

FRAGMENTATION AND DIMERIZATION OF POLYHALOGENATED NITRO-
BENZENE AND BENZONITRILE RADICAL ANIONS AS A ROUTE TO
BIPHENYL DERIVATIVES.

V.F.Starichenko, N.V.Efremova, G.A.Selivanova, V.D.Shteingarts
Institute of Organic Chemistry,
USSR Academy of Sciences, Siberian Division,
630090, Novosibirsk

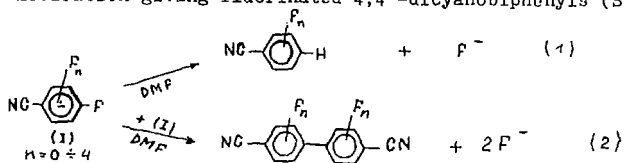
Electrochemical reduction of benzonitrile and nitrobenzene derivatives with 1 to 5 fluorine or chlorine atoms has been studied in DMF using cyclic voltammetry [1,2]. The analysis of data on fluorine effect on the half-wave reduction potential ($E_{1/2}$) of benzonitrile derivatives (see Tab.1) has shown both increased general stability of the radical anion state and increased value of the stabilizing effect of fluorine with accumulation of fluorines in the molecule. This is mainly due to the changed fluorine effect from para-position to the cyano group. While fluorine introduction into the 4-position of benzonitrile destabilizes its radical anion state by 0.04 eV, for 2,3-difluoro-, 2,3,4-trifluoro-, 2,6-difluoro-, 2,4,6-trifluoro-, 2,3,5,6-tetrafluoro- and pentafluorobenzonitriles, para-fluorine introduction produces the stabilizing effect, as shown by comparison of their $E_{1/2}$ values, which is comparable to that of ortho- and meta-fluorines. The leveling of ortho-, meta- and para-fluorine effects with fluorine accumulation may be attributed to the changed geometry of the starting molecule after its transformation to the radical anion state [3].

In the nitrobenzene series, introduction of one fluorine ortho to the nitro group stabilizes the radical anion state, whereas with two ortho-fluorines their total stabilizing effect is twice as low. In view of this, one can draw a conclusion about the additivity of fluorine effect on the reduction potential with fluorine accumulation at positions remote from the nitro group. This conclusion agrees with ideas about preservation of the planar structure of the aromatic moiety in the series of fluoronitrobenzenes.

Using the standart and OD ESR technique, the ESR spectra have been recorded for fluorobenzonitrile radical anions (RAs) generated in DMF and squalane. As opposed to RAs of some fluoronitrobenzenes [2], for fluorobenzonitrile RAs (see Tab.2) accumulation of fluorine

nes in the benzene ring leads to sharply increased a_F constant. The quantum-chemical analysis has shown that such a behaviour of a_F constant may be interpreted in terms of the Jan-Teller pseudo-effect which gives rise to the out-of-plane distortion and the pseudo- $\dot{\sigma}$ -radical state with characteristic growth of a_F constants.

Fluorobenzonitrile RAs with para-fluorine have been found to decompose by fluoride anion elimination (Scheme 1) with concurrent dimerization giving fluorinated 4,4'-dicyanobiphenyls (Scheme 2)

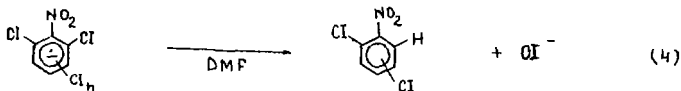
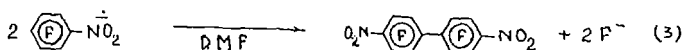


For fluorobenzonitrile RAs containing no fluorine para to the CN group, the dimerization at these positions is reversible, and elimination of the fluoride anion may occur both from the ortho- and meta-positions of the benzene ring.

With fluorine accumulation in the series of fluorobenzonitrile RAs the rate of decomposition and dimerization increases. This is due to peculiarities in the electronic structure of these RAs which are the pseudo- $\dot{\sigma}$ -type RAs.

