=47.8, dH=15.8), -186.1(dH=21.0, 29.7 ,dF=16.2)
IXa	-183.8(AA'XX' 62.8)
IXb	-187.1(AA'XX' 64.8)
X	-188.6(dF=14.8, dH=49.0, 23.2, 26.0, 14.8), -228.3(dF=14.8, tH=47.8, dH=18.5)
XI	-216.7(tH=51.0, dH=11.2)
XII	-150.9(septet H=23.4, septet H=4.1, perturbed $AA'X_6X_6'$)
XIII	-151.1(dF=9.9, septet H=21.1, dH=13.0, qH=0.7), -183.7(dF=9.9, dH=47.5, qH=24.4, septet H=1.7)
XIV	-97.9(qH=18.7, dH=12.8)
XVIa	-133.3(dF=11.8, dH=58.7, 11.0), -175.7(dF=11.8, dH=56.0)
XVIb	-146.0(dF=16.5, dH=62.0, 14.0), -200.0(dF=16.5, dH=55.0)
XX	-123.8(AA'XX' 34.4)
XXI	-123.8(dH=10.5)
XXII	-111.0(dF=135.0), -116.0(dF=135.0), -198.9
XXIII	-151.5
XXIV	-121.3
XXVI	-92.7(2F), -103.5
XXVII	-104.8(dF=209.6, 3.6, dH=14.0, 5.0), -114.9(dF=209.6, 3.2, dH=11.0, 5.7), -199.6(dF=3.2, 3.6, dH=46.9, 7.0)
XXIX	-132.8(dH=3.8, 6.0, 11.0) in DMSO-d_6
XXX	-124.7(dH=5.5, 7.4, 9.4) in benzene-d_6
XXXI	-134.5(dH=3.3, 10.3) in methanol-d_4/CF_3CO_2H

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