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Transformations of Perfluoroxylenes and Perfluoro-p-cymene under the Action of Zn(Cu)-DMF-H_2O.[1]

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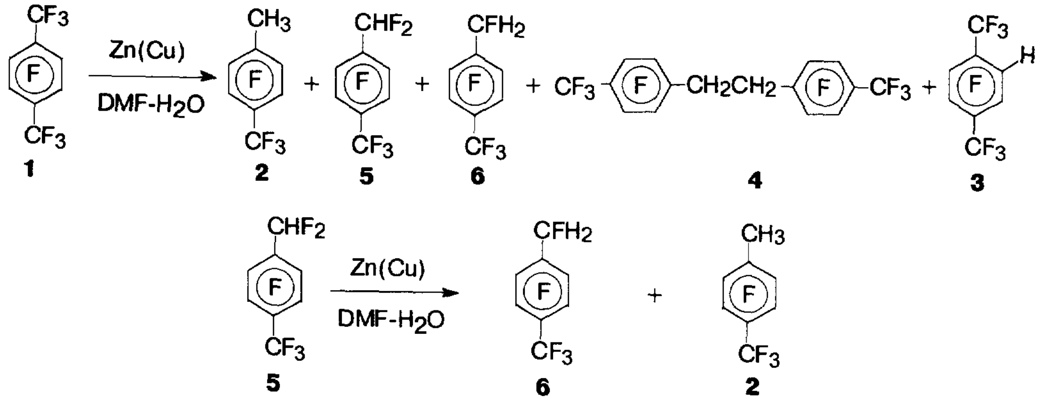
Dedicated to Professor Alois Haas, on the occasion of his 65th birthday.

Abstract. Perfluorinated xylenes and perfluoro-para-cymene undergo hydrodefluorination under the action of Zn(Cu)-DMF-H_2O. Hydrogen enters mainly at the benzyl position of para-dialkylbenzenes and at the *para* position to perfluoroalkyl groups of perfluorinated *ortho-* and *meta-*xylenes. The process presumably involves radical anions as intermediates. A product of perfluoro-4-methylbenzyl radical trapping by hexene-1 was obtained. Quantum-chemical calculations of radical anions of the compounds under investigation have been carried out.

The most general use of zinc for hydrodehalogenation is to exchange iodine, bromine and chlorine for hydrogen [2]. Nucleophilic agents such as $LiAlH_4$ are usually employed for hydrodefluorination of polyfluoroarenes [3]. The study of regularities in hydrodefluorination initiated by an electron transfer to an organic molecule is of interest, as the fundamental mechanistic difference of this process from nucleophilic substitution can offer novel ways for the synthesis of fluoro-containing substances [4]. In this connection the electrochemical reduction of partially fluorinated benzoic acids, nitriles and polyhalonitrobenzenes are also noteworthy [5]. The action of reagents such as dissolving metals is another method of realizing electron transfer. We have found the reducing system Zn(Cu)-DMF-H_2O to be efficient in the hydrodefluorination of polyfluorinated aromatic compounds [1]. Hydrogenolyses of C-F bonds both in benzyl position and in the aromatic ring take place under the action of this reagent. Regularities in the reactions of perfluorinated para-, meta-, ortho-xylenes, perfluoro-para-cymene, and products arising from their transformations with Zn (Cu)-DMF-H_2O are considered in this paper.

Transformation of one trifluoromethyl group into methyl was found to be the main reaction on treatment of perfluoro-p-xylene (**1**) with Zn(Cu)-DMF-H_2O (Scheme 1). At 70°C (20 hours) and with the ratio of the reactants as given in the Table 1 (exp 3), xylene **1** was converted almost completely into the reaction products, 1-trifluoromethyl-4-methyl-2,3,5,6-tetrafluorobenzene (**2**) being the dominant component. The product of aromatic ring C-F bond hydrogenolysis - 1,4-bis(trifluoromethyl)-2,3,5-trifluorobenzene (**3**), and the coupled product - 1,2-bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)ethane (**4**) were also obtained but in lower yields. Decrease in the reaction time and in the proportion of zinc (exps 1,2) lowered the conversion of the starting xylene **1**, although the product **2** was still predominant. Products of partial substitution of hydrogen for fluorine in CF_3-group (**5** and **6**) were found in small amounts. Hydrodefluorination of **1** into compounds **2** and **3** also took place under the action of Zn-DMF-H_2O, when the zinc was activated with HCl (exp 5), but the extent of conversion was small. Hardly any hydrodefluorination was observed when treating perfluoro-p-xylene with activated zinc in dimethylformamide in the absence of water (exp 6).



Scheme 1

The xylenes **2** and **6** were the major products, when 1-trifluoromethyl-4-difluoromethyl-2,3,5,6-tetrafluoro-benzene (**5**) was reacted with Zn(Cu)-DMF-H_2O (Table 1, exps 8 and 9). The process is likely to proceed via the formation of 1-trifluoromethyl-4-fluoromethyl-2,3,5,6-tetrafluorobenzene (**6**). When treating compound **2** with Zn(Cu)-DMF-H_2O (exp 7), the starting compound was recovered in high yield, with no evidence for the formation of other compounds.

Table 1. Reactions of xylenes **1**, **2** and **5** with Zn(Cu)-DMF-H_2O.

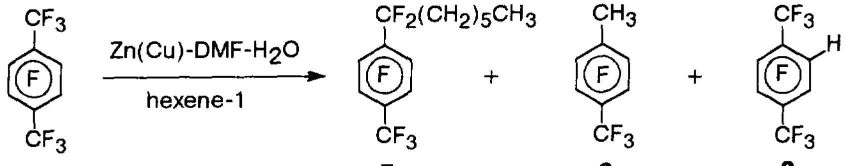
No.	Starting compound, g	Reaction temperature and time	Reactants mole ratio arene:Zn:Cu:DMF:H_2O	Reaction products, yields, %						
				1	**2**	**3**	**4**	**5**	**6**	**7**
1	**1**, 1.45	70°C, 5 h.	1 : 6 : 3 : 30 : 46	49	9	<1	-	1.5	2	
2	**1**, 1.45	70°C, 10 h.	1 : 6 : 3 : 30 : 46	39	22	2	-	1	1.5	
3	**1**, 14.40	70°C, 20 h.	1 : 12 : 3 : 30 : 46	<1	76	7	2			
4	**1***, 14.40	65°C, 20 h.	1 : 12 : 3 : 30 : 46	41	20	2	-	<0.5		5
5	**1**, 14.40	70°C, 20 h.	1 : 12 : 0 : 30 : 46	77	7	<1				
6	**1****, 1.80	70°C, 20 h.	1 : 12 : 0 : 30	67★	<1					
7	**2**, 3.32	70°C, 20 h.	1 : 12 : 3 : 30 : 46		88					
8	**5**, 0.45	70°C, 5 h.	1 : 6 : 3 : 30 : 46	-	25	-		8	33	
9	**5**, 0.45	70°C, 10 h.	1 : 6 : 3 : 30 : 46		40			-	10	
10	**1**, 0.72 + **5**, 0.67	70°C, 10 h.	1 : 6 : 3 : 30 : 46	11	44	2		<0.5	1	

* In the presence of hexene-1 (see Experimental).

** With an activated zinc (see Experimental) without water addition.

★ 1.26 g of a mixture containing 88% of xylene **1** was obtained.