Contrary to fluorobenzonitrile RAs, fluoronitrobenzene RAs are stable against decomposition. Pentafluoronitrobenzene RA undergoes dimerization to form 4,4'-dinitrooctafluorobiphenyl (Scheme 3). For RAs with 4 or less fluorines, no dimerization was observed.

Chloronitrobenzene RAs did not undergo dimerization [4]. The RAs of polychlorinated nitrobenzenes containing two ortho-chlorines undergo decomposition by the chloride anion elimination from these positions to form the dechlorination products (Scheme 4). The RAs of chloronitrobenzenes with one ortho-chlorine are more stable against decomposition.



$h = 0 - 3$

Table 1. The half-wave potentials of electrochemical reduction ($E_{1/2}$) of fluorosubstituted nitrobenzenes and benzonitriles relative to NCE.

Compound	$-E_{1/2}$, $v(R=NO_2)$	$-E_{1/2}$, $v(R=CN)$
C_6H_5R	1.05	2.14
3- FC_6H_4R	0.91	2.01
4- FC_6H_4R	1.01	2.18
3,4- $F_2C_6H_3R$	0.90	1.99
3,5- $F_2C_6H_3R$	0.80	1.88
3,4,5- $F_3C_6H_2R$	0.79	1.83
2- FC_6H_4R	0.99	2.00
2,4- $F_2C_6H_3R$	0.98	1.99
2,3- $F_2C_6H_3R$	0.89	1.81
2,5- $F_2C_6H_3R$	0.88	1.76
2,4,5- $F_3C_6H_2R$	0.87	-
2,3,5- $F_3C_6H_2R$	0.78	1.68
2,3,4,5- F_4C_6HR	0.78	1.51
2,6- $F_2C_6H_3R$	1.02	1.85
2,4,6- $F_3C_6H_2R$	1.00	1.76
2,3,6- $F_3C_6H_2R$	0.90	-
2,3,4,6- F_4C_6HR	0.89	-
2,3,5,6- F_4C_6HR	0.80	1.37
C_6F_5R	0.78	1.35

Table 2. Hfi constant of fluorobenzonitrile RAs.

Compound	Hfi constants in gauss	Solvent
C_6H_5CN	$a_N^{CN}=2.15$, $a_H^{2,6}=3.63$, $a_H^{3,5}=0.30$, $a_H^4=8.40$	DMF
$3,5-F_2C_6H_3CN$	$a_N^{CN}=2.17$, $a_H^{2,6}=2.98$, $a_H^{3,5}=0.93$, $a_H^4=6.94$	DMF
$2,6-F_2C_6H_3CN$	$a_H^{2,6}=8.5$, $a_H^4=8.5$	squalane
$4-FC_6H_4CN$	$a_H^4=26.3$	squalane
$2,4-F_2C_6H_3CN$	$a_H^2=8.0$, $a_H^4=30.5$	squalane
$2,4,6-F_3C_6H_2CN$	$a_H^{2,6}=15.5$, $a_H^4=55.5$	squalane
$3,4,5-F_3C_6H_2CN$	$a_H^{3,5}=35.0$, $a_H^4=99.0$	squalane
$3-HC_6F_4CN$	$a_H^2=55.5$, $a_H^4=97.5$, $a_H^5=11.3$, $a_H^6=57.5$	squalane
$4-CH_3C_6F_4CN$	$a_H^{2,6}=9.3$, $a_H^{CH_3}=9.3$	squalane
$4-NH_2C_6F_4CN$	$a_H^{2,6}=34.6$, $a_H^{3,5}=34.6$	squalane
$4-CH_3OC_6F_4CN$	$a_H^{2,6}=37.2$, $a_H^{3,5}=37.2$	squalane
$4-CF_3C_6F_4CN$	$a_H^{2,6}=12.2$, $a_H^{CF_3}=24.5$	squalane
$1,4-(CN)_2C_6F_4$	$a_N^{CN}=1.96$, $a_F=4.48$	DMF

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