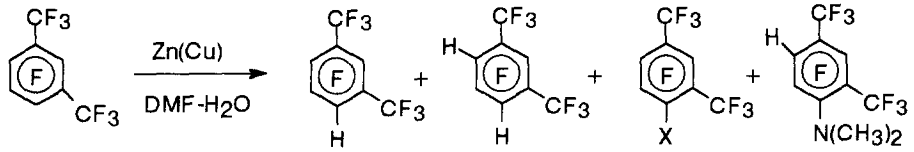
The reaction of perfluoro-p-xylene with Zn(Cu)-DMF-H_2O in the presence of hexene-1 (exp 4) resulted in the formation of several products in addition to the compounds **2** and **3** observed under the usual conditions, though the dimer **4** was not found. We succeeded in isolating the main component - 1,1-difluoro-1-(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)heptane (**7**) from the mixture of additional products which had close boiling points.



1 **7** **2** **3**

Scheme 2

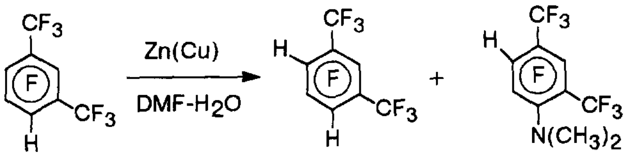
Under the conditions of complete conversion (Table 2, exp 13) perfluoro-m-xylene (**8**) reacted to give 1,3-bis(trifluoromethyl)-2,4,5-trifluorobenzene (**9**) as the main product, along with 1,3-bis(trifluoromethyl)-2,5-difluorobenzene (**10**), 1,3-bis(trifluoromethyl)-4-dimethylamino-2,5,6-trifluorobenzene (**11a**) and 1,3-bis(trifluoromethyl)-4-dimethylamino-2,5-difluorobenzene (**12**), isolated by steam distillation. Furthermore, 2,4-bis(trifluoromethyl)-3,5,6-trifluorophenol (**11b**) was separated in small amounts.



8 **9** **10** **11** **a** X=$N(CH_3)_2$ **b** X=OH **12**

Scheme 3

Decrease in reaction time and zinc amounts (exp 11 and 12) resulted in the formation of monohydroderivative **9** without compounds **10** and **12**. The nonafluoroxylene **9** was shown to give the hydro derivative **10** and dimethylamino derivative **12** when treated with Zn(Cu)-DMF-H_2O (exp 14). Octafluoroxylene **10** was recovered in high yield when treated with Zn(Cu)-DMF-H_2O (exp 15); no products of its further hydrodefluorination were found.



9 **10** **12**

Scheme 4

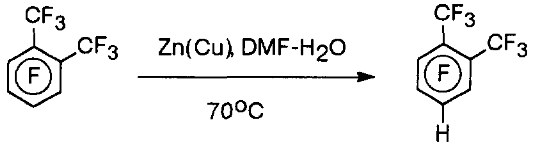
Table 2. Reactions of xylenes **8**, **9**, **10** and **13** with Zn(Cu)-DMF-H_2O.

No.	Starting compound, g	Reaction temperature and time	Reactants mole ratio arene:Zn:Cu:DMF:H_2O	Reaction products, yields, %					
				8	**9**	**10**	**11**	**12**	**14**
11	**8**, 1.45	70°C, 5 h.	1 : 3.2 : 3.2 : 32 : 48	42	12	-	**a**-3	-	
12	**8**, 2.80	70°C, 10 h.	1 : 4 : 4 : 33 : 36	10	43	-	**a**-3	-	
13	**8**, 5.70	70°C, 20 h.	1 : 12 : 3 : 30 : 46	-	53	15	**a**-3, **b**-4	8	
14	**9**, 1.35	70°C, 10 h.	1 : 6 : 3 : 30 : 46	-	67	3	-	2	
15	**10**, 0.75	70°C, 20 h.	1 : 12 : 3 : 30 : 46			60*			
16	**13**, 0.30	70°C, 7 h.	1 : 5 : 5 : 40 : 56						38**

* The starting compound only (0.45 g).

** 0.12 g of a mixture containing 2.5% of **13**, 91% of **14** (GLC) was obtained.

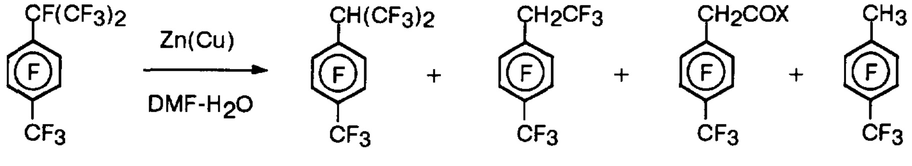
The product of substitution of one fluorine atom in the aromatic ring - 1,2-bis(trifluoromethyl)-3,4,5-trifluorobenzene (**14**) has been obtained by hydrodefluorination of perfluoro-o-xylene (**13**) (Table 2, exp 16).



13 **14**

Scheme 5

Perfluoro-p-cymene (**15**) gave a number of products from the reaction of the heptafluoroisopropyl group on treatment with Zn(Cu) in aqueous DMF (Scheme 6). 1-Trifluoromethyl-2,3,5,6-tetrafluoro-4-(2,2,2-trifluoroethyl) benzene (**17**) was produced in more than 60% yield at 70°C and 90°C (Table 3, exps 22, 24). The p-xylene derivative **2** (exps 22, 24) and the dimethylamide derivative of (4-trifluoromethyl-2,3,5,6-tetrafluorophenyl) acetic acid (**18b**) (exp 24) were found in small amounts. Moreover, 1-trifluoromethyl-2,3,5,6-tetrafluoro-4-(1,1,1,3,3,3-hexafluoro-2-propyl)benzene (**16**) was formed at 70°C (exp 22). The yield of the compound **16** increased at 50°C and when the reaction time was shortened to 5 hours (exps 18, 20, 21). However, further lowering of temperature to the room temperature slowed the reaction down, the overall yield of products being only 17% with the same ratio of the reactants (exp 17).



15 **16** **17** **18** **2**

a) X=OH

b) X=N(CH_3)$_2$

Scheme 6

Table 3. Reactions of cymene **15** and its products of transformation with Zn(Cu)-DMF-H_2O*.

No.	Starting compound, g	Reaction temperature and time	Reaction products, yields, %				
			15	**16**	**17**	**18**	**2**
17	**15**, 1.85	25°C, 10 h.	76	13	4		
18	**15**, 11.20	50°C, 5 h.	13	52	29		
19	**15**, 0.95	50°C, 5 h.**	74***				
20	**15**, 1.85	50°C, 10 h.	<1	38	31		
21	**15**, 1.85	50°C, 10 h.★	<1	35	35	**a**- 5	
22	**15**, 1.85	70°C, 10 h.	-	6	64		<1
23	**15**, 1.85	70°C, 10 h.★★	23	14	22	**a**- 4	-
24	**15**, 3.70	90°C, 5 h.	4	-	69	**b**- 3	4
25	**16**, 0.40	70°C, 10 h.		4	27★★★		
26	**17**, 1.50	90°C, 5 h.			69	**b**- 1	5

* The reactants mole ratio is arene:Zn:Cu:DMF:H_2O= 1 : 3.2 : 3.2 : 32 : 48.

** Without water addition.

*** Only the starting compound (0.70 g).

★ The reaction mixture treatment without steam distillation.

★★ With an activated zinc without copper.

★★★ 0.11 g of a mixture containing 80% of **17**, 15% of **16** was obtained. The low yield is due to a small quantity of the starting material used for reaction.

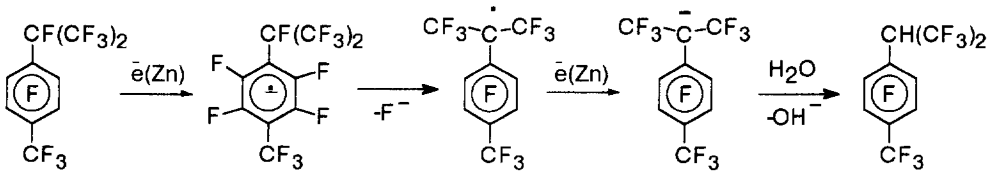
4-Trifluoromethyl-2,3,5,6-tetrafluorophenyl acetic acid (**18a**) was isolated in low yield from the products of the reaction of perfluoro-p-cymene **15** with Zn(Cu)-DMF-H_2O at 50°C avoiding a conventional reaction mixture treatment by steam distillation (exp 21). Compound **16** is converted into compound **17** under the action of Zn(Cu)-DMF-H_2O (exp 25). Compound **17**, in turn, gives products **2** and **18b** at 90°C (exp 26).

It should be noted that the hydrodefluorination of perfluoro-p-cymene (**15**) was also accomplished under the action of activated zinc in DMF-H_2O (exp 23). In this case, the same transformations were observed, but the conversion of the starting material was less than in a similar experiment with Zn(Cu)-DMF-H_2O (exp 22). No hydrodefluorination products were found on treatment of the cymene **15** with Zn(Cu) in dimethylformamide (50°C, 10 hours) in the absence of water (exp 19).

On the basis of the experimental results, we can conclude that hydrodefluorination reaction readily takes place in the treatment of perfluorodialkylbenzenes with Zn(Cu)-DMF-H_2O. This process is a key one in the case of further transformations of perfluoro-p-cymene. Distinctions in the direction of the substitution of hydrogen for fluorine are revealed which depend on the position and structure of the perfluoroalkyl group. Thus, the reactions of perfluorinated meta- and ortho-xylenes involve aromatic ring C-F bond, the trifluoromethyl groups remaining intact. Conversely, side chain hydrodefluorination predominates in the case of perfluorinated para-dialkyl benzenes: fluorine atoms in benzyl position are replaced by hydrogen. At the same time, in the reaction with perfluoro-p-xylene, some hydrodefluorination in aromatic ring was observed while with perfluoro-p-cymene no products of this type were detected. In contrast, fluorine atoms in aromatic ring are replaced in all the above perfluorodialkyl benzenes in the reaction with nucleophilic reactants [3c,3d,6].

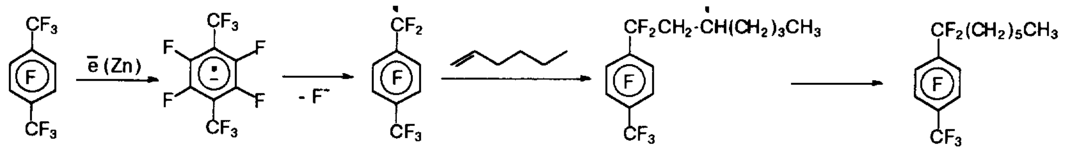
One of possible mechanisms of benzyl and aryl C-F bonds hydrogenolysis involves electron transfer from zinc surface to polyfluoroarene molecule, resulting in radical anion formation followed by its decomposition. It was reported [7] that non-halogenated arenes can form radical anions under the action Zn-DMSO-OH$^-$. The formation and decomposition of radical anions is suggested to account for perfluoroalkyl halogenides reactions initiated by reaction with zinc [8] and the defluorination of perfluorocycloolefins with Zn-DMF [9]. We suggest that the hydrodefluorination pathway can take place by a radical anion decomposition, which is determined by the electronic and spatial structure of the radical anion. Consequently, quantum-chemical (INDO UHF) calculations of radical anions and their decomposition products have been performed. Radicals of phenyl and benzyl type which result from fluoride ion elimination from various positions in radical anions were considered as such products. The choice of the method of calculation is a consequence of its successful (as distinct from MNDO) employment in the interpretation of structure and properties of a wide range of radical anions of polyfluorobenzene derivatives [10].

Scheme 7 illustrates the proposed mechanism for the hydrogenolysis of benzylic C-F bonds found in perfluoro-p-xylene (**1**) and perfluoro-p-cymene (**15**), using the conversion of the latter. The resulting radical anion fragments to benzyl radical and fluoride-ion. The radical is likely to form a hydrogen derivative by accepting an electron to generate a carbanion, which then reacts with water. Water in the hydrogenolysis seems to be more than a proton source, since the reaction hardly occurs without water. Water is known to accelerate sharply the fragmentation of radical anions with fluoride-ion elimination via transition state solvation. Thus, the fragmentation rate of 4-fluorobenzonitrile radical anion obtained in water is higher by 4 orders of magnitude than the corresponding value found in DMF solution. [5e,5f,11a]



Scheme 7

The formation of compound **4** provided support for the formation of benzyl-type radicals in the hydrogenolysis of perfluoro-p-xylene. Moreover, carrying out perfluoro-p-xylene hydrogenolysis in the presence of hexene-1 resulted in the trapping of perfluoro-(4-methylphenyl)methyl radical to yield the compound 7. The formation of the latter can be illustrated by the following scheme.



1

7

Scheme 8

Compound **2**, which resulted both from perfluoro-p-xylene (**1**) and perfluoro-p-cymene (**15**), seems to be considerably deactivated towards reaction with Zn(Cu)-DMF-H_2O (exp 7). Low reactivity of the compound **2** may be attributable to the decrease in the electron affinity of polyfluoroarene when a perfluoroalkyl group in the compounds **1** and **15** is replaced with an alkyl one, [11] which makes difficult the formation of a reactive radical anion. Our calculated values of electron affinity of xylene **1** and its hydrogen derivatives (Table 4) decrease with the substitution of hydrogen for fluorine in benzyl position. Therefore, inhibition of hydrogenolysis reaction might be expected at the stage of formation of xylenes **5** and **6**. With respect to the above it seems to be surprising that intermediates **5** and **6** containing CF_2H and CFH_2-groups are not found in considerable quantities. We have found that compound **2** is a predominant product even in the conversion of the starting compound to different extents. Xylenes **5** and **6** are found in small or trace amounts in the reaction mixtures. Xylene **5** was demonstrated (exp 10) to react essentially faster than xylene **1** by treatment of their mixture with Zn(Cu)-DMF-H_2O. To explain this, we have to take into account another factor which may affect the reactivity of the polyfluoroarene. The substitution of hydrogen for fluorine is known to lead to a lower bond strength of the remaining C-F bonds [12]. It has been previously shown that the rates of dehalogenation for radical anions of $ArCH_2Hal$ increase with decreasing of the C-Hal bond strength [13]. If a set of compounds **1**, **5**, **6** and corresponding radical anions is considered in terms of energy of bond cleavage (Table 4), it should be noted that the effect of bond strength shows a reverse trend to that of electron affinity. The C-F bonds strength in CF_2H- and CFH_2- groups are lower than those in CF_3- group. This factor may be also responsible for the participation of a less fluorinated substituent in the conversion of compounds **5** and **6**.

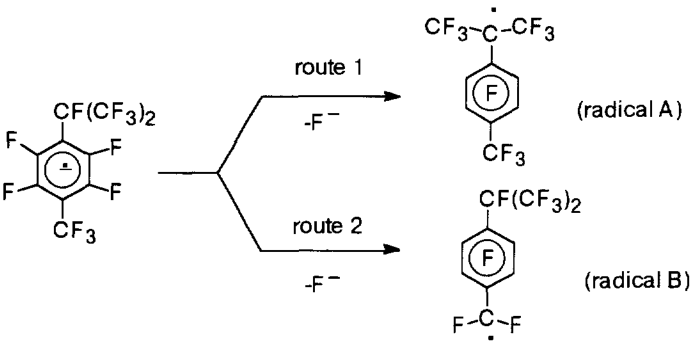
Table 4. Calculation results for the relative values of electron affinity (EA), energy of C-F-bonds dissociation* (D_{CF}) for neutral compounds (ArF), and radical anions (ArF^-).

Radical anion	**1**	**5**	**6**	**2**
EA, kcal/mol	0	- 9.78	- 15.65	- 25.98
D_{CF}(ArF), kcal/mol	0	-3.98	-6.05	2.60
D_{CF}(ArF^-), kcal/mol	0	-13.76	-21.70	-23.38

* C-F bonds in CF_3, CF_2H, CFH_2 and CF_3-groups of the compounds **1**, **5**, **6** and **2** correspondingly are considered.

Calculations based on two benzyl radicals formed from compound **5** by cleavage of the CHF-F and CF_2-F bonds have been carried out to verify the reasoning. The difference in their total energies can be considered also as the difference in the dissociation energies of the corresponding C-F bonds. $ArCF_2$-F bond are estimated to be stronger than ArCHF-F by 5 kcal/mol.

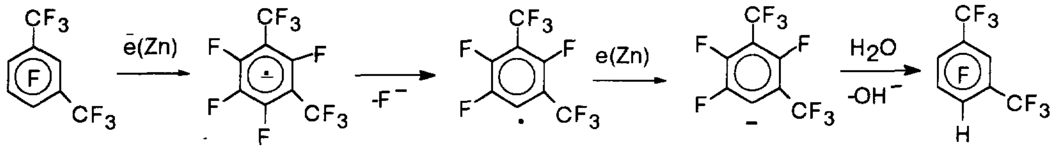
Based on the experimental results (exps 1,2,8,9,10), one may notice that the conversion rate of xylenes **5** and **6** is higher in the presence of xylene **1** than in its absence. For example, compound **5** afforded xylene **6** in 33% or 10% yields when treated with Zn(Cu)-DMF-H_2O for five or ten hours (exps 8,9), whereas the reactions of xylene **1** (exps 1,2) or mixture of xylenes **1** and **5** (exp 10) gives a small yield of **6**. Also, the amount of intermediate xylene **6** relative to final xylene **2** formed under equivalent conditions was found to be different. Thus, ratio of **6** to **2** is 1:4 in the case of pure xylene **5** transformation (exp 9), but decreases to 1:15 (exp 2) and 1:44 (exp 10) when mixture contains xylene **2**. Elucidation of reasons for this phenomenon is the subject for further investigations. It is not inconceivable that perfluoro-p-xylene is capable of favouring the transformations of xylenes **5** and **6**, acting as a mediator in the process of electron transfer.



Scheme 9

A greater stability of the radicals A as compared with the radicals B (by 39 kcal/mol according to quantum-chemical calculations) or, correspondingly, less strength of C-F bond in the case of route 1 (Scheme 9) is one of the possible reasons for perfluoro-p-cymene to react via transformation of heptafluoroisopropyl group rather than trifluoromethyl one.

Two mechanisms for C_{ar}-F bond defluorination are usually discussed [5b] when the decomposition of radical anions occurs in protic media. The first one is similar to that shown in Scheme 10, and involves both an intermediate radical anion and an aryl radical. The second one includes radical anion protonation. The available data on the kinetics of the fragmentation of radical anions of benzoic acids in protic medium being dependent on pH, [5b] bear witness to the first mechanism. Consequently we have used a mechanism of hydrodefluorination of perfluoro-m-xylene illustrated by Scheme 10, as example, to explain the obtained results on C_{ar}-F bonds hydrogenolysis. A similar scheme might also be suggested for perfluoro-o-xylene hydrogenolysis and transformation of para-xylene **1** into compound **3**.



Scheme 10

The total energy calculations for the phenyl- and benzyl-type radicals resulting from polyfluoroarene radical anion fragmentation in two different ways, predict benzyl type radicals to be more stable. The calculated difference in energies comprises 10.0, 6.2 and 12.3 kcal/mol for the radicals which resulted from **1**, **8** and **13** correspondingly. Moreover, the process of halogenarene π-radical anion fragmentation into a phenyl radical and a halogenide-anion is symmetry forbidden, since its energy barrier corresponds to the π and σ therms crossing [14]. It is also one of the reasons for an easier release of halogenide-anion from the benzyl position in the radical anion as compared with the one from the aromatic ring, which has been experimentally verified with, for example, data on the fragmentation rate for radical anions of halogenbenzonitriles and cyanobenzylhalogenides [15]. Consequently, the observed hydrogenolysis of an aromatic C-F bond with benzyl C-F bonds available in the molecule seems to be unusual.

Recently, a theoretical approach concerning the symmetry-forbidden fragmentation reaction of polyfluorobenzene radical anions with the elimination of a ring fluorine ion has been proposed [10]. It is based on the consideration of a vibronic interaction between the ground (π) and lower excited (σ) radical anion states, which allows the π and σ therms crossing to be avoided due to out-of-plane deviation of the leaving fluorine atom. Vibronic interactions of radical anion π- and σ-states account for its ability of out-of-plane distortion and is defined by the ratio value of squared vibronic coupling constant $\lambda_{\pi\sigma}$ to the excitation energy $\Delta E_{\pi\sigma}$. The constant $\lambda_{\pi\sigma}$ depends on the electron transition density between these states, and hence on the coincidence of SOMO localization in π- and σ-states.

The results of geometry optimization suggest radical anions of perfluorinated xylenes, and cymene **15** to be planar π-radicals. The SOMO in π- and σ-states are schematically depicted and the values of energy splitting $\Delta E_{\pi\sigma}$ are given in Figure 1. For comparison, similar values are represented in Table 5 for some fluoro-containing radical anions, from which only 3,5-difluorobenzonitrile radical anion has got a planar structure, as ESR and calculations indicate. At the same time, geometry optimization in the INDO frames reproduces the fact of out-of-plane distortion availability only in hexafluorobenzene and pentafluorobenzene radical anions. Having regard to this and comparing $\Delta E_{\pi\sigma}$ values, some out-of-plane distortion is likely to be expected also in the case of perfluoro-m-xylene **8** radical anion.

Table 5. Energy of the lower $\pi\sigma$-excitations in radical anions of perfluorinated compounds, radical anions structure and decomposition rate constants.

Radical anion	$\Delta E_{\pi\sigma}$[10], eV	Structure [5d,10]		k_{decomp} (in DMF)
		INDO	ESR	
C_6F_6	2.49	non-planar	non-planar	- *
C_6F_5H	2.15	non-planar	non-planar	- *
2,4,6-F_3-C_6H_2CN	2.97	planar	non-planar	$0.8 \cdot 10^3$ [5c]
4-F-C_6H_4CN	3.25	planar	non-planar	$1.1 \cdot 10^1$ [5f]
3,5-F_2-C_6H_3CN	3.80	planar	planar	$<1.7 \cdot 10^{-4}$ [5d]

* No data.

The Hartree-Fock solutions obtained for excited σ-states of perfluorinated xylene radical anions (see MO (b) in Fig.1) turned out to be symmetrically unstable: that is, there exists some additional broken-symmetry solutions of lower energy (MO (c) in Fig.1). Note, that these broken-symmetry solutions have no physical sense by themselves. However, the Hartree-Fock instability observed is suggestive of an essential role of correlation effects, the consideration of which allows a relative lowering of the σ-states levels. This tendency is roughly represented by $\Delta E_{\pi\sigma}$ values, obtained with regard to the energy of broken-symmetry σ-solutions (see Fig. 1). Ortho- and meta-isomers are of lower πσ-excitation energy ($\Delta E_{\pi\sigma}$ splitting) as compared to para-isomer. According to Fig.1, positions of preferential localization of the electron transition density are also distinguished in this case. These data are collectively representative of regularities in the behaviour of perfluoroxylenes under the action of Zn(Cu): meta- and ortho-isomers are reacting at C_{ar}-F bond to a rather greater extent than para-isomer.

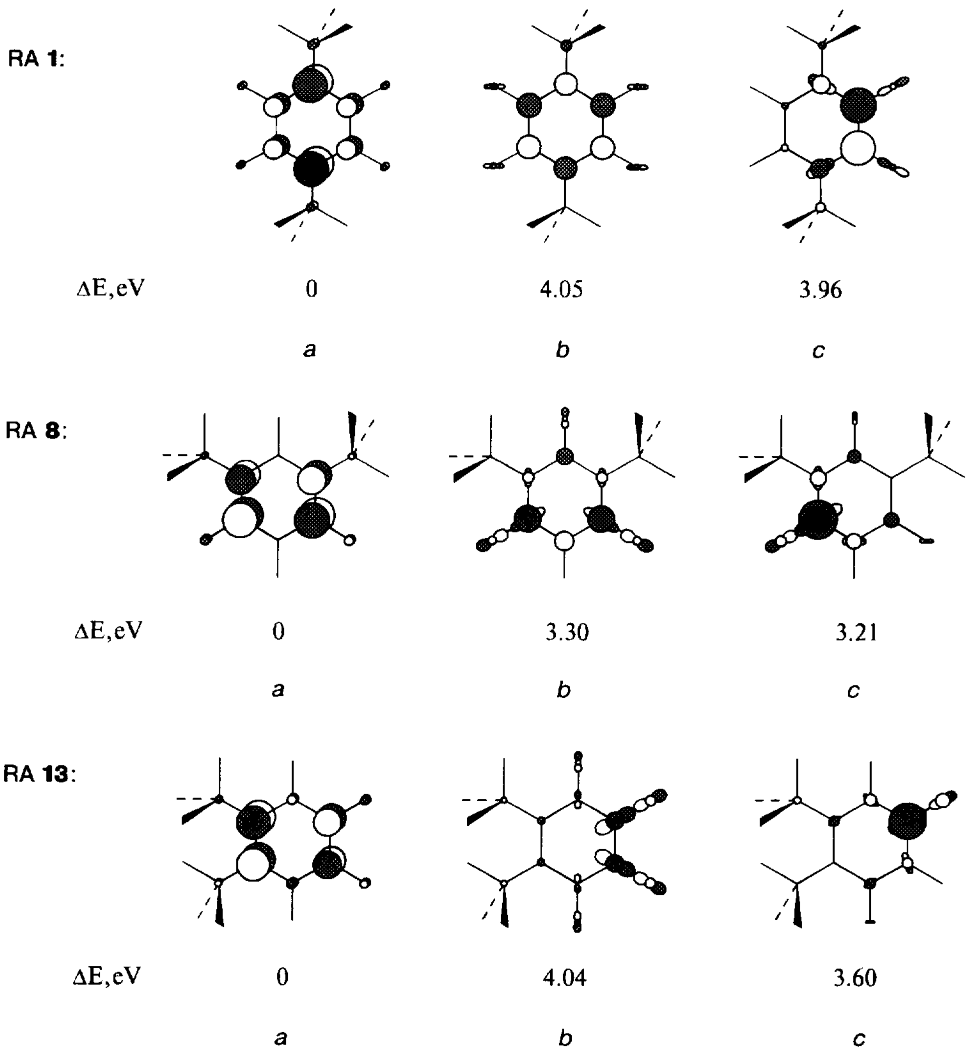


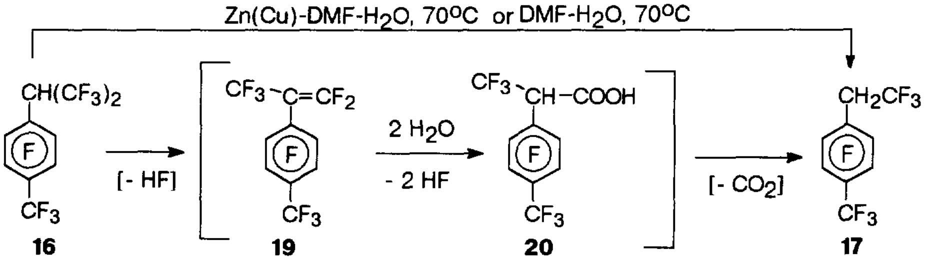
Fig.1. SOMO view and relative energy for radical anions of isomer perfluoroxylenes **1**, **8**, **13** in the ground π-state (a) and in the lower excited σ-state: (b) - symmetrical solution, (c) - broken-symmetry solution.

As it was mentioned earlier, the formation of the products from the hydrogenolysis of C_{ap}-F bond of the cymene **15** was not found, whereas xylene **1** gives hydrodefluorination products with substitution both for the benzyl and the "ring" fluorine atoms (ratio ~11:1). It seems likely that this difference may be attributable to the effect of bond strength on hydrogenolysis. Quantum-chemical calculations (see above) suggest a lower strength of $(CF_3)_2C$ — F bond as compared with F_2C — F. It can result in a greater ratio between the rates of hydrodefluorination at the side chain and at the ring of cymene **13** as compared with xylene **1**.

A peculiarity of the reaction of the hydrogenolysis of the C_{ar}-F bonds under the action of Zn(Cu)-DMF-H_2O is its reduction in speed with the reduction in the number of fluorine atoms in the aromatic ring. Thus, the comparison of the results of compounds **8** and **9** hydrodefluorination (Table 2, exps 12 and 14) suggests that C_{ar}-F bond in perfluoro-m-xylene undergoes hydrogenolysis rather easier than the C_{ap}-F bond in its hydrogen derivative **9**. It allows the synthesis of the hydrogen derivative **9** without the formation of the dihydrogen derivative **10** (Table 2, exps 11,12). Octafluoro-m-xylene **10** shows no hydrodefluorination under the action of Zn(Cu)-DMF-H_2O (70°C, 10 h) (Table 2, exp 15).

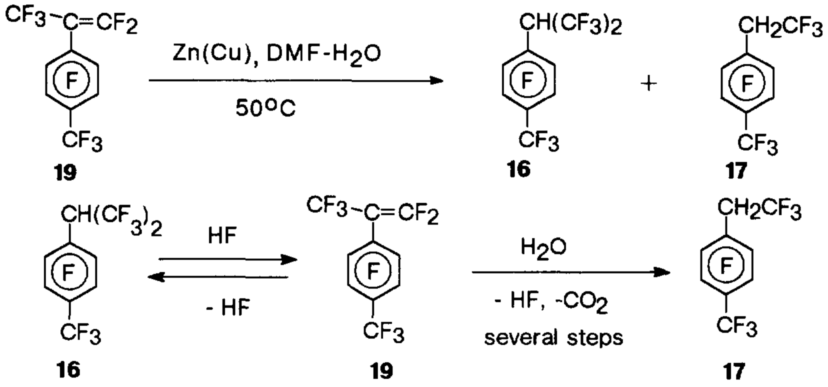
Also, perfluoro-o-xylene reacted through only one C_{ar}-F bond hydrogenolysis resulting in **14** (Table 2, exp 16). The restriction of hydrodefluorination depth in the above examples, as it is in the case of xylene **2**, is likely to be attributable to the decreased electron affinity of polyfluoroarenes with the substitution of hydrogen for fluorine [5d, 5f, 11b]. Moreover, it is known that the decrease of a number of fluorine atoms attached to an aromatic ring results in the increase of the value $\Delta E_{\pi\sigma}$ [10a]. This also can indicate that the second C_{ar}-F bond undergoes hydrogenolysis less readily than the first one.

Compounds **2** and **17** were found to result from perfluoro-p-cymene reaction with Zn(Cu)-DMF-H_2O along with hydrodefluorination products. These compounds arise formally from C-C bonds fission. Cymene **16** was found to give trifluoroethyl derivative **17** when heated in aqueous dimethylformamide both in the presence and in the absence of metals. Therefore, its transformation is likely to proceed through dehydrofluorination resulting in the formation of perfluoro-α,4-dimethylstyrene **19**, which further reacts with water to give the acid **20**. Decarboxylation of the latter gives compound **17**.



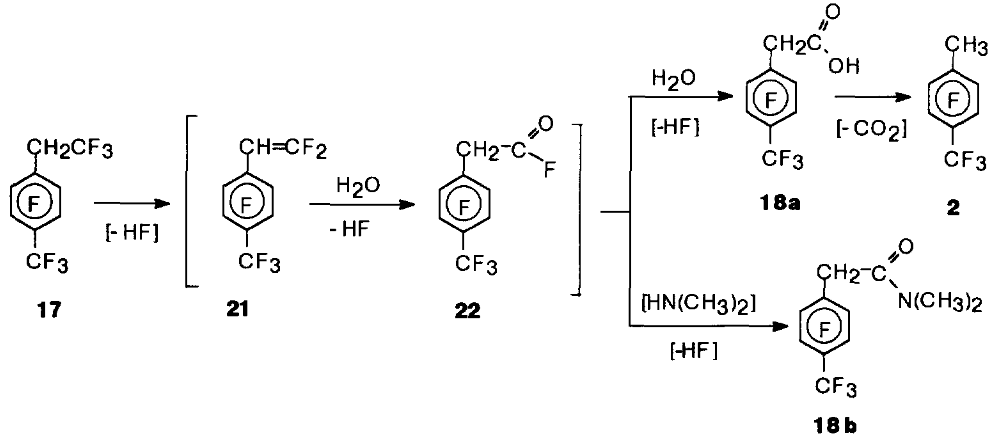
Scheme 11

The formation of a trifluoroethyl group from a pentafluoropropenyl fragment as well as the corresponding intermediate acid, was previously observed by the examples of reaction of pentafluoromethylacrylonitrile and perfluoroisobutylene with water [16]. Dimethylformamide is likely to favour dehydrodefluorination of **16** into **19** [17]. The basic capacity of this solvent can also favour further processes resulting in **17**. Intermediates **19** and **20** suggested in Scheme 11 were not observed. This circumstance could speak in favour of their further transformations under the reaction conditions. Actually, styrene **19** gives product **17**, accompanied by **16** rather readily, being completely converted within 5 hours when allowed to react with Zn(Cu)-DMF-H_2O (see Experimental). Formation of the latter is probably attributable to HF nucleophilic addition to styrene **19**, as it takes place in the chemistry of compounds containing a pentafluoropropenyl fragment [18].



Scheme 12

Xylene **2** formation in perfluoro-p-cymene reaction with Zn(Cu)-DMF-H_2O can be represented by the Scheme 13 similar to the above one. Both xylene **2** and dimethylamide **18b** were shown to result from compound **17** being heating with Zn(Cu)-DMF-H_2O (Table 3,exp 26). Acid **18a**, a possible precursor of xylene **2**, was identified in the products from the perfluoro-p-cymene reaction carried out at 50°C. The detection of acid **18a** rather than acid **20** does not contradict their expected comparative resistance to decarboxylation.



Scheme 13

Dimethylformamide decomposition resulting in dimethylamine formation is a usual process on heating, especially, in alkali media [19]. Dimethylamine is likely to be produced under the reaction conditions at 90°C, giving rise to the formation of product **18b** (Scheme 13). Moreover, other products, containing dimethylamino group (compounds **11a** and **12**) can be formed similarly. Phenol **11b** may be derived from nucleophilic substitution of hydroxy group for fluorine in xylene **8**.

Experimental.

General procedure and starting materials. The ^{19}F and ^{1}H NMR spectra were obtained on a Bruker WP-200SY spectrometer (188.6 and 200 MHz). HMS (0.04 ppm) or C_6F_6 were used as internal standard. Samples were dissolved in CCl_4. Mass spectra were recorded on a Finnigan MAT 8200 spectrometer. Infrared spectra (IR) were recorded on a Specord M-80 for 1% solutions in CCl_4. GLC analyses were carried out on a LHM-72 chromatograph with columns (4000 x 4 mm) and a thermal conductivity detector using silicon elastomer as stationary phases (SKTFT-50, SKTFT-803) on Celite. The ratio of stationary phase to solid carrier was 15:100, column temperatures 50-270°C with a linear temperature programme of 10°C · min^{-1}; detector temperature was 270°C. Dimethylformamide was stored over KOH and redistilled under reduced pressure. A copper powder was obtained by reaction of copper sulphate with zinc. Samples of compounds **3**, **9**, **11b**, **14**, **18a**, **19** for identification were obtained by common procedures [20].

Reaction of perfluoro-p-xylene (1) with Zn(Cu)-DMF-H_2O. A mixture of xylene **1** (14.4 g), zinc dust (40 g), copper (10 g), water (42 g), and DMF (120 mL) was stirred under argon at 70°C for 20 hours. Steam distillation yielded 10.3 g of a mixture, containing 88% of **2**, 7% of **3**, 2% of **4** according to GLC. The residue was extracted with ether; the extract was dried (Na_2SO_4) and evaporated to yield 1.2 g of unidentified compounds. Xylene **2** was isolated by distillation of mixture (b.p. 137-138°C). The residue (1.0 g) which resulted after **2** and **3** had been distilled off was recrystallised from CCl_4, then sublimed *in vacuo*. A final recrystallisation from n-heptane gave 1,2-bis(4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)ethane (**4**), (colourless needles), m.p.122.5-123.5 °C. MS, m/z: 462 (M^+, 20%), 231 (1/2 M, 100%), 181 (25%), M^+: 462.00947; calculated for $C_{16}H_4F_{14}$: 462.00891. ^{1}H NMR: 3.10 (s). ^{19}F NMR: 105.2 (3F, t, J=21 Hz, CF_3), 21.8 (2F, m, 3,5-F), 19.3 (2F, m, 2,6-F). Analysis: calc. C 41.58, H 0.87, F 57.55%; found C 41.19, 41.45, H 0.72, 0.79, F 57.69, 57.74%.

Other reactions of polyfluoroarenes with Zn(Cu)-DMF-H_2O were performed similarly. The reaction conditions, compositions of the resultant mixtures and yields are given in Tables 1-3. The reaction mixture treatment without steam distillation (Table 3) was conducted as follows. The solution was decanted. Metals were treated with 15% HCl to dissolve zinc, then mixture was filtered off and washed with DMF. All the solutions were poured in a 3% HCl and an organic layer was separated.

Reaction of xylene (1) with Zn-DMF-H_2O. A suspension of zinc dust (40 g) in water (39.5 g) was stirred with 2.5 g of 35% HCl for 30 min (argon). Then DMF (120 mL) and xylene **1** (14.4 g) were added. Further procedures were conducted as described above.

Reaction of xylene (1) with Zn-DMF. Zinc dust was activated by washing with 1.7% HCl, then washed with water and dried *in vacuo* (30-35°C/~20 mm Hg, argon flow). A mixture of activated zinc dust (6 g), DMF (12 mL) and xylene **1** (1.8 g) was stirred under argon at 70°C for 20 hours. Steam distillation yielded 1.26 g (after drying with $CaCl_2$) of organic liquid. According to GLC and NMR the product contained 90% of initial compound and 1% of xylene **2**; compounds **3**, **4**, **5**, **6** were not detected.

Reactions of perfluoro-p-cymene (15) with Zn-DMF-H_2O and Zn(Cu)-DMF were performed similarly using dry copper powder.

Reaction of perfluoro-α,4-dimethylstyrene (19) with Zn(Cu)-DMF-H_2O. 1.45 g of the product, containing 78 mol% of perfluoro-α,4-dimethylstyrene (**19**), 11 mol% of compound **16** and 11 mol% of compound **17** were allowed to react with Zn (1 g), Cu (1 g), DMF (12 mL) and H_2O (4.2 g) for 5 hours at 50°C. 1.03 g of a mixture, containing only compounds **16** and **17**, each with a yield of 37%, resulted.

Reaction of perfluoro-p-xylene (1) with Zn(Cu)-DMF-H_2O in presence of hexene-1. A mixture of zinc dust (40 g), copper (10 g), water (42 g), DMF (120 mL) and hexene-1 (17 g) was heated under argon up to 65°C (boiling) and 14.4 g of xylene **1** was added on stirring. The mixture was further stirred at 65°C for 20 hours, then distillated with steam, and dried over $CaCl_2$. Distillation gave hexene-1 (11g, b.p.64-65°C), and a mixture (9.25 g, b.p.40-45°C / 40 mm Hg), containing (GLC): the starting compound - 63%, **2** - 29%, **3** - 2.5%, **5** - 0.7%, and a residue (2.0 g), containing 48% of **7**. The residue was distilled (b.p. 107-110°C /

2-3 mm Hg) and then separated by preparative GLC (15% SKTFT-50 on chromosorb W, 150°C, nitrogen) giving 0.4 g of the liquid which was shown by GLC to contain compound 7 - 90% and 10% of unidentified component; (analytical GLC was performed using SKTFT-803). **1,1-Difluoro-1-(4-trifluoromethyl-2,3,5,6-tetraphenyl) heptane (7)** (the yield from an isolated product comprised 2.2%) MS, m/z: 352 (M^+, 30%), 333 (7%), M^+: 352.08857; calculated for $C_{14}H_{13}F_9$: 352.08734. ^1H NMR: 2.20 (2H, m, 2-H), 1.50 (2H, m, 3-H), 1.31 (6H, m, 4-,5-,6-H), 0.88 (3H, m, 7-H). ^{19}F NMR: 104.8 (3F, t, J=21 Hz, CF_3), 70.0 (2F, tt, J= 27.5, 16 Hz, 1-F), 22.6-23.6 (4F, m, 2-,3-,5-,6-F).

Reaction of 1-trifluoromethyl-2,3,5,6-tetrafluoro-4-(1,1,1,3,3,3-hexafluoro-2-propyl)benzene (16) with DMF-H_2O. A mixture of compound **16** (0.40 g), DMF (4 mL) and water (1 g) was stirred at 70°C for 10 hours. It was diluted with 50 mL of water and steam distilled. The product (0.23 g), analysed by GLC, contained compound **16** (14%), **17** (84%), **2** (2%).

Synthesis of 1-trifluoromethyl-4-difluoromethyl-2,3,5,6-tetrafluorobenzene (5). 1-Trifluoromethyl-4-brom-2,3,5,6-tetrafluorobenzene (29 g, 98 mmol) was added slowly, with stirring, to magnesium shavings (2.85 g, 117 mmol) in dry ether (100 mL) at 5-10°C and the reaction mixture stirred under argon at 0-5°C for 2 hours. The resulting solution was added to a solution of N-methylformanilide (29.3 g, 197 mmol) in 150 mL of dry ether at 0-2°C over 1 hours and stirring was continued for 2 hours on heating to 20°C. The mixture was poured in water (0.5 L) and acidified with 36% HCl (25 mL). The ether layer was separated, washed until neutral pH, and dried over $MgSO_4$. After filtration, the ether was evaporated and the dark residue fractionated. 4-Trifluoromethyl-2,3,5,6-tetrafluorobenzaldehyde **(23)** (15 g, b.p. 52°C / 2 mm Hg) was isolated as a white low-melting crystalline solid. Efforts to achieve a good melting point by recrystallisation failed, probably because of oxidation of aldehyde **23**. The yield was 63%. MS, m/z: 246 (M^+, 100%), 245 (M-H, 89%), 217 (M -CHO, 45%), 199 (M-CFO, 65%), 168 (M-C_2F_2O, 76%). M^+: 245.99135; calculated for C_8HOF_7: 245.99155. IR, cm^{-1}: 2875 (C-H), 1720 (C=O). ^1H NMR: 10.31. ^{19}F NMR: 104.8 (3F, t, J=22 Hz, CF_3), 23.1 (2F, m, 3,5-F), 18.6 (2F, m, 2,6-F). The aldehyde **23** (3.5 g) was added in portions to phosphorus pentachloride (5.4 g) with stirring, the temperature being maintained at 20-25°C. The mixture was stirred for 4 hours, then kept for 48 hours without stirring, filtered from excess PCl_5 and distilled under reduced pressure to give 1-trifluoromethyl-4-dichloromethyl-2,3,5,6-tetrafluorobenzene **(24)** (3.3 g), a colourless liquid, b.p. 85-87°C (15 mm Hg). Yield is 77%. MS, m/z: 300 (M^+, 15%), 265 (M-Cl, 100%), 215 (M -Cl, -CF_2, 25%), M^+: 299.93450; calculated for $C_8HF_7Cl_2$: 299.93451. ^1H NMR: 6.94. ^{19}F NMR: 104.9 (3F, m, CF_3), 23.4 (4F, m, 2-,3-,5-,6-F). A mixture of compound **24** (2.1 g) and CsF (9 g) was heated in a sealed ampoule at 250 °C for 8 hours. Steam distillation gave a liquid (1.4 g), containing 85% of 1-trifluoromethyl-4-difluoromethyl-2,3,5,6-tetrafluorobenzene **(5)**. Purification was achieved through distillation to give a colourless liquid (64% yield), b.p. 136-138°C. MS, m/z: 268 (M^+, 100%), 249 (M-F, 55%), 218 (M-CF_2, 60%), 199 (M-CF_3, 60%), M^+: 267.99404; calculated for C_8HF_9: 267.99344. ^1H NMR: 6.93 (t, 52 Hz). ^{19}F NMR: 104.8 (3F, t, J=21.5 Hz, CF_3), 48.8 (2F, dt, 52, 8.5 Hz, CF_2H), 23.5 (2F, m, 2-,6-F), 20.7 (2F, m, 3-,5-F).

1-Trifluoromethyl-4-fluoromethyl-2,3,5,6-tetrafluorobenzene (6) was separated from the reaction mixture (exp 8) by preparative GLC. M^+: 250.00308; calculated for $C_8H_2F_8$: 250.00288. ^1H NMR: 5.51 (d, 47 Hz). ^{19}F NMR: 105.0 (3F, t, J=22 Hz, CF_3), 23.5 (2F, m, 2-,6-F), 21.1 (2F, m, 3-,5-F), -15.4 (1F, t, 47 Hz, CFH_2).

1,3-Bis(trifluoromethyl)-2,5-difluorobenzene (10). A solution of hydrazine hydrate (0.9 g) in ethanol (5 mL) was added to a solution of compound **9** (2.4 g) in ethanol (5 mL). The mixture was boiled with stirring for 2 hours, then poured into water, and extracted with chloroform. The extract was dried over Na_2SO_4. Filtration and evaporation of the solvent gave 2.2 g of a crystalline substance. A solution of the obtained substance in acetonitrile was added dropwise to 18% aqueous solution of $CuSO_4 \cdot 5H_2O$ (25 mL) with stirring and boiling. The treatment was continued for 2 hours. Steam distillation gave a liquid (1.7 g) which was distilled to give compound **10** (1.4 g, 63% yield), a colourless liquid, b.p. 117-118°C. MS, m/z: 250 (M^+, 10%), 231 (M-F, 90%), M$^+$: 250.00305; calculated for $C_8H_2F_8$: 250.00287. ^{1}H NMR: 7.54 (dd, J= 7 and 5 Hz). ^{19}F NMR: 99.6 (6F, d, J=13 Hz, 2CF_3), 48.0 (1F, dt, J= 18 Hz, 7 Hz, 5-F), 41.1 (1F, m, 2-F).

1,3-Bis(trifluoromethyl)-4-dimethylamino-2,5,6-trifluorobenzene (11a). Dimethylamine (5.6 g of 8% solution in DMF; 10 mmol) was added to the solution of 4.29 g of xylene **8** (15 mmol) and 1.43 g of xylene **1** (available mixture) in 5 mL of DMF. The reaction mixture was stirred, kept for 48 hours, and poured into water. The organic layer was separated, dried over $MgSO_4$ and the resultant mixture (4.2 g) was distilled *in vacuo* to give compound **11a** (0.8 g), a colourless liquid, b.p. 49-50°C (20 mm Hg). MS, m/z: 311 (M$^+$, 55%), 310 (M-H, 100%), 298 (20%), M$^+$: 311.03693; calculated for $C_{10}H_6NF_9$: 311.03564. ^{1}H NMR: 2.96. ^{19}F NMR: 105.6 (3F, t, J=23 Hz, 1-CF_3), 105.0 (3F, d, J=29 Hz, 3-CF_3), 48.7 (1F, m, 2-F), 32.0 (1F, m, 6-F), 13.7 (1F, m, 5-F). Analysis: calc. C 38.60, H 1.94, F 54.95, N 4.50%; found C 38.66, 39.26, H 1.79, 1.93, F 55.19, 55.18, N 4.37%.

1,3-Bis(trifluoromethyl)-4-dimethylamino-2,5-difluorobenzene (12). Compound **12** was similarly prepared from 1.3 g (4.85 mmol) of xylene **9** and dimethylamine (9.7 mmol) (0.75 g, yield 53%), a colourless liquid, b.p. 83-84°C (40 mm Hg). MS: m/z: 293 (M$^+$, 55%), 292 (M-H, 100%), 274 (10%), M$^+$: 293.04525; calculated for $C_{10}H_7NF_8$: 293.04506. ^{1}H NMR: 7.40 (1H, dd, 11 and 6 Hz, 6-H), 2.90 (6H, $N(CH_3)_2$). ^{19}F NMR: 104.7 (3F, d, J=30 Hz, 3-CF_3), 100.2 (3F, d, J=14 Hz, 1-CF_3), 46.2 (1F, m, 2-F), 39.8 (1F, m, 5-F).

Dimethylamide of (4-trifluoromethyl-2,3,5,6-tetrafluorophenyl)acetic acid (18b). A solution of thionyl chloride (1.5 g) in DMF (0.2 g) was added to acid **18a** (2.72 g) with stirring and boiled for 30 min. A 30% solution of dimethylamine in DMF was added to the mixture until neutral pH. The mixture was stirred for 15 min more, then poured into water and extracted with chloroform. The extract was dried over $CaCl_2$, and the solvent evaporated to give the dimethylamide **18b** (2.8 g, yield 92%). An analytical sample, prepared by sublimation with further recrystallization from CCl_4 and then from heptane, gave colourless plate crystals, m.p. 104-105°C. MS, m/z: 303 (M$^+$, 20%), 231 (10%), 181 (10%), 72 (100%), M$^+$: 303.04987; calculated for $C_{11}H_8NOF_7$: 303.04940. IR, cm^{-1}: 1665 (C=O), 2930. ^{1}H NMR: 3.69 (2H, s, CH_2), 3.12 (3H, s, CH_3), 2.93 (3H, s, CH_3). ^{19}F NMR: 105.4 (3F, t, J=21 Hz, CF_3), 20.4 and 20.0 (4F, m, 2-,3-,5-,6-F). Analysis: calc. C 43.58, H 2.66, F 43.86, N 4.62%; found C 43.21, 43.54, H 2.59, 2.87, F 43.62, 43.88, N 4.77%.

Procedure of quantum-chemical calculations. The calculations employed the INDO UHF method with full geometry optimization. The modified PC-version of the SPIN-HAMILTONIAN programme was used [10c]. SCF solutions for excited σ-states of radical anions were found at the ground state geometry varying the initial density matrix. The employment of an asymmetric initial density matrix allowed broken-symmetry solution of a lower energy.

